Inductively Coupled Plasma Optical Emission Spectrometry in Effective Condition Based Maintenance Engineering Plan

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Abstract— The Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES) is a powerful tool for the determination of many wear down elements in a variety of different sample matrices. The Sri Lanka Navy commenced analysis of used lubricating oils in on-board main machineries and shore-based generators since the year 2017 which assists to implement Condition Based Maintenance (CBM) philosophy in the Sri Lanka Navy as a vital component in the P-F curve of machinery maintenance reliability. As per ASTM D 5185, the testing has been carried out. Results of the analysis capture only the particle sizes below 10 microns where the elements are necessary to be oil-solvable. In this, soluble residues are not counted. The paper is focuses on appraising the process practiced by the SLN to study the elemental behaviour of machineries fitted on-board to support the CBM development plan. The annual oil condition monitoring schedule has been published, and sample testing is done according to the promulgated directives. The findings of the analysis are plotted against each of the machinery, and the machinery health is monitored accordingly. Several failures were pre-identified and preventive actions were initiated. The numerical results against each similar type of engines with respect to the running hours of the machinery are compared and specific limitations against each make/model are identified. This will enable us to find the safe operating parameters as a baseline measurement and to promulgate the threshold limits.

Keywords: ***inductively coupled plasma optical emission spectrometry, oil analysis, condition monitoring***

I. INTRODUCTION

Machinery maintenance is a vital role of an Engineer which involves measuring, servicing, carryout functional tests, overhauling, repairing, etc. Various maintenance categories have been introduced to optimize the schedules according to the industrial /user requirements. The Condition Based Maintenance is a strategy that monitor the real time condition of the machinery/equipment which is an asset that decides the real maintenance requirement. Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) is a widely used analytical tool that is used globally as a versatile method of inorganic analysis. This is used as one of the main components of Condition Based Monitoring in SLN Oil analysis for wear down analysis. This will identify and quantify the element presence in the provided oil sample.

A. The Operating concept of ICP-OES

A plasma is a gas, in this case argon, which contains a significant number of argon ions. The plasma is formed by seeding the argon gas passing through a plasma torch with electrons. The electrons are accelerated and collide with argon atoms releasing more electrons and forming argon ions. Elements, in the form of atoms, are introduced into the plasma. A proportion of these atoms will be become ionized within the plasma. When an atom or ion is excited within the plasma, its electrons jump from a lower to a higher energy level (Figure 1). Upon relaxation of these electrons to their initial 'ground' state, energy is emitted in the form of photons. The emitted photons possess wavelengths that are characteristic of their respective elements.

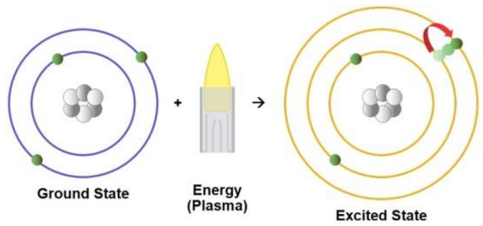


Figure 1. Excitation of an atom by a Plasma

One element can have multiple electron excitations and relaxations; therefore, it can have wavelengths with multiple characteristics. However, during the analysis, the Analyst will select the most suitable wavelength which will not interfere with any of the other elements that exist in the provided oil sample. An example of an emission spectrum for calcium is shown in figure 2.

Figure 2. Emission of spectrum of Calcium in visible range

The main aim of this wear down analysis is to formulate safety margins for machinery fitted on board fleet units and also to identify unforeseen failures prior major failures. The oil analysis spectra assessment is to be performed during each oil draining interval, major repairs, major routines or installation of new equipment to understand the elemental behaviour of specific regimes.

II. METHODOLOGY

The wear elements presence in provided oil samples are tested through ICP-OES. Following methods are identified as the essential components of the testing;

A. Sampling & Sample / Equipment Preparation

The objective of sampling is to obtain a test specimen that represents the entire quantity. Therefore, the sampling procedure is done according to the laid down ASTM D 4057 standard.

The samples were prepared as per the Laid down procedure in ASTM D 5185. The following elements are tested by ICP-OES and results were recorded accordingly. The elements determined and tested wavelengths are as follows;

Table 1. Elements Determined and Suggested Wavelengths

Element	Wavelength, nm
Aluminium	308.22, 396.15, 309.27
Chromium	205.55, 267.72
Copper	324.75
Iron	259.94, 238.20
Lead	220.35
Nickel	231.60, 227.02, 221.65
Silicon	288.16, 251.61
Tin	189.99, 242.95

As an example, the Figure 3 indicates how the elements will interfere against other elements presence in the sample. It is visible that Vanadium (V), Antimony (Sb), Barium (Ba), Radium (Ra), Tungsten (W), Tantalum (Ta) elements interfere with the Iron (Fe) (252.851) element. However, that can be neglected due to none of the wear elements which need to be tested are present in the interference list.

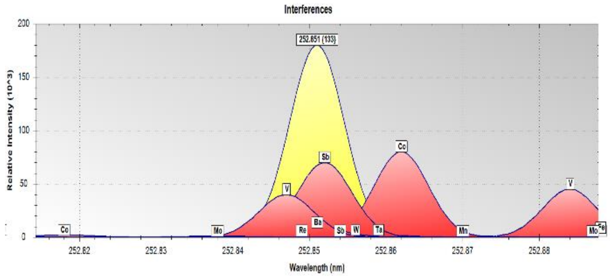


Figure 3. Interference between elements

However, in the ICP-OES plasma temperature is above 9000 K which is considered as higher in temperature, which will help to chemical interferences, This will be sufficient to break down the most spices into the atoms or irons for excitation and subsequent emission.

B. Calibration

The instrument calibration is one of the most important factors in which the linear range must be maintained. This is performed prior to each analysis. At the beginning of the analysis blank, three specimens of Oil Analysis standards were prepared.

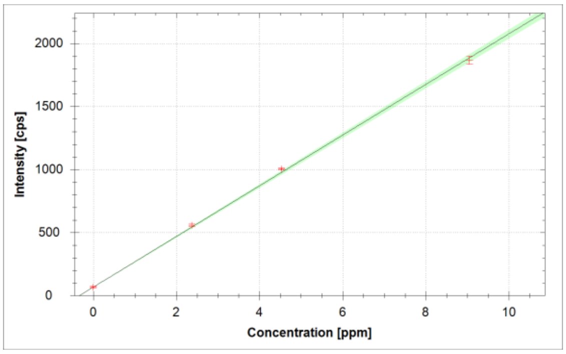
The concentration of the Oil Analysis standard was 1000ppm. Therefore, three specimen samples will be prepared to perform three-point calibration.

Following mathematical calculation was used to prepare the specimen samples.

$$c_1 \text{ x } V_1 = c_2 \text{ x } V_2$$

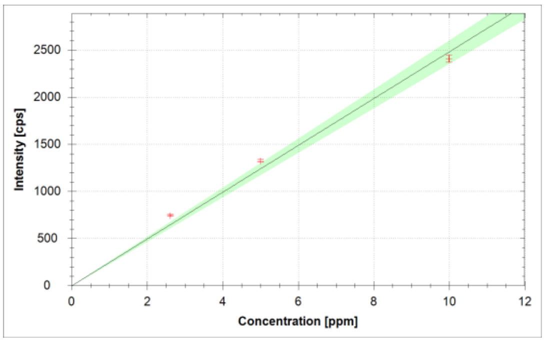
where,
c_1 = Initial concentration or molarity
V_1 = Initial volume
C_2 = Final concentration or molarity
V_2 = Final volume

Therefore, 2.5 ppm, 5 ppm and 10 ppm sample specimens are prepared and by running the samples in ICP-OES as per the procedure, the calibration curves were plotted as per Figure 4 to Figure 8. Therefore, the linearity will confirm the calibration process.



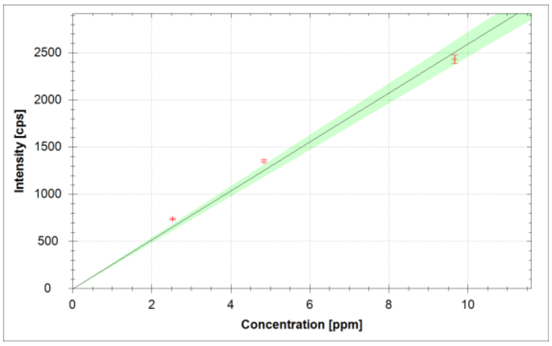
f(x) = 200.8345*x + 67.7000
R^2 = 0.9993
LoD = 0.0817 ppm

Figure 4. Calibration curve of "Al" element



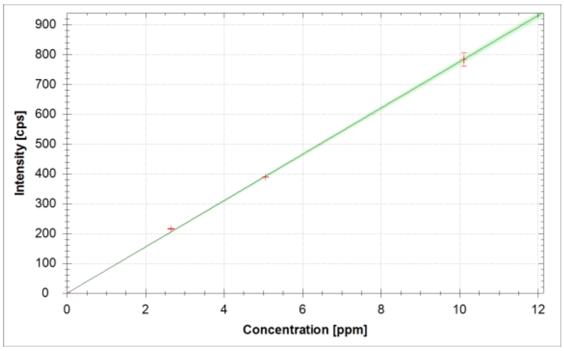
f(x) = 209.2875*x + -15.6444
R^2 = 0.9988
LoD = 0.0526 ppm

Figure 5. Calibration curve of "Cr" element



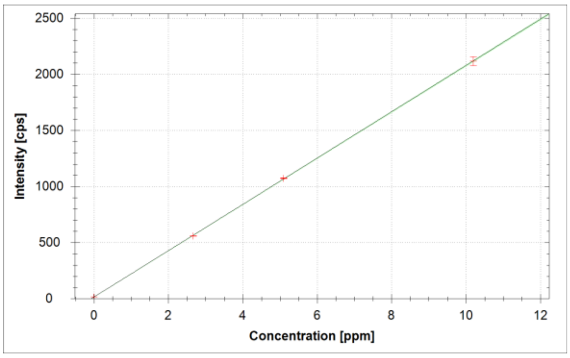
f(x) = 259.3706*x + -4.2986
R^2 = 0.9929
LoD = 0.0195 ppm

Figure 6. Calibration curve of "Cu" element



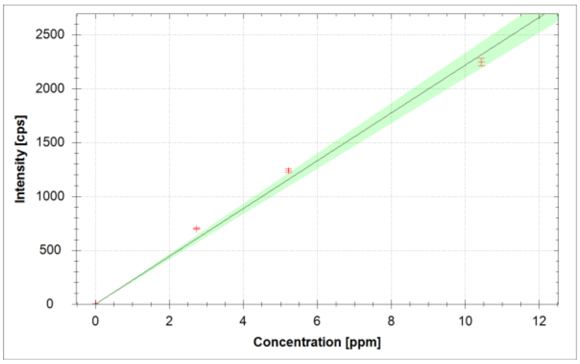
f(x) = 77.5786*x + -0.1661
R^2 = 0.9996
LoD = 0.0554 ppm

Figure 7. Calibration curve of "Pb" element



f(x) = 206.3070*x + 15.0743
R^2 = 1.0000
LoD = 0.0114 ppm

Figure 8. Calibration curve of "Sn" element



f(x) = 221.7207*x + 0.1000
R^2 = 0.9923
LoD = 0.0215 ppm

Figure 9. Calibration curve of "Fe" element

If the R^2 value is closer to 1 the calibration is considered as accepted. If the calibration curve is not passing through the origin or the blank shows some amount of count, then there is a possibility of having low concentration or having analyte in the sample which will show negative results if the blank is different or use a different weight/volume of blank. Mostly it is recommended to have a low Limit Of Detection (LOD). However, if the analysis results are lower than the LOD value, those results should not be considered. If the results are not large negative numbers that indicate the element(s) which are measured is not present in the particular oil sample.

Basically, the calibration curve is plotted to understand the relationship between concentration and intensity.

C. Testing frequency

In order to standardize the oil sample testing intervals (except specific cases), an oil analysis schedule has been introduced which recommends the time interval for oil sample testing for ships/craft (main engines, gear boxes and generators). Therefore, the end-users will forward the oil samples as per the prescribed schedule.

D. International Standards Followed

The ASTM D 5185 method "Standard Test Method for Determination of Additive Elements, Wear Metal, and Contaminants in used lubrication oils and determination of selected Elements in base oils by Inductively Coupled Plasma Optical Emission Spectrometry (ICP-OES)" are practised as the international standardized test method.

III. RESULTS AND DISCUSSION

The focus was mainly placed on the wear metal concentrations of Fe, Cu, Al, Si, Pb, Cr, Sn, Ni elements in the oil samples to prevent unforeseen failures. Basically to find out the wear metal presence in lubricating oil samples.

The analysis was carried out for 16 cylinder V type reciprocating engines as per the promulgated schedule. Both the engines had clocked approx. 40000 Hrs. All the wear metals were found within acceptable regimes in the initial stage of analysis and it was noticed that the "Cu" elemental concentration in Port Main Engine was abnormal compared to Stbd Main Engine. Therefore, it was recommended to flush the entire lubricating oil system of Port Main Engine and re-fill with fresh oil to address this abnormality.

Port Main Engine

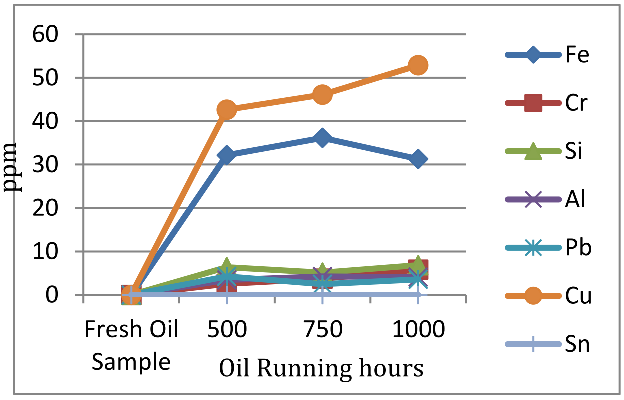


Figure 10. Variation of element concentrations in the lubricant oil as a function of engine operating hours in Port Main Engine

Stbd Main Engine

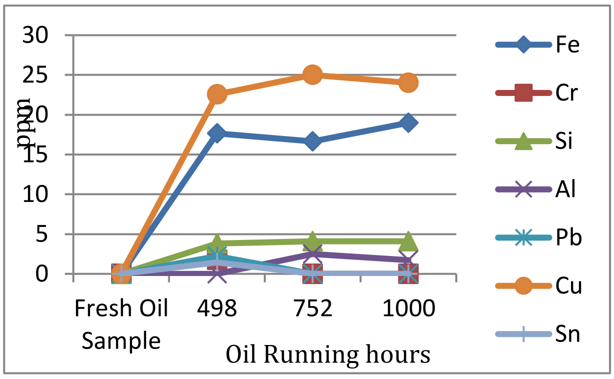


Figure 11. Variation of element concentrations in the lubricant oil as a function of engine operating hours in Stbd Main Engine

The general standard guidelines for this type of engine series elemental concentration are as follows;

Port Main Engine

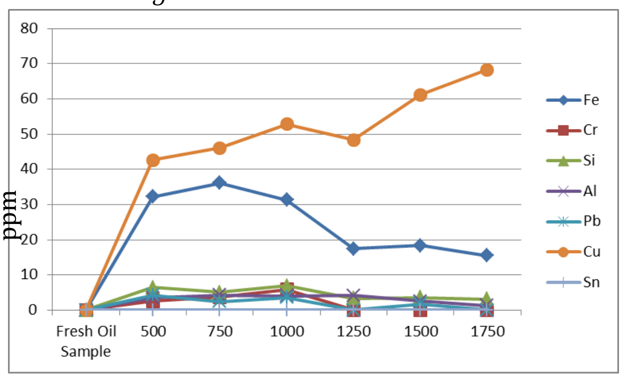


Figure 12. Variation of element concentrations in the lubricant oil as a function of engine operating hours in Port Main Engine

Comparing results with this particular series of engines, Port Main Engine values were beyond the general referred guidelines as well as the previous trend pattern.

The wear rate of "Cu" element concentration was carried out by using the following formula;

$$Wear\ Rate = \frac{(ppm\ of\ wear\ metal)}{(Total\ Hours)} x \left(1 + \frac{(oil\ added)}{(sump\ capacity)}\right)$$

Therefore, it was found that the wear rate also increasing with the running hours. Hence, it was recommended the repair authority to carry out in depth investigation to find root causes for this specific metal wear down giving special attention to inspecting bearings, bushes, sleeves, bearing cages, coolant core tubes, valve guides, thrust washers, alloyed with Si-Ti.

The inspections were carried out by the repair authority and found heavy metal deterioration in Main bearings as shown below;

Figure 13. Metal wear down of No 09 bearing lower half

Table 2. Standard safety limits of wear element concentration of 16 cylinder V type reciprocating engine

Element	Maximum permissible limits
Fe	80
Cr	10
Si	15
Al	20
Pb	20
Cu	25
Sn	10
Ni	10

Figure 13. Metal wear down of No 01 bearing upper half

The second stage of oil analysis was carried out on completion breakdown repairs and a similar trend analysis pattern to Stbd Main Engine was observed. Therefore, these particular findings confirmed the metal wear down of bearings of a particular engine. The statistical data of the first stage and second stage are shown in Table 3.

Table 3. Statistical data of the first stage and second stage

Stage 01							
Element	**Oil R/H Fresh oil sample**	500	750	1000	1250	1500	1750
Fe	< 1.000	32.178	36.153	31.257	17.446	18.344	15.51
Cr	< 1.000	2.54	3.74	5.82	< 1.000	< 1.000	< 1.000
Si	< 1.000	6.404	5.121	6.851	3.36	3.56	< 1.000
Al	< 1.000	3.455	4.255	4.056	2.529	2.529	1.305
Pb	< 1.000	4.254	2.457	3.587	1.7	1.7	< 1.000
Cu	< 1.000	**42.628**	**46.083**	**52.857**	**61.153**	**61.153**	**68.248**
Sn	< 1.000	< 1.000	< 1.000	< 1.000	< 1.000	< 1.000	< 1.000
Stage 02							
Element	**Oil R/H Fresh oil sample**	50	250	500			
Fe	< 1.000	22.147	18.141	17.217			
Cr	< 1.000	1.78	< 1.000	< 1.000			
Si	< 1.000	4.584	3.5013.851				
Al	< 1.000	2.415	1.215	1.946			
Pb	< 1.000	4.414	3.417	3.457			
Cu	< 1.000	**50.248**	**30.013**	**25.204**			
Sn	< 1.000	< 1.000	< 1.000	< 1.000			

With these statistics, it was evident that the "Cu" element concentration increment is due to the bearing failure and the replacement of the particular bearing had normalised the elemental behaviour.

The SLN plan is to transfer the existing maintenance schedules to condition based predictive maintenance in which at present the oil will be drained on completion of OEM recommended intervals. This case was one of the key instances in which the findings had paved the path to prevent a catastrophic failure to an engine. These specific findings will also be utilized to systematically extend the Oil Draining Intervals (ODI) of machinery fitted on board the SLN fleet.

IV. CONCLUSION

Many of the findings of wear down analysis, had helped MTTU of SLN to reveal the information on machinery health. This instance had identified the developing malfunctions, damages to the machinery at the initial stage which had finally led to prevent catastrophic failures to the particular machinery. With the help of the findings, it will be beneficial to the relevant repair authorities of SLN to carry out a root cause analysis to identify the process environment, uneven mechanical loads such as stresses and strains or surface oil chemistry.

These findings will be correlated with the vibration analysis, thermography, ultrasound and non-destructive testing results as a productive approach to maximise the life of machinery. When conducting these techniques independently, only a portion of machinery fault is identified, therefore, integrating all these concepts will be more beneficial to predict the failure and also to extend the life cycle of the machinery.

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