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Strictly as per the compliance and regulations of:

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I. INTRODUCTION

Oil analysis (OA) is the sampling and laboratory analysis of a lubricant's properties, suspended contaminants, and wears debris. OA is performed during routine preventive maintenance to provide meaningful and accurate information on lubricant and machine condition. By tracking oil analysis sample results over the life of a particular machine, trends can be established which can help eliminate costly repairs [1-5].

OA was first used after World War II by the US railroad industry to monitor the health of locomotives. In 1946, the Denver and Rio Grande Railroad's research laboratory successfully detected diesel engine problems through wear metal analysis of used oils. A key factor in their success was the development of the spectrograph, an instrument that replaced several wet chemical methods for detecting and measuring individual chemical element such as iron or copper. This practice was soon accepted and used extensively throughout the railroad industry [5-9].

Used oil analysis is comparable to a medical analysis with a blood test. Like blood, lubricating oil contains a good deal of information about the envelope in which it circulates. Wear of metallic parts, for example, produces many minute particles, which are carried by the lubricant. These small metal particles can give information about the machine elements that are wearing. In addition, variations of physical properties such as viscosity, viscosity index, flash point and etc, can give valuable information about engine and lubricant performance [5-9].

A number of techniques such as inductively coupled plasma [10] , Fourier transformation infrared spectroscopy [11,12], atomic absorption spectroscopy [13], , differential scanning colorimetry [14] , x-ray fluorescence spectroscopy [15], laser induced break down spectroscopy [16], spectrography [17], ferrography [18], mass spectrometry [19], and chromatography [20] have been applied for the oil analysis.

We have been recently involved in the investigation of lubrication oils [21-23]. In this paper, we report the results of the comparative physical and chemical analysis of fresh and used gasoline engine oil with mineral base, by ICP-OES and some other techniques.

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Experimental

a) Materials

All of the materials were used directly without any further processing. The employed materials, as well as the name of the corresponding manufacturer are as follows:

Material	Manufacturer	Material	Manufacturer
Gasoline oil Speedy SL	Sepahan Oil Company	Potassium Hydroxide	Merck
Ethanol	Merck	Acetic acid	Merck
Hydrochloric acid	Merck	Acetic anhydride	Merck
Lithium chloride	Merck	Chlorobenzene	Merck
Methanol	Merck	Sodium perchlorate	Merck
Propane-2-ol	Merck	Sodium carbonate	Merck
Buffer	Merck	Xylene	Merck
Chloroform	Merck	Acetone	Merck
Perchloric acid	Merck	Solid carbon dioxide	Merck

b) Test Methods

The test methods were followed as: ASTM D-445 for viscosity @ 40^{0}c and 100^{0}c, ASTM D-2270 for viscosity index, ASTM D- 92 for flash point, ASTM D-97 for pour point, ASTM D-1298 for specific gravity, ASTM D-1500 for color, ASTM D-664 for total acid number, ASTM D-6304 for water content,

c) Instrumental

All of the viscosities, viscosity indices and specific gravities were determined by viscometer Anton Paar model SVM 3000. Flash points were evaluated by flash point tester Herzog model HC 852. Pour points were determined by pour point tester Herzog model HC 852. The colors were determined by Dr. Long instrument. TBNs were determined by robotic titro sampler Metrohm model Dosiono 800. TANs were determined by titrator Methrohm model Titrino MPT 789. FTIR spectrum was recorded on a FTIR spectrum Perkin Elmer model Spectrum 65 using KBr pellet. The elemental analysis were performed by ICP-OES Perkin Elmer model Optima 5300V

d) Sampling

The sampling was performed immediately after turning off the car. An adequate amount of oil sample was taken by 100 mL syringe.

II. RESULTS AND DISCUSSION

Typical properties such as vis@40°c, vis@100°c, viscosity index, flash point and etc of fresh and used oil are compared in Table 1. As it can be seen, all of the properties have been changed approximately. This means that upon the usage of motor oil and during the performance of the oil several changes has been occurred in the oil composition [24].

Consistency, flow properties, or viscosity in the case of oils, are key parameters to create lubrication efficiency and the application of lubricants [25]. The viscosity of used engine oil can drop for reasons of fuel dilution, or as a result of high water content and/or shearing of the VI improver [1]. Viscosity can increase because of heavy contamination of the oil by soot, polymerization, vaporization losses, and emulsions due to water contamination and/or oxidation of the oil [1].

Obviously, the final status of the oil viscosity depends on the combination effects of decreasing and increasing factors. If the falling factors overcome to the rising ones, the drop in viscosity will happen. An increase in the property will be observed, in the reverse conditions.

There is no signal of fuel dilution. Therefore, the appearance of water in the used oil and the drop of viscosity index (as a result of shearing of the VI improver) are the main viscosity reducing agents.

It is well known that heavy contamination of the oil by soot causes the appearance of a band at 2000 cm-1 in the IR spectrum of corresponding oil [1]. Because of the absence of such band in the spectrum of used oil (Fig. 1) viscosity increase by soot formation is discarded. On the other hand, considerable reduction in the volume of the oil was not observed. Which means that the evaporation loses through usage of the oil are minimal. Furthermore, there is no evident of polymerization. Thus, among the viscosity increasing factors the main role can be attributed to the oxidation. This is further confirmed by the increase of TAN, density and color, as some of the oxidation signals.

The data in Table 1 indicate that vis@40°c and vis@100°c have been increased. Based on the discussion on previous paragraph it can be claimed that viscosity-increasing factors have been overcome to the decreasing ones.

The flash point is the lowest temperature at which an ignition source causes the vapors of the specimen (lubricant) to ignite under specified conditions [2]. Like viscosity, the flash point test has always been a standard part of a lubricant's specification. Because of the low flash points of most fuels, a sudden drop in flash temperature in crankcase oil can usually be relied upon as an indication of dilution. Occasionally, very high, localized temperatures can lead to thermal cracking within the oil. As there is no evident of fuel dilution, the observed reduction (Table 1) can be attributed to thermal cracking. Because of lower flammability of lighter molecules, the flash point has been reduced. The production of lighter molecules is further confirmed by decreasing of pour point. As it can be seen, the pour point has been reduced for 4 degrees of celicious.

The total acid number is a measure of the acidic constituents in petroleum products. The acidity of unused oils and fluids is normally derived from the type and concentration of specific additive material whereas the acidity of used oil is of interest to measure the degree of oxidation of the fluid. The total base number (TBN) characterizes the alkaline reserve in petroleum products [24, 25]. It is particularly used for engine oils where by acidic combustion products use up the alkaline reserve. Both TAN and TBN can be obtained by acid base titration. Sample titration curve is shown in Fig. 2. The resulting data indicate that TAN of used oil has been increased relative to fresh oil. In contrast, TBN has been decreased. The increasing of TAN can be attributed to production of acidic products due to oil oxidation. In fact, in high temperature of motor conditions some of the oil constituents oxidize. The carboxylic acid is produced. The reduction of TBN can be assigned to depletion of additives, which mostly do have basic character. The appearance of carbonyl band in IR spectrum of used oil (Fig. 1) further confirms the production of acidic adducts.

The concentration of different elements was measured by ICP-OES. The final results are given in Table 2. According to the data, different elements can be categorized to three groups: (i) the elements, which have high concentration in fresh oil, (ii) elements, which have low concentration in fresh oil, and (iii) elements that do not exist in fresh oil. Based on this categorization sulfur, zinc, phosphorus, magnesium, silicon, calcium and barium can be located in first group. Bohr molybdenum, aluminum, silver, chromium, nickel and sodium in second group and manganese, iron, copper, tin, titanium, vanadium, led, cadmium, antimony and potassium in third group.

Among the elements of the first group, the highest concentration belongs to sulfur. Keeping in mind that the examined motor oil do have mineral character and mineral base oils do have relatively high sulfur content [25], such an observation is not unexpected. On the other hand, the decrease in the concentration of this element in the used oil can be attributed to oxidation followed by evaporization of some of the sulfur containing constituents.

The high concentration of other elements such as Zinc, Phosphorous, magnesium, silicon and barium indicate that these elements are the constituents of employed additives. The existence of these elements can be attributed to ZDDP, barium sulfonate, and other additives. The decrease in the concentration of these elements indicates that during the performance of the oil the additives have been depleted.

The low concentration elements (group (ii)) origin from the additives which are used in very low concentration or the elements which in the process of oil production have been produced in the oil.

The encounter with the elements which initially are absent in the fresh oil but appear in the used oil (group (iii)) can be attributed to the wearing of motor parts during the oil performance, contamination or both o them. Equipment as it operates will deposit microscopic amounts of wear metals in the lubricant. For example iron originates from the wearing of cylinders, copper from bushings, bearings, cam bushings, oil coolers, valve train bushings, thrust washers, oil pumps, aluminum from pistons, bearings, blocks (some), bushings, housing, oil pumps, blowers, thrust bearings, cam bearings/bushings, chromium from rings, roller/taper bearings (some), liners, exhaust valves, wear treatment, lead from bearings, gasoline, octane improver .Molybdenum from plating or surface hardening agent in certain bearings, rings.

Under normal conditions, wear will be very low and under abnormal conditions, the wear will be high Among these elements the concentration of iron and manganese show drastic change, which indicate drastic wear of iron alloy occurs such as. Because the concentration of wear elements is not very high, it can be concluded that considerable wearing has not occurred.

III. Conclusions

Based on obtained results it can be concluded that due to depletion of additives, oxidation, thermal cracking and wear, some of the physical and chemical properties of the selected oil have been changed. Minor wearing has been occurred. It general it can be claimed that the oil shows acceptable performance characteristics.

IV. Acknowledgements

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Table 1 : Typical properties of fresh oil Speedy SL from Sepahan oil Company

Typical Properties	**Test Method**	**Fresh oil**	**Used oil**
Viscosity@40°c cSt	ASTM D-445	141.6	152.2
Viscosity@100°c cSt	ASTM D-445	16.51	18.4
Viscosity Index	ASTM D-2270	125	118.3
Flash Point	ASTM D-92	222	218
Pour Point	ASTM D-97	-26	-30
Specific Gravity	ASTM D-1298	0.8910	0.9037
Color	ASTM D-1500	2	8
TAN (mg KOH/g)	ASTM D-664	1.52	3.2
TBN (mg KOH/g)	ASTM D-664	12.37	9.75
Water content	ASTM D-6304	0	1%

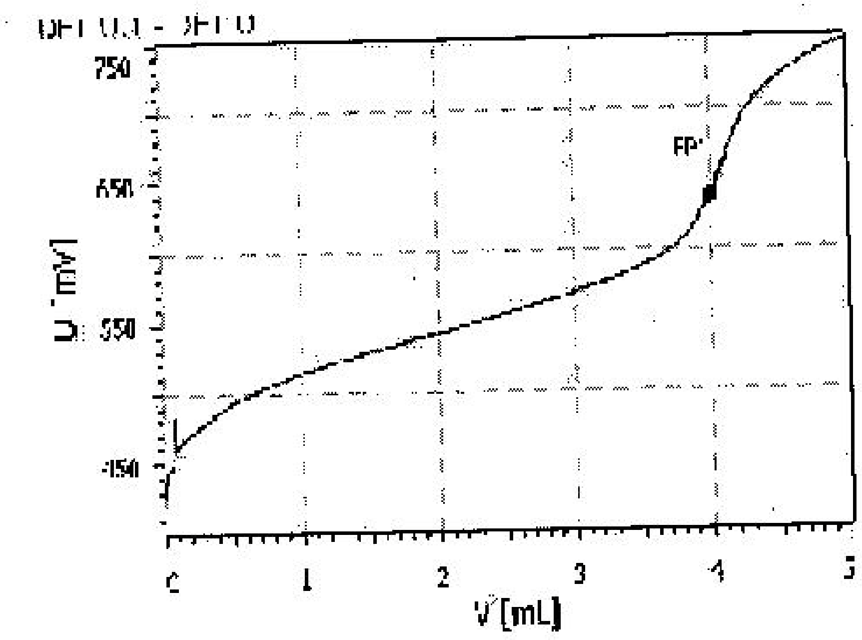

Figure 1 : Titration curve due to TBN determination of fresh oil.

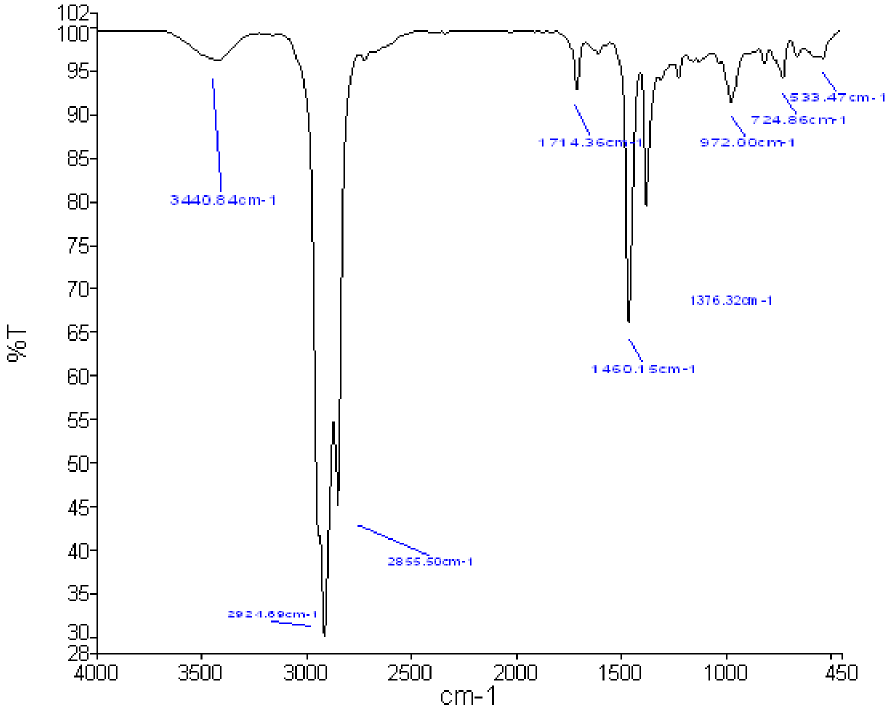

Fig. 2 : IR spectrum of used oil

Table 2 : Concentration of different elements in fresh and used oils

No.	**Element**	**Fresh oil**	**Used oil**	**No.**	**Element**	**Fresh oil**	**Used oil**
1	Sulfur	1108.0	938.0	13	Nickel	1.1	2.0
2	Zinc	784.0	160.0	14	Sodium	0.5	1.1
3	Phosphorous	811.2	318.8	15	Manganese	0.0	25.3
4	Magnesium	228.9	185.9	16	Iron	0.0	12.8
5	Silicon	61.4	45.5	17	Copper	0.0	2.8
6	Calcium	56.7	16.1	18	Tin	0.0	1.6
7	Barium	29.4	22.8	19	Titanium	0.0	1.6
8	Bohr	6.7	2.9	20	Vanadium	0.0	1.5
9	Molybdenum	6.5	8.9	21	Lead	0.0	0.6
10	Aluminum	5.0	10.6	22	Cadmium	0.0	0.5
11	Silver	1.7	2.3	23	Antimony	0.0	0.4
12	Chromium	1.1	2.2	24	Potassium	0.0	0.0