



Comparative analysis of metal contents in fresh and used lubricating oils

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Abstract

The study compared the analysis of wear metals in fresh and used lubricating oils. Four samples of fresh lubricating oils were categorized as A₁, B₁, C₁ and D₁ while their used oil counterparts were designated as A₂, B₂, C₂ and D₂ respectively. A dry ash method was adopted for digestion of the samples in a 10:1 (oil: acid) ratio (W/V). The digested sample solutions were subjected to Atomic absorption spectroscopy (AAS) for the detection and quantification of six wear metals. The wear metal concentrations determined for fresh oil were in the range 508-1097.5, 172.1-3557, 574.45-1009.90, 2.5-3.95, 3.15-16.45, 3.05-10.45 ppm for Ca, Mg, Zn, Fe, Cr and Ni respectively, their corresponding oil metal concentrations were in the range of 570.05-934.25, 110.55-400.55, 761.15-1004.39, 2.10-5.50, 2.40-34.55 and 5.40-303.40 ppm respectively for the same metal ions. Among the investigated metal ions of A₂, Cr made up 1.54%. The information about these metal concentrations will be helpful in monitoring and maintaining generators and machine engines while also indicating which metals could be quantitatively recovered and thereby being used to solve environmental problems.

Keywords: Atomic absorption spectroscopy, fresh oil, used oil, index ratio, generator engine oil

Introduction

Oil analysis involves sampling and analysing oil for various properties and materials to monitor wear and contamination in an engine, transmission or hydraulic system (Mortier, Fox & Orszulih, 2010) [19]. The purpose of the test is to measure the concentration of wear metals (machin wear), oil additives (oil health) and contaminants. (John, 2012) [22]. The industries as well as other financial institutions operate on generator due to lack of constant electricity supply. These generators and machineries need lubricants especially lubricating oil for proper functioning of engine parts and reduction in its wear (Aucelio *et al.*, 2007) [3]. The newly manufactured generators and machines of various categories also need lubricating oils.

Lubricating oil is a slippery viscous liquid or liquefiable substance primarily used to reduce friction between moving parts of various equipment or machinery. The use of lubricating oil minimizes material wear and contributes to improves efficiency of equipment or machinery and fuel and energy saving (Vahaoja, 2005) [25]. All liquids will provide lubrication of a sort, but some do it a great deal better than others. The difference between one lubricating materials and another is often the difference between successful operation of a machine and failure (Ludema, 1996, Leslie, 2003, Rizvi, 2009) [16, 17, 23]. The Principal function of the engine oil (lubricant) is to extend the life of moving parts operating under many different conditions of speed, temperature, and pressure. At low temperatures the lubricant is expected to flow efficiently in order that moving parts are not short of oil.

At higher temperatures they are expected to keep the moving parts apart to minimize wear. Lubricating oils from petroleum are mainly composed in paraffinic, naphthenic and to a lesser extent, aromatic hydrocarbons. Several additives, including metallo-organic ones are also part of

the final composition of commercial lubricating oil. (Yang *et al.*, 2003) [28]. Therefore, the monitoring and the determination of the metal contents in lubricating oils, which may come from either metallo-organic compounds or nanometric metal debris would provide an efficient way to alert and diagnose any defective functioning in oil lubricated engines, and if possible before the failures occur (Troyer & Fitch, 2001) [24]. It has been noted that the effectiveness of lubricating oil contributes to the life span of an engine (Maten, 2008) [18]. The monitoring of wear metal concentration ions in the oil of moving parts of a machine is an important indicator of the internal condition of the machine. The basic concept is that moving contact between oil lubricated metallic components is accompanied by friction which causes the transformation of the contacting surfaces into small particles which are deposited into the lubricating oil (Duyck *et al.*, 2000) [9] such compounds involve a large number of elements, for example Mg, Si, Ca, Zn and Ba (Goncalves *et al.*, 1998).

The elemental analysis of used lubricating oil may indicate the need for preventive, maintenance of engines or turbines before irreversible damage occurs which brings economic benefits and saves lives (Aucelio *et al.*, 2007) [3]. Engine and turbine components undergo continual wear under normal operating conditions; this is minimized by the use of lubricating oils (Evans, 2008) [10].

Thus, lubricating oil functions by preventing friction between sliding or rolling engine parts; protection of surfaces from corrosion, transportation of wear metal particles and contaminants as well as transfer of heat through the engine parts.

Materials and Methods

Materials: The lubricating oils that were used for the conduct of this experiment are as outlined on Table 1.

Table 1: Lubricating oils and their manufacturers

S/N	Type of oil	Manufacturer	SAE class
1.	Oando Oleum Super	Oando lubricants oil Co., Plc	SAE 40
2.	Oando Super Duty	Oando lubricants oil Co., Plc	SAE 40
3.	Conoil Golden Super	Conoil lubricants Co., Plc	SAE 40
4.	Total Rubia XT	Total oil Co., Plc	SAE 40

Oil Sampling

Four samples of used lubricating oils were collected from generators in four different banks in the Sokoto Metropolis and Yauri, Northern Nigeria and stored in 5L plastic container. The used oil samples from four different monograde oil products Conoil Golden Super diesel oil (SAE 40), Oando Oleum Super oil (SAE 40), Oando Super Duty oil (SAE 40) and Total Rubia XT diesel oil (SAE 40) of lubricating oil used in four different brands of diesel generators (K750 Kalip, FG Wilson Perking, LS Leroy Somer and Mikano) from Unity bank, Access bank, Skye bank and First bank respectively were collected from Yauri, Kebbi State and Sokoto Metropolis. Oando Oleum Super diesel oil was obtained from Unity bank Yauri along Sokoto road, Oando Super Duty Oil as well as Conoil Golden Super Diesel Oil were collected from Access bank and Skye bank respectively in the campus, while Total Rubia XT was obtained from First bank Head Office located at Kano road, Sokoto, using the drain stream method, that is by drawing the oil from underneath the engine compartment called the sump within thirteen (13) hours after the engine had been shut down as adopted from Evans (2008) [10]. Each sample

container was then labelled and properly sealed to prevent any contamination during transit as recommended by John (2012) [15]. The samples were designated as used lubricating oil samples. Engine oil analysis is a quick, nondestructive way to gauge the health of an engine by looking at what is in the oil. It is a process that involves a sample of engine oil whether fresh or used by analyzing it for various properties and materials in order to monitor wear metals and contamination. The approach in this work is to analyze used engine oil of brands of generators of different age group that may differ in quality make of crankshaft, cylinders, pistons to assess the nature of wear and tear metals generated due to long period of service, drain engine oil interval, overloading and the fresh oil as the control.

Quantitative Analysis of Used Oil

The spectrometric analysis of lubricating oil is common practice where large amounts of lubricating oils are involved (Cosnier, 2008) [6]. The analysis covers the determination of six (6) elements in used lubricating oils which include additive elements wear metals and contaminants by Atomic Absorption Spectroscopy (AAS). Fresh lubricated oils were purchased from three petrol filling stations in Sokoto.

Description of Generators

The descriptions of generators used in the study are outlined on Table 2.

Table 2: Description of Generators used in the study

Source of lubricating oil	Symbol type	Generator	Manufacture year	Period of oil contact with engine (month)
Virgin Oil	A1 Fresh OO5	Nil		0
	B1 Fresh OSD	Nil		0
	C1 Fresh CGS	Nil		0
	D1 Fresh TR-XT	Nil		0
Used Oil	A2 Used OO5	K750 Kalip	2010	2
	B2 Used OSD	FG Wilson Perking	2007	1
	C2 Used CGS	LS Leroy Somer	2009	1
	D2 Used TR-XT	Mikano	2014	2

Sample treatment

Ashing of the sample

Ashing was carried out to burn off carbonaceous materials in the used and fresh oil samples. A mixture of used and fresh lubricating oils (10.0 g each) and concentrated sulphuric acid (1.0 ml) in a pyrex beaker (250 cm³) was transferred into a round bottom flask and heated in a heating mantle in the fume cupboard for 45 minutes. The carbonaceous materials were burnt off and the metals form sulphate with sulphuric acid which are non-volatile. The charred sulphated part was transferred into silica crucible and was kept in the muffle furnace at 550°C ± 25°C until all traces of carbon were removed. This was indicated by the absence of a charcoal color till the sample was reduced to ash in 4-5 hours (David, 2011) [8].

Preparation of Aqueous solution of the sample

To the ash (1 g) in a crucible, concentrated hydrochloric acid (20 cm³) was added and the mixture heated till the volume reduced to 2-3 cm³. Concentrated nitric acid, HNO₃ (2 drops) was added to the coloured sample to decolorize it. The solution was then transferred to volumetric flask (50.0 cm³) and the crucible was washed thoroughly with distilled water and made up to the mark (Duyek *et al.*, 2000).

Results and Discussion

Results

The results of the AAS analysis carried out on fresh and used oil samples from four generator models of different age bracket are outlined on Table 3 and Figure 1.

Table 3: Wear Metal Concentration (ppm)

Commercial lubricant oil types	Ca	Mg	Zn	Fe	Cr	Ni	Description of oil sample
A ₁	508.00±0.002	300.30±0.005	574.45±0.041	3.95±0.002	12.50±0.033	3.05±0.024	Fresh
B ₁	592.40±0.003	355.70±0.073	1009.90±0.057	3.05±0.003	16.45±0.049	9.40±0.002	Fresh
C ₁	1097.50±0.005	172.10±0.065	1000.81±0.003	2.45±0.005	3.15±0.002	4.65±0.004	Fresh
D ₁	950.25±0.002	281.95±0.041	1001.95±0.002	2.70±0.001	5.15±0.060	10.45±0.006	Fresh

A ₂	778.60±0.010	110.55±0.024	1004.39±0.005	5.50±0.020	34.55±0.041	303.40±0.002	Used oil
B ₂	570.05±0.033	400.55±0.003	989.65±0.041	3.15±0.002	2.40±0.024	26.15±0.006	Used oil
C ₂	934.25±0.004	121.90±0.020	992.20±0.024	3.85±0.004	11.95±0.044	38.20±0.033	Used oil
D ₂	622.05±0.057	385.55±0.033	761.15±0.049	2.10±0.002	7.05±0.016	5.40±0.007	Used oil

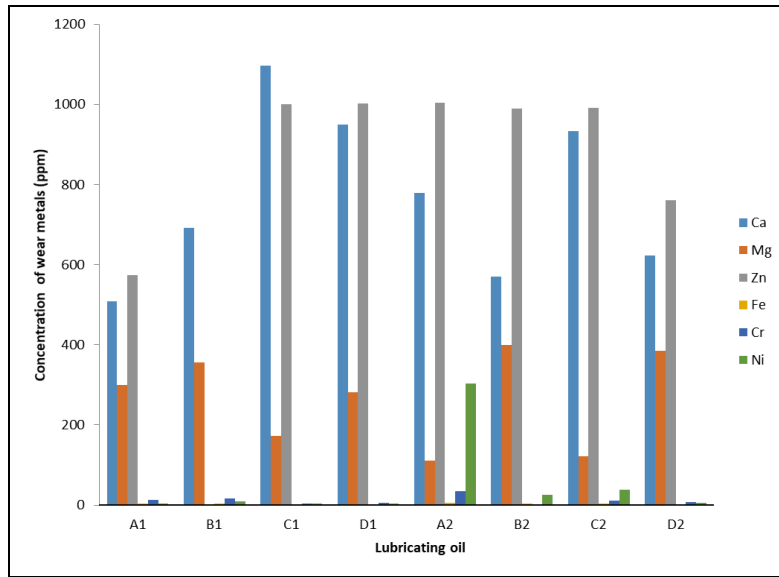


Fig 1: Results of AAS analysis on the various samples of the lubricating oils

Discussion

The result of analyses of the used lubricating oil from A₁, (K, 750 Kalip), B₁, (FG Wilson perking), C₁, (LS Leroy Somer) and D₁, (Mikano) generators of different age brackets were shown in Table 3 and Figure 1.

From the results, the concentration of Ca in fresh oil decreased from 692.40 to 570.05 ppm in type B lubricating oil and from 1097.50 to 934.25 ppm in type C lubricating oil while type D decreased from 950.25 to 622.05 ppm. However, an increase in concentration was observed for A-type lubricating oil. The high concentration of Ca in fresh oil of B, C and D makes them better than A₁ fresh oil because the oils are viscous by virtue of high concentration of Ca and thus prevents wear of corrosive which is exhibited effectively in FG Wilson perking, LS Leroy Somer and Mikano generators. The decrease in calcium concentration also indicated that calcium is consumed as suggested in literature (Casap, 2008 and Maten, 2008) [5, 18] [5].

According to Burke (2001) [4] [4], levels of calcium can be as high as 4000 or 5000 parts per million (ppm) in some high base diesel engine oils, but generally it is found in the 500-800 ppm range in today's gasoline engine oils. The concentration of calcium in both the fresh and the used oil were within the 500-800 ppm range for gasoline engine as reported in the work of Burke (2001) [4] and Quesnel (2001) [4]. Since calcium is an anti-corrosion additive that provides acid neutralization, providing a level of protection against corrosive acid build-up, its concentration would therefore, decrease with increase in the age of the generator. These observations are consistent with the findings in this work.

Magnesium (Mg): Source of magnesium in used oil are usually from detergent additives and some aluminum alloys or in form of magnesium oxide used in the lubricating oils to neutralize acids as reported by Evans (2008). According to Burke (2001) [4, 10] [4], in industrial anti-wear (AW) and extreme pressure (EP) industrial lubricants, the concentration of magnesium is usually found below 150 ppm while in new lubricants and automotive engine oils, its

concentration may be up to 300 ppm or even higher depending on the formulation and base number. From the figure, the concentration of Mg in fresh oil decreased from 300.3 to 110.55 ppm in type-A lubricating oil while type-C decreased from 172.10 to 121.90 ppm. However, an increase in concentration was observed for B and D types lubricating oil. The high concentration of Mg in the fresh oils of A₁ and C₁ makes them better than B₁ and D₁ fresh oils because the oils are more viscous by virtue of high concentration of Mg and they prevent wear or corrosion which is exhibited effectively in A₂ and C₂, K. 750 Kalip and LS Leroy Somer generators respectively. The decreases in Mg concentration also indicated that Mg is consumed as suggested in literature (Casap, 2008; Maten, 2008) [5, 18] [5]. The fact that magnesium was used as an additive metal such as antioxidant in the lubricating oils (Evans, 2008) [10], its concentration is therefore, expected to decrease with increase in the age of the generator. This is so because according to Evans (2008) [10], older systems typically generate more oxidation products than fairly new ones of the same model. The results generated from this work clearly demonstrate the consequential decrease of magnesium with increase in age of the generator due to its role as an additive. The amounts of magnesium in all the generator oil samples were all above the 150 ppm. Similar results were obtained by Hamad *et al* (2003) [14] for used oils.

Zinc (Zn): Zinc is also a metal introduced into the oil from engine oil additives, such as anti-wear additives, oxidation and corrosive inhibitors (Leslie, 2003). According to Quesnel (2001) [16, 20], high values of zinc in lubricating oils are usual from the lubricating oil additive package, e.g. detergent, extreme pressure additives and dispersants used as anti-wear additives, oxidations and corrosion inhibitors (Leslie, 2003) [16]. Figure 1 outlined the levels of wear metal in used engine oil from different brand of generators. It was observed that D₂ Mikano model had the least value (761.15 ppm) of zinc followed by B₂ and C₂, FG Wilson perking and

Leroy Somer models both had 989.65 ppm and 992.20 ppm respectively. The highest concentration of 1004.39 ppm was recorded in A₂, K, 750 Kalip generator. These values are different from those of the fresh lubricating where there was decrease in values for B₁, C₁, and D₁, but increase in A₁.

The concentration of Zinc is expected to be depleted over time because it is usually from the lubricating oil additive package, such as detergent, dispersants, and extreme pressure additives and as explained by Burke (2001)^[4] should usually be below 200 ppm and opined by Fitch (2002). This therefore, indicates that the values obtained for zinc in all the samples were all above the tolerable limits 200 ppm reported by Fitch (2002).

However, the results are in agreement with the works of Hamad *et al.* (2003)^[14] who reported a concentration of 701 ppm for used oils and Casap (2008)^[5] who recorded 1038 mg/kg for fresh oils, but are lower than the results reported in the work of Raymond *et al.* (1975) where they measured 1500 mg/kg Zn and Cotton *et al.* (1977)^[7] who reported a concentration of 2500 ppm Zn.

Iron (Fe): Iron emanates from many places in the engine such as liners, camshafts, crankshaft, valve train etc. (Dolan, 1998 and Burke, 2001)^[4]. The concentration of iron in the used engine oil is usually expected to be higher since iron constitutes the principal element in most mechanical systems and in a lubricant, it is considered a wear metal (Evans, 2008)^[10]. The result of the analysis of iron in the generators suggest the amount of iron in all the samples are less than the 76 ppm reported by Hamad *et al.* (2003)^[14] and the range of 100-200 ppm reported by Fitch (2002). The value of Fe content for all the fresh lubricating oil types are in 2.70-3.95 ppm range which is in line with that reported by Casap (2008)^[5] (2.76 mg/kg) and within the range of (1.5-5.41 mg/kg) reported by Friday *et al.* (2008)^[12]. There is increase in the wear metal Fe in the used oil (Figure 1) which indicates cylinder liners, piston, rings, ball roller bearing wear (Aucelio, 2008)^[2]. However, the Fe content in the used oil ranged from 2.10 to 5.50 ppm which is in line with that reported by (Friday *et al.* 2008)^[12] (3.2-6.2 mg/kg). The concentration of iron in used engine oil sample should fall within 100-200 ppm range.

Very high concentrations are indicative of excessive wear of the engine components Chromium (Cr): Chromium is a wear metal normally associated with piston and rings (William, 2005)^[27] or dirt coming through the air intake or broken rings (Evans, 2008)^[10] AAS analysis of used oil samples do not followed any trend, the highest concentration of 34.55 ppm was found in A₂, K, 750 Kalip generator follow by the C₂ LS Leroy Somer model with a concentration of 11.95 ppm and then D₂ the Mikano model having 7.05 ppm. The least concentration (2.40 ppm) was observed in B₂, the FG Wilson perking. These numbers are substantially lower than those reported in the earlier work of Raymond *et al.* (1975) where 21.00 ppm Cr was found in the used oil Cotton *et al.* (1977)^[7], who reported a concentration of 24.00 ppm Cr in used oil. The concentration of Cr in FG Wilson perking is in conformity with the work of Casap (2008)^[5] and Rahimi *et al.* (2012)^[21] who reported a concentration of 2.5 ppm and 2.20 ppm respectively for used oil while k, 750 Kalip, LS Leroy Somer fall within the acceptable range of 10-30 ppm reported by Fitch (2002). This result is below the findings of Vazquez-Duhalt (1989)^[26] who reported 10 mg/kg Cr and 6.5 mg/kg reported by the Agency for Toxic Substances and

Diseases Registry (ATSDR). The concentration of K, 750 Kalip generators increased from 12.50-34.55 ppm which is an indicative of slight wear of piston and rings.

On the other hand, the value of Cr content for all the fresh lubricating oil types are in the 3.15-16.45 ppm range which is in line with the report of Casap (2008)^[5] (16.0 mg/kg). However, the Chromium content ranged between 3.15 ppm -16.45 ppm, a bit higher than those reported by Anderau *et al.* (1999)^[1] (<3 mg/kg) and in conformity with the work of Friday *et al.* (2008)^[12] who reported a concentration ranged between 3.2-14.1 ppm.

Nickel (Ni): Nickel is a metal usually found in stainless steels and can be an indicator of shaft wear roller or ball bearing wear (John, 2012)^[15]. The result of the analysis of Nickel in the fresh and used SAE 40 lube oil samples for the four generators were reported in Table 1 and figure 1 the results of the used oil showed that Mikano had the least concentration of 5.40 ppm while that of the FG Wilson perking had 26.15 ppm. In the other brands. LS Leroy Somer had 38.20 ppm and 303.40 ppm was obtained in the k 750 kalip model. However, the value 0.48 ppm (Casap, 2008)^[5] and 2.3-8.44 ppm Friday *et al.* (2008)^[5] is lower than 5.40-303.40 ppm obtained for the used oil investigated These results are in agreement with the results reported by Anderau *et al.*, (1999)^[1] (<70 meke). The concentration of Nickel in the fresh oil was, however, 3.05-10.45 ppm. An increase in the levels of nickel is indicative of bearing wear, which if detected early enough, a relatively simple bearing replacement can be made, rather than an overhaul and crankshaft replacement (John, 2012)^[15].

Conclusion

The monitoring of wear metal concentration of the moving parts of a machine is an important indicator of the internal condition of the machine. The effect of engine wear on metal composition of used engine oil was determined. The quality of wear metals in used lubricating oil was determined and compared with unused so as to be able to determine the extent of wear. Based on obtained results it can be concluded that due to depletion of additive the concentration of additive metals have been changed. It has been found that there is generally an increase in concentration of most wear metals (that are not used as additive) in used oil when compared to their fresh corresponding lubricating oil. It has also been shown that considerable concentration of heavy metal like Cr which is injurious to living things and human is contained in the used disposed. Although the value is insignificant high concentration of heavy metals is a signal of danger to life in areas where the used oil is not properly disposed. The study has also been able to predict which components parts of the four generators need attention of machines for physical dismantling of the engine and replacement of the damages engine parts.

This research suggests that the fresh oil produced by manufacturers investigated contain additives required for good lubricating oils.

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