INVESTIGATION ON THE SENSITIVITY OF X-RAY FLUORESCENCE(XRF) DETECTION SYSTEM FOR LIQUID SAMPLE OF MEDIUM Z-ELEMENT, ZINC (Zn)*

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ABSTRACT

The sensitivity of X-ray fluorescence (XRF) detection system for liquid sample of medium Z-element, zinc (Zn) was investigated and the optimal method was determined. In this study, Zinc sulphate ($ZnSO_4.4H_2O$) liquid sample was analyzed using (SPECTRO XEPOS) EDXRF system to investigate the sensitivity of the detection system for medium Z-element. The determination was performed by using five different sample preparation methods namely Method 1 (one drop method), Method 2 (two drops method), Method 3 (three drops method) and Method 4 (seven drops method), Method 5 (fourteen drops method). Sensitivity of the X-ray detection system increases with the sample amount. Among the five methods, Method 1 has easy sample preparation and more suitable for comparison analysis. But for precise analysis, it is needed to choose Methods 5 and careful sample preparation is required. From the correlation graphs (Sensitivity versus 'Z'), Method 5 has the best smooth curve from the comparing to five different methods. Therefore, it is found that Method 5 is the most suitable method for liquid sample of zinc.

Keywords : sensitivity, X-ray fluorescence , liquid sample, medium Z-element, correlation graphs

1 INTRODUCTION

Energy dispersive X-ray fluorescence technique has become a powerful technique for non-destructive multi-element analysis of materials. M. Rozmaric and V. Orescanen (2005) [1] reported the concentrations of the elements Pb, Rb, Sr, Y, Zr, K, Ca, Ti, V, Cr , Mn, Fe, Ni, Cu, Zn and Co were determined in the ash-samples of writing copying and computer printing papers by energy dispersive X-ray fluorescence (EDXRF). Non colored white papers of various manufactures and grammages were considered. Michael B. Biddle (2012) [2] have reported the concentrations of the elements Cl. Br, Sb, Ti, Pb, Cd, Zn, S, P, Ca and Fe were determined in plastics by using Energy Dispersive X-ray Fluorescence (EDXRF). Joshi *et al* (1998) [3] reported energy dispersive X-ray fluorescence (EDXRF) technique to determine the concentrations of different elements in water samples collected from different locations of famous Nainital Lake, including tap water and spring water sample Nainital(Uttaran chal). Campbell *et al* (2012) [4] demonstrates that the X-ray Fluorescence (XRF) technique is capable of performing elemental analysis of all of the pharmaceutical (liquid, powder and solid) materials with high sensitivity, precision and accuracy. Havrilla *et al* (1996) [5] reported that the program offers new approaches to actinide characterization. The dried spot method has the potential for rapid, multielemental analysis on small masses of volumes of material. The method utilizes 10-ml to 50-ml drops of solution, which are dried. The resulting dried residue is analyzed with sensitivities approaching less than 1 part per billion.

From the above research findings, the energy dispersive X-ray fluorescence (EDXRF) technique is simple, non destructive and simultaneous determinations of multi-elements from Na to U in a variety of solids, powders, liquids and films. EDXRF technique has numerous applications and great advantages in various fields for the determination of trace elements. However, the study is still wide open for investigation and for accurate measurements.

There are many compounds of medium Z-elements ($20 \leq Z \leq 40$). Among them, Zinc sulphate ($ZnSO_4.7H_2O$) were chosen for the study. In this research work, the investigation of sensitivity of XRF detection system for liquid sample of medium-Z element, zinc (Zn) would be carried out and find out the optimum method for elemental analysis for liquid sample using EDXRF.

2 MATERIALS AND METHODS

2.1 Materials

Three filter paper samples such as China made filter paper, Whatman No 1 filter paper, and Whatman No 2 filter paper were purchased from Able Lab ware Co.Ltd, Mandalay. Zinc sulphate ($ZnSO_4.7H_2O$) was also purchased from Able Lab ware Co.Ltd, Mandalay. Among the five water samples, the purified water, distilled water and rain water were collected from Able Lab ware Co.Ltd, Mandalay. Tap water and air-condition condensed water were also collected.

2.2 Methods

In this research work, measurements were made at University of Mandalay using SPECTRO XEPOS spectrometer. In this system, the X- ray tube was excited with a 50 watt palladium (Pd) anode target. To achieve sensitivity, the exciting radiation can be optimized by using secondary targets. Secondary target emits radiation when they are hit by radiation themselves. The secondary target used were Molybdenum (Mo), aluminium Oxide (Al_2O_3) and Highly Orient Pyrolytic Graphite (HOPG). X-ray emitted from the secondary target were counted by Si(Li) detector with resolution of 160 V at Mn(K_α), was used 50 keV bias voltages and tube current was automatically adjusted. The analyzed energy range was 0-50keV. The irradiation chamber was operated in air. The automatic sample changer could be equipped with 12 samples maximum. The prepared samples were measured two times for determination of sensitivity of the system. Each measurement has been carried out for 900 sec in three targets of the XRF spectrometer system. The sensitivity of XRF detection system and R^2 levels for selected medium Z-elements were determined by using five different methods.

The elemental content of the filter paper samples were determined by EDXRF technique.

The elemental content of the water samples were analysed by EDXRF technique.

Among many compounds of medium Z-elements ($20 \leq Z \leq 40$), Zinc sulphate ($ZnSO_4.7H_2O$) was chosen for the study. Molecular weight of zinc sulphate is 287.40 g. Zinc sulphate crystal (28.74 g) was dissolved in 100 ml of water and stirred thoroughly to obtain homogenous one molarity solution. The solution was assumed to be 100% solution.

To obtain 80% solution, 8 ml 100% solution was taken, 2 ml water was added and stirred thoroughly. 4 ml water was added to 6 ml 100% solution and stirred thoroughly to get 60% solution. 6 ml water was added to 4 ml 100% solution and stirred thoroughly to obtain 40% solution. 2 ml 100% solution was taken, 8 ml water was added and stirred thoroughly to get 20% solution. Gradurated pipette (one drop = 0.05 ml) was used for putting solution.

The diameter of the selected pre-analyzed whatmann no.1 filter paper is 30 mm. For Method 1, one drop (0.05 ml) of 100% solution was put onto the centre of the pre-analyzed whatmann no.1 filter paper and dried by using drying chamber. Then, dry paper piece was kept in plastic bag. For Method 2, the same procedure as described in Method 1 was performed two times and dried by using drying chamber. Then, dry paper piece was kept in plastic bag. For Method 3, the same procedure as described in Method 1 was performed three times and dried by using drying chamber. Then, this dry paper piece was also kept in plastic bag. For Method 4, the same

procedure as described in Method 1 was performed seven times and dried by using drying chamber. Then, dry paper piece was kept in plastic bag.

For Method 5, the procedure was same but 7 drops was applied two times and dried by using drying chamber. Then, dry paper piece was kept in plastic bag. The study was extended for 80% solution, 60% solution, 40% solution and 20% solution. After sample preparations, the filter papers that contain different amount of selected zinc compound were determined by using EDXRF.

3 EXPERIMENTAL RESULTS AND DISCUSSION

The concentrations of the elements of the filter paper samples were determined by EDXRF technique. The results were shown in Table-1.

Table 1 Concentrations of elements of filter samples analyzed by EDXRF

No.	Code Name	Concentrations of Elements (mg/l)					
		Ca	Fe	Cu	Mn	Cr	Total
1	FC	96.44	66.332	24.118	21.976	15.696	224.63
2	FT	75.58	76.811	30.767	26.452	18.826	228.436
3	FW	92.92	60.415	25.353	22.867	15.718	217.27

FC = China filter paper, FT = Whatman filter paper 2, FW = Whatman filter paper 1

Among the filter paper samples, Whatman No 1 filter paper consists of the least total concentrations of elements. Therefore, Whatman No 1 filter paper was chosen for the detection of the sensitivity of XRF system.

The elemental content of the water samples were analysed by EDXRF technique. The results were shown in Table-2.

Table- 2 Comparison of Element Concentrations and Physicochemical Values of Water Samples

No	Sample code name	pH	Conductivity	Alkalinity	Element Concentration (mg/l)						
					Ca	Fe	Cu	Mn	Zn	Cr	Total
1	PW	6.8					min		ND	min	min
2	DW	6.8			min						
3	IW	6.75	min	min			max	min	min		max
4	TW	7.3	max	max		min		max	max		
5	AW	6.8			max	max			ND	max	

PW = Purified Water DW = Distilled Water ND = Not Detect
IW = Injection Water TW = Tap Water min = minimum
AW = Collected Water of Air-conditional Room max = maximum

The concentrations of copper and manganese in purified water are less than that of other water samples and zinc can not be detected. Therefore, the purified water was selected for the study.

By using EDXRF, the sensitivity of XRF system was determined by changing the concentration of zinc for five methods. Various zinc concentrations prepared for this research work is shown in Table-3.

Table -3 The concentration of Zinc in Zinc Sulphate ($ZnSO_4$) under different Strength

No	Strength(%)	Concentration of $ZnSO_4$ ($g\ l^{-1}$)	Concentration of Zinc ($g\ l^{-1}$)
1	100	287.40	65.40
2	80	229.90	52.30
3	60	172.45	39.20
4	40	114.90	26.00
5	20	57.50	13.00

The peak area of chromium peaks were determined from the x-ray spectra. The results were described in Table -4.

Table- 4 The net peak area (counts) of Zinc in different percent concentrations for different methods

No.	Method	Counts for different concentrations				
		100%	80 %	60%	40 %	20 %
1	Method 1	5602789	5104974	4174772	1919981	1095685
2	Method 2	7574872	6998540	5530098	2347769	1534002
3	Method 3	11201125	9877455	5438331	3921220	1983991
4	Method 4	14022110	11667055	10997433	5649089	3500114
5	Method 5	16088442	13859554	12666347	7789322	4655781

The Zinc sensitivity graphs were plotted by using the concentration of liquid sample (g/l) with the peak area (counts) for five different methods. From the graphs, the sensitivity values were obtained by finding the slope of the graph line. The sensitivity graphs for Zinc are shown in Figure- 1 to Figure -5. The counts were observed from X-ray energy spectrum of Zinc Sulphate ($ZnSO_4$) Solution (Figure-6).

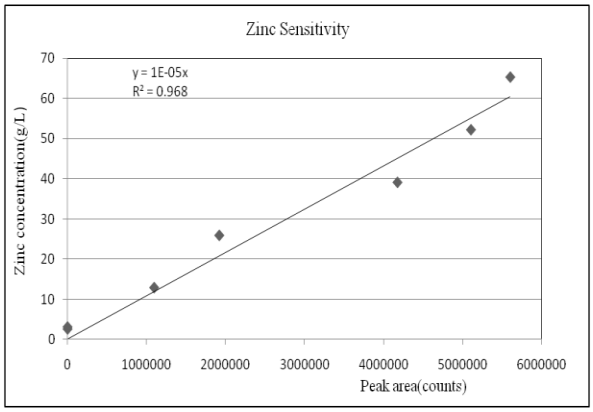

Figure-1 Zinc sensitivity curve for Method 1

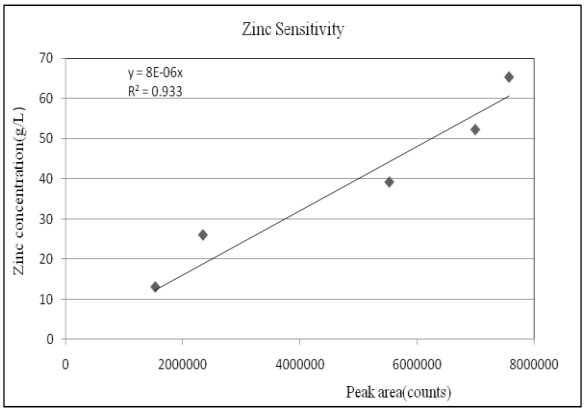

Figure-2 Zinc sensitivity curve for Method 2

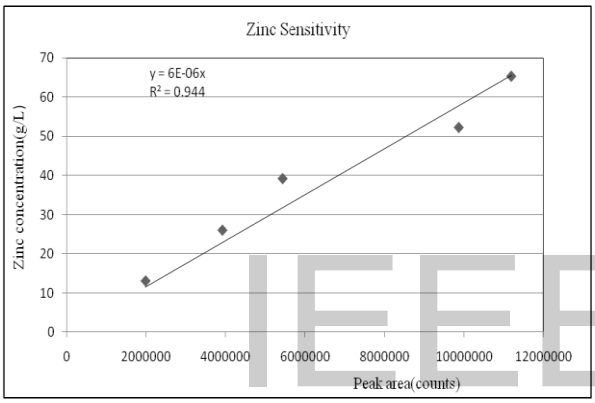

Figure-3 Zinc sensitivity curve for Method 3

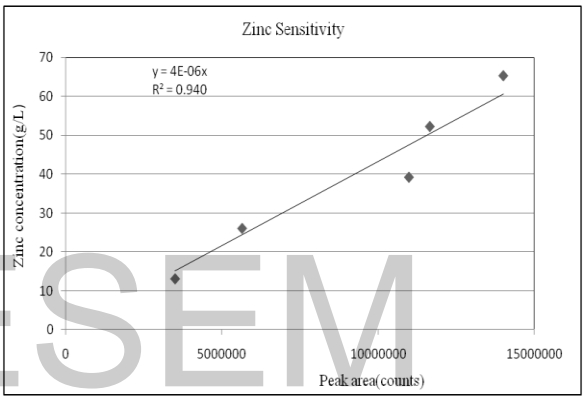

Figure-4 Zinc sensitivity curve for Method 4

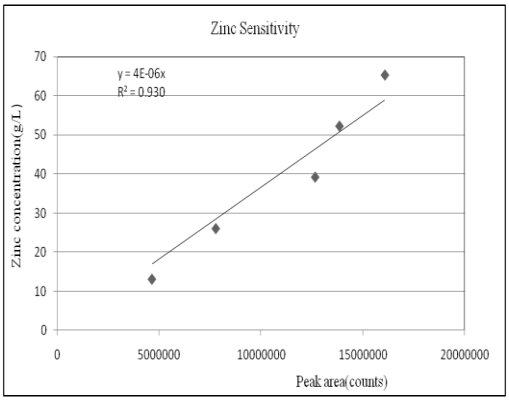

Figure-5 Zinc sensitivity curve for Method 5

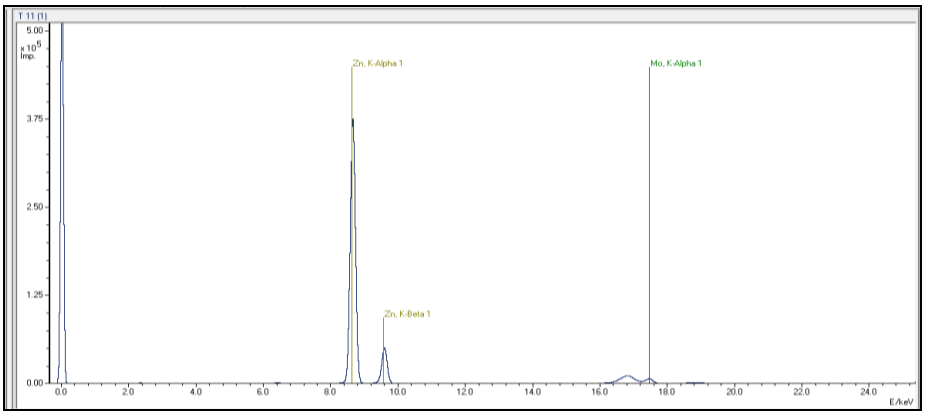

Figure -6 X-ray energy spectrum of Zinc Sulphate ($ZnSO_4$) Solution

The Sensitivity of Zinc for different methods were displayed in Table-5. R^2 values (linear with correlation coefficient) of the sensitivity graphs are tabulated in Table-5.

According to Table-5, Method 1 (one drop method) gives the least sensitivity value 1 x 10^{-5} g l^{-1} C^{-1} and Method 5 (fourteen drops method) gives the best sensitivity value 4 x 10^{-6} g l^{-1} C^{-1}. Method 2 improves sensitivity to 20% than that of Method 1. Method 3 improves sensitivity to 40% than that of Method 1. Method 4 and 5 improve sensitivity to 60% than that of Method 1.

Table-5 Sensitivity and R^2 levels of Zinc for different methods

No.	Method	Sensitivity (g $L^{-1}C^{-1}$)	R^2
1	Method 1	1 x 10^{-5}	0.9685
2	Method 2	8 x 10^{-6}	0.9333
3	Method 3	6 x 10^{-6}	0.9442
4	Method 4	4x 10^{-6}	0.9401
5	Method 5	4 x 10^{-6}	0.9309

Comparison of R^2 levels of the five sample preparation methods for Zinc sample are shown in Figure -7.

Comparison of Zinc sensitivity of five sample preparation methods is shown in Figure -8.

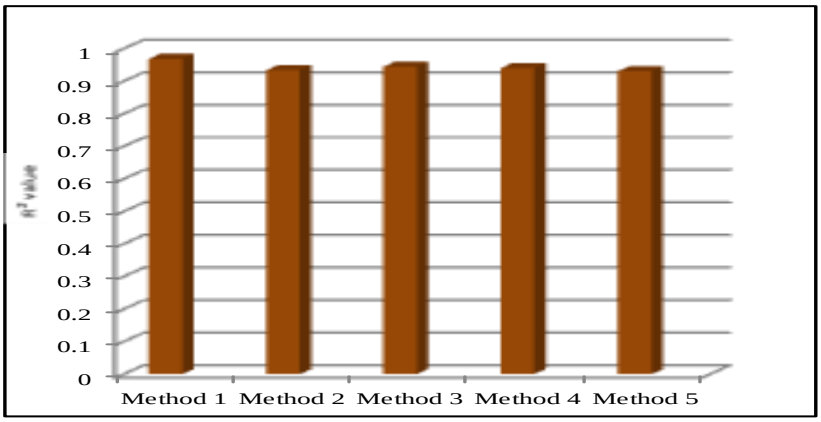

Figure-7 Comparison of R^2 levels of Zinc for different methods

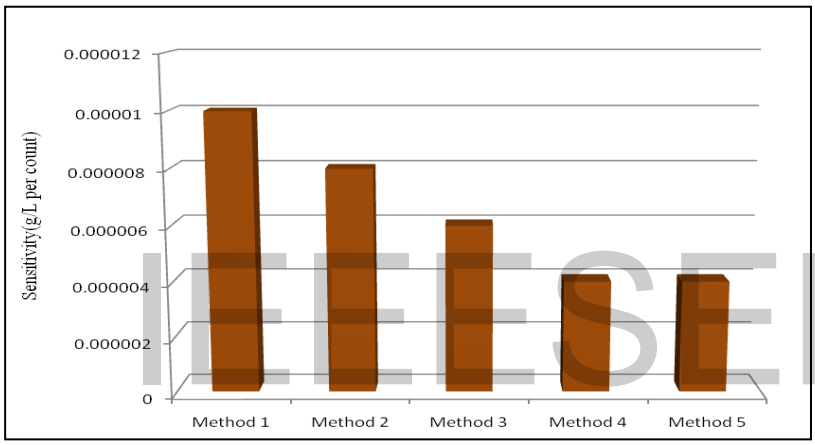

Figure-8 Comparison of sensitivity of Zinc for different methods

According to this figure, all methods have R^2 values greater than 0.9 and not so much different. Method 1 has the highest R^2 value and this means that it has the most reliable data set.
The Zinc sensitivity increases with the increasing the number of drop.

4 CONCLUSION

According to data of this research work, sensitivity of the X-ray detection system increases with the sample amount. So that, among the five methods, Method 5 (14 drops) gives the best sensitivity. Method 1 has the best R^2 value for medium 'Z' elements by the comparing to five different methods. Therefore, Method 1 has easy sample preparation and more suitable for comparison anslysis. But for precise analysis, it is needed to choose Methods 5 and careful sample preparation is required. From the correlation graphs (Sensitivity versus 'Z'), Method 5 has the best smooth curve from the comparing to five different methods. Therefore, it is found that Method 5 is the most suitable method for XRF detection system for medium Z-elements. Therefore, XRF detection system is very useful, convenient, precise and sensitive for the investigation on the sensitivity of medium Z-elements of liquid sample.

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