DETERMINATION OF WEAR METALS IN LUBRICATING OIL BY X-RAY FLUORESCENCE ANALYSIS

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Abstract

DETERMINATION OF WEAR METALS IN LUBRICATING OIL BY X-RAY FLUORESCENCE ANALYSIS. Energy dispersive X-Ray Fluorescence (EDXRF) method was used to analyze Cr, Fe, Pb and Zn in lubricating oil, associated with engine components, since it requires a small amount of sample and minimal sample preparation. Methodology was developed for the use of a Mo filter for the determination of Cr, Fe and Zn, while a Cd filter allowed the determination of Pb. The results obtained, for the most part, were in good agreement with the results obtained by the Atomic Absorption (AA) and Neutron Acivation Analysis (NAA) methods.

INTRODUCTION

Analysis of metals in oils from diesel engines used on railroads, ships, and from other lubricated machines have been done for more than forty years [1]. Measuring concentrations of elements, such as Cr, Fe and Pb in oil taken regularly from these machines can be used as an indicator of the internal condition for predicting future failure.

Atomic absorption spectrometry has been used for many years to analyze wear metals in lubrication oil. However, the conventional aspiration and flame atomization system suffers from an inherent drawback in dealing with the high viscosity of the oil, and the presence of particulate material which may be only partially aspirated and or atomized [3,4]. Neutron activation analysis (NAA) may also be used for analyzing wear metals in oil because it is sensitive, has a multielement capability, and allows for the simultaneous determination of several elements in one sample. Most metals, except lead, can be analyzed by NAA [6,7].

Energy dispersive X-Ray Fluorescence (EDXRF) is a very attractive alternative for analyzing metals in both liquid and solid sample, often with minimal pretreatment. EDXRF enables non-destructive, multielements analysis to be done rapidly with high precision on a variety of sample types. Both qualitative and quantitative analysis may be done simultaneously. An X-ray spectrum is relatively simple as there are only a few lines for each element.

More commonly, analysis is done by referring the measurement of the unknown to measured values obtained from a standard or a series of standards. Calibration requires that the matrix of both samples and standards

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be matched very closely. Analysis of speciemens then gives the calibration curves relating measured X-ray intensity to true elemental concentration. However, intensities of lines to any particular element are usually linear over only a relatively small concentration range. Outside this range, negative or positive deviations may occur due to enhancement or diminution effects caused by other elements in the matrix [8]. An alternative methode of calibration involves the addition of a small amount of known analyte to the sample being analyzed. By doing so, the matrix of the original species remains almost unchanged before and after the addition of standard analyte. This method is particularly well suited to liquids because of the ease of mixing to achieve homogeneity. The intensity of analyte will differ before and after the addition of standard analyte; on the other hand, intensities of other elements should remain unchanged. This method requires that the relationship between intensity and added concentration is linear. Least squares equations have often been employed for the extrapolation of this line to zero intensity of the original sample. In some cases a single addition of prescribed volume of a standard solution is added to a know volume of the sample. Alternatively and preferably, multiple additions may be made. Energy dispersive X-ray fluorescence using standard addition calibration has many attractive features for the analysis of metals present in dissolved forms as well as those found in fine particulate materials (should produce fluorescence). Multielement analysis may be done, and there are no large variations in sensitivity such as those found with neutron activation analysis.

EXPERIMENTAL REAGENTS

Standards containing 0, 10 and 50 ppm of typical wear elements (Cr, Fe, Ni, Cu, Zn and Pb) in oil were obtained from Department of Chemistry and Chemical Engineering., Royal Military College (RMC), Kingston, Ontario, Canada. The standards had been prepared for the Spectrometric Oil Analysis Program (SAOP), used by Canadian Air Force and United States Air Force (USAF), by adding know quantities of organometallic compounds to a clean base oil. A blank base oil in the SOAP program was also analyzed in this work. The 50 ppm standard was used for optimizing the analytical conditions. Four standard solutions were used for standard addition :

- A solution of 602 ppm Cr was made up by dissolving 0.10098 g of chromium (III)-acetylacetonate Cr{acac}₃ (Department Chemistry, Queen's University, Kingston, Ontario, Canada) in 25 mL of methyl isobutyl ketone (MIBK).
- A solution of 2240 ppm Fe was made up by dissolving 0.18817 g of dicyclopentadienyl iron Fe(C₅H₅)₂, purity 98 % (J.T Baker Chemical Co-New Jersey) in MIBK solvent.

- A solution of 1831 ppm Pb was made up by dissolving 0.11403 g from tetraphenyllead Pb(C₆H₅)₄, purity 98 % (Alfa Inorganic - Ventron) in benzene.
- 4. A solution of 2.3 % Zn was made up by dissolving 1.98700 g Zn(acetate)₂ 2H₂O, purity 99.9 % (Merck) in methanol. The standard CuO (link Analytical, U.K) and PbO (SPEX industries, USA) pellets (31 mm x 5 mm) were used for checking the energy calibration of the XR 200 Spectrometer.

SAMPLES

The samples, as shown in Table 1, analyzed in this work consisted of used oils from various types of engines on marine vessels. The oils had been previously analyzed by atomic absorption spectrophotometry [15] and instrumental activation analysis [5]. Samples were prepared by weighing approximately 1 g of a well shaken oil into a cup (SPEX industries). Four subsamples of each sample were taken so that standard addition for each element of interest (Cr,Fe,Zn and Pb) could be carried out using a "new" oil sample. This method was used to ensure that each element did not exhibit a matrix effect due to the other elements during analysis.

Standard addition (10 μ L) was added to the samples through a small hole in the top of the cup. After each standard addition the sample was shaken to insure a homogeneous distribution of the spike in the oil.

EQUIPMENT

The XR 200 energy dispersive X-Ray Fluorescence Spectrometer (Link Analytical, England) has a 30 kV, 0.3 mA rhodium anode in side window Bremsstrahlung x-ray tube. The X-Ray tube was operated at fixed filament current, but the potential could be varied between 10 and 29 kV. Detection was with a 10 mm² lithium drifted silicon detector Si(Li) with an 8 micron beryllium window and an energy resolution of 155 eV for the Mn K α peak at 5.9 keV. The Si(Li) detector was interfaced to an integrated power supply and pulse processor which in turn was connected to an IBM compatible microcomputer. A general diagram of the system is shown in Figure 1. The system was also equipped with 6 and 8 mm of id (inner diameter) aluminum collimators, the inner holes of which was coated with carbon paint to attenuate Al X-rays. The collimator assembly also houses any filter that may be required (ie. Al, Ti, Mo and Cd in this work) and this assembly is housed in a special recess on the primary X-ray beam side of spectrometer.

PROCEDURES

During the development of the XRF technique the XR 200 was operated with the X-ray tube anode current set at 0.15 mA and the X-ray tube voltage varied from 15 to 29 kV. The pulse processor was set for a range of 20 keV over 1024 channels of the MCA and the pulse processing time was 20 μ sec. The system was calibrated for enegry by comparing the K α peak of Cu from the CuO pellet (Link Analytical, England) with the X-ray library file provide in the software. Fine gain adjusments were made in the pulse processor to align the marker in the library file with the centroid of the peak. Linearity in the enegry calibration was checked using the PbO pellet by comparing the macth of the peak centered with the Pb L α and Pb L β marker for Pb from library. In addition a strobe peak produced by the pulse processor was centered at zero energy for possible future spectrum processing using more sophisticated software.

Standards and samples were analyzed for 1000 seconds live time (except for Zn-samples which were analyzed for 100 seconds live time) and the three variables of X-ray volatge, filter and collimator were adjusted to obatain the best peak-to-background ratio for the elements under study.

PRELIMINARY EXPERIMENTS

The ideal conditions for carrying out X-ray fluorescence analysis was to produce a spectrum where the lines from the analyte elements, in this case, Cr, Fe, Zn and Pb, would produce large peaks, while the background under these peaks would be small. Preliminary experiments were done in order to observe what potential of X-ray tube is required in order to obtain a reasonable spectrum. Both the analyte and bremsstrahlung fluorescent radiation may be seen resulting of an oil standard containing 50 ppm wear metals. Filtering may be useful to reduce the large background, but it also reduces the intensity of the characteristic lines. In order to choose an appropriate filter it is desirable that it has a K absorption edge near to the energy of the background radiation which is to be removed.

Preliminary experiments were done using a Mo and a Cd filter. The Mo filter is able to remove more background radiation, however the characteristic secondary line spectra are also reduced in intensity. Therefore, it was decided that the Mo filter would be the most appropriate for determining Cr, Fe, Zn. It was found that the Cd filter removes additional background radiation and also significantly reduces the peak sizes of Cr, Fe and Zn, but it was now possible to observe the Pb peak [26]. In the present experiment, two collimators of 6 mm and 8 mm inner diameter were evaluated with respect to their use in analysis of wear metals in oil samples. The intensity of the peaks is higher with the 8 mm collimator than with the 6 mm one.

Using the information obtained from the preliminary experiments, further experiments were done to more clearly define the experimental conditions required to give optimum analytical properties. The filters chosen as indicated above were for Cr. Fe and Zn analysis and Cd for Pb analysis. The potential applied in the X-ray tube was varied from 15 to 29 kV for experiments with the Mo filter and from 20 to 29 KV when using the Cd filter. At the same time, measurements were made using both 8 mm and 6 mm diameters collimator. The intensity of each peak was measured under the various experimental conditions along with the intensity of the background peak. Optimization was based on a calculated relative standard counting error for each peak[18]. In these experiments, the relative standard counting error was determined using the standard oil sample containing 50 ppm wear metals. A second factor to be taken into account in choosing the optimal experimental conditions is the dead time. If exceessively high counts rate are being measured, the counting time will appear as dead time and this leads to inefficiency of the detector. Therefore, it was arbitrarily decided that a maximum dead time of 35 % would be allowed in this experiment. From these experiments it can be seen that in each case, the relative standard counting error using the 8 mm collimator is lower than that obtained using the 6 mm collimator. In general, it can be found that the relative counting error was high at low x-ray tube potentials and decrease in relative counting error is small. In order to minimize this error the highest possible potential should be used. However it was also necessary to consider the dead time in order to ensure that excessive inefficiency in counting did not occur. Therefore, an intermediate potential was chosen to give on the one hand a small relative counting error, and at the same time, a relatively small dead time. For the the particular elements being studied, an x-ray tube potential of 23 kV was chosen for Cr. Fe and Zn analysis, while 29 kV was chosen for Pb analysis in conjuntion with the Mo and Cd filters respectively.

RÉSULTS AND DISCUSSION ANALYSIS OF STANDARD SAMPLES

In order to achieve reliable quantitative results for all the elements, a series of measurements was carried out for each element of interest (Cr, Fe, Pb and Zn) using two SOAP (Spectrometry Oil Analysis Program) standards, one containing 0 and 10 ppm of each wear metals respectively. For the elements of interest, standard additions were done on subsamples in order to obtain quantitative result. As can be seen, the intensities of the Pb L α and Pb L β x- ray lines increase with each standard addition while the intensities of the x- ray peaks of Cr, Fe, Cu, Ni and Zn remain unchanged as shown in Figure 2.

In order to determine the concentration of the analyte in the original sample the X-ray peak areas (Y-axis) are plotted against the concentration of standard added (X-axis). A linear regression is then carried out on the data and the intercept on the X-axis yields the concentration of the analyte in the original sample as shown in Figure 3.

The uncertainty for the result is determined from the computed standard addition deviation of the linear regression using a data analysis program. The results obtained from the analysis of the SOAP "blank" and 10 ppm standard using NAA [6] method and this work are given in Table 2. The results given in Table 2 indicate that EDXRF is a feasible non destructive analytical technique for the determination of the specified wear metals in engine lubricating oils. The rather large standar deviations plots and are probably also due in part to the simple method of peak integration used in this work, especially at the lower concentration. Because each element was analyzed separately from a new subsample it is not thought that enhancement or suppression effects (matrix effects) would contribute to any appreciable deviation from linearity. However, a certain amount of intermittent instability in the x-ray analyzer was observed. While every effort was made to ensure that the system was stable during this work, the possibility of instability in the system contribution to deviation in the standard addition plots can not be ruled out. A further reason for the larger standard deviation is because only four measurements in total were made on the sample. Nevertheless, the feasability of the EDXRF technique has been demonstrated.

ANALYSIS OF SAMPLES

Analysis of Cr, Fe, Pb and Zn in a variety of actual engine oils containing variable amount of wear metals was also done using EDXRF procedure developed in this work. Eight used oil samples from engines on naval vessels were analyzed as shown in Table 3. The samples chosen for analyses had been previously analyzed by AAS and NAA and these results are also included in Table 3. For Fe, Pb and Zn, with a single exception, all results obatined are above the calculated detection limit for the respective of the elements. For Cr all results but one are below the detection limit for that element. Therefore these results using the present method can not be considered as reliable values for Cr concentration in the oil sample. The fact that these results are below the detection limit is also reflected in the large standard deviation which were obtained in the analyses. Peaks were observed in all cases, and improvement in the methods of measuring areas (see below) should lead to the possibility of using this method for Cr analyses. Results for the elements indicate, in a number of cases, that the scatter of the data about a linear curve resulted in a large standard deviation. For example, the

Fe result for sample 684-870 was 10 ± 27 ppm. In contrast, the Fe result for sample 684-832 was 14.6 ± 1.0 ppm. As stated previously, possible reason for the large standard deviations are the simple method of peak integration used in this work, instability in the EDXRF analyzer and the used of a small number of measurement data points. Towards the end of this work sample 684-868 was reanalyzed and triplicate analyses were done on the unspike sample and after each standard addition.

The results obtained (Table 3) indicate fairly good agreement in most cases with previous analyses by AAS. Agreement with NAA is generally not as good, but NAA is not a procedure of choice for most of these elements. The differences results between obtained by XRF and AAS may be partly due to technichal problem in the pulse processing unit. These have been found to be the instability. The results obtained for the analyses of Zn is an additive in all of the engine oil samples and therefore this element does not constitute a wear metal. All samples were therefore not analyzed for Zn. Nevertheless, the analyses of this element may be important from a quality control aspect.

CONCLUSION

The purpose of this investigation was to develop a method for the determination of Cr, Fe, Pb and Zn in used engine oils using the energy dispersive x-ray flourescence analysis. Methods were developed which involved minimum effects from matrix elements. Standard addition technique was adopted and each element was analyzed separately.

A number of standard and previously analyzed samples were analyzed using the developed procedures and the results for Fe, Zn and Pb are in reasonable agreement with those obtained by other methods.

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61

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Table 1. Description of oil sample	taken fron	n various of ships	5.
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Sample Description	Ship	Date of Collection
684-805	Port Dauphine	No.2 D/G04/29/87
684-810	Chignecto	No.1 D/G04/30/87
684-816	Endeavour	Aux RM D/G04/30/87
684-832	Miramichi	No.1 D/G05/05/87
684-867	Fort Steele	Port M/E05/23/87
684-868	Fort Steele	Stbd M/E05/22/87
684-869	Fort Steele	Port D/G05/22/87
684-870	Fort Steele	Stbd D/G05/22/87
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Table 2. Analysis Cr, Fe Zn and Pb in SOAP samples containing blank and 10 ppm wear metals of interest using NAA [6] and EDXRF method.

Methods	Standar (p	d Solution opm)	Elements (ppm)						
			Cr	Fe	Zn	Pb			
EDXRF NAA EDXRF NAA	Blank Blank	10 10	<d1 <0.05 9.5±3.1 10.2±0.2</d1 	<d1 <60 10.2±2.5 <60</d1 	<dl <2 8.2±3.6 11.2±0.2</dl 	<dl * 9.2±2.7 *</dl 			

* Pb can not be analyzed by NA d l is detection limit.

Table	3.	Results	of	anal	lysi	s of	wear	metals	in	oil	using	XRF	(in	ppm)).
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Sample No.	a	Chromium			Iron			d	Zinc		
	XŔF	AAS	NAA	XRF	AAS	NAA	XRF	AAS	XRF	NAA	
684 - 805	1.5 ± 5.2	1	0.6	14.9 ± 1.4	15	32	7.4 ± 1.5	10	485 ± 230	441	
684 - 810	2.0 ± 3.1	0	1.3	7.6 ± 1.3	5	22	6.0 ± 0.4	8	-	1123	
684 - 816	1.4 ± 8.1	0	0.8	11.1 ± 1.5	10	17.4	3.5 ± 0.8	8	378 ± 311	392	
684 - 832	5.9 ± 0.8	7	5.9	14.6 ± 1.0	13	27	9.9 ± 3.2	11	1190 ± 243	1127	
684 - 867	0.7 ± 0,1	1	0.5	17.0 ± 12.7	10	21	17.2 ± 11	15	-	423	
684 - 868	2.1 ± 0.5	1	< 0.5	6.3 ± 0.9	7	< 10	15.9 ± 2.6	15	414 ± 344	390	
684 - 868 ^{*)}	0.9 ± 0.1	1	< 0.5	9.1 ± 2.6	7	< 10	8.2 ± 7.2	15	435 ± 86	390	
684 - 869	0.6 ± 3.3	1	< 0.5	20.5 ± 4.9	19	36	17.4 ± 3.9	17	-	568	
684 - 870	2.4 ± 0.2	1	< 0.5	10.0 ± 27	9	< 10	20.5 ± 6.7	18	473 ± 235	458	

64







Figure 2. Intensities of Pb Lα dan Pb Lβ increase after spiking standard lead solution while matrix unchanged.





66