The Determination of Lower Limit Detection of X-Ray Fluorescence for Zinc Powder Suspended in Engine Oil

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Abstract:

In this work Different weight of pure Zinc powder suspended particles in 4ml base engine Oil were used.

Intensity of K_α Line was measured for the suspended particles ,also for mixture which consist from Zinc particle blended with Engine base Oil. Calibration Curve was drawn between $I_{k\alpha}$ line Intensity and Zinc concentration at different operation condition. The Lower Limit detection (LLD) and Sensitivity (m) of Spectrometer were determined for different Zinc Concentration (Wt%). The results of LLD and m for Samples were analyzed at Operation Condition of 30KV,17mA is best from Samples were analyzed at Operation Condition of 25KV,15mA.

تحديد الحد الأدنى للتحسس لتألق الأشعة السينية لمسحوق الزنك العالق في زيت المحرك

زاريه ازات سركيس وزارة العلوم والتكنولوجيا

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الخلاصة:

في هذا البحث أوزان مختلفة من مسحوق الزنك النقي عالق في أربعة ميليلتر من أساس دهـــن المحـــرك ، وتم إجراء عملية الخلط بعناية ، ثم أجريت قياسات الشدة للخط Kα لعينة تحتوي على ٤ مل من الدهن الأساس لوحدة وكذلك تم قياس الشدة لعينات مكونة من خليط دهن أساس مع مسحوق الزنك.

رسم منحني معايرة بين الشدة Kα وتركيز الزنك وتحت ظروف تشغيلية مختلفة ، وتم إيجاد الحـــد الأدنى للتحسس وحساسية مطياف الأشعة السينية لمختلف تراكيز الزنك ، تبين أن الحد الأدنى للتحسس للنماذج التي تم تحليلها بظروف تشغيلية (30KV, 17mA) أفضل من تلك التي تم تحليلها بظروف تشغيلية (25KV, 15mA) وكذلك الحال بالنسبة لنتائج الحساسية.

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 Zinc particle in engine oil is established as valuable means of assessing concentration of Zinc particles in engine oil as a final product which was involved base oil and additives[1]. In 1954 Gunn[2] 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 [3] was analyzed the engine oil The larger field of oil analysis which includes analysis of suspended particles, further evaluates the filter for chemical elemental content using X-ray fluorescence technique.
lubricant for its condition and for the presence of other contaminates, such as fuel , coolant and Water[4].

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[5] .
There are two standard deviations of the total background counts N_b taken will be given by.

$$2S(N)=2\sqrt{N}_b =2\sqrt{R_b}\,t_b \text{ (in counts)} \quad (1)$$

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

$$2S(R)=2\frac{\sqrt{R_b t_b}}{t_b}=2\sqrt{\frac{R_b}{t_b}} \text{ (in count rate)} \quad (2)$$

To convert count rate to concentration we divide by sensitivity (m) which is defined as [6]

$$2S=\frac{2}{m}\sqrt{\frac{R_b}{t_b}} \text{ (in concentration)} \quad (3)$$

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 $2\sqrt{2} \sim 3$ we have the formula for the lower limit of detection LLD .

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

Equation (4) represents the minimum detection limit (MDL) or lower limit detection (LLD)for the wave length dispersive system in X-ray fluorescence spectrometry (WXRF) [7].

II- Sensitivity (m)

The sensitivity is still very high for x-ray fluorescence technique. 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. Table (1) shows the sensitivities of X-ray fluorescence and other analytical chemical methods [8].
The sensitivity of the spectrometer is determine from the equation (5)

Sensitivity(m)=count rate/concentration in C/S %[5] (5)

Table (1) Ultimate sensitivities of methods for the most sensitive elements under the most instrumental conditions

Method	Minimum detectable amount (gm)
X-ray fluorescence spectrometry	10^{-9}
Optical Emission spectrography	10^{-10}
Optical absorption spectrometry	10^{-10}
Auger electron spectrometry(AES)	10^{-11}
Ion-Induced x-ray spectrometry	10^{-12}
Mass spectrometry	10^{-13}

Experimental

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) .

A molybdenum(Mo)tube was used to obtain maximum sensitivity and minimum lower limit detection (LLD), for Zinc suspended particles in engine Oil.

Table(2) Operation parameter of X-ray fluorescence system

X-ray tube anode	Mo
Power	30KV , 17mA and 25KV ,15mA
Analyzing Crystal	LiF(100)
Collimator	$0.^{0}15$
Atmosphere	Air
Element Line	Zn K_{α}
Angle (2θ)	41.73[9]
Detector Type	Scintillation Counter

The main materials used in this investigation are Zinc Powder, Base Engine Oil, and Final engine Oil Product.

Some properties of these Materials are listed in table (3)

Table (3)Represent some properties of the main materials used in this Investigation[10]

Materials	Properties	Suppliers
Zinc Powder	Pure Zinc Metal Powder of fine Particle size	Merck Company (Germany Product)
Base Engine Oil	Engine Oil without additives	AL Dura Refinery Baghdad-Iraq

II-Sample preparation and final checking**:**

Liquid sample holders (Fig.(1)) which were designed and manufactured from Tephlon Material were used in this work , the bottom window was fitted with 6μm Mylar Film Fine percent by weight of Zinc powdered was blended with base Oil to preparation Samples of Zn-1 , Zn-2, Zn-3, Zn-4 and Zn-5 Fig.(2) represents microscopic photograph for one of these samples to conducted the Calibration Curve, and shown the distribution of particles in engine oil.

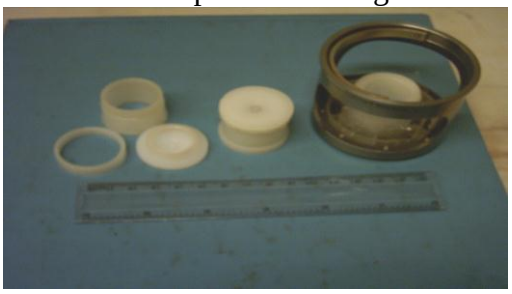

Fig. (1): a photograph of Liquid Sample Holder

Fig (2): Microscopic Photograph of Zinc Powder blended with base engine Oil

Counts were accumulated for 10 seconds and averaged to 1second for the Zinc K_{α} Peak and also for either side to obtain background. The average of the background intensities were calculated to give net counts of Zinc K_{α} line.

Samples were analyzed one at time to reduce inaccuracies due to setting of Zinc particles in Sample.

The rate of increase in Zinc intensity Signals were Plotted for all Samples.

Results and Discussion

I- Intensity Measurements:

Tables (4) and (5) represent the results of $I_{k\alpha Zn}$ line Intensity for standard samples which were prepared

from 4 ml base engine oil mixed with fine percent by weight of pure Zinc (Zn) powder at different operation conditions. The Intensity value of base oil only is approximately equal to 150c/sec and represented the average background count rate.

These results were used to made calibration curve as shown in Fig.(3) which represented the relationship between the net count rate of X-ray fluorescence Intensity and Zinc concentration (wt%), and from this figure it can be seen that the intensity increased when Zn wt% and Voltage operation are increased. The calibration curve can be used to determined Zn concentration in final engine oil product.

Table(4)Intensity measurements of $I_{k\alpha Zn}$ line at 30KV , 17mA

Zn wt%	$I_{k\alpha Zn}$ peak (c/s)	$I_{k\alpha Zn}$ background(c/s)	Net count (c/s)
0.025	4907	275	4632
0.050	12920	420	12500
0.075	18440	480	17960
0.100	23515	535	22980
0.125	26800	618	26182

Table(5)Intensity measurements of $I_{k\alpha Zn}$ line at 25KV , 15mA

Zn wt%	$I_{k\alpha Zn}$peak (c/s)	$I_{k\alpha Zn}$ background(c/s)	Net count (c/s)
0.025	1983	180	1803
0.050	6280	280	6000
0.075	9081	312	8769
0.100	12292	360	11932
0.125	15340	400	14940

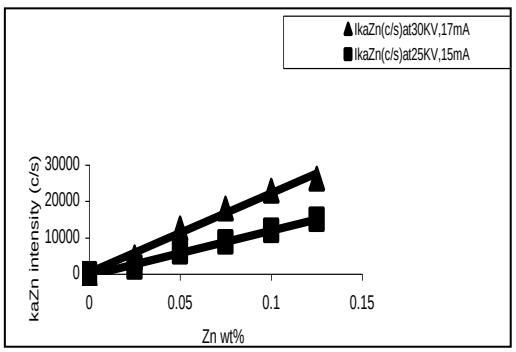

Fig. (3): X-ray intensity as a function of Zn wt% for different energies

II-Sensitivity and Lower Limit Detection Results:

From Tables (4) and (5) we can determine Sensitivity (m) and lower limit detection (LLD) of X-ray Fluorescence Spectrometer according to Eq.(3) and (4) and these results are tabulated in Table (6).

Table (6) Lower Limit Detection and Sensitivity Results

Sample no.	Zn Wt%	At30KV,17mA		At 25 KV,15mA	
		LLD %	Sensit .(c/s%)	LLD%	Sensit .(c/s%)
Zn-1	0.025	0.000268	185280	0.000558	72120
Zn-2	0.050	0.000245	250000	0.000418	120000
Zn-3	0.075	0.000274	239466	0.000453	116920
Zn-4	0.100	0.000300	229800	0.000477	119320
Zn-5	0.125	0.000356	209456	0.000500	119520

Table (6) and Figs. (4), (5) shows the Correlation between the lower limit detection and Sensitivity for Zinc concentration at different operation condition, and shown that the Lower limit detection and sensitivity of Samples analyte at operation condition 30KV, 17mA is best than that the sample were analyte at operation condition 25KV, 15mA because the absorption effect of X-ray at 30KV is lower than that 0f 25KV and the statistical error is reduce when the intensity is increased and we can show the best case at the condition of 30 KV, 17mA in Figs. (4), (5) and in Table (6). The LLD and m are affected by the background and inter element effect and the absorption parameter .the effect of these factors is reduce at operation condition KV,17mA. As shown in Fig. (4) and (5).

The lower limit detection is generally defined as that Concentration equivalent to a certain number of standard deviation of the background count rate [8]. This means that three major factors will affect the detection limit for a given element, first the sensitivity of the spectrometer for that element, second, the background photons which can be reduced by increased photon energy, and third, the

available time for counting peak and background photons.

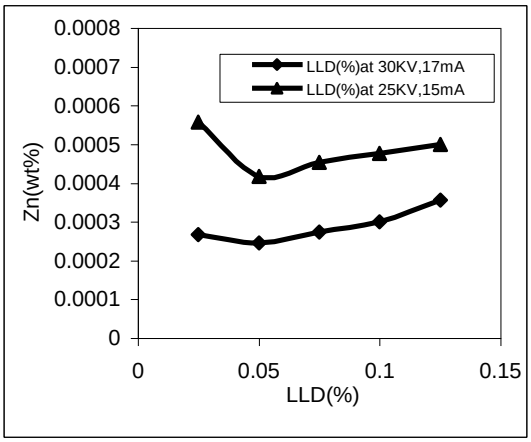

Fig. (4): Lower limit detection(%) versus against Zn concentration

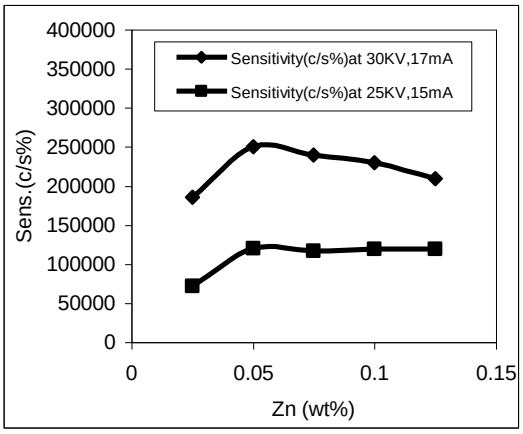

Fig. (5): Sensitivity (c/s%) as a function of Zinc concentration

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