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Atomic Emission Spectrometric Analysis in the Assessment of Wearing of Vehicle Engines

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Internal combustion engines are exposed to very difficult exploitation conditions: heavy loads and high temperature. Oil is used to reduce friction and wear of the mechanism parts. Different physical and chemical characteristics of the oil play a crucial role during the performance because of the change of regime: the oil preventing from one type of wear may not be suitable to prevent another type of wear. One of the experimental ways to determine the influence of the oil on the wear processes is to estimate the amount of wear products, i.e. wear metals. Employing the inductively coupled plasma emission spectrometer "Spectroflame ICP" one can carry out such used oil analysis. This equipment is not specifically modified to the oil analysis and this paper presents the method for engine oil sample preparation and its application for the "Spectroflame ICP".

Keywords: engine oil, spectrometric emission analysis, oil sample preparation.

1. INTRODUCTION

Modern mechanisms employ oil in especially difficult working conditions: heavy loads and, often, high temperatures. Oil is used to reduce friction and wear of the mechanisms. In any machine application the most important aspect for insuring maximum machine and lubricant life is the selection of the correct oil. In an internal combustion engine, oil is constantly mixed with fuel combustion corrosive products and can reach the temperature of 300 °C or higher. The efficiency of the oil in 100 °C – 150 °C depends on its thermal stability. Composition of oils changes during their performance due to the external factors. Some of the characteristics change to such an extent that the oil can no longer serve its functions. During performance oil undergoes oxidation, vaporization, and contamination with mechanical impurities and water. Oxidation takes place when oil is exposed to the air. Metallic additives in the oil also act as catalysts for oxidation of the oils [1]. What regards oxidation, lead is the most active metal, while iron and other metals are not very active, and aluminium does not cause oxidation at all [2]. During performance alloy oils lose part of their active additives, which, on their part, react with lubricated metal surfaces, to some oil components and impurities. On the other hand, alloy components are being used up. Oil additives can break down into fragments because of the water, which appears in cases of high performance temperatures or other physical phenomena. If these additives are polymeric they can depolymerize, i.e. disintegrate, due to the broken mechanical polymeric circuits during oil circulation. This irreversibly changes the composition of the oil. Big part of oil ageing products as well as worn metal of the mechanisms fall into precipitates. Characteristics of the same oil would depend on the working conditions, ageing of the oil and composition of the products that develop during the ageing process. During performance the regime is constantly changing and thus different physical and chemical characteristics come into play in the process of lubrication; thus the oil preventing from one type of wear can become useless in the prevention against another type of wear (abrasive, erosive or adhesive wear). There are various standard methods for evaluating the performance characteristics of oils [1 – 11]. Experimental analysis has to be carried out in order to evaluate the set of the phenomena and processes that take place in oils during the wear of lubricated machine parts, and the efficiency of lubrication. One of the experimental ways to determine the impact of a particular oil on the wear is the analysis of the wear products, i.e. metals. Oil analysis has to be carried out during which the amount of metals in the waste oil can be estimated as follows [5]:

Amount of metals = metals in the oil + metals of the active additives + worn metals,

where:
Metals in the oil: Ca, K;
Metals of the active additives: Mg, Ca, Ba, Zn;
Worn metals of the engine mechanism: Fe, Cr, Al, Mo, Pb, Cu, Sn, Ni, Ti.

Oil analyses are globally undertaken by conducting predictive maintenance programs. By monitoring oil conditions the statistics of oil analyses help to determine the time interval for changing oils. These time intervals are usually determined by oil producers or equipment manufacturers, who base themselves on wear metal analysis in the oil.

For example, US National Tribology Services provide alarm limits from three engine manufacturers (Cantepillar, Cummins and Detroit Diesel) (see Table 1). Metal alarm limits depend on engine model, i.e. on chemical characteristics and amount of wear metals in an engine, and engine performance characteristics.

During the condition monitoring of equipment performance in modern oil research laboratories,

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comprehensive oil analysis is carried out according to the tests indicated in Table 2.

Table 1. Alarm limits of chemical elements in waste engine oil (according to engine manufacturers) [7]

Metal tested by spectro analysis	Alarm limits of metals in engine oils of three engine manufacturers, ppm*		
	Caterpillar (all models)	Cummins (all models)	Detroit Diesel (all models)
Iron	100	84	150
Copper	45	20	90
Lead	100	100	–
Aluminium	15	15	–
Chromium	15	15	–
Tin	20	20	–
Sodium	40	20	50
Boron	20	25	20
Silicon	10	15	–

*ppm – part per million.

Table 2 presents three required and advisable tests methods namely, particle count, Rotrode Filter method and spectrometric analysis for the estimation of metals amount in oil. Application areas of the required tests are given in Figure 1. Other tests, outlined in the table, and employed for the research of oil organics, are not further discussed in the present work.

Spectrometric Analysis is designated as the main method for the estimation of the amount of metals in the internal combustion engines during monitoring. Such analysis is most efficient when the size of metal particles is up to 1 µm, and less efficient when metal particles are of 5 µm in size. When the majority of the particles in the oil is of about 10 µm in size, the particles are counted by applying analytic ferrography method (see Fig. 1).

There wear magnetic particles are separated and etched on a glass plate and called ferrogramma. Microscopic test helps to describe the way of the wearing and a possible reason of wearing. This technique is called analytic ferrography. Automatic technique of this magnetic separation is called DR (Direct Read) ferrography. It can be used to determine the amount of small and big parts, as well as the concentration and intensity index of small and big parts. The latter two are the parameters that define wearing tendencies and act as indicators of irregular wearing. This method can also be used for the determination of the size and an amount of non-metalic parts.

According to the US National Tribology Service, oil research laboratories have been used inductive plasma atomic emission spectrometers, specially adapted to the oil research, for the last seven years.

In the Institute of Welding and Materials Science Problems at Vilnius Gediminas Technical University there is an inductive plasma atomic emission spectrometer “Spectroflame ICP”, which has not been manufactured particularly for oil analysis. In order to adapt this spectrometer to the oil analysis, a specific method has to be created; preparation of the sample is one of the main parts of it. A specialized emission spectrometer requires the sample for the oil analysis to be prepared by attenuating the necessary amount of oil by an organic solvent, e.g. kerosene or n-heptane. Such a sample, however, would not be suitable for the base model of the owned “Spectroflame ICP”.

Table 2. Test equipment of oil condition monitoring [6]

Equipment	Spectro Analysis	Viscosity	FT-IR*	Particle Count	Amount of water, Karl Fisher method	Total Acid No.	Total Base No.	Rotrode filter method
Internal combustion engines	R	R	R	R			R	A
Compressor	R	R	R	R	A	R		A
Gearboxes	R	R	R	R				R
Bearings	R	R	R	A	A			R
Hydraulics	R	R	R	R	R	A		R
Turbines	R	R	R	R	R	R		R
Motors (other engines)	R	R	R					R

* – Infrared Analysis for detecting the organic contaminants; R – Required test; A – Advisable test, provides extra details, particularly during problem solving

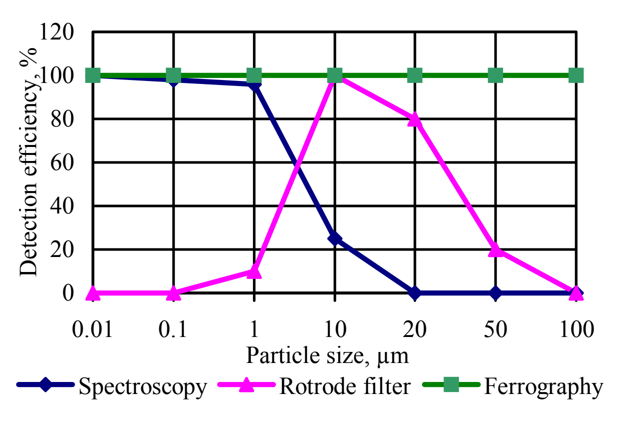

Fig. 1. Dependence of the efficiency of the metal particle detection in oil on the particle size [6]

2. EXPERIMENTAL

The purpose of this work is to develop the method for dissolving the oil sample in acid medium but not in the organic one. Such method will allow the solving of small as well as big metal particles in the oil sample. The traditional way of preparation of acid oil solvents is oxidation of oil organics and further solving in sulphuric acid at high temperature about 300 ºC. The oxidizing in high temperature makes part of the element to evaporate. Thus the sample must be prepared at a low temperature and ensure the dissolving of wear metals.

2.1. THE METHOD OF OIL SAMPLE PREPARATION IN ACID MEDIUM

In order to avoid the aforementioned drawbacks, the following sample preparation method was developed.

About 0.2 g of oil to be analyzed is put into a flask and about 1 – 1.5 ml of concentrated high pure sulfuric acid is added. The content of the flask is slowly heated in a sand bath up to 40 – 60 °C, this temperature is maintained for about three hours while constantly mixing. After the content of the flask is heated up to 120 °C and the acid evaporates. When the content has cooled down, about 3 ml of concentrated nitrogen acid of special purity is added. The temperature is gradually raised up to 60 °C and this temperature is maintained until the solution becomes even. Then the content is heated up to 100 °C and is evaporated until 1 ml is left. This amount is added to the single-mark 100 ml-measure volumetric flask by rinsing. The sample is suitable for analysis after distilled water is added to reach the amount of 100 ml. Such sample allows to melt even big metal particles (>5 μm). That is why there is no need to filter bigger particles before this sample undergoes analysis. These particles are otherwise calculated by using the aforementioned Rotrode Filter or Ferrography methods.

2.2. ANALYSIS OF THE ACID OIL SAMPLE

According to the specially developed method the sample of the internal combustion waste engine oil in a motorcar was analyzed applying the atomic emission equipment "Spectroflame ICP". For verify created method the same sample was analyzed outside (Vilnius Fuel apparatus plant) by atomic absorbtion method. The results obtained for Cr, Fe and Cu are shown in Table 3.

Table 3. Amount of metals in the engine oil after the 20-hour performance of the engine 18P-T

Method of waste engine oil analysis	Amount of metals, ppm*		
	Iron	Chromium	Copper
Atomic emission ICP spectrometry	29.06	0.9605	1.1320
Atomic absorbtion spectrometry	29.56	0.9088	1.1020

*ppm – part per million.

Two research methods received the same result with admissible error for methods. Employing the inductively coupled plasma emission spectrometer "Spectroflame ICP"one can carry out such used oil analysis.

These results do not constitute alarm limits presented in Table 1. It should be noted that this analysis is useful for the purpose of information, i.e. in order to make sure whether there is a need to change the oil under analysis.

However, this analysis does not help to describe the performance characteristics because the change of the oil in an engine, still leaves 18 % to 4 % of the old oil in the engine. It is obvious that the information is not sufficient for the comprehensive oil analysis.

3. CONCLUSIONS

1. The developed sample preparation methodology provides with the possibility to conduct metal amount analysis in oil by applying the base model of the inductive plasma spectrometer "Spectroflame ICP".
2. By using the developed sample preparation methodology for the spectrometer "Spectroflame ICP" it is possible to determine the total amount of metal particles in the waste oil.

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