STUDY OF METALLIC CONTENT IN LUBRICATING OIL WITH PREDICTIVE PURPOSES

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SAMPLE ABSTRACT:
Aims: To determine the concentration of the metals present in a lubricating oil of mineral base, before, during and after its use in the engine of a truck, to know its variation for predictive purposes.

Study design: In the study, we used a truck in which the lubricating oil of mineral base, diesel grade 15W/40 is tested. Periodically, a sample of the oil contained in the crankcase is taken and the concentration of the metals present in it is determined to know its variation.

Duration of Study: The study is carried out during the period corresponding to 57000 km of operation of the lubricating oil in the engine.

Methodology: The determination of the metals content of both new and used lubricating oil samples, extracted from the crankcase after regular periods of use, is carried out by atomic absorption spectrophotometry.

Results and Conclusion: The analysis of the lubricating oil allowed to know what was happening inside the engine; helping to detect wear problems of its components, as well as detecting contamination and degradation suffered by the lubricating oil itself. Thus, it can be considered a valid method in the predictive maintenance of the engine.

Keywords: lubricating oil, metallic content, atomic absorption spectrophotometry, predictive analysis.

1. INTRODUCTION

During operation, an engine is subject to normal wear and tear of its construction elements due to the continuous friction of its moving parts. Any mechanical system has mobile components that when in contact with each other produce frictions whose fundamental consequences are the resistance to movement, the increase in temperature and the wear of them. Lubricating oils are used to reduce these problems [1, 2].

Motor oils are, mostly, liquid products derived from petroleum, complex mixtures of various types of hydrocarbons, with additives to improve their performance. The so-called multigrade oils which are used at present, which came into use for engines in the 1950's, are designed to work in applications where the temperature changes are considerable. Current lubricants

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are a combination of base oils of mineral or synthetic origin and additives, chemicals of complex formulation whose mission is to improve the performance of oils.

The additives for lubricating oils were used for the first time in 1922 and since then their use has been increasing to the point that nowadays all types of oils has additive. The additives are added in order to:

- Decrease the speed at which certain reactions that are undesirable in the oil occur during your period of service.
- Improve the stability of the lubricating film with respect to variations in operating temperature.
- Protect lubricated surfaces from the aggression of certain contaminants such as water, acids, etc.
- Improve the physical-chemical properties of the oil or provide new ones.

The main types of additives used are viscosity index improvers, pour point depressants, corrosion inhibitors, anti-emulsifiers, defoamers, anti-wear and extreme pressure. The percentage by volume of additives in a lubricating oil is variable and the additives used in its formulation can have harmful side effects, especially if the dose is excessive or if reactions occur between them [3, 4].

In internal combustion engines, the lubrication system is responsible for lubricating the parts in relative movement. When internal wear occurs, due to the friction between them, the small particles of detached material pass to the oil; the larger ones are deposited in the bottom of the crankcase or are trapped in the filter, the rest will remain in suspension in the oil. The concentration and type of metal particles in suspension in the lubricating oil will determine the origin of the wear and if this can be considered normal or accelerated, table 1.

Table 1. Possible origin of metals in lubricating oil
http://noria.mx/lublearn/analisis-de-elementos/

Element	Symbol	Origin	Most common source
Aluminium	Al	Wear metal, Contaminant	Plungers, Bearings, Contaminants, Lubricating grease.
Barium	Ba	Additive	Detergent additive
Calcium	Ca	Additive, Contaminant	Detergent additive, Lubricating grease, Water.
Copper	Cu	Metal wear, Additive	Bearings, Radiators, Bronze.
Chrome	Cr	Wear metal	Cylinders, Rings, Crankshafts, Gears.
Tin	Sn	Wear metal	Bearings, Bushings, Push systems, Welding material
Iron	Fe	Wear metal	Cylinders, Crankshafts, Gear, Rust, Water.
Magnesium	Mg	Additive, Contaminant	Bearing, additives, seawater.
Nickel	Ni	Wear metal	Camshafts, Gears, Rings, Turbine alloys.
Lead	Pb	Wear metal	Bearings, Babbitt
Sodium	Na	Additive, Contaminant,	Additives, Coolants, Seawater, Lubricating grease.
Zinc	Zn	Metal wear, Additive	EP Additive, Bearings, Coatings

In table 2, we can see the limits for the metallic content normally accepted in the industry for diesel engines, independent of the brand and without considering km or hours of operation [5].

Table 2. Limits normally accepted in industry for diesel engines
http://widman.biz/boletines/46.html

M = Element		Normal	Abnormal	Critical
		ppm		
Aluminium	Al	<20	20 - 30	>30
Chrome	Cr	<10	10 - 25	>25
Copper	Cu	<30	30 - 75	>75
Nickel	Ni	<10	10 - 20	>20
Iron	Fe	<100	100 - 200	>200
Sodium	Na	<50	50 - 200	>200
Lead	Pb	<30	30 - 75	>75
Tin	Sn	<20	20 - 30	>30
Silicon	Si	<20	20 - 50	>50

These limits can be considered high within a proactive maintenance plan, in which we must also define the kilometres or hours of use for which they are established.

The analysis of lubricating oil is considered a method of predictive maintenance in internal combustion engines. It is a technique that allows to know what is happening inside the engine, helping to quickly detect wear problems of the engine components, as well as contamination and degradation of the lubricating oil, problems that can even have environmental consequences [6, 7]. The control of the oil must be supported by a series of periodic and continuous analyses, which can establish the tendency of wear and the need for its replacement.

The lubricating oil analysis [8] is carried out with two different objectives:
1. Check your formulation.
2. Evaluate, the concentration of metals after use:
   - Coming from additives, such as barium, zinc, calcium and magnesium, to check their stability and correct functioning.
   - That allows to establish the degree of engine wear such as iron, aluminium, chromium, copper, lead or tin.
   - That may appear as a consequence of some kind of external contamination such as sodium.

The analysis of lubricating oil as a tool for the predictive maintenance of diesel engines is still important for the researchers [9], the evaluation of measurement methods for the different parameters of the lubricating oil is interesting from the point of view of diagnosis, with widely accepted techniques or with techniques still in development [10].

In recent years, it has been noted that the determination of the metallic content of the oil by atomic absorption spectrophotometry [11, 12] continues to be of interest from multiple and varied approaches [13, 14, 15, 16].

2. MATERIALS AND METHOD

2.1. Equipment

- Perkin Elmer - Atomic Absorption Spectrophotometer.
- Atomic flame absorption spectrophotometry (EAAF) allows the detection and determination of metals in any type of sample as long as it can be solubilized.
- Monoelement hollow cathode lamps. The type of tube according to the metal being analysed.

2.2. Material and reagents

- Volumetric flasks, 25 mL.
- Automatic pipette and disposable tips.

- White oil free of metals, Merck, of adequate viscosity.
- Fat-soluble standards, Merck, of each of the metals to be determined in the test.
- Methyl isobutyl ketone (MIBK).

- Nitrogen oxide, N_2O.
- Acetylene.

2.3. Method

For the determination, the atomic absorption spectrophotometry is used [17]; an excellent method for the determination of metals at the trace level, comply Beer's Law and based on the absorption of electromagnetic radiation.

The determination of the metal content of the lubricating oil samples, both new and used, was carried out based on the method of the principles of ASTM D4628 [18], through the following steps:

2.3.1. Preparation and dissolution of the samples

Methyl isobutyl ketone (MIBK) is used for the dissolution of the samples since its viscosity is small and it is relatively easy to obtain a dimmed flame by decreasing the flow of fuel or by supplying an auxiliary oxidant.

2.3.2. Adjustment of the ratio of fuel and oxidant flows

The flow of oxidant is regulated to achieve optimal fogging, and then the fuel flow is varied until an optimum signal is obtained.

2.3.3. Selection of the appropriate wavelength for each element

2.3.4. Calibration

The determination of each element requires its own calibration curve, the patterns used for its realization have the same matrix as the sample. The limits of detection of the elements determined in the study are shown in table 3.

Table 3. Detection limits (µg/L) EAAF [19]

Element	Detection limits *(µg/L)*
Fe	6
Cu	2
Cr	4
Sn	15
Mn	2
Ni	3
Al	30
Ag	3
Pb	5
Na	0,2
Mg	0,2
Ba	20
Ca	1
Zn	1

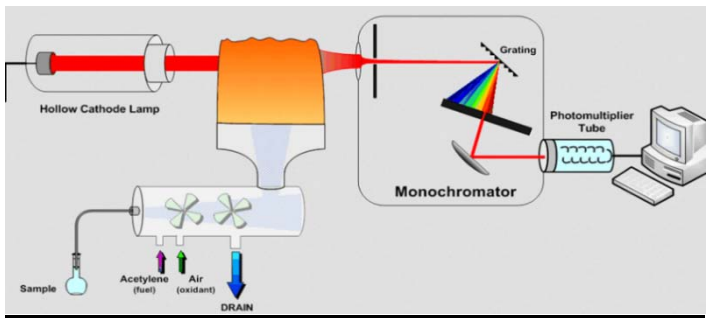

Figure 1. Atomic Absorption Spectroscopy
http://testingposts72014.blogspot.com.es/2014/08/atomic-spectroscopy.html

2.3.5. Analysis of the samples

The diesel oil grade 15W/40 used in the study is a multigrade mineral oil, suitable for all types of diesel engines including supercharged, optimal for vehicles working in severe conditions both service and environmental. It is formulated to achieve a high detergent-dispersant level and contains anti-wear additives.

The vehicle used in the study belongs to a fleet of industrial vehicles that at the beginning of the study had been in service for several years complying with the oil changes pre-established in its maintenance program.

Throughout the study, three total oil changes were made, at 0, 17000 and 37000 km of engine operation during the study period, table 4; the crankcase has a capacity of 22 L. The control samples were periodically removed from the crankcase and always before proceeding to the scheduled oil change.

Table 4. Volume of oil added to the crankcase

Sample	Series 1	Series 2	Series 3	Series 4	Series 5	Series 6	Series 7
km traveled	0	5,000	17,000	27,000	37,000	47,000	57,000
Added oil, L	22	0	22	0	22	0	22

* oil change and filter

3. RESULTS AND DISCUSSION

The metal drum of 208 L containing the new oil, once opened, remains in good condition. Throughout the study, through periodic controls, the oil suffers a level of oxidation that affects its appearance but not its composition.

The results obtained for the concentration of the metals determined in the new lubricating oil extracted from the drum, series 1, shown in table 5; these concentrations act as reference level in the study. Among the metals checked (second column of table 5), barium, aluminium or tin were not found in the new oil.

In the analysis of the data related to the concentration of metals in the samples tested, it was taken into account that the study begins with the substitution of a mineral lubricating oil of inferior quality that was using in the engine for grade diesel oil 15W/40 used in the study. In the lubrication circuit the new oil was mixed with traces of the old oil and the analysis of the results were affected by this problem.

The chosen method for the determination is an analytical technique exhaustively studied and used successfully, on very varied matrices, for the determination of elements at trace level; in the case of the determination of metals in lubricating oil, several studies have endorsed and endorse their effectiveness [20,21] even in comparison with other techniques [22, 23].

The metallic content in the samples oil is shown in table 5 and figures 2, 3, 4, 5: the new oil (series 1) and the used lubricating oil (series 2 to series 7); extracted from the crankcase respectively to the 5000, 17000, 27000, 37000, 47000 and 57000 km of operation of the engine.

Table 5. Metal content of lubricating oil samples

Nº	M = Element		0	Period 1		Period 2		Period 3	
			Series 1	Series 2	Series 3	Series 4	Series 5	Series 6	Series 7
1	Aluminium	[M] ppm	0.0	4.3	4.7	11.0	13.0	25.2	26.6
2	Chrome		8.0	7.5	8.0	14.0	15.0	28.0	33.0
3	Copper		6.0	1.3	2.1	18.0	20.0	11.0	12.0
4	Nickel		4.6	3.0	4.0	4.6	4.7	4.4	4.8
5	Iron		11.0	24.0	47.0	59.0	69.0	192.0	207.6
6	Sodium		5.6	22.0	22.0	28.0	28.6	72.0	104.0
7	Manganese		1.5	1.3	1.8	2.6	2.6	28.4	28.8
8	Lead		25.0	19.8	23.6	29.8	33.0	74.0	84.0
9	Magnesium		47.5	24.4	27.8	42.5	42,5	40.0	4.0
10	Tin		0.0	0.0	0.0	0.0	0.0	0.0	0.0
11	Barium		0,0	0.0	0.0	0.0	0.0	0.0	0.0
12	Calcium		1,500.0	1,040.0	1,010.0	1,340.0	1,310.0	1,300.0	1,280.0
13	Zinc		2,400.0	1,559.0	1,559.0	2,380.0	2,370.0	2,340.0	2,340.0

The study of the variation in metal content was carried out for predictive purposes, based on the metal content of the new oil, series 1.

The determination of the metallic content of the oil samples taken periodically from the crankcase, during the period of duration of the test, allowed the comparative study in three periods, limited by the successive and programmed oil changes at 0, 17000 and 37000 km.

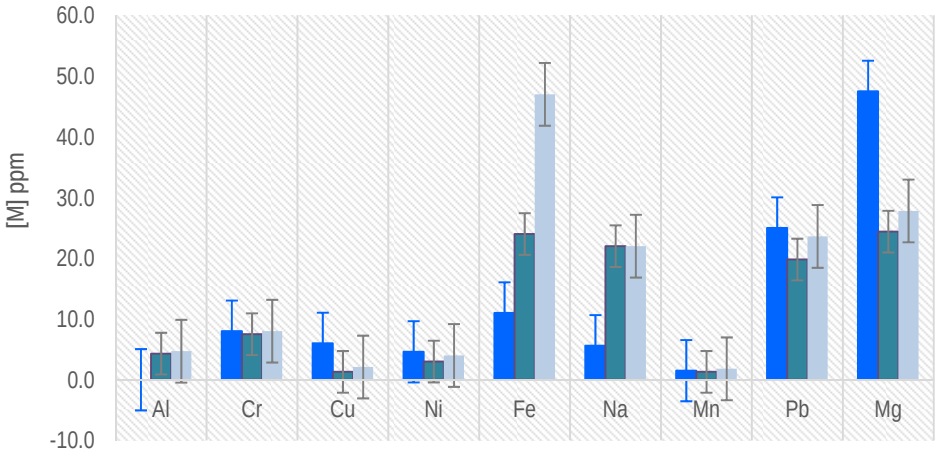

Figure 2. Variation in metal content, 1 al 11, series 1-2-3.

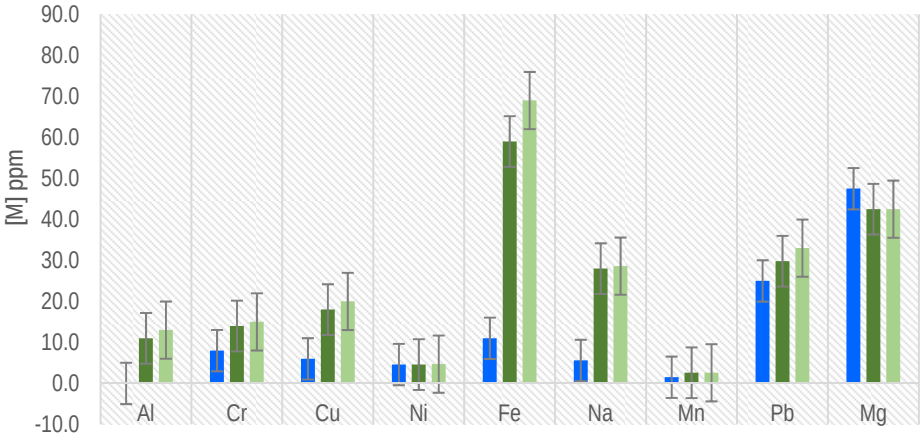

Figure 3. Variation in metal content, 1 al 11, series 1-4-5

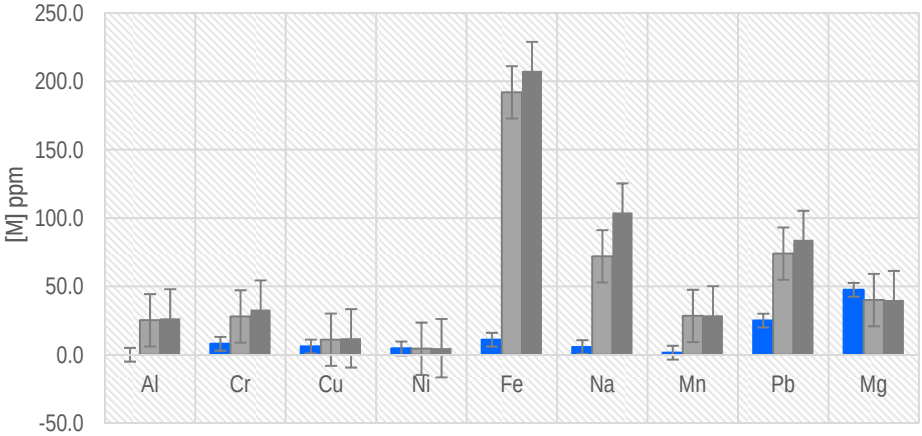

Figure 4. Variation in metal content, 1 al 11, series 1-6-7

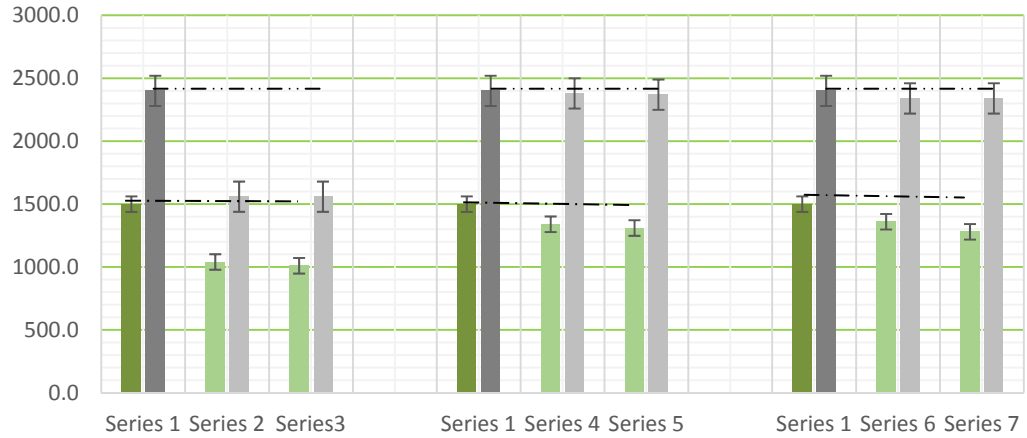

Figure 5. Variation of the content of Ca y Zn [ppm], periods 1-2-3

Table 6. Content of [Ca] and [Zn] in lubricating oil samples

[M] ppm	Series 1	Series 2	Series 3	Series 4	Series 5	Series 6	Series 7
Ca	1,500.0	1,040.0	1,010.0	1,340.0	1,310.0	1,360.0	1,280.0
Zn	2,400.0	1,559.0	1,559.0	2,380.0	2,370.0	2,340.0	2,340.0

Between the first two oil changes, a lubricating oil consumption was found, not very high for the type of oil and condition of the vehicle. The data are consistents with the fact that in modern diesel engines the operating conditions of the piston are harder than in the past, increasing the average temperatures of the piston, which is cooled by the crankcase oil, which leads to an increase in its consumption.

- The **calcium and zinc** content (tables 5, 6 and figure 5), metals from the additives that are part of the oil formulation, decreases substantially in period 1, series 2 and 3, calcium decreases by 30% and zinc by 35%. This decrease is related to the fact that it is the first time that the oil is used in the vehicle that previously used an oil of different characteristics and lower quality.

  At the beginning of the study there are still remains of the old oil in the lubrication circuit as it is shown by the differences observed when comparing the results obtained for the series 1-2-3 with respect to the series 1-4-5 and 1-6-7, in which it is observed that the variation in concentration of calcium and zinc follows the same pattern in relation [M]/ service time.

  Calcium and magnesium originate from the detergent / dispersant additives used to combat the soot, neutralize the acids formed during combustion and keep pollutants and sludge in suspension until they reach the filter, preventing them from adhering to metal surfaces. Detergent / dispersant additives are consumed when performing the function for which they were designed.

  The speed with which the degradation occurs depends on the quality of the fuel used, the way in which the combustion process takes place and the temperature reached in the engine. The formation of acid compounds as a result of poor combustion and low temperature implies a rapid degradation of this type of additives, so it is essential to know the initial concentration of each additive in order to determine its degradation.

At 17000 km, before the planned change to 20000 km, were changed the oil and the oil and air filters to correct the combustion problems detected. In periods 2 and 3 of the study, calcium and magnesium maintain the concentration within adequate levels.

Zinc comes from ZDDP (zinc dialkyl dithiophosphate) used in the formulation of extreme pressure additives. ZDDP (zinc dialkyl dithiophosphate) is an organometallic salt [24], composed of zinc, sulfur and phosphorus that forms a sulphate layer iron on the surface of the pieces, where the sulfur can act to attract zinc, leaving three soft layers to avoid steel-steel contact [25, 26]. During the lifetime of the oil, the limit concentration of ZDDP is the one which is insufficient to achieve its adhesion to the surfaces it must protect. A good oil for a diesel engine (API CI-4) has usually more than 1,550 ppm of zinc, and 1,450 of phosphorus [5].

The variation in Zn concentration observed in the used oil is due to:
- The losses due to the volatility of the additive used, as a result of the absorption by the soot.
- The adhesion to the metal parts.

Zinc works to provide limit lubrication when hydrodynamic lubrication is not enough to tackle the problems caused by pressure and friction.

- The increase in **sodium** indicates the existence of possible contamination, usually by water directly or through humid air entering the engine. The water may have entered due to a mechanical problem or accidentally.

  In the second study period the data reveal a significant increase, although not worrisome, of the concentration of sodium, indicative of contamination by water and attributed to humid air entering the engine; in the third period, the increase is more significant and seems to be related to the accidental entry of water into the engine after high pressure washing.

  Sodium is an element that depends, to a great extent, on the locality where we are working: in a country without sea, a value greater than 10 ppm is an indicator of radiator contamination and more than 15 ppm a water problem in the engine. A value greater than 40 ppm of sodium may be normal near the sea or in countries where they melt the snow with salt.

- The presence of water causes rust, which agrees with the elevation of the iron content. **Iron** is the main wear metal, some studies postulate that the iron content in the used oil should not be higher than 250 ppm. It is found in used oil as a product of normal wear and tear, as a result of friction between the walls of the cylinders and the rings or by the wear of other metal parts: connecting rods, camshaft, crankshaft, valves, bearings, pump oil, gears, the turbo...

- Regarding the other metals determined in the test, increased levels of **lead, aluminium, chromium and copper** are detected as a result of the wear of the metal parts of the engine that have these elements in their composition.

  In the case of **aluminium**, although most of it is a consequence of wear, a small part can come from contaminated air that is introduced into the engine.

The concentration of chromium in the used oil is almost exclusively due to the wear of the chromed piston rings. Most heavy-duty diesel engines use chrome rings and the amount found in the oil sample indicates wear on the rings. A chromium concentration of 10 to 25 ppm is already indicative of significant wear.

Copper is a metal commonly used in the engine and normally used in bearings, bushings, oil coolers, thrust washers, valve guides and connecting rod bushings. The wear or corrosion of these elements results in the presence of concentrations higher than 75 ppm in the oil used, the levels detected are not indicative of significant wear.

When analysing the analysis data, tables 7, 8, 9, it is important to see not only the absolute value of each element, but also to see the trend line, the change in the concentrations of elements in consecutive samples. This type of change rate analysis can be very valuable in locating early signs of wear and pollution.

Table 7. Data analysis, period 1

M = Element		0	Period 1		Normal	Abnormal	Critical	Period 1	
		Series 1	Series 2	Series 3	Limit			Series 2	Series 3
Aluminium	[M] ppm	0.0	4.3	4.7	<20	20 - 30	>30	Normal	Normal
Chrome		8.0	7.5	8.0	<10	10 - 25	>25	Normal	Normal
Copper		6.0	1.3	2.1	<30	30 - 75	>75	Normal	Normal
Nickel		4.6	3.0	4.0	<10	10 - 20	>20	Normal	Normal
Iron		11.0	24.0	47.0	<100	100 - 200	>200	Normal	Normal
Sodium		5.6	22.0	22.0	<50	50 - 200	>200	Normal	Normal
Lead		25.0	19.8	23.6	<30	30 - 75	>75	Normal	Normal

Table 8. Data analysis, period 2

M = Element		0	Period 2		Normal	Abnormal	Critical	Period 2	
		Series 1	Series 4	Series 5	Limit			Series 4	Series 5
Aluminium	[M] ppm	0.0	11.0	13.0	<20	20 - 30	>30	Normal	Normal
I". Chrome		8.0	14.0	15.0	<10	10 - 25	>25	Abnormal	Abnormal
Copper		6.0	18.0	20.0	<30	30 - 75	>75	Normal	Normal
Nickel		4.6	4.6	4.7	<10	10 - 20	>20	Normal	Normal
Iron		11.0	59.0	69.0	<100	100 - 200	>200	Normal	Normal
Sodium		5.6	28.0	28.6	<50	50 - 200	>200	Normal	Normal
Lead		25.0	29.8	33.0	<30	30 - 75	>75	Normal	Abnormal

Table 9. Data analysis, period 3

M = Element		0	Period 3		Normal	Abnormal	Critical	Period 3	
		Series 1	Series 6	Series 7	Limit			Series 6	Series 7
Aluminium	[M] ppm	0.0	25.2	26.6	<20	20 - 30	>30	Abnormal	Abnormal
Chrome		8.0	28.0	33.0	<10	10 - 25	>25	Critical	Critical
Copper		6.0	11.0	12.0	<30	30 - 75	>75	Normal	Normal
Nickel		5.6	4.4	4.8	<10	10 - 20	>20	Normal	Normal
Iron		11.0	192.0	207.6	<100	100 - 200	>200	Abnormal	Critical
Sodium		5.6	72.0	104.0	<50	50 - 200	>200	Abnormal	Abnormal
Lead		25.0	74.0	84.0	<30	30 - 75	>75	Critical	Critical

The analysis helps the vehicle owner with the identification of very serious problems, and indicates where the problem may be located when the data show values above what established as "normal".

In a complete analysis of the oil, the determination of the metallic content during its use provides an extremely valuable information of the additives that are part of its formulation, of the wear of the metallic components of the engine and of the possible contaminations, as consequence of mechanical or accidental problems.

4. CONCLUSION

Maintenance is a complex and continuous process that involves all the personnel that touch or use a vehicle and includes different actions, among which it is important to maintain the lubrication system in optimum conditions.

Checking the condition of the lubricating oil is an important part in maintaining the engine. A detailed analysis of the lubricating oil is fundamental, since it allows to know thoroughly:

- Its state, for lengthen the periods between oil changes.
- The state of the engine, becoming an important part its predictive maintenance; thus achieving to extend its lifetime.

It is irresponsible to extend the intervals between oil changes without implementing a proactive procedure that allows establishing the appropriate moment in which to carry it out. Proactive maintenance requires understanding the differences between:

- **Condemnatory limits:** The limits published by manufacturers that indicate a critical situation that requires an oil change with the recommended revisions in their catalogues.
- **Commonly accepted limits:** Limits based on what often seen.
- **Proactive limits:** These are limits set by benchmarking or comparisons with the best results, looking for the best for our company, car, truck, etc.

High temperatures, high shear rates, corrosive environments, external and internal contamination are the main causes of alterations in the physicochemical properties of the oil, causing its degradation and consequently the malfunction of the engine.

To determine the metallic content of the lubricating oil is an important step to know its condition and in case of degradation act on its possible causes before there is a catastrophic failure in the engine.

Although currently there are widely accepted analytical methods for determining the metallic content in oily substances such as plasma spectroscopy (ICP-OES), atomic absorption spectrophotometry can be used for the same purpose with acceptable results.

For proactive purposes, it is convenient to perform an analysis of the oil in which, in addition to the metal content, other characteristics of the oil are determined, such as viscosity, acid number (TAN) or total number of base (TBN) to obtain a more complete information of what happens in the engine.

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