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Concentration of heavy metals in virgin, used, recovered and waste oil: a spectroscopic study

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Abstract

As a result of the changes that occur during their use, oil from many machinery products tend to differ in term of physical and chemical composition from virgin oil. The analysis of additive, wear and contaminants element is oil will aid to understand the possible processes that alter the oil compositions. This study examine the heavy metal distribution in virgin, used, waste and recovered oil in term of their additives, contaminants and wear elements using simultaneous analysis of ICP-OES for 23 elements based on ASTM D5185 method. The results demonstrate that there is no significant change for additive element in virgin and used similar virgin oil samples. The metals for contaminants and wear elements in used, waste and recovered oil show indistinct distribution suggest that the oil lubricating, introduction of contamination foreign substances and recovery process play a role in discriminating the oil samples.

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Keywords: heavy metals, oil analysis, ICP-OES, additive elements, wear metals, contaminants

1. Introduction

The analysis of new and used oil for concentration trends of wear metals and for formulation or depletion of additive package metal has been around for many years. Moreover analysis of heavy metals in engine oil has been

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introduced to detect the failure of the engine component in early stage prior to major damage. Wear metals such as iron (Fe), chromium (Cr), aluminium (Al), lead (Pd) and cadmium (Cd) may indicate wear in engine or any oil-wetted compartment. However for Silicone (Si), Sodium (Na) and Boron (B) may explain the contamination from dirt and antifreeze that might lead to system failure [1]. Many additives elements such as calcium (Ca), phosphorus (P) and zinc (Zn) was blended with oil for metallic detergents, ashless dispersants, anti-oxidant, anti-wear, friction modifier and antifoam purposes [2]. In Malaysia, a guideline on standard and specifications of recovered waste oil was established in year 2009. Typically waste oil contains physical and chemical impurities that can affect living creatures and classified as scheduled waste under First Schedule of the Environment Quality Regulation 2005 [3]. Waste oil should be managed properly according to the regulations and for waste oil that still has potential economic values can still be recovered by licensed facilities listed by Department of Environment, Malaysia. Nevertheless, if the waste oil does not meet the standard and regulation, it is still categorized as scheduled waste and must be disposed in a proper ways. Table 1 show the standard and specification of recovered waste oil. Nowadays, Inductively Coupled Plasma- Optical Emission Spectrometer (ICP-OES) instrument was widely used in oil analysis and offers the possibility to simultaneously measure all the element of interest and some non-metals compared to flame atomic absorption spectrometer (FAAS) [4]. This technique is useful for differentiation purposes, giving information on whether the metal concentration could be an appropriate feature for discriminating various oil samples. The objective of this study is (1) to determine the concentration of 23 elements in virgin, used, recovered and waste oil and (2) to study the differentiation between oils samples in heavy metals perspectives.

Table 1. Standard and specification of recovered waste oil

Parameters	Allowable level
Arsenic (As)	5 ppm maximum
Cadmium (Cd)	2 ppm maximum
Chromium (Cr)	10 ppm maximum
Lead (Pb)	100 ppm maximum

2. Material and methods

Sixteen oil samples were obtained from enforcement program of schedules wastes from various factories in Selangor states and at the workshop of the cars and motorcycles for virgin, used, recovered and waste oils. The oil analysis was based on American Standard for Testing and Materials (ASTM D5185) which covers the determination of additive elements, wear metals and contaminations in used and unused lubrication oils and base oil via Inductively Coupled Plasma- Atomic Emission Spectrometry (ICP-AES) [5]. All standard solution and QC standards was prepared in standards mixture in base oil using organometallic standard S-21AccuStandard contain Al, Ba, B, Ca, Cr, Cu, Fe, Pb, Mg, Mn, Mo, Ni, P, Na, Si, Ag, Sn, Ti, V, Zn and Cd and As and Sulfur in single element with series of four calibration point (0.05 mg/kg, 0.1 mg.kg, 2 mg/kg and 5 mg/kg) with QC samples is 2.5 mg/kg. The samples were dissolved in oil soluble solvent, kerosene prior to analysis with ICP-OES. Internal standard yttrium (Yt) was used in order to compensate of different viscosity between samples. The samples were reported in mg/kg up to three significant figures for all elements. Furthermore to evaluate the similarity between variables in the samples, cluster analysis using XLSTAT 2015 software was executed on the results dataset.

3. Results and discussion

Fig. 1 demonstrates the concentration of 23 additive, wear and contaminants elements in sixteen oil samples. The stack column chart show that the additive elements such as Ca, P, S and Zn dominate the virgin oil samples with low concentration for contaminants and wear metals. The comparison between virgin lubricating oil 1 and used lubricating oil 1 signify the increase of wear element such as Al, Cr, Fe, and contaminants such as B, Mn and Na. Nonetheless the concentration of additives such as Ca and P show no significant changes for these two samples. Considerable amount of Pb and Na were observed in waste oil 3 and waste oil 5 compared to used oil samples signify that this element was essential in determining the waste oil. Pb and Na were categorized as wear metals and

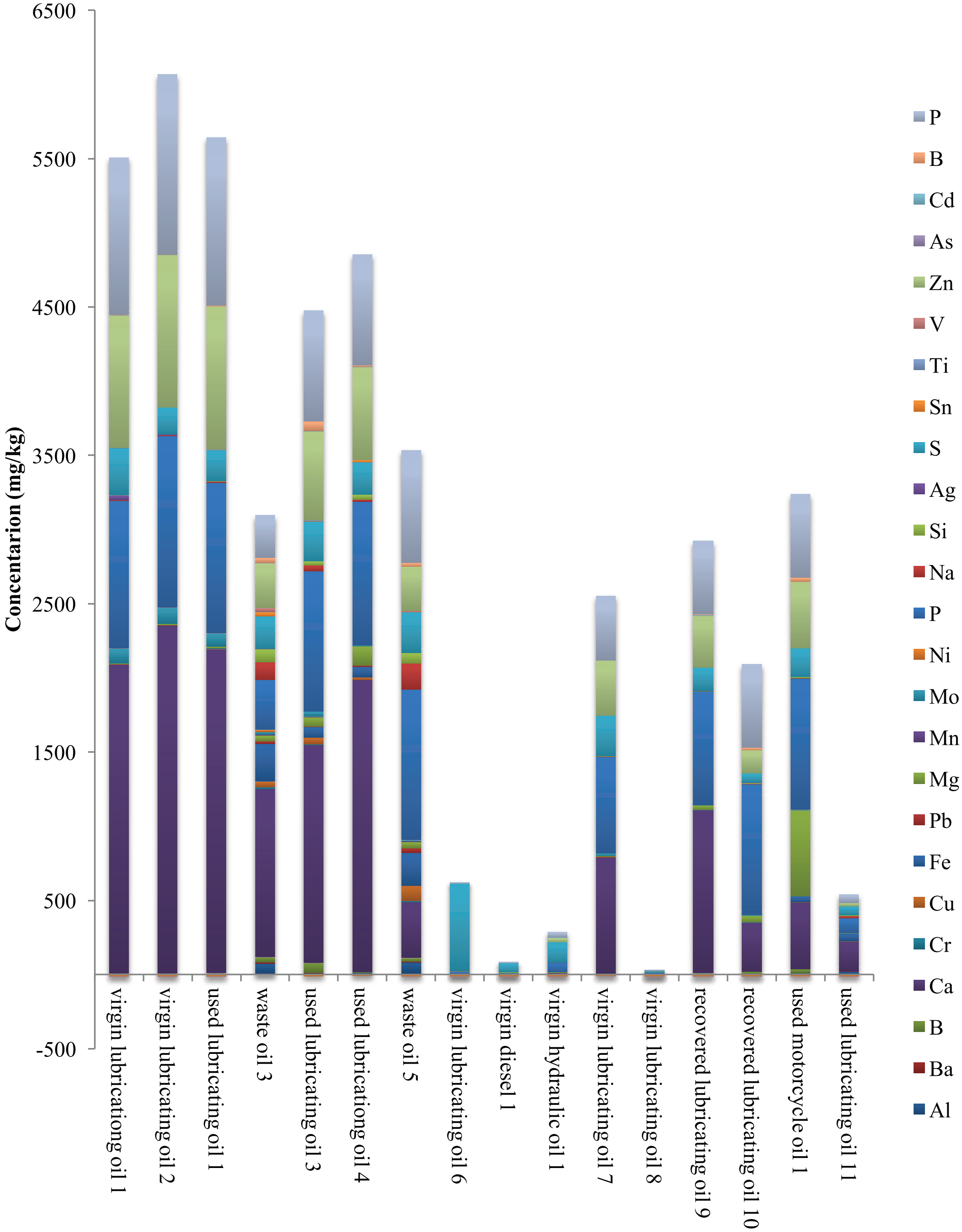

Fig. 1. Distribution of additive, wear and contaminants elements in various oil samples

contaminants metals respectively where Pb can be generated from main and rod bearings while Na can be derived from coolant inhibitor or salt water contaminations [6]. Fig. 2 illustrates the cluster analysis result for 23 elements for analysed oil samples. Three significant groups was computed with Group 1 consists of additive element (Ba and Mg), wear and contaminants metals (Al, B, Cr, Cu, Fe, Pb, Mn, Mo, Ni, Na, Si, Ag, Sn, Ti, V, Cd and As), Group 2 is additive element (Ca) and Group 3 is additive element (P and Zn). The mixing of additive, wear and contaminants elements in Group 1 elucidate that the metals in this group were low compared to additives such as Ca, P and Zn.

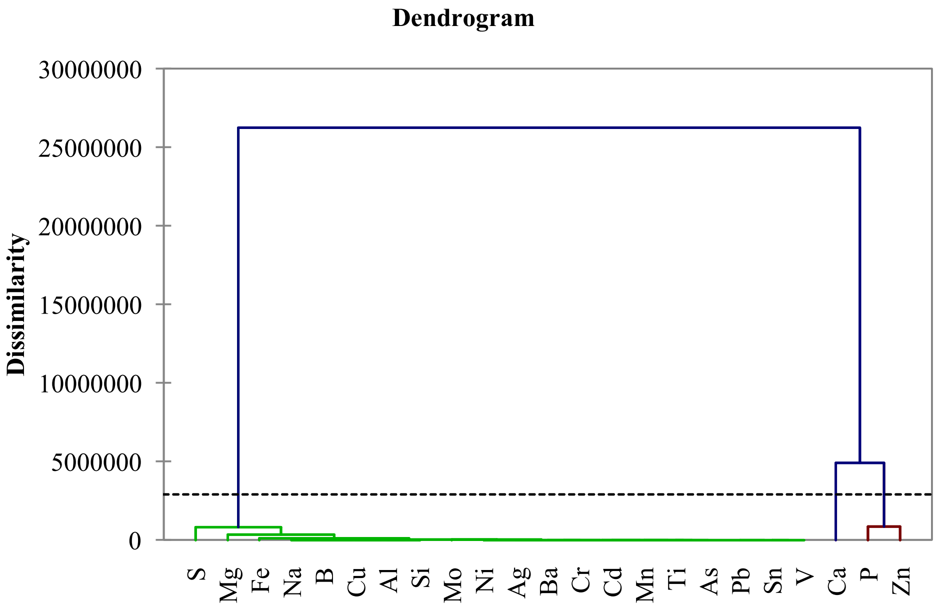

Fig. 2. Cluster analysis of heavy metals for oil samples

4. Conclusion

The analysis of additive, wear and contaminants elements was vital in order to determine the possible types of oils (virgin, used, waste and recovered oils). Heavy metal distribution is one part in discrimination the features of oil samples besides chemical fingerprinting and isotopes distributions. The different between virgin and used oil was need for further investigation as the additives element was still abundant after the oil was used. The dissimilarity of waste and recovered oil revealed that Na and Pb were among the significant element in characterizing the virgin and waste samples. More samples and study need to be performed in order to illuminate the potential of heavy metals in oils differentiation and fingerprinting.

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