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DETERMINATION OF HEAVY METALS AND SULPHUR IN WASTE ENGINE OILS

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ABSTRACT. A technique for the determination of heavy metals and sulphur concentration in waste engine oils by energy dispersive X-ray fluorescence (EDXRF) is presented. The sample preparation does not require acid digestion or pre-concentration but only production of a homogenous "pellet" on a mylar backed aluminium ring. Waste oils (n = 100) were collected from garages in and around the Nairobi central business district. The sulphur (S) concentration of used engine oils ranged from 1000-10400 mg/L; lead (Pb), 20-788 mg/L; iron (Fe), 9-1550 mg/L; copper (Cu), 6.5-170 mg/L whereas mercury and arsenic were below 3.3 mg/L, the detection limit of the machine. A comparison of some results obtained using both EDXRF and atomic absorption spectrometry (AAS) showed a good correlation of the two methods, giving a r^2 value of 0.98.

INTRODUCTION

The presence of heavy metals and sulphur in waste oils pose a great danger to living organisms and the environment if the waste oils are dumped carelessly. This calls for better ways of waste oils disposal [1]. Grahams and Jean [2] observed, that recycling of waste oils for energy generation might be an alternative self-sustaining disposal method. Recycling such oils for energy generation would involve combustion. This would mean emission of sulphur dioxide into the atmosphere. Sulphur dioxide has been established to have several harmful effects to both animals and plants [3-5]. It has also been linked to the corrosion of buildings, monuments and works of art due to its acidic properties [5].

The annual global emission of sulphur dioxide was previously estimated at about 294 million tons. Fossil fuel combustion accounts for approximately 90 percent of the total man-made emissions of sulphur dioxide [7]. The sulphur content of most oils range from trace to 80,000 mg/L, mostly in the 5,000-150,000 mg/L range [8].

Estimate of heavy metals output so far mined and thus ultimately released into the atmosphere are: cadmium - 0.5 million tons, chromium and copper - 350 million tons each, and zinc 250 million tons [9]. Most of these heavy metals have been confirmed to have some toxic effects at the given concentrations [9,10].

The aim of this study is to develop a fast non-destructive technique for the determination of elements in waste oil samples by Energy Dispersive X-ray Fluorescence (EDXRF). The technique is based on fundamental parameter [11], an adaptation of a calibration procedure for PIXE system [12] and software developed for EDXRF analysis of environmental samples [13]. The sample preparation required the configuration of a homogenous pellet on a mylar backed aluminium ring.

THEORY OF EDXRF ANALYSIS

Elemental analysis using x-ray fluorescence technique was performed more than sixty years ago

[14]. Since then, the utility of this technique has increased tremendously. This has been due to the development of fast-counting electronic modules and detector systems.

Calculation of concentration in a sample is based on intensity recorded (I) being taken as a product of sensitivity (S), concentration (C), absorption correction (T) and enhancement factor (H) [13].

$$I_i = S_i . C_i . T_i (C_1 . C_2 \dots C_n) . H_i (C1 . C_2 \dots C_n),$$

where C_i is the elemental concentration in the sample. The absorption and enhancement correction factors generally depend on the sample composition and make the above relationship non-linear in concentration of a particular element. Only in the case of extremely thin samples do both correction factors become one (1) and the above relationship becomes linear:

$I_i = S_i . (\rho d)_i . T_i$, where $(\rho d)_i$ is the density of element *i* in the sample.

In this particular work, the intensity (I_i) that is, elemental area under the peak was read from the spectrum fitting by AXIL (Analysis of X-rays by Iterative Least Square Fitting) program [15]. The sensitivity, S_i, was determined from a calibration curve generated from a standard oil reference material NIST-SRM-1634b, whereas, the absorption correction factor, T_i, were determined by the use of a pure target of molybdenum. The enhancement factor was assumed to be one (1) because additional excitation to the fluorescence radiation by other elements was minimal because the samples were thin.

EXPERIMENTAL

Heavy metals and sulphur concentration in the oils were determined by energy dispersive x-ray fluorescence analysis [16]. The EDXRF system utilised consisted of 28 mm^2 x 5 mm thick Ortec Si (Li) detector with beryllium window thickness of 25 μm, a Canberra amplifier/pulse processor with pile-up rejector Model 2020, and a Canberra S100 PC based Multi-Channel Analyzer system.

One hundred (100) samples from different petrol stations and garages within Nairobi were analysed. For each sample analysed, three replicate determinations were performed. Sample preparation consisted of shaking the oils in the bottles so as to homogenise them, then pouring them into 30 mm diameter Mylar (SPECTRO - FILM grade: SOMAR INC., USA) supported on aluminium rings. The oils were accurately weighed and their mass-per-unit area calculated. The samples were then irradiated with x-rays from a ^{109}Cd source for 500 seconds. To obtain the absorption correction factor and maintaining the same geometry, a pure target of molybdenum was substituted for the sample after every analysis and collection done for about 10 seconds. The sensitivity curve was generated from the use of an oil standard reference material NIST-SRM-1634b whereas the intensity (area under the peaks) was read from the spectrum fitting by AXIL [15]. Quantitative analysis was by QAES software [13]. For the intercomparison and verification of results, a few of the samples were analysed for Zn, Cu and Pb using atomic absorption spectrometry. 1-mL aliquot of each sample was digested using a mixture of AnalaR concentrated hydrochloric and nitric acids for 8 hours [17]. The samples were then run on a Spectr AA-10 (Varian Techlron, Mulgrave, Victoria Australia) atomic absorption spectrometer.

RESULTS AND DISCUSSION

Elemental sensitivity for the EDXRF system used for K_α elements is shown in Figure 1 while Figure 2 shows the correlation between analytical results obtained by intercomparison of some EDXRF and AAS values. Typical EDXRF spectra of a used engine oil sample is shown in Figure 3. Sulphur and heavy metal concentrations in the oils are shown in Table 1.

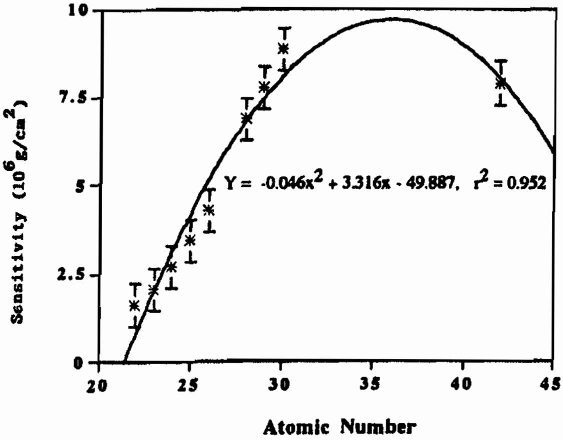


Figure 1. Sensitivity curve.

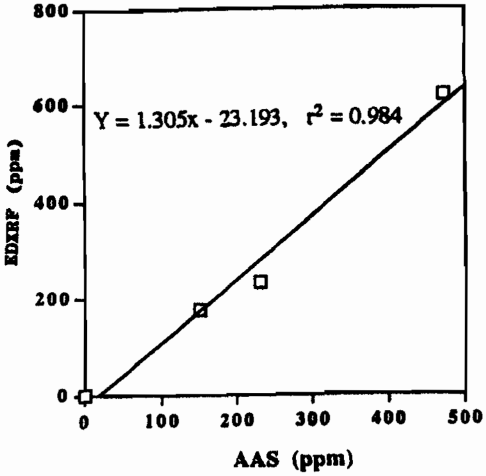
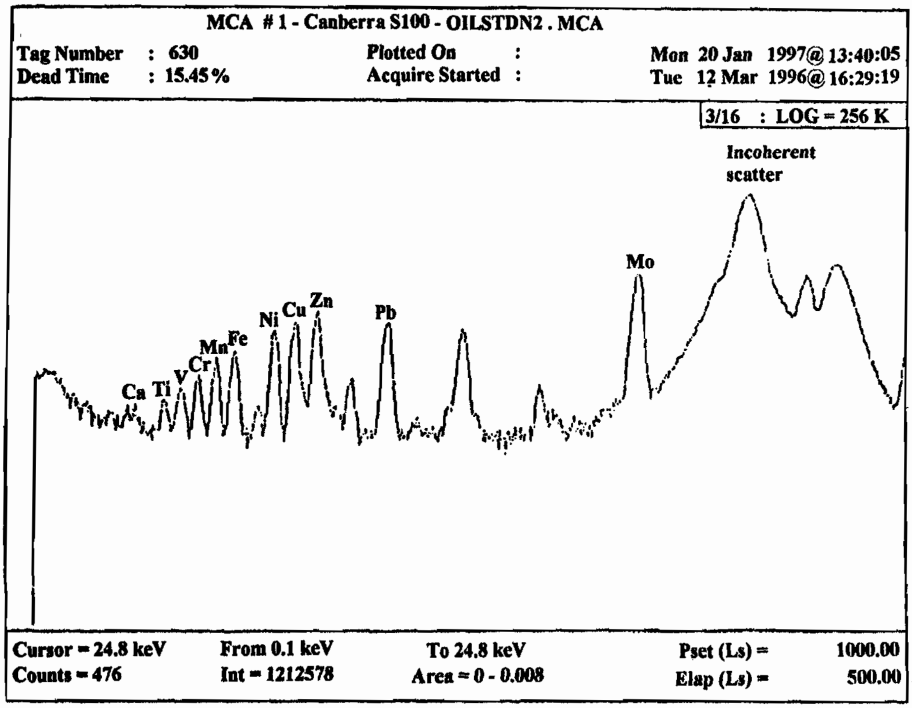


Figure 2. Intercomparison of EDXRF and AAS.

There are four significant findings of this study. First, the sulphur concentration of used and fresh oils were not significantly different. Secondly, the waste oil had higher concentrations of Fe, Cu, Zn and Pb. Thirdly, the analytical technique is fast and compares very well with AAS measurements ($r^2 = 0.98$). Finally, there were big differences in the elemental concentrations between samples collected from different garages.

The sulphur concentration in used engine oils on average had levels ~ 4000 ± 2000 mg/L sulphur (± 1s.d., n = 100). Crude oil has sulphur concentration that ranges from 5000-4000 mg/L [7]. Henderson-Seller [6] gives the sulphur concentration of diesel and fuel oils to be 3000-9000 and 5000-4000 mg/L, respectively. The values obtained in this work are thus lower than the quoted values for fuel oils. Fresh engine oil will on average have 5000-40000 mg/L sulphur [6], a value found not to be significantly different ($p \leq 0.05$) from the values obtained from this study. One can thus deduce that sulphur concentration in oils is dependent on the geological source and that very little sulphur is introduced into the oils during usage or storage.



MCA # 1 - Canberra S100 - OILSTDN2 . MCA

Tag Number : 630
Dead Time : 15.45 %
Plotted On : Mon 20 Jan 1997@ 13:40:05
Acquire Started : Tue 12 Mar 1996@ 16:29:19

3/16 : LOG = 256 K

Cursor = 24.8 keV
Counts = 476
From 0.1 keV
Int = 1212578
To 24.8 keV
Area = 0 - 0.008
Pset (Ls) = 1000.00
Elap (Ls) = 500.00

Figure 3. A spectrum of the oil standard.

Table 1. Elemental concentration (mg/L) in fresh and used oil samples.

Element	Fresh engine oil (n = 10, ± 1 s.d.)	Used engine oil (n=100, ± 1 s.d.)
S	3700 ± 1000	4000 ± 2000
Ca	2300 ± 1300	3700 ± 1600
K	340 ± 250	480 ± 260
Fe	60 ± 40	260 ± 300
Cu	< 6.3	25 ± 28
Zn	500 ± 400	960 ± 800
Pb	24 ± 10	110 ± 160

The elements determined are potassium, calcium, iron, copper, zinc, and lead. The concentrations of titanium, vanadium, chromium, manganese, cobalt, nickel, arsenic and mercury were found to be below their detection limits. The detection limits for mercury and arsenic, the two most important toxic elements, was found to be 3.05 and 3.27 mg/L, respectively.

Lead concentration in the used oils ranged from 20-788 mg/L with an average value of 106 mg/L. The maximum permitted level of lead in fuels is150 mg/L [18]. Assuming that the specific gravity of fuel is 0.84 g/ml [5], then this value translates to 180 mg/L. Iron, whose average concentration in fuels is estimated to be 2.5 mg/L [19], was found to be 59 mg/L in fresh oil, and 258 mg/L in used oil. Concentration of zinc and copper in the used oil were found to be 800 and 28 mg/L, respectively. From these results, it is quite evident that the heavy metal concentrations in used engine oil are high. On combustion of used engine oils, many of the heavy metals present would be left in the residue ash. It would be a lot easier to safely dispose the ashes than the oils and this would support the recycling of the oils for energy generation.

A comparison of heavy metals in the used and fresh oil samples shows that higher levels of Fe, Cu, Zn and Pb are registered than those in fresh oil. This difference and the large deviations between the results can be attributed to several factors, like sample inhomogeneity, the introduction of the metals during storage of the oils, corrosion of storage tanks and machine parts as well as the addition of anti-knock agent in the gasoline. These results agree with previous findings by Kinyua *et al.* [16] who reported that the metal concentration of used engine oil will depend on the wear and tear of machine parts. The use of plastic containers rather than metal containers for the storage of the oils would ensure minimum metal contamination of the oils.

CONCLUSION

There was good correlation of the results obtained by EDXRF and AAS methods. Although EDXRF method is faster than AAS, it is less sensitive but it also has the advantage over the AAS method in that many elements can be analysed at the same time. The concentrations of mercury and arsenic, the most toxic elements were below the detection limit of EDXRF method. The concentration of sulphur (1000-10400) mg/L was generally lower than the reported values in crude and other oils.

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