Asian Journal of Chemistry; Vol. 25, No. 5 (2013), 2557-2560

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2013.13454

Effect of Analysis Time on Detection Limit by Energy Dispersive X-Ray Fluorescence Spectrometry

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(*Received*: 16 January 2012; *Accepted*: 12 November 2012) AJC-12400

The influence of analysis time on detection limits in energy dispersive X-ray spectrometry was experimentally investigated. We utilized a high resolution Si(Li) detector (full width half maximum=160 eV at 5.9 keV) with a Camberra DSA-1000 desktop spectrum analyzer and Am-241 and Cd-109 radioactive point sources to collect X-ray spectra. The results showed that the detection limit decreased with increasing analysis time.

Key Words: Energy dispersive X-ray fluorescence, Detection limit, Fluorescence intensity.

INTRODUCTION

Energy dispersive X-ray fluorescence is one of the fundamental techniques used for multi-element analysis of archeological, geological, environmental and biological materials. This technique allows the determination of the trace elements' concentration in different types of materials with a very low detection limits. The detection limit (abbreviated by DL) can be defined as the minimum detectable amount, minimum detection limit must be removed, lower limit of detectability (LLD) or concentration at the detection limit.

Therefore, it shows the relative measure of the performance of applied technique. In X-ray fluorescence measurements, its most common definition is the amount of analyte that gives a net line intensity equal to three times the square root of the background intensity for a specified counting time or the amount that gives a net intensity equal to three times the standard counting error of the background intensity. Hence, detection limit is related to the capability of instrument to distinguish a peak intensity from the fluctuations of the background intensity due to counting statistics, or background noise. In above, the amount signifies concentration (per cent or mg/mL) for infinitely thick specimens, area density (mg/cm^2) for moderately thick specimens, or mass (mg) for extremely small particulate specimens.

Detection limit depends on experimental conditions such as sample matrix (absorption and enhancement), physical state of the sample (heterogeneity, surface, thickness, particle size, and mineralogy), instrument (energy resolution and quantum efficiency of detector), geometry, concentration and atomic number of analyte, matrix compositions, excitation conditions (X-ray tube or radioisotope source) and analysis time[1]. For example, the peak intensity of the sample response to a source decreases with decreasing the concentration of analyte and finally disappears in the background noise[2]. It can be deduced that detection limit depends mainly on two parameters; the background intensity (I_B) and the net area intensity per unit analyte mass (I_A/C_A) eqn. (4). It also varies with the specimen matrix composition. For instance, for a given analytical context and concentration of an analyzed analyte, we can say that the detection limit will be smaller when the matrix composition becomes lighter. It is because the degree of absorption decreases with light matrices and, therefore, the measured intensity is higher from samples with light matrices. detection limit may change with different X-ray energy levels since the sensitivity factor will be affected by the efficiency of characteristic lines to excite the element of interest. It also varies with the atomic number (Z) of the analyte. For example, let us take a given X-ray tube anode and divide the periodic table in three wavelength regions. The short wavelength region (0.3-0.8 Å), *i.e.*, for Zr (40) to Ba (56), is characterized by a moderate slope value, high background and excitation condition far from optimum, which lead to moderate detection limit values. The medium wavelength region (0.8-3 Å), *i.e.*, for Ca (20) to Zr (40) for K lines and for Ba (56) to U (92) for L lines, is characterized by a high slope value, low background and optimum excitation conditions, which lead to the best detection limit values. The long wavelength region (3-12 Å), *i.e.*, for Na (11)

to Ca (20), is characterized by a small slope value, low background and the poorer excitations, which lead to the poorest detection limit values[3].

Experimental measurements of detection limit have been performed since the early days of X-ray studies. Detection limit and estimate of uncertainty of analytical X-ray spectrometry results have been described[3]. In addition, matrix effect on detection limit and accuracy in total reflection X-ray fluorescence analysis of trace elements in environmental and biological samples have been experimentally investigated[4]. Furthermore, mercury in environmental samples using energy dispersive X-ray fluorescence and cold vapour atomic absorption (CV-AAS) have been analyzed[5]. Random left censoring approach to analyze trace elements in biomedical samples has been discussed[6]. An improved total reflection X-ray fluorescence setup has been proposed to obtain detection limit values in low ppm ranges[7]. While theoretical calculation of detection limits in total reflection X-ray fluorescence analysis has been presented[8], theoretical estimation of detection limits in inductively coupled plasma mass spectrometry has been investigated[9]. Furthermore, X-ray fluorescence detection limits for dental tissues of human teeth have been discussed[10]. Also, portable X-ray fluorescence techniques for the analysis of environmental samples have been successfully utilized[11]. The survey of detection limit has been carried out[12]. In addition, limit of detection criteria in analytical chemistry has been specified[13]. The effect of sample thickness on the accuracy of results has been explored[14]. Samples of healthy and carcinoma tissues, of colon, breast and uterus using total reflection X-ray fluorescence and energy dispersive X-ray fluorescence have been analyzed, too[15]. The influence of analyte mass concentration on detection limits in X-ray fluorescence spectrometry has been investigated[16].

In this research paper, we investigated the influence of analysis time on detection limits in Cu, Fe, Mn and Ni and their different compounds using Am-241 and Cd-109 radioactive point sources using energy dispersive X-ray fluorescence. In case there may not be any certified reference materials in every laboratory, in this study, we used an equation [eqn. (4)] for finding the concentration of detection limit different than that in the literature, which requires a conversion from measured net intensities to concentration[3], to analyze the effect of analysis times on detection limits[17].

EXPERIMENTAL

Detection limit has been defined in terms of standard counting error of the background intensity. If σ_P and σ_B are the counting errors of the individual peak and the background, respectively, then the standard counting error for a net count can be expressed as:

$$\sigma = \sqrt{\sigma_P^2 + \sigma_B^2} \quad (1)$$

In the limit of detection one can assume $\sigma_P \approx \sigma_B$. Therefore, we can write (1) as:

$$\sigma \approx \sqrt{2\sigma_B} \quad (2)$$

For 95 % confidence level, which demonstrates the reliability of measurements[18], the counting error would be:

$$2\sigma = 3\sqrt{N_b} \quad (3)$$

By taking into account the counting time T and the slope *m* of fluorescence intensity *vs*. analyte concentration curve, one can write the expression for minimum detectable concentration for an analyte element as:

$$C_{DL} = \frac{3}{m}\sqrt{\frac{N_B}{T}} \cdot m = \frac{I_A}{C_A}$$

$$\text{or } C_{DL} = \frac{3\sqrt{I_B}}{(I_A / C_A)} \quad (4)$$

where, I_A, C_A, N_B and C_{DL} denote, respectively, the net area intensity, the mass concentration of analyte, the background counts in a given time T and the minimum detectable concentration of analyte and I_B is the background intensity (N_B/T) and $m = I_A/C_A$, *i.e.*, slope of analyte counts-concentration curve.

Experimental setup: The experimental setup used in this work is shown in Fig. 1. X-ray spectra were collected using a Si(Li) detector with a Camberra DSA-1000 desktop spectrum analyzer. The energy resolution of the spectrometer was 160 eV at 5.9 keV. This procedure was based on the measurement of fluorescence intensity for 59.5 keV photon emitted from Am-241 radioactive point source and 22.1 keV photon emitted from Cd-109 radioactive point source. The main advantage of radioisotope excitation over X-ray tube excitation is the monoenergetic character of radioisotope-emitted X-rays, inexpensiveness and commercially availability. For X-ray tube excitation, the spectral distribution relationship between scattered and background radiation intensities is more complex as a result of the bremsstrahlung continuum. In this study, Mn, $MnBr_2$, $MnCl_2$, Fe, $FeBr_2$, FeSe, Ni, $NiBr_2$, NiSe, Cu, $CuBr_2$, $CuCl_2$ and $CuSeO_3.2H_2O$ were chosen as test sample elements. Samples were prepared in the form of pellets of mass -0.1 g. The advantage of making these pellets is that interelement enhancement effects in the sample are minimized. The effects of the matrix composition on the measured analyte-line intensity are known as matrix-, interelement-, self-absorption- and absorption-enhancement effects. Whatever absorption-enhancement effects a specified analyte-matrix system may be subject to, they are most severe at and above infinite thickness, decrease in severity as thickness decreases below infinite thickness, and substantially disappear in thin samples[1].

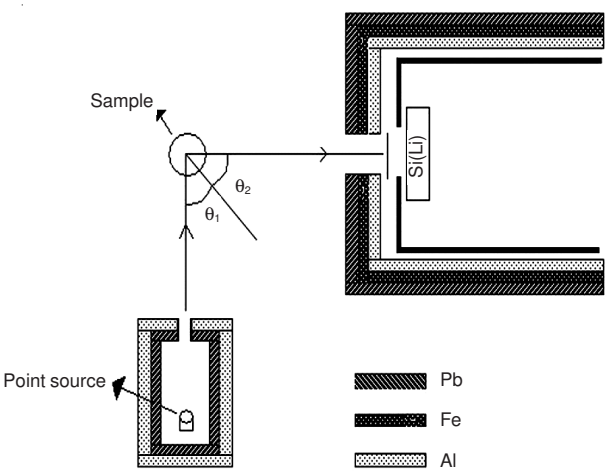

Fig. 1. Experimental set up for energy dispersive X-ray fluorescence analysis

TABLE-1
DETECTION LIMIT VALUES (ppm) WITH USING Am-241 RADIOACTIVE POINT SOURCE

	Sample	Analysis time (second)			
		500	1000	5000	10000
Detection limit (ppm)	Cu	42.56 ± 0.11	39.44 ± 0.15	30.86 ± 0.10	29.81 ± 0.09
	$CuBr_2$	33.14 ± 0.07	31.71 ± 0.07	26.72 ± 0.10	21.94 ± 0.05
	$CuCl_2$	51.87 ± 0.07	46.73 ± 0.09	37.35 ± 0.09	34.23 ± 0.04
	$CuSeO_3.2H_2O$	29.38 ± 0.09	27.57 ± 0.08	20.38 ± 0.06	18.81 ± 0.06
	Fe	94.46 ± 0.09	71.96 ± 0.10	40.38 ± 0.06	39.11 ± 0.06
	$FeBr_2$	70.33 ± 0.12	64.55 ± 0.15	39.41 ± 0.09	34.79 ± 0.05
	FeSe	164.99 ± 0.11	126.12 ± 0.08	69.52 ± 0.07	48.60 ± 0.08
	Mn	108.14 ± 0.16	89.68 ± 0.08	65.16 ± 0.06	57.81 ± 0.06
	$MnBr_2$	110.39 ± 0.12	95.36 ± 0.10	46.85 ± 0.06	45.83 ± 0.06
	$MnCl_2$	184.65 ± 0.09	120.48 ± 0.15	37.52 ± 0.09	36.79 ± 0.09
	Ni	56.87 ± 0.11	48.64 ± 0.05	17.05 ± 0.05	14.46 ± 0.03
	$NiBr_2$	71.91 ± 0.21	61.55 ± 0.12	30.56 ± 0.12	29.25 ± 0.06
	NiSe	143.10 ± 0.15	115.83 ± 0.12	47.63 ± 0.07	45.81 ± 0.05

TABLE-2
DETECTION LIMIT VALUES (ppm) WITH USING Cd-109 RADIOACTIVE POINT SOURCE

	Sample	Analysis time (sec)			
		500	1000	5000	10000
Detection limit (ppm)	Cu	15.02 ± 0.07	13.72 ± 0.05	9.47 ± 0.03	8.56 ± 0.02
	$CuBr_2$	13.29 ± 0.08	12.84 ± 0.04	11.67 ± 0.05	11.34 ± 0.04
	$CuCl_2$	12.37 ± 0.05	11.55 ± 0.06	9.38 ± 0.05	9.15 ± 0.02
	$CuSeO_3.2H_2O$	5.45 ± 0.13	4.61 ± 0.07	3.63 ± 0.04	3.34 ± 0.05
	Fe	164.12 ± 0.04	162.97 ± 0.02	161.01 ± 0.02	160.53 ± 0.02
	$FeBr_2$	14.72 ± 0.03	13.59 ± 0.06	12.11 ± 0.04	12.07 ± 0.02
	FeSe	181.48 ± 0.05	180.35 ± 0.06	177.10 ± 0.04	176.72 ± 0.03
	Mn	29.71 ± 0.08	26.802 ± 0.04	22.60 ± 0.07	20.47 ± 0.05
	$MnBr_2$	188.14 ± 0.05	179.10 ± 0.06	166.18 ± 0.04	163.94 ± 0.05
	$MnCl_2$	164.34 ± 0.04	158.76 ± 0.04	151.23 ± 0.02	150.74 ± 0.02
	Ni	17.19 ± 0.11	16.14 ± 0.03	14.19 ± 0.02	14.08 ± 0.02
	$NiBr_2$	12.82 ± 0.03	11.94 ± 0.05	8.87 ± 0.05	8.39 ± 0.02
	NiSe	14,44 ± 0.11	14.19 ± 0.08	13.51 ± 0.06	13.34 ± 0.05

To determine the contributions of the background and scattering from sample holder and air, measurements without sample were performed. To determine the effect of analysis time on detection limit, without changing the system geometry, every sample was measured for 500 s, 1000 s, 5000 s, and 10000 s. The incidence angle and angle of reflection on system geometry were chosen to decrease the contributions from the background.

RESULTS AND DISCUSSION

Detection limit of an element depends on some experimental conditions mentioned before. To investigate the effect of analysis time on the detection limits, in the present study, Cu, $CuBr_2$, $CuCl_2$, $CuSeO_3.2H_2O$, Fe, $FeBr_2$, FeSe, Mn, $MnBr_2$, $MnCl_2$, Ni, $NiBr_2$ and NiSe samples were chosen as test samples. Tables 1 and 2 demonstrate the detection limits of these samples *versus* some analysis times. The general tendency of detection limit values in Tables 1 and 2 is that they decrease with analysis time. For example, detection limit values for the Mn sample using Am-241 radioactive point source for 500 s, 1000 s, 5000 s and 10000 s are 108 parts per million (ppm), 90 ppm, 65 ppm and 57 ppm, respectively. In the same way, detection limit values for Mn sample using Cd-109 radioactive point source for the above corresponding analysis times are 29 ppm, 26 ppm, 22 ppm and 20 ppm, respectively. The above results are completely in good agreement with eqn. (4), which shows the relation between the detection limit concentration and analysis time.

Since the general tendency of decrease of detection limit *versus* analysis time is not easily seen from Tables 1 and 2. However obtained their curve-fitted plots to reveal this tendency or behaviour. For instance, corresponding curves for the Ni sample using Am-241 and Cd-109 radioactive point sources are given in Figs. 2 and 3. It is seen from these figures that detection limit values can significantly decrease for smaller values of analysis times whereas they slightly decrease with larger analysis time values. For instance, in Fig. 2, while the time analysis period between 500 s and 1000 s (ΔT = 500 s) corresponds to a decrease of nearly 8.23 ppm in detection limit, another period between 5000 s and 10000 s (ΔT = 5000 s) results in a minute decrease of approximately 2.59 ppm in detection limit. In addition that the curve-fitted data in Figs. 2 and 3 show the general trend of detection limit over analysis time, it can also demonstrate the optimum analysis times for a specified detection limit. It is seen from Fig. 2 that, for minimum detection limit can be attained for an analysis time of approximately 10000s.

Detection limit varies not only with Z (atomic number) of the analyte but also with the specimen composition. From Tables 1 and 2, detection limit values for ^{25}Mn, ^{26}Fe, ^{28}Ni, ^{29}Cu

elements ($24 < Z < 30$) show that the detection limits are better for elements with larger atomic numbers. Considering 500s as an example, detection limit values of ^{25}Mn, ^{26}Fe, ^{28}Ni, ^{29}Cu elements are 108, 94, 57 and 42 ppm. It is understood that the detection limit decreases for lower atomic numbers.

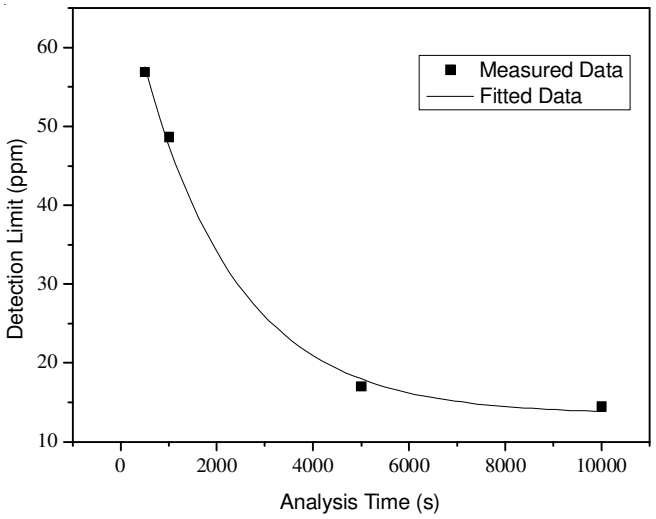

Fig. 2. Graph of Ni detection limits plotted against analysis times for Am-241 radioactive point source

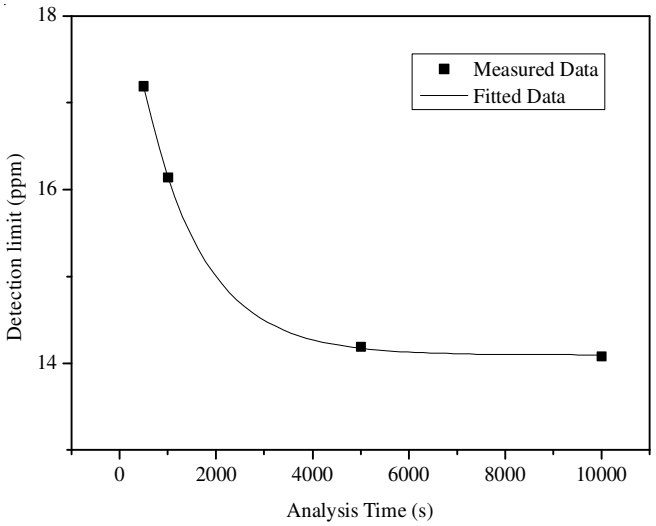

Fig. 3. Graph of Ni detection limits plotted against analysis times for Cd-109 radioactive point source

Errors are unavoidable concomitant of every measurement. They can arise from net area intensity, sample preparation, statistical error, and/or geometry reproducibility. To calculate the relative error in detection limit measurement, ten successive measurements were made for each measurement time. While the relative error contributing to detection limit measurement for Am-241 radioactive point source has been found to vary between 2 and 20 %, the same error for Cd-109 radioactive point source has been found to be between 1 and 12 %.

Present investigation can give some insight on the stability of the employed X-ray source. For example, considering the R^2 values, which show how the measured data fit to the exponential curve (or any other curve depending on the type of the behaviour of the function) for the Ni sample in Figs. 2 and 3, we can deduce from our preliminary data that the Cd-109 radioactive point source seems more stable than the Am-241 radioactive point source. To fully assess those sources and any other sources for their stability, more measurement data are needed, which we left as a future study.

In conclusion, the detection limit is an important parameter for direct analysis in energy dispersive X-ray fluorescence and can yield an optimum analysis time for a given sample. In addition, it can also give a chance to analyze the stability of the employed source for energy dispersive X-ray fluorescence measurements.

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