

# Spectrometric investigation of internal combustion engine oil

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**Abstract.** One of the ways to improve the efficiency of internal combustion engines is by reducing fuel and lubricant costs. The major cost of engine oil is due to the need to replace it regularly. Extending the service life of the oil based on the evaluation of its actual condition provides a significant reduction in operating costs. The article presents the results of the evaluation of changes in oil performance using spectrometric methods of oil sample analysis. Spectrometric methods allow to estimate promptly the intensity of accumulation of wear products, impurities, additives degradation degree, its viscosity index, oxidation, alkalinity in the oil. The results of spectrometric analyzes can also be used to assess the technical condition of the engine and the intensity of wear of its main parts. Results of researches confirm a possibility of scientific substantiation of prolongation of term of use of engine oils of internal combustion engines that provides decrease in operational expenses. The application of spectrometric methods of engine oil analysis also provides perfection of the engine maintenance system based on an objective estimation of the condition of the knots and mechanisms of the engine and the exception of not forced repairs and service. To increase the efficiency of the use of spectrometric methods of engine oil analysis, it is necessary to accumulate and generalize experience of their practical application and increase the duration of tests.

## 1 Introduction

Internal combustion engines are the most common type of heat engine. Due to their high level of reliability and sufficiently high efficiency, internal combustion engines find application in all branches of transport and stationary installations for various purposes [1, 2]. A feature of internal combustion piston engines design is a great number of friction units, caused by the movement conversion processes in the crank mechanism. To ensure the reliable and efficient operation of friction components, a high quality lubricant is essential. Lubricants, used in internal combustion engines, provide reduction of wear of rubbing parts

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of mechanisms, reduction of mechanical losses on friction, removal of a considerable amount of the heat allocated at friction.

Change of oil properties during operation occurs under the influence of: contamination of oil by falling into it metal particles, dust, water fouling and fuel; formation of oxidation products in oil; reduction of additive concentration. Oil degradation due to external contamination is not dependent on the original oil quality. The intensity of formation of oxidation products in the oil under the same operating conditions of the lubricated unit or machine, on the contrary, depends entirely on the initial oil quality.

These causes a gradual deterioration of oil quality, which in turn leads to increased wear of friction parts, shortening the service life of mechanisms and units, increasing their repair costs. Deteriorating oil quality leads to the need for periodic oil changes. Frequent oil changes are disadvantageous due to the increased cost of oil and the cost of replacing the oil. It is important that the oil retains its high quality for as long as possible.

Monitoring of the physical and chemical properties of operating materials enables their condition to be correctly evaluated and the decision to change them or to correct their properties through treatment or additive use to be made.

Improving quality control of engine oil requires solving several interrelated tasks:

- selection of controllable (reject) indicators and definition of their threshold (limit) values;
- choice of devices and measuring instruments to determine the monitored parameters of the engine oil with the required accuracy;
- creation of an effective system of oil quality control, which ensures the prolongation of oil life and its timely replacement.

During exploitation quality of engine oil constantly changes due to oxidation of oil, accumulation of wear products and degradation of additives, which are part of oil [3]. The analysis of engine oil allows to receive the information not only about quality of engine oil, but also about intensity of wear of details and engine mechanisms. Obtaining of reliable and timely information about condition of engine oil allows to solve two interconnected problems: decision-making on necessity of replacement of engine oil or prolongation of its service life, evaluation of intensity of engine parts wear and forecasting of its remaining life for the purpose of maintenance works. The solution of these tasks allows to reduce operating costs and increase economic efficiency of transport and stationary installations with diesel engines.

## **2 Methods and materials**

Many methods and means of quality control of engine oils exist. Among applied approaches it is possible to allocate operative methods of analyses of a condition of oils which are spent directly in operating conditions [4, 5], and also the laboratory, applied for the purpose of more qualitative estimation of a general condition of a diesel engine and its separate details and units. Since to determine the degree of engine parts wear it is necessary to analyze a wide range of indicators, for these purposes special laboratory equipment is used, which allows quickly enough to conduct the required research in accordance with the approved methods. Use of modern laboratory methods of estimation of technical condition of engines by indicators of engine oil are described in works [6-9]. Results of spent researches provide the organisation of rational service of engines on the basis of the analysis of engine oil. Similar approaches to estimation of intensity of wear on condition of lubricating oil are applied also for other technical systems [10, 11], that confirms their efficiency. The most promising directions of development of methods of diagnosing of internal combustion engines, as well as other complex technical systems, are application of

probabilistic methods [12, 13], machine learning in the process of diagnosing [14], monitoring of engine oil condition in the process of operation of engines in real time [15].

Timely detection of worn diesel engine parts reduces the probability of engine failure and, consequently, the costs associated with ship downtime. Prediction of service life of parts can be built on regular comparison of oil additives and metal impurities concentrations. For example the atomic emission spectrometry method is used to determine metal wear in engine couplings.

Spectral analysis determines the following parameters: physical and chemical parameters (the content of fuel, water, soot and acids in the engine oil), metal impurities (iron, aluminium, titanium, copper, etc.), viscosity, alkali number and oxidation stability.

These parameters are an extensive set of data, which indirectly tells you about the technical condition of the diesel engine. Such characteristics as the iron and aluminium content in the engine oil sample can give an indication of the wear of pistons and cylinders. Bearing wear, as well as the presence of water and fuel in the oil in use, are also detected in advance.

One of the devices developed for online optical emission spectrometry is the OSA4 MetalLab system. The spectrometer principle is based on emission spectral analysis with sample excitation by means of a spark. The spectrometer comprised the excitation source, optical system (polychromator), vacuum system, system for temperature control of the polychromator, argon feeding system, power units and controller, which allows the control of the analysis process and recording of results by means of an IBM-compatible computer.

The use of the spectrometer enables not only determination of the range of metallic impurities but also recommendations for engine oil replacement or further engine oil use. Conducted analyses are in compliance with ASTM 97414-10 standard, and the error of analysis does not exceed permissible intervals for determination of metal content according to ASTM D6595-00 and ASTM D5185-09 standards. Metal content is determined in accordance with high precision (up to 1 mg/l). Therefore it is important to take samples using a dedicated sampler. The OSA4 MetalLab determines the metals iron, chromium, tin, aluminium, nickel, copper, lead, molybdenum, titanium, manganese, vanadium, calcium, magnesium, boron, zinc, phosphorus, barium, silicon, potassium and sodium. Such system is not so complex and expensive as complete monitoring systems [16], but is capable to present sufficient information both about operational properties of engine oil, and about a technical condition of the engine, intensity of wear of its basic details.

The object of research was an engine oil of Gazpromneft Ocean TPL 4040 brand, designed for use in lubrication systems of engines running on fuels with high sulphur content (up to 4.5 %). This oil was used in the lubrication systems of two engines Wartsila 6L20, used as the main ones in the power plant of motor ships of project 19614, mixed "river-sea" sailing.

Physical and chemical data of the tested oil are given in table 1. Table 2 shows technical characteristics of the Wartsila 6L20 engine.

**Table 1.** Characteristics of engine oil Gazpromneft Ocean TPL 4040.

Viscosity class SAE	40
Kinematic viscosity at 100 °C, mm <sup>2</sup> /s	14.5
Flash point in open crucible, °C	238
Curing temperature, °C	-12
Alkaline value, mg KOH/g	41
Viscosity index	96
Sulphate ash content, %	5.0
Density at 20 °C, g/cm <sup>3</sup>	0.915

**Table 2.** Diesel technical data Wartsila 6L20.

Rated (continuous) power, kW at crankshaft speed $n=1000 \text{ min}^{-1}$	930
Number of cylinders	6
Cylinder diameter, mm	200
Piston stroke, mm	280
Average effective pressure at 930 kW and crankshaft speed $n=1000 \text{ min}^{-1}$ , MPa	2.46
Fuel consumption, with min. calorific value 42700 kJ/kg	190 g/(kW·h) $\pm 5 \%$
Oil consumption, g/(kWh)	0.6 (tolerance 0.3)

The purpose of the research carried out was to determine the intensity and qualitative patterns of change in a wide range of internal combustion engine oils for marine engines during operation.

### 3 Results

Preliminary measurements have shown that after 100 hours of use most of the engine oil's indicators remain practically unchanged, so in order to reduce the number of analyses it was decided to analyse samples taken after 300 hours. The OSA4 MetalLab's interface allows the analysis results to be divided into the following groups

- elements of contaminants;
- elements of wear or additives;
- elements of additives;
- contaminants;
- physical properties.

Data from spectrometric analyses of engine oil samples are shown in Table 3.

**Table 3.** Results of engine oil sample tests.

Test series		first			second		
Oil running hours		100	400	700	100	400	700
Elements of depreciation	Iron, ppm	3	2	5	3	4	6
	Chrome, ppm	2	2	2	2	4	4
	Aluminium, ppm	2	2	5	4	4	5
	Copper, ppm	12	22	14	4	14	11
	Lead, ppm	5	3	2	2	2	2
	Tin, ppm	4	2	4	2	2	3
	Vanadium, ppm	26	33	12	1	7	8
Contamination elements	Silicon, ppm	3	2	2	2	2	3
	Sodium, ppm	88	54	45	50	26	60
	Potassium, ppm	11	2	2	6	9	2
Elements of wear or additives	Titanium, ppm	0	0	0	0	0	0
	Molybdenum, ppm	2	2	2	2	2	2
	Nickel, ppm	2	0	2	0	1	1
	Manganese, ppm	3	0	2	2	2	2
	Bor, ppm	3	2	0	0	0	0
Additive elements	Magnesium, ppm	253	83	47	39	40	52
	Calcium, ppm	2967	-	7032	7332	5402	8759
	Barium, ppm	0	0	0	0	0	0
	Phosphorus, ppm	2008	50	368	340	380	432
	Zinc, ppm	2038	1281	499	538	648	517

Pollutants	Fuel	-	D	D	D	D	D
	Soot, %	0.1	0.3	0.3	0.1	0.3	0.1
	Water, %	0.1	0.1	0.1	0.1	0.1	0.1
	Glycol, %	0	0	0.6	0.8	0	0.8
Physical properties	Nitration, A/cm	5.1	2	2	2	2	2
	TBN, (mg KOH/g)	8.3	17.3	17.6	19.5	15.9	19.2
	Oxidation, A/cm	2	3.5	4.5	3.9	2.5	5
	V40 °C	158	158	159	159	158	159
	V100 °C	14.4	8	8.3	8.2	8.7	8.1
	V index	87	<3	<3	<3	<3	<3

Indicator D defines the presence of fuel in the oil. Fuel reduces the viscosity of the oil and leads to a reduction in its lubricating power. The detection of fuel in an oil sample may indicate the formation of lacquer deposits on the inner surfaces of the cylinder, which are washed away by the engine oil.

Soot, which is a product of the combustion of fuel, forms a deposit on the parts of the cylinder and piston group, which is washed away by the oil and accumulates in the oil. An increased concentration of soot indicates a malfunction in the fuel system, an incorrect ratio in the fuel/air mixture, or poor mixture preparation.

Significant presence of water in the oil, or an increase in its quantity, indicates a violation of the tightness of the lubrication system.

Nitration is a process of accumulation of nitrate compounds in oil formed during fuel combustion. Lubricant nitration occurs when there is sufficient temperature, pressure and oxygen in the combustion chamber to break down the stable N<sub>2</sub> form of atmospheric nitrogen into individual atoms. These reactive atoms can combine with free oxygen to form nitrogen oxides NO<sub>x</sub> (i.e. NO and NO<sub>2</sub>). Two types of nitrogen compounds can be formed from these oxides: organic nitrates on the walls of cylinders, piston and piston ring surfaces, intake and exhaust valves; nitro compounds in oil pumps, lubrication system channels, oil coolers, etc. Organic nitrates usually lead to nitration in the oils of natural gas engines. Once formed, the nitrates penetrate into the engine crankcase. Nitrates are initially soluble in the engine oil, but in excessive amounts they precipitate out of the lubricant and form fouling and deposits. These deposits can also lead to lodged piston rings and clogged oil filters. Nitration products cause corrosion and accelerate oil ageing. Nitration of oil leads to thickening of the oil, formation of deposits or lacquer-like deposits on engine parts and formation of soluble nitrogen compounds. Nitration of oil is common in natural gas engines and also in the oils of low-speed diesel engines with engine oil temperatures below 80 °C.

The alkali number (TBN) describes the oil's ability to neutralise acidic products of nitration and oxidation. The control of the alkali number enables the oil's change intervals to be determined accurately. An alkali number below 3 (as a general rule) means that the oil's alkaline additives are exhausted and must be changed immediately. In the case of a recent oil change, however, a rapid drop in the alkali number indicates that the engine has overheated.

Oxidation is a characteristic process of oil ageing by interaction with air oxygen at higher temperatures. The oxidation of oil in the engine occurs most intensively in thin films of oil on the surfaces of parts heated to high temperature and in contact with hot gases (piston, cylinder, piston rings, valve guides and valve stems). Oil oxidises less intensively in the volume, as the temperature in the crankcase sump, radiator and oil pipes is lower and the contact surface of the oil with the oxidising gas medium is smaller. Inside the engine, filled with oil mist, the oxidation is more intensive. During the oxidation process, carboxylic acids are released from the oil, which have a corrosive effect on engine parts, as

well as sludge and sludge that clog the oil clearances. Sludge and deposits form which reduce engine performance and increase the risk of engine failure. Oil oxidation leads to higher oil viscosity, increased fuel consumption, accelerated degradation of additives - which reduces the efficiency of the oil itself and shortens the oil change interval. At values above 25 the oil must be changed.

Viscosity describes the oil's ability to circulate inside the lubrication system and lubricate moving engine parts. The OSA4 MetalLab has a dual-temperature viscometer (DTV) working on the principle of overpressure. The oil sample is pumped into the reservoir chamber, then blown out at constant pressure through a precision tube in the bottom of the chamber. The blowing time of the sample is directly dependent on the viscosity of the sample and can be calculated from the time measurement. Tests are carried out at 40 °C and 100 °C. From the measurements the viscosity index (V index) is calculated.

The most significant changes in the oil condition indices are shown in Figures 1, 2, 3.

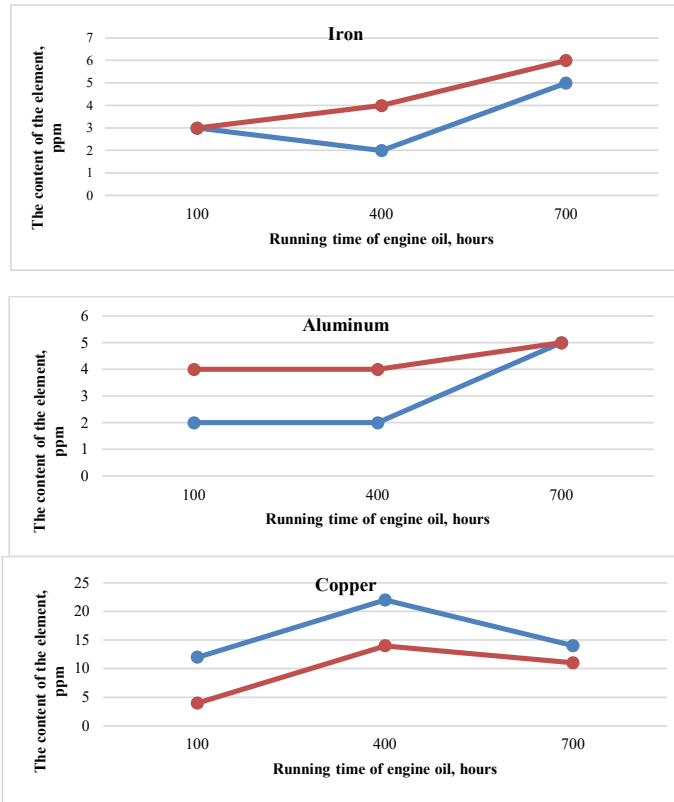
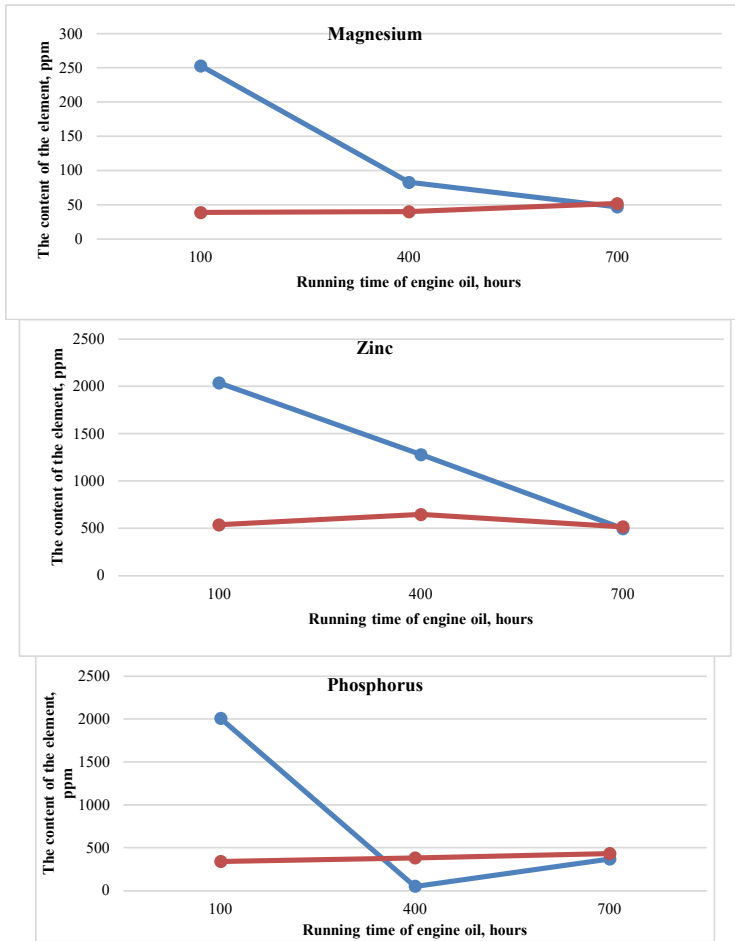
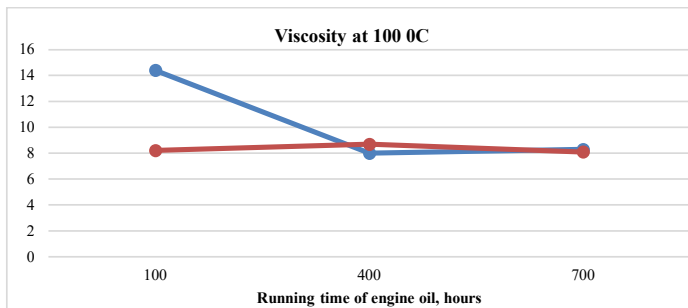


Fig. 1. Change in oil concentration of wear products.



**Fig. 2.** Change in concentration of additive components in oil.



**Fig. 3.** Change in oil viscosity.

## **4 Discussion**

The conducted research on changes of properties of engine oil during operation showed that in both series of experiments the accumulation of such wear products as iron, aluminium, copper swells quite slowly, which indicates the low intensity of wear of the main engine parts and confirms the reliable operation of its components. No unscheduled engine repairs or maintenance are required.

Both series of tests showed a gradual reduction in the concentration of additives, such as magnesium, zinc, phosphorus. The content of the other components remained virtually unchanged. No additional additive injection into the oil is required.

In both test series, the presence of fuel in the engine oil was detected. This is probably the reason why the oil's viscosity at 100°C and the low viscosity index value were observed. The information obtained is a signal to identify the causes of fuel in the oil and to eliminate them.

Accumulation of soot in oil is not critical, which indicates quality combustion of fuel, provided by good condition of fuel equipment and good technical condition of parts of the cylinder-piston group.

Moisture content in the oil is insignificant and constant. Minor watering of the oil is likely to have occurred during storage. The high tightness of the lubrication system prevents an increase in moisture content.

Oil nitration is at a low level, indicating high oil quality and good engine condition.

Oil oxidation gradually increases with increasing service life, with values well below the critical threshold requiring oil changes.

The alkaline index (TBN) changed insignificantly during the tests. Its value is much higher than the threshold value requiring an oil change. Thus, the oil also has a sufficiently high level of performance that it does not need to be changed.

## **5 Conclusion**

The following conclusions can be drawn from the research carried out.

Spectrometric analyses of engine oil samples confirmed good technical condition of diesel engines in which the oil was used, absence of increased wear and excluded the need for unscheduled repairs.

By the time the oil is changed, as specified in the engine manual, the engine oils retain their operational properties, allowing them to be used in the future. Extending the oil's lifespan by their actual condition can reduce operating costs and minimise the impact on the environment.

Using technologically advanced spectral analysis systems makes it possible to determine metal impurities in engine oils, basic physico-chemical characteristics and to assess the overall condition of the oil in a relatively short time. Spectrometers of the OSA4 MetalLab type and techniques applied in these devices are capable to become a part of the engine oil monitoring system during diesel operation in order to prevent undesirable failures. A comprehensive approach to engine oil monitoring using a wide range of tools will improve the economics of combustion engines and the efficiency of transport and stationary applications.

To ensure maximum utilisation of engine oil life, further research is required to develop systems to monitor the physical and chemical characteristics of oils during the operation of marine diesel engines.



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