Determined the parameters effected on sensitivity and lower limit detection of XRF–WDS for different metals particles suspended in engine oil.

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Abstract

In this work Different weight of pure Copper,Nickel,Cobalt and Iron fine powders were blended carefully with engine Oil.X-ray fluorescence system was operated at 30KV and 17mA,the XRF intensities of K_α lines for all samples were measured at the peak and at background.The Lower Limit detection (LLD) and Sensitivity (m) of XRF Spectrometer were determined for different metal particles with different Concentrations (Wt%).The results of LLD and sensitivity of all suspended samples were plotted as a function of concentration , and the average values of LLD and m were calculated and plotted as a function of atomic number of metal particles suspended in engine oil.

Introduction

X-ray fluorescence analysis(XRF)is a well established convenient method for qualitative and quantitative elemental compositional analysis of solid and liquid and its Nondestructive techniques for chemical analysis of materials.In recent year(XRF)has been found to offer advantages of speed and accuracy. The determination of different metal particles in engine oil is established as valuable means of assessing concentration of metal particles in engine oil as a final product which was involved base oil and additives (Robert.R.w.,1996).in 1954 Gunn(Gunn.E.L ,1964)study the application of X-ray fluorescence to the analysis of suspended particles in liquid hydrocarbons and study the effect of particle size on X-ray fluorescence intensity,and in 1998 Darrel (Darrell.B.C.,1998)was analyzed the engine oil filter for chemical elemental content using X-ray fluorescence technique. The larger field of oil analysis which includes analysis of suspended particles, further evaluates the lubricant for its condition and for the presence of other contaminates,such as fuel, coolant and Water(Robert.R.w.,1997).

I-Lower Limit Detection

The X-ray fluorescence method is particularly applicable to the quantitative and qualitative analysis of low concentrations of elements in a wide range of samples as well as allowing the analysis of elements at a

higher concentrations in limited quantities of materials.the generally accepted definition for the lower limit of detection is that concentration equivalent to two standard deviations of background counting rate(Ron,J.,2000).there are two standard deviations of the total background counts N_b taken will be given by:

$$\mathbf{2S(N)=2}\sqrt{N}_{\mathbf{b}}\mathbf{=2}\sqrt{R_b t_b} \quad \ldots(1)$$

Where t_b is the time spent counting on the background and R_b is count of background.to convert count to count rate we divide by time

$$2S(R) = 2\frac{\sqrt{R_b t_b}}{t_b} = 2\sqrt{\frac{R_b}{t_b}} \quad \ldots(2)$$

To convert count rate to concentration we divide by sensitivity (m) which is defined as(Ron,J.,1998)

$$2S = \frac{2}{m}\sqrt{\frac{R_b}{t_b}} \quad \ldots\mathbf{(3)}$$

where m is a sensitivity which will defined carefully in section II.Since two measurements have to be made(peak and background)the error is increased by $\sqrt{2}$ and taking $2\sqrt{2}$ ~3 we have the formula for the lower limit of detection LLD.

$$LLD = \frac{3}{m}\sqrt{\frac{R_b}{t_b}} \quad \ldots(4)$$

Equation(4)represents the minimum detection limit(MDL)or lower limit detection(LLD)for the wave length dispersive system in X-ray fluorescence spectrometry wavelength X-ray fluorescence(Clark&Mark,2000).

II-Sensitivity (m)

Different parameters such as,instrument components,accessories and condition may be made chosen for optimum sensitivity for a given analysis with a given X- ray tube target,crystal,collimator system and detector. Sensitivity of the pure analyte is a relatively simple function of atomic number.Elements having about the same atomic number are likely to have about the same sensitivity in a given system.The sensitivity of the spectrometer is determine from the following equation (Ron,J.,2000) and(Eugene,B.1975)

Sensitivity (m)=count rate/concentration …(5)

in C/S %

Experimental part

I-Equipment and materials properties

a Siemens SRS 200 Sequential X-ray Spectrometer complete with Kirstalloflex 805 X-ray Generator and measuring cabinet with electronic measuring system and Kompensograph X-T.The instrumental parameters are listed in table(2.1).the diffracted angles of K_α lines were tabulated in table(2.2).a molybdenum(Mo)tube was used to obtain maximum sensitivity and

Table(2.1):Operation parameters of X-ray fluorescence system.

X-ray tube anode	Mo
Power	30KV , 17mA
Analyzing Crystal	LiF(100)
Collimator	$0.^{0}15$
Atmosphere	Vac.10^{-3}(m bar)in both sample and analyzing chamber
Detector Type	Scintillation Counter

Table(2.2):The diffracted angles of X-ray fluorescence system[9]

K_α lines	diffracted angles
Cu	44.96
Ni	48.60
Co	52.74
Fe	57.46

II-Sampling and measurements procedure

The main materials used in this work are Cu,Ni,Co,Fe fine powders and Iraqi engine oil.Liquid sample container which were designed and manufactured by us from Tephlon were used in this work,the bottom window was fitted with 6μm Mylar Film.Different percent by weight of Cu,Ni,Co,Fe fine powders were blended carefully with Iraqi engine oil to prepared the suspended samples and these samples were subjected to XRF system.Counts of XRF intensities were accumulated for 10seconds and averaged to 1second for K_α Peak and also for either side to obtain background of all suspended samples.The average of the background intensities were calculated to give net counts of Cu K_α,Ni K_α,Co K_α and Fe K_α lines.Samples were analyzed at the same time to reduce inaccuracies due to setting of metal particles in samples.

Results and discussion

Tables(4.1-4.4)shows the XRF intensity measurements of peaks and background for all metal particles suspended(mentioned in section 2)in

Iraqi engine oil and by using the equations(4) and(5)can be calculated the sensitivity(m)and the lower limit detection(LLD).Figures(3.1)and(3.2) represents the results of sensitivity and the lower limit detection for all suspended samples versus with the concentration of metals particles in engine oil.In general can be shown from these figures that the sensitivity of XRF spectrometer is increased when the metals particles concentrations increased and the LLD is decreased when the concentration of metals particles increased.the minimum value of LLD is desired and that's means the spectrometer can be used to detect the minimum quantities of metal particles suspended in any hydrocarbons materials and the maximum value of m is desired because it is means the accuracy of XRF measurements for metal particles suspended in any hydrocarbons with high concentrations are greater than that of low concentrations.the average values of m and LLD were calculated for all metal particles suspended in engine oil.fig.(3.3) shows the relation between the averages values of sensitivity and the atomic number of metal particles suspended in engine oil,while fig.(3.4) shows the relation between the averages values of LLD and the atomic number of metal particles suspended in engine oil,from these figures one can be noticed that m and LLD improved when the atomic number increased and can be employed the equation of the best fitting to determine the optimum values of m and LLD for such samples.

Table(3.1):intensity measurements of different Cu particles concentration in engine oil

Cu(wt%)	$I_{K\alpha\ Cu}$ peak(c/s)	$I_{K\alpha\ Cu}$ background(c/s)	$I_{K\alpha\ Cu}$ net count (c/s)
1	1660	110	1490
2	2680	150	2530
3	5000	220	4780
4	7800	300	7500
5	12300	420	11180

Table(3.2):intensity measurements of different Ni particles concentration in engine oil

Ni(wt%)	$I_{K\alpha\ Ni}$ peak(c/s)	$I_{K\alpha\ Ni}$ background(c/s)	$I_{K\alpha\ Ni}$ net count(c/s)
1	1500	100	1400
2	2500	140	2360
3	4600	190	4410
4	6900	240	6660
5	10500	320	10180

Table(3.3):intensity measurements of different Co particles concentration in engine oil

Co(wt%)	$I_{K\alpha\ C0}$peak(c/s)	$I_{K\alpha\ C0}$ background(c/s)	$I_{K\alpha\ C0}$ net count(c/s)
1	1400	90	1310
2	2300	130	2170
3	4100	180	3910
4	6300	220	6080
5	9200	300	8900

Table(3.4):intensity measurements of different Fe particles concentration in engine oil

Fe (wt%)	$I_{K\alpha\ Fe}$ peak(c/s)	$I_{K\alpha\ Fe}$ background(c/s)	$I_{K\alpha\ Fe}$ net count(c/s)
1	1310	80	1230
2	2000	110	1890
3	3600	150	3450
4	5600	200	5400
5	8200	270	7930

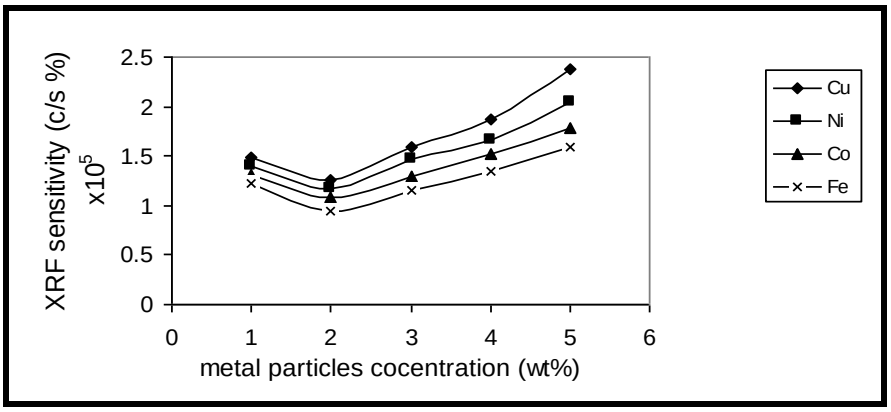

Fig.(3.1):XRF sensitivity as a function of copper concentration in engine oil

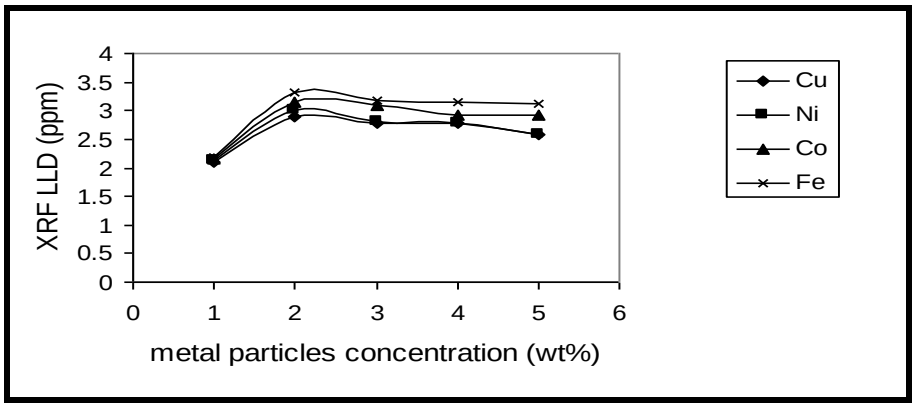

Fig.(3.2):XRF lower limit detection(LLD)as a function of copper concentration in engine oil

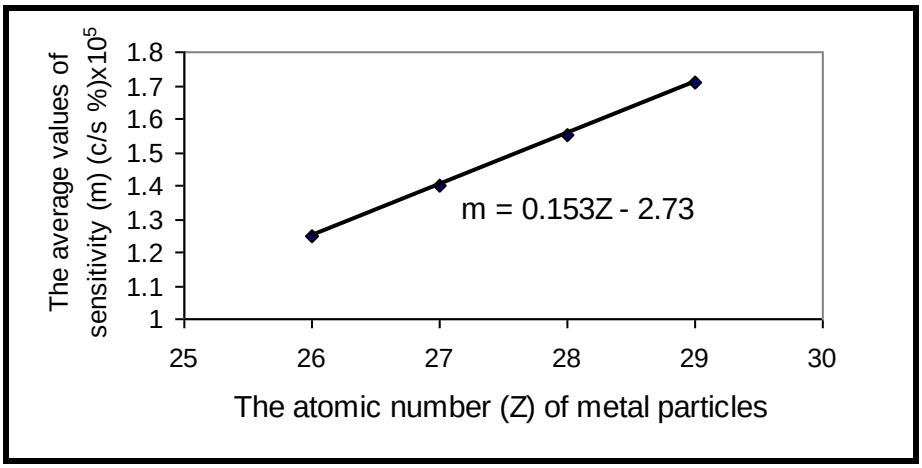

Fig.(3.3):The XRF sensitivity(m)as a function of atomic number(Z)of metal particles suspended in engine oil.

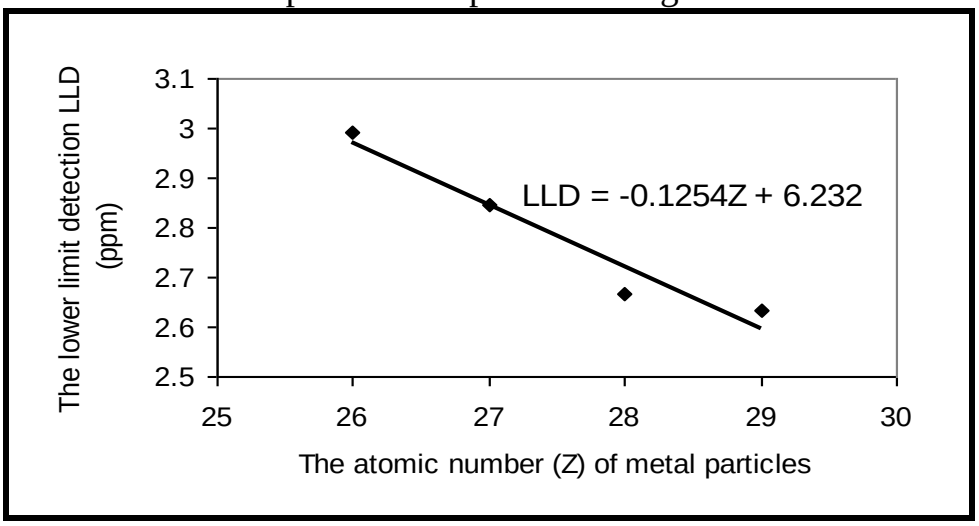

Fig.(3.4):The XRF lower limit detection(LLD)as a function of atomic number(Z)of metal particles suspended in engine oil.

Conclusions

1- The major parameters affected on XRF sensitivity and lower limit detection for suspended metal particles in engine oil are namely,the concentrations and the atomic number.
2- In all samples the values of sensitivity are low for concentration of 2wt % due to that the concentration rapidly increased from 1wt% to 2wt% .
3- The XRF sensitivity is proportional to concentration and to atomic number of metal particles while the lower limit detection is inversely proportional to concentration and to atomic number of metal particles suspended in engine oil.

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تحديد المعلمات المؤثرة على الحساسية والحد الادنى للتحسس لمطيافية تألق الاشعة السينية لمختلف الجسيمات المعدنية العالقة في زيت المحرك

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الخلاصة

اخذت أوزان مختلفة من المساحيق النقية لمعادن النحاس والنيكل والكوبلت والحديد خلطت بعناية مع زيت المحرك.اذ تم استخدام منظومة تألق الأشعة السينية وتم تشغيلها بظروف تشغيلية30KV,17mA.تم قياس الشدة للخط $k\alpha$ للقمة وللأستطارة الخلفية ولجميع النماذج الحد الأدنى للتحسس والحساسية لمطياف تألق الأشعة السينية وجد لمختلف الجسيمات المعدنية وبمختلف التراكيز.نتائج الحد الأدنى للتحسس والحساسية للنماذج العالقة رسم كدالة للتركيز وتم إيجاد معدل قيمة الحد الأدنى للتحسس والحساسية ورسمت كدالة للعدد الذري للجسيمات المعدنية العالقة في زيت المحرك.