DETERMINATION OF WEAR ELEMENTS IN TRACTOR LUBRICATING OIL: COMPARISON BETWEEN AAS AND ICP-OES TECHNIQUES

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ABSTRACT

Determination of appropriate tractor engine lubricating oil change based on hours of operation or distance travelled lead to wastage of resources/ premature failure of machine components as some tractor operators unnecessarily use to over throttle engines during clutching in order to impress others. Oil analysis has been used to assess the overall stress being encountered during operations with varied torque/speed characteristics. This study was conducted to determine the presence and level of wear elements in engine lubricating oil of tractors using inductively coupled plasma and optical emission spectroscopy (ICP&OES) technique and comparing the results with earlier results obtained using atomic absorption spectroscopy (AAS) on the same samples. The comparison between AAS and ICP&OES was based on analysis of variance (ANOVA) and Duncans Multiple range test (DMRT). The two statistical methods show significant differences between the tractors in five elements (Zinc, Chromium, Nickel, Copper and Iron) using AAS versus seven (Chromium, Nickel, Lead, Copper, Iron, Cobalt and Manganese) with ICP&OES. The ICP&OES results precisely showed that tractor number six was the most mishandled by its operator. The study recommends regular monitoring of wear elements using ICP&OES technique over AAS.

KEYWORDS: Metal wear, lubrication oil, lubricant additive, wear monitoring.

1. INTRODUCTION

The tractor engine develops power by converting the chemical energy contained in fuels into mechanical and other forms of energy. Tractor operators' behaviors play a vital role in ensuring proper maintenance and availability of machines. A consistent quality assurance program is necessary to avoid performance issues in vehicle engines and inorganic constituents in the final product can promote residue build up in the engine, cause corrosion and ultimately affect engine life (Iqbal et al., 2010). Since metallic elements in fuel are undesirable even at lower concentrations, their determination in fuel is necessary to evaluate fuel quality, to see their effect on auto engines, and to control environmental pollution.

The purpose of oil test is to measure the concentration of wear metals (machine health), oil additives (oil health) and contaminants. These parameters are determined by the concentrations of various elements from the periodic table. ICP&OES measures these elements and they fall into the various categories such as copper which is wear metal, calcium which forms part of an oil additive or silicon which is a constituent of dirt (contaminant). Note that quite a few elements can belong to more than one category as shown in Table 1.

Element	Category		
	Wear	Contaminant	additive
Aluminum, Al	Х	Х	
Boron, B		Х	Х
Calcium, Ca		Х	Х
Copper, Cu	Х	Х	
Chromium, Cr	Х		
Iron, Fe	Х	Х	
Lead, Pb	Х		
Magnesium, Mg		Х	Х
Molybdenum, Mo	Х		Х
Phosphorous, P		Х	Х
Potassium, K		Х	
Silicon, Si		Х	Х
Sodium, Na		Х	Х
Tin, Sn	X		
Zinc, Zn	X		Х

Table 1: Categorization of elements found in engine lubrication oil analysis

Source: Johnson and Spurlock, 2009

By far the biggest category is the wear metals, of which iron is the most common wearing element (Evans, 2012). Oil analysis by X-ray fluorescence spectrometry (XRF) is very fast but limited in concentration range. ICP&OES has the concentration range necessary to determine additives, wear metals and contaminates in oils (Hilligoss and Wee, 1999). A study (Hilligoss and Wee, 1999) compares the performance of ICP&OES with XRF for 5 elements (calcium, magnesium, phosphorus, sulfur and zinc) commonly determined by XRF and found that the ICP&OES results show good agreement with XRF on the high concentration elements in the oils tested.

Just as humans undergo a battery of tests to understand the state of their health, conducting oil analysis provides similar insight into the health of a machine. Subtle changes in the chemical health of the oil/lubricant and in the cleanliness of the machine's sump as well as increases in the types and concentrations of wear metals, point to solvable problems. When the analysis is conducted systematically, the relative state of the machine health can be observed. Armed with information about the machine's changing health, the machine owner can adjust operating and maintenance practices to protect the machine's long term usefulness.

As is the case with human health monitoring, there are hundreds of tests that could be recommended to deliver a particular piece of the puzzle representing overall health. A key to health management, whether human or machine, is understanding which test to use and what to look for within that test.

There are 702 discrete petroleum and lubricant tests listed in the 2009 ASTM (American society of testing and materials) catalog (Johnson and Spurlock, 2009). Some of these tests tell a broad characteristic about the test specimen, and some tell a narrow concern. In addition to the ASTM methods, there are several other standardization organizations providing test methods, including Din (German Institute for standardization), ISO (International Standards Organization), SAE (Society for Automotive Engineers), API (American Petroleum Institute and IP (Institute of Petroleum test methods). Each has standards and test methods useful for measurement of variety of lubricant properties.

Any sample that can be dissolved or digested into an aqueous solution can be analysed with ICP&OES technique (www.els.co.nz). The ICP&OES has many benefits for the analysis of oils. The samples are simply diluted, in kerosene or other suitable solvent, and aspirated directly into the ICP&OES. The ICP&OES analysis is very fast, and gives accurate, precise results (Johnson, 2010).

The analytical principle used in the ICP&OES system is optical emission spectroscopy. A liquid sample is nebulized and then vapourized within the argon plasma in same way as the Inductively Coupled Plasma-Mass Spectroscopy (ICP-MS). Unlike the Mass Spectroscopy however, the atoms and ions contained in the plasma vapour are excited into a state of radiated light photon emission. The radiation emitted is passed to the spectrometer optics, where it is dispersed into its spectral components. From the specific wavelengths emitted by each element, the most suitable line for the application is measured by means of a charge couple device (CDD). This instrument is capable of determining the concentrations of 40 to 70 elements simultaneously to very low detection limits (ppm to ppb).

ICP&OES provides the highest and lowest levels for 29 elements which include Al, As, B, Bi, Ca, Cd, Co, Cr, Cu, Fe, Li, Mn, Ni, P, Pb, Se, Sr, Ti, Tl, V, and Zn (www.wearcheck.co.za). The ICP&OES technology allows for very low-level determination and uncertainty of many elements. Other strengths of ICP&OES technique include (ELS, 2011):

- i) High sensitivity
- ii) Large dynamic range from detection limit to the maximum working concentration (order of 8 compared to 2 in graphite furnace atomic absorption)
- iii) Short elemental concentration determination time
- iv) The ability to measure individual isotopes

The ICP&OES is most moderate in terms of cost versus performance consideration when compared to flame atomic absorption spectroscopy (AAS) and ICP&OES-MS (Sarojam, 2010) and precision of its results confirmed by ICP&OES-MS (UWLAB, 2012).

In order to determine all possible elements present or being produced in engine combustion and lubricating processes, the use of highly sensitive analytical technique is required (Iqbal et al., 2010). Hence the objective of this study was to analyse the samples earlier analysed with AAS (Ahmad et al., 2012) using ICP&OES technique and compare the two results for eight elements (Co, Cr, Cu, Fe, Mn, Ni, Pb and Zn).

2. MATERIALS AND METHODS

2.1 Experimental Procedure

Ten tractors from Refuse Management and Sanitation Board (REMASAB) concerned with refuse collection and disposal in Kano Metropolitan area of Kano State of Nigeria were used for elemental engine oil analysis. The lubricating oil from each tractor was sampled at an interval of one week from the date of oil change until it is drained out during routine oil change. On the day of sampling, the tractor engine was warmed up in the morning before starting the day's operation for about five minutes to ensure proper mixing of the engine oil throughout the various engine components. After warming, the engine is stopped and the area around the bottom plate nut thoroughly cleaned and gently loosened to collect about ten ml of the engine oil into plastic containers. This small quantity may not cause shortening of the oil level below the lower mark to warrant topping up. In this kind of experiment, topping up use to dilute the oil concentration and lead to wrong inference after analysis. The importance of recording oil top-ups needs to be emphasised to the operators.

This was repeated within a period of two months for all the tractors. Some tractors had two, three and even four samples taken between two consecutive oil changes. A replication is the interval between two consecutive oil changes. A total of sixty one samples were collected for the ten tractors within the two oil change periods. The samples were labelled in three number codes (1:1:1, 7:2:3). The first number indicating tractor, second number indicating oil change and third number indicating sample number within the oil change interval.

The above samples were earlier analysed with AAS at Soil Science laboratory of Faculty of Agriculture, Bayero University, Kano. The AAS machine (Buck 210 VGP) was warmed up for 30 minutes and the hollow cathode lamp of respective metal of interest at a time was set with wavelength of maximum absorption as directed in the manufacturer's instruction guide. The blank, calibration standards, and digested samples were aspirated separately and their absorbencies recorded. Calibration curves of the standards were plotted and regression equations obtained. The concentrations of the analytes/samples in mg/dm³ were computed by either extrapolation from calibration curves or obtained as dependent variables in the calibration equations.

Similar analysis was done on the same samples using ICP&OES technique with a machine (PerkinElmer Optima 7300 DV) at Chemical and Environmental Engineering Department, Universiti Putra Malaysia. The results obtained were analysed using SAS procedures and ANOVA table and DMRT rankings generated for comparison with AAS results.

2.2 Specification and Operating Parameters of ICP&OES Machine

The operating conditions for the equipment used in this study are given in Table 2.

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Plasma gas flow	15 L/min
Auxillary gas flow	0.2 L/min
Nebulizer gas flow	0.6 L/min
RF power	1450 watts
Plasma view	Axial or Radial
Read delay	90 sec
Read parameters (s)	2.0 min, 5.0 max
Peristaltic pump flow rate	1.8 mL/min
Spray chamber	Cyclonic
Nebulizer	Low flow GemCone
Injector	Alumina, 2.0 mm i.d
Sample tubing	Standard 0.76 mm i.d
Drain tubing	Standard 1.14 mm i.d.
Quartz torch	Single slot
Sample capillary	Teflon® 1 mm i.d
Replicates	3
Resolution	Normal

Table 2. Optima 7300 DV Operating Conditions

2.3 Measurement by ICP&OES

2.3.1 Instrumentation

The measurements were performed using the PerkinElmer® Optima[™] 7300 DVICP&OES- OES instrument (PerkinElmer, Inc. Shelton, CT, USA) equipped with WinLab32[™] forICP&OES Version 4.0 software for simultaneous measurement of all analyte wavelengths of interest. The Optima 7300 DV has been optimized to provide high speed analysis. By combining an SCD detector and an echelle optical system, the Optima 7300 DV can measure all elements simultaneously. Its wavelength flexibility allows the end users to easily add new elements as their program needs change. The measurement procedure as outlined by U. S. EPA 200.7 requirements for instruments is given in Table 3.

Check Code	Check Name	Purpose	Frequency of Check	Specified Limits
ССВ	Continuing Calibration blank Checks	Check calibration validity	After calibration, after every 10 analyses and at the end of analyses	<idl< td=""></idl<>
LRB	Laboratory Reagent Blank	Checks the laboratory reagents and apparatus for possible contamination	1 per batch	<2.2 MDL
LFB	Laboratory Fortified Blank	Checks the analyte recovery of spiked blank	1 per batch	85-115% recovery
LFM	Laboratory Fortified Matrix	Checks the analyte recovery in sample matrix	10% of total samples	85-115% recovery
QCS	Quality Control Standard	Checks the accuracy of the calibration by analyzing a second source standard	Post calibration	95-105% recovery
IPC	Instrument Performance Check	Checks the accuracy and drift by analyzing a standard as a sample.	Every 10 analyses and at the end of analyses	95-105% immediately after calibration, 90- 110% thereafter
SIC	Spectral Interference Check	Checks the presence of spectral interferences	Periodically	No criteria specified
CRM	Certified Reference Material	Checks the accuracy of the developed method	Immediately after calibration	Should be analysed whenever available

Table 3. U.S. EPA Method 200.7 Requirements

Source: Sarojam (2010)

The PerkinElmer S10 Autosampler was used for high throughput and automated analysis. The autosampler automates standard and sample introduction for instrument calibration and sample analysis.

2.3.2 Initial Performance Demonstration

An Initial Performance Solution (IPC) was run (for all analytes at the levels of their respective standards used) immediately following calibration and the recoveries were found to be within the limits of 89.5-105% specified by EPA (Table 4) with the exception of Copper which has a recovery of -64.29. This is an important parameter used to evaluate the performance of the instrument system with respect to a defined set of method criteria. Precision (%RSD) was also monitored to ensure the short term stability of emission signals.

Analyte	IPC Avg.	%	% RSD	Monitored
	Conc.	Recovery		wavelength
	(mg/L)			(nm)
Со	0.004	100.01	0.94583333	267.7160
Cr	0.018	86.08	2.06683333	228.616
Cu	-1.635	-64.29	0.71983333	327.393
Fe	0.344	89.69	0.73183333	238.204
Mn	0.466	97.39	3.45166667	257.610
Ni	0.486	97.99	1.936	231.604
Pb	0.042	97.92	44.1398333	220.353
Zn	0.032	99.00	0.80783333	206.200

2.3.3 Internal Standards

All samples were spiked with 1.5 mg/L of yttrium and 2.5 mg/L of tellurium. The spiking solution was made from 1000 mg/L single element stock solutions.

2.3.4 Calibration

The calibration blank and standards were prepared in 1% nitric acid. Calibration was performed using a calibration blank and a single standard containing all elements at 1 mg/L. The calibration standard was prepared from a combination of single element and multi-element stock solutions, all containing elements at 1000 mg/L.

2.4 Data Processing after ICP&OES Measurement

2.4.1 Data Handling

All data obtained from the Optima 7300 DV was collected using the WinLab32 software loaded on a desktop PC attached to the instrument. Analytical results were computed using the WinLab32 software and exported into Microsoft Excel. The text and data tables used in this report were created using Microsoft Excel and Word.

2.4.2 Data analysis

Data were analysed using computer programmes (SAS 2009 version 9.2) to determine the relation between various measures made during the study.

3. **RESULTS AND DISCUSSION**

The summarized comparison between AAS and ICP&OES results on elemental basis is shown in Table 5 for the eight common elements found present in the ten tractors' engine lubricating oil.

	<u>parison or re</u>			
Element	AAS	ICP	TRACTOR(S) NO(S)	
			WITH HIGHEST	
			CONC. For ICP&OES	
			RESULT	
Zinc	S	NS	T6	
Chromium	S	S	T6	
Nickel	S	S	T6	
Lead	NS	S	T6	
Copper	S	S	T6	
Iron	S	S	T6	
Cobalt	NS	S	T6	
Manganese	NS	S	T6	

Table 5: Comparison of results between AAS and ICP&OES

Key: S- Significant difference between the tractors for the element.

NS- Not significant difference between the tractors for the element

It can be seen from Table 5 that only Zinc showed significant difference under AAS but not significant with ICP&OES even though it has the second highest recovery rate of 99% (Table 4). Zinc is found in chemicals used to make antiwear, anti-oxidant, detergent and corrosion inhibitor additives. Zinc is alloyed with copper to make brass so it can be evident as a wear metal (Evans, 2012). Thus, not a major constituent of principal wearing components of the engine such as liners, pistons, rings (Figure 1) and bearings.

All other elements maintained significance between AAS and ICP&OES or an improvement in analysis sensitivity of ICP&OES over AAS. Lead, Cobalt and Manganese were not significant under AAS but showed significance under ICP&OES. Thus, the ICP&OES technique has added two more elements as criteria in augmenting the hypothesis that variation exists between tractors due to attitudinal behaviors of tractor operators.

This sensitivity has also produced the most operator attitudinal behavioral contribution to the tractors differences in elements concentrations. In the AAS results (Ahmad et al., 2012), one cannot single out the worst operator as tractor number one (T1) recorded highest element concentration in Zn, T8 (Chromium), T9 (Ni and Pb), T6 (Cu and Co) and T4 (Fe and Mn). From Table 4, tractor number 6 recorded the highest concentrations in all eight elements! Thus maintenance management strategies should include aspects of personnel behavior and attitudes in discharging duties as machinery operators are also responsible for following applicable laws, keeping logs of their activities, and making sure that their equipment is in good working condition (BLS, 2012). This has been buttressed in computerised maintenance management system (CMMS) (Tuomo Honkanen, 2004) where it was stated that the resulting maintenance systems seem to be a heterogeneous combination of methods and systems in which the integrating factor of the information and business processes is the maintenance personnel. The information in the maintenance systems goes through these human minds forming an organisational information system and creating a high reliance on the expertise of the maintenance staff.



Figure 1: Piston, ring and liner wear (Source: www.wearcheck.co.za)

A study (Adekoya and Otono, 1990) has attributed the relatively higher repair costs of tractors to misuse by operators, among other factors. Also, the DMRT for ICP&OES equipment produced only two categories (A and B) (Table 6) while the AAS equipment result (Ahmad et al., 2012) had four categories (A, AB, BC and C) making clear distinction not easy.

Hours of operation by each tractor may contribute to these differences. However, if the Duncan Multiple Range Test (DMRT) for Chromium (Table 6) is looked at, tractor numbers 6, 3, 5 and 7 are having same number of samples (with seven each) which indicates been used for similar periods of time during the experiments and tractor number 1 with only four samples having the least but not significantly different from tractors number 3, 5 and 7.

Tractor	Chromium element	
No.	Mean	Ranking ^a
1	0.02825	В
2	0.03180	В
3	0.05100	В
4	0.04333	В
5	0.03743	В
6	0.09029	А
7	0.02900	В
8	0.03083	В
9	0.03533	В
10	0.04000	В

Table 6: DMRT of means of ten tractors for Chromium element

^aMeans with similar letters are not significantly different at 5% level.

4. CONCLUSIONS AND RECOMMENDATIONS

4.1 Conclusions

This study conducted an analysis of Steyr tractor engine lubricating oil using ICP&OES technique on samples previously analysed using AAS and compared the results for eight common elements. From the study, the following conclusions can be derived:

- i) That ICP&OES technique has shown its higher sensitivity and precision over the AAS.
- ii) Out of eight elements analysed from the oil samples, seven showed significant differences between the tractors against five for AAS.
- iii) Only Zinc element showed variance in the trend by being not significant with ICP&OES and significant under AAS
- iv) ICP has clearly shown that tractor number 6 was highly mishandled by having highest concentrations in all the eight elements analysed.
- v) Operator attitude may be playing significant contribution in the deterioration of machines.

4.2 Recommendations

The work presented in this study has clearly shown that full machinery/tractor management involves determining factors/elements leading to machine health, oil health, level of contamination/environmental pollution and operator behavior in discharging their duties. It is therefore recommended that:

- i) Comprehensive analysis of likely elements that would lead to complete diagnosis of machinery health is conducted on regular basis.
- ii) Tractor maintenance management should be extended to operator attitudinal/welfare assessment as all investment in technical infrastructure could be wasted by a psychologically depressed or irresponsible staff.

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