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# DETERMINATION OF TRACE METAL LEVELS IN USED LUBRICATING OIL IN AQUEOUS MEDIUM USING ATOMIC ABSORPTION SPECTROMETRY.

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## ABSTRACT

Used lubricating oil samples from a 125 kVA diesel power generator were put into aqueous solution by carbornization using fuming $H_2SO_4$ followed by heat - assisted digestion in a mixture of Caro's acid (peroxymonosulfuric acid) and concentrated $H_2SO_4$. Flame atomic absorption spectrometric (AAS) analysis of the resulting solutions revealed a linear increase of Mg, Zn and Cr concentrations with the time of running the machine. This is consistent with the normal wear of the moving parts of a machine and the loss of quality of the lube oil with time. This trend is further confirmed by the result of analysis of fresh lube oil samples from the same batch. Unlike the other metals, Cu concentration was found to remain practically constant in both used and unused samples, indicating this element as an additive or a contaminant in the oil. This digestion method was found to be fast (6 samples digested within 1 hour) and effective in eliminating wear particle size effects commonly encountered in this sort of study. An excellent precision was also achieved (up to 0.2 %) through the obvious elimination of chemical interferences and viscosity - induced inaccuracies often associated with direct AAS analysis of oil samples.

**Key Words** : Lube Oils, Wear Metals, Peroxymonosulfuric Acid, Aqueous Solutions, Atomic Absorption Spectrometry.

## INTRODUCTION

Tribological and environmental imperatives make it desirable to carry out regular and reliable monitoring of trace metal levels in used lubricating oils. To avoid catastrophic breakdown due to extensive wear of moving components of an oil lubricated machine, it is necessary to effect periodic checks on the levels of elements such as Cr, Fe, Al, Ni, Cu and Mg which are characteristic of most machine components. Levels of elements such as Ca, Na and Zn, which are typical additives in lubricating oil, could also constitute early warning signals on oil quality degradation due to use. Other elements like Pb, Cd and Hg are also known to be non-biodegradable with enormous impacts on human health ( Pier and Bang, 1980 ) and need to be quantitatively assayed and possibly removed before used oil is discharged into the environment.

Various instrumental analytical techniques have been fully developed and are currently used to characterize such metals in petroleum, its products and oil related materials. These include AAS (Hofstader et al, 1976; Welz, 1985; Nadkarmi, 1991 ), energy dispersive X-Ray fluorescence ( Bhat et al, 1989; Wheeler, 1991 ), particle induced X-Ray emission (Al-Kofahi, 1997), instrumental neutron activation analysis (Oluwole et al, 1987; Duke and Cowles, 1993) and Rutherford backscattering spectroscopy (Racolta, 1995 ). A common problem with these techniques is the matrix effect necessitating more or less extensive sample preparation steps.

A major feature of lubricating oils is the high viscosity value, which constitutes a major hindrance in the exploitation of the otherwise easily applicable direct AAS. A common method for overcoming this problem is dilution with an organic solvent such as methyl iso-butyl ketone (MIBK), kerosine or xylene ( Welz, 1985 ). The aspiration and nebulization process of the resulting sample thus becomes easy. Obviously, comparable organo-metallic salt solutions are then required for the preparation of a calibration curve. However the use of combustible organic solvents could lead to incessant variations of the fuel/oxidant ratio and general instability of the flame conditions. Also, large metallic particulates from extensive wear and tear usually fail to reach the flame, thus escaping detection. To avoid these constraints, we have adapted a method earlier used in the determination of total Nitrogen ( Hach et al, 1985 ) to effect a rapid digestion of used lubricating oil in aqueous medium and subsequently analysed the resulting solution for Mg, Zn, Cr and Cu using an air / acetylene flame AAS and aqueous standard solutions for calibration. The procedures and results obtained are presented in this paper.

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## EXPERIMENTAL

### Sampling and Sample Preparation

Used lubricating oil samples were collected for seven consecutive days from the 125 kVA Rolls Royce diesel power generator of the Centre for Energy Research and Development (CERD), Obafemi Awolowo University (OAU), Ile-Ife, Nigeria after 10 hours operation on each day. Three replicate samples of 20 ml each were successively collected immediately after stopping the engine. Also, three similar samples were taken from the remaining unused oil. After rigorous shaking, aliquots of 0.5g were then weighed from each sample into a Kjeldahl flask. Portions of 4 ml of an analar grade fuming $H_2SO_4$ as were added to each sample inside the flask and the mixture heated on a heating racket at 70°C until charring. This is generally accomplished within 30 minutes. The carbonized samples were then digested by addition of 4 ml Caro's acid (peroxymonosulfuric acid), which is a 4:1 mixture of $H_2O_2$ and concentrated $H_2SO_4$. The acid mixture reacts violently and was therefore added slowly and gradually to the charred sample. When necessary, an additional 4 ml of Caro's acid was added and the mixture heated at 70°C for 30 minutes at the end of which complete digestion was achieved as indicated by a colourless digest. The solution was then air cooled, transferred into a 25 ml volumetric flask and made up to the mark with distilled water.

### Analytical Procedure

Sample analysis was carried out using the ALPHA 4 (ChemTech Analyticals) AAS of the CERD, Ile-Ife. Nigeria. Major working conditions of the equipment have been presented elsewhere (Oladipo et al, 2002) and will not be detailed here. Appropriate operating conditions were employed for each metal determined. In all cases, the conventional air-acetylene flame was used for atomization. Primary absorption lines were used for each element and serially diluted inorganic aqueous standard reference solutions used to construct linear calibration curves by the standard addition technique. All measurements were taken within the linear range of the absorbance-concentration equation (Christian, 1994). Necessary dilutions were done to ensure this in all cases. This was particularly true of Mg for which AAS sensitivity is exceedingly high.

### Determination of optimum fuel/ oxidant ratios:

Among other experimental conditions, the luminosity of the flame is known to exert considerable influence on elemental sensitivity in AAS work (Welz, 1985). This is particularly true of Cr, which incidentally is of great importance in this sort of study - being a key addition to steel (hence a valuable indicator of wear and tear in

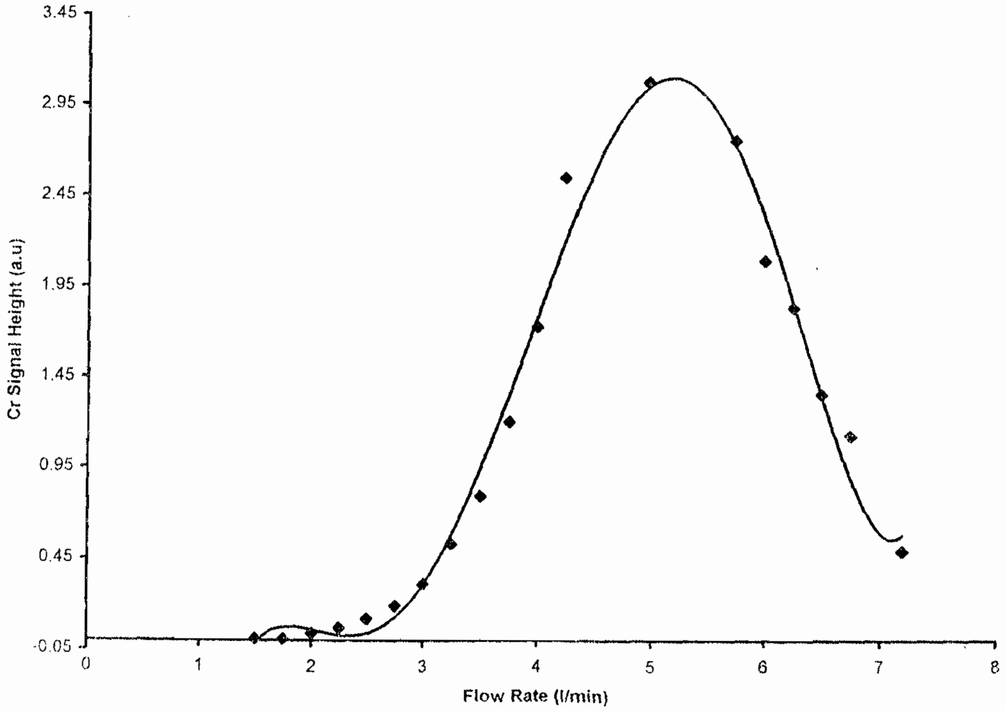

FIGURE 1. Variation of Cr (20ppm) Absorbance Signal Height (arbitrary units) with the Fuel ($C_2H_2$) Gas Flow Rate (l/min.).

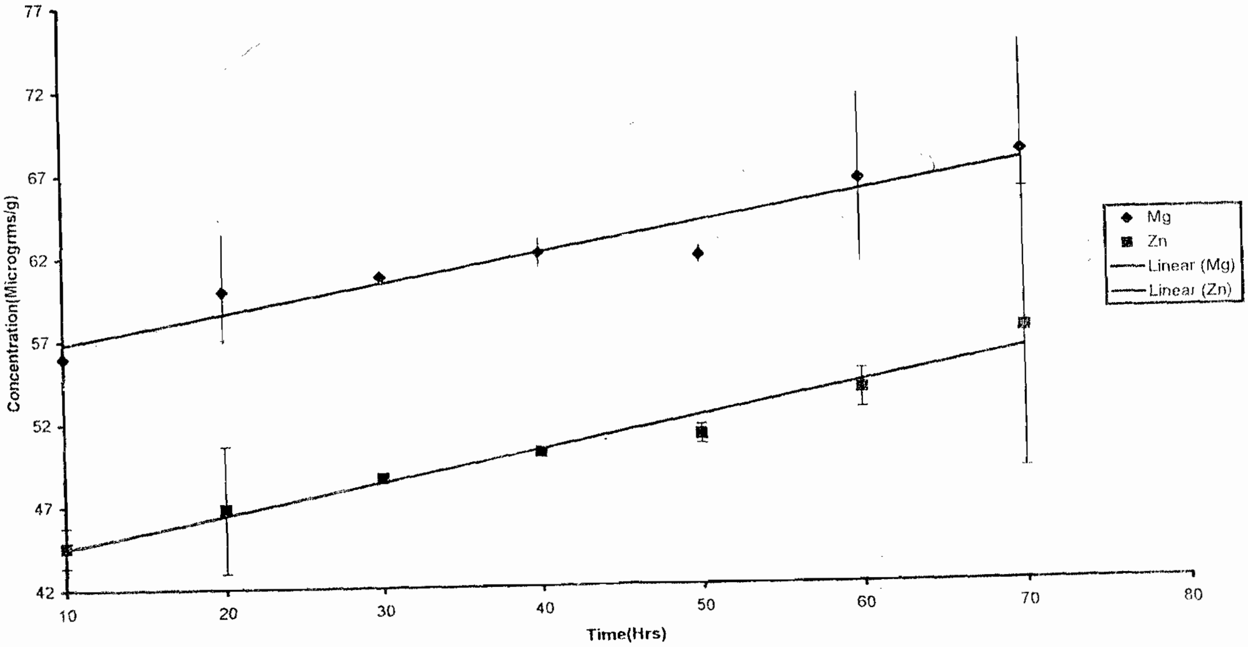

FIGURE 2. Plot of Mg and Zn Concentrations (µg/g) in Used Lube Oil as a function of Generator Operation Time (hr).

engines) and a major toxin. While a transparent flame was found to give maximum sensitivity for all the elements analysed in this work, an insignificant absorbance signal was obtained for Cr in a standard solution of 20 ppm under this flame condition. For this element therefore, the flame luminosity was varied by progressively increasing the fuel ($C_2H_2$) pressure from 1.5 to 7.0 l/min while keeping the oxidant (air) flow rate constant at its maximum value of 13.5 l/min. The Cr absorbance signal height was recorded for the 20ppm solution and plotted as a function of the varying fuel flow rate.

## RESULTS AND DISCUSSIONS

A demonstration of the result of optimization of experimental conditions to achieve excellent sensitivity for the analyte elements is presented in Figure 1 for Cr. A very gradual increase of the 20 ppm Cr signal height is observed between fuel flow rates of 1.5 and 3.0 l/min. After this, the sensitivity increased sharply to reach a maximum at flow rate 5.0 and thereafter fell off rapidly till the experiment was terminated at 7.0 due to excessive noise. All measurements for Cr in the samples and standards were therefore carried out at a constant oxidant flow rate of 13.5 l/min and a fuel pressure of 5.0 l/min

### Variation of Elemental Concentration with Time

The measured concentrations (µg/g) of Mg and Zn in the seven used lube oil samples are plotted as a function of the accumulated time (hr) of generator operation in Figure 2. The corresponding plots for Cr and Cu are presented in Figure 3. The experimental points shown in the two figures represent mean values of the result of consecutive analysis of the 3 replicate samples. A cursory look at Figure 2 shows a close similarity in the variation of Mg and Zn with time. There is a linear increase in the concentration of both elements with the time of operation of the machine. A similar linear increase is also observed for Cr in Figure 3. The concentration of Cu presented no such clear trend as the values alternated between a minimum of 1.00 and a maximum of 1.97µg/g over the whole study period (Figure 3).

Another major feature of these results is the excellent precision (about 0.2%) recorded between the three replicate samples for the 4 analyte elements. Throughout the experiment, only in four exceptional cases (out of a total reading of 28) were relatively poor precisions of about 3-10 % obtained. This could as well be due to experimental errors.

Over the total accumulated study period of 70 hrs, the concentration of Zn increased from 44.57±1.20 to 57.13±4.41µg/g representing a 28 % increase. The Mg level also moved from 55.97±1.32 to 67.80±6.52µg/g - indicating a 21 % increase. Another percentage variation is 190 % increment for Cr whose concentration moved from 1.47±0.02 to 4.27±0.09µg/g. The linear increase observed for these three elements could

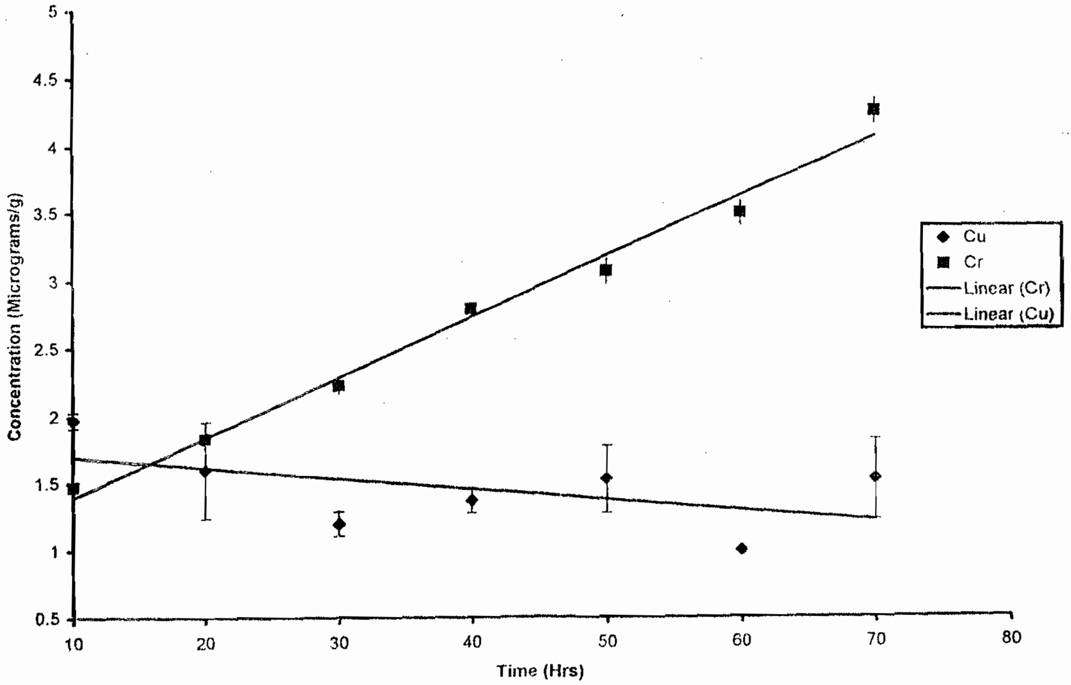

FIGURE 3. Plot of Cu and Cr Concentrations (μg/g) in Used Lube oil as a function of Generator Operation Time (hr).

be attributed to their systematic introduction into the lube oil from the normal wear occurring on the surface of the engine. Zn is normally used in Neoprene seals and in galvanized piping, Mg in cylinder liners and Cr in seal ring and cylinder liners (Nardkarni, 1991). The fact that the concentration of Cu remained practically constant over the study period is an indication that the engine casing is neither made of Cu nor of a Cu - containing material.

## Comparison of Used and Unused Oils

Mean concentration values of the four elements in three replicate samples of unused oil from the same batch are presented on Table 1. The overall mean values of the concentrations of the 4 elements in the 7 used oils are also presented on the same Table for comparison. In agreement with the trend noted earlier, the Cu concentration in the unused oil (1.42±0.08μg/g) is practically the same as the mean value in the used oils (1.46±0.02μg/g), thus confirming this element as a contaminant or possible additive to the base oil. Cr has a concentration value of 0.11±0.01μg/g in unused oil compared to an average value of 2.74±0.06μg/g in used oil samples - representing a 25 times increment. Similar observation holds for Mg and Zn which have base concentrations of 4.50±0.20 and 5.72±0.06μg/g (or increment factors of 14 and 9) respectively in unused oil. The implication of this is that though the increasing trend of these three elements with time is definitely due to their introduction into the lube oil as micro-particulate

**Table 1 Overall Mean Values (μg/g) of Mg, Zn, Cu and Cr in Seven Used Lube Oils as Factors of Their Concentration Values in Unused Lube Oil.**

| Element | Overall Mean Conc. in 7 Used Oils | Concentration in Unused Oil. | Used/Unused |
|---|---|---|---|
| Mg | 62.11±2.55 | 4.50±0.20 | 13.8 |
| Zn | 50.23±1.65 | 5.72±0.06 | 8.8 |
| Cr | 2.74±0.06 | 0.11±0.01 | 24.9 |
| Cu | **1.46±0.03** | 1.42±0.08 | 1.03 |

wears from the engine surface, a certain proportion (between 4 and 7 %) is also present in the base oil as additives. This is hardly surprising since Zn as dialkyldithiophosphate, dithiocarbamates or phenolates is often added to oil as antioxidants, corrosion inhibitors and anti-wear agents. Magnesium sulfonates are detergent inhibitors while chromium salts are grease additives.

## CONCLUSIONS

Rapid digestion of lube oil by Caro's acid and $H_2SO_4$ followed by AAS analysis for Mg, Zn, Cr and Cu has been shown to be useful in monitoring engine wear rates and oil quality degradation. The use of the aqueous solution that results from this digestion process serves to enhance the precision of the method by eliminating organic chemical interferences and flame instabilities. Efforts are on in our laboratory to extend the study to more hazardous elements such as Cd and Pb as well as engine - specific metals like Fe and Al.

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