Evaluation of Detection Limits with Wavelength Dispersive X-Ray Fluorescence Spectrometry

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Abstract

The influence of analyte mass concentration on the determination of detection limits has been investigated by using WDXRF (Wavelength dispersive X- ray fluorescence) spectrometry. Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Y, Zr, Nb, Mo, Ag, Cd, Sb, Nd, Gd, Er elements and binary and triple combination of these elements have been used. The samples have been selected considering the absorption edges due to the importance of the effect of matrix absorption and enhancement. The elements which have absorption edges that are close to each other have been used observe the matrix absorption and enhancement. From this results corresponding to the interval of 5-25 times the best value of the detection limits of analytical concentration values are found to be the ideal values. It is concluded that WDXRF spectrometry is a suitable technique for the determination of detection limits.

Keywords: analyte, detection limits, WDXRF, matrix, absorption and enhancement.

1. Introduction

X-ray fluorescence spectrometry is one of the appropriate techniques for elemental analysis of materials. This technique is based on the sample excitation with the release of the secondary X-rays. They contain a concentration of the elements in an unknown sample by comparison with standards of known values located in another sample PITSCH (2000).

A commercial WDXRF (Wavelength dispersive X-ray fluorescence) spectrometer (Bruker S4 Explorer, Karlsruhe, West Germany) was used for analysis of the different samples. All the elements in the sample can be determined simultaneously in the WDXRF spectrometry. This instrument is usually equipped with a 1 kW Rh-anode tube working at a voltage range of 20-50 kV and a current from 50 to 20 mA. It is possible to use primary beam filters (made of Al or Cu) between the primary radiation and the sample holder to reduce the background continuum and to improve the signal-to-noise ratio. Energy resolution and efficiency for each analytical line also depend on the collimator aperture and the analyzer crystals in use. Detection can be performed using a flow proportional counter (light elements) or a scintillation counter (heavy elements) GONZALEZ-FERNANDEZ et al. (2009). In this work, analyses were made in vacuum atmosphere.

The detection limits, is of interest to analytical chemists due to the trace detection of the compound. In many literature, improved analytical methods used to determine the detection limit and new instruments used are mentioned. THOMPSON (1998) mentioned in his theoretical work that the limit of detection can never be fully interpreted, in fact it seems to be a very difficult subject to be understood and defined on the basis of this seemingly simple matter.

Then, CURRIE (2000) noted that despite the successful work on the detection limit, some problems still exist in this work. The problem of determining the limit of detection has been shown to occur more in biological and environmental samples. ROUSSEAU (2001) investigated the effect of analytical errors on the detection limit, using some chemical samples, and calculated how much the systematic and random error sources affected the result. In the following years TIWARI et al. (2005) investigated the effect of analyte mass concentration on the detection limit using total reflectance X-ray fluorescence (TXRF) and energy X-ray fluorescence (EDXRF) spectrometers. As a result, they observed that the analyte mass concentration affected the detection limit values. SHALTOUT et al. (2007)

determined the detection limit values by atomic absorption spectroscopy using Cd, Ni, Pb and Zn samples and showed that the detection limit value could be decreased by adjusting the absorption mode and counting time. KARJOU (2007) investigated matrix effects on the detection limit by using TXRF spectrometry using multiple standard solutions of the NH_4NO_3 sample at various concentrations. He observed that the low matrix concentration did not affect the detection limit, but the high matrix concentration strongly affected the detection limit. He also investigated the effect of sample mass on the detection limit using soil and blood samples and showed that the detection limit increased with increasing sample mass in the concentration unit but the detection limit increased with increasing sample mass in mass unit.

In studies carried out until today, the effects of matrix effects and analytical mass concentration on the detection limit have been investigated using various instruments, liquids and biological samples on the detection limit. But we know that since the detection limit is an indication of sensitivity, the most accurate analytical mass that should be used to obtain the most accurate measurement should be determined in scientific studies. In this study, a study was carried out to investigate the values of appropriate analyte concentrations and obtain more accurate results. Here, it is aimed to achieve accurate sample standards using WDXRF spectrometer.

2. Experimental Details

The detection limit is usually defined as the smallest amount of an analyte that can be detected in a specimen. However, it is often misinterpreted as the smallest concentration of an analyte that can be determined with reliability in a given sample ROUSSEAU (2001). 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 peak intensity from the fluctuations of the background intensity due to counting statistics, or background noise EKINCI et al. (2013) (Furthermore, the detection limit calculations are based on background measurements, which are below any peak intensity used for a possible determination.

The following formula is commonly accepted to define the detection limit in XRF techniques VAN GRIEKEN (1993) and KLOCKENKAMPER (1997),

$$C_{DL} = \frac{3}{S\left(\frac{N_B}{T}\right)^{1/2}} \qquad (1)$$

Where C_{DL} is the detection limit (mass or concentration unit), N_B is the intensity of the background under the respective peak in count per second (cps), S is the sensitivity (net peak counts per second, per mass or concentration unit and T is the counting time (s). The equation shows that increasing S and T, and reducing N_B improves the C_{DL}.

Mathematically, as per the IUPAC recommendation, the detection limit has been defined in terms of standard counting error of the background intensity BERTIN (1975). 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,

$$\sigma = \sqrt{\sigma_p{}^2 + \sigma_b{}^2}$$

In the limit of detection one can assume $\sigma_b \approx \sigma_p$. Therefore

$$\sigma = \sqrt{2\sigma_b}$$

For 95% confidence level, the counting error would be

$$2\sigma = 3\sigma_b = 3\sqrt{N_B}$$

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

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

or

$$C_{DL} = \frac{3\sqrt{I_b}}{\frac{I_A}{C_A}}, \quad m = {I_A}/{C_A} \qquad (2)$$

Where I_b= background intensity (N_B/T); I_A= net area intensity; C_A= mass concentration of analyte; N_B=

background counts in a given time T; m= I_A/C_A, i.e. slope of analyte counts concentration curve; $C_{DL}=$ minimum detectable concentration of analyte. From Eq. (2), it is clear that, for a specified counting time, the minimum detectable concentration of analyte or 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) TIWARI (2005).

XRF is often studied in solid samples. However, analysis of the solution can be performed using a suitable apparatus. Solid samples or adjusting surface sample is irradiated directly or tablet then made into a powder before irradiation. Sample will be considered in the preparation to ensure homogeneity biggest point is. Quick and simple way to prepare powder is directly pressed into the pallets of equal density. Samples were irradiated by placing the cell sample prepared by the method of assembly.

In this study, ZSX 1000e wavelength X-ray fluorescence device produced by Rigaku Company was used. In the WDXRF spectrometer, the analyzer crystal distributes the secondary characteristic X-ray so that each wavelength can be measured separately.

X-ray fluorescence spectroscopy usually involves working with solid samples. However, the analysis of the solutions can also be carried out using appropriate tool. The solid samples are either irradiated directly by smoothing a surface such as in steel analysis, or first powdered and then tableted and irradiated. The greatest point to note in preparing the sample is to ensure homogeneity. If the sample is in the form of very fine powder or if it can be crumbled to the grain size below 200 mesh, the powder sample is mixed with the necessary materials and then pressed into a tablet.

Analytical information for long wave length will be generated when well powdered powders are pressed at high pressure. Powders can be pressed into aluminum containers and steel circles. Alternatively, a boric acid binder or a hard pressing binder may be used.

In this study, samples have been selected considering the absorption edges due to the effect of matrix absorption and enhancement. The elements which have absorption edges that are close to each other have been used observe the matrix absorption and enhancement. Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Y, Zr, Nb, Mo, Ag, Cd, Sb, Nd, Gd, Er elements and binary and triple combination of these elements have been used. A total of 69 samples were prepared, including the pure substance and mixtures. Mixtures to study the effect on the detection limit of the concentration of analyte and matrix were prepared at different concentrations. Powdered samples were first milled using an agate mortar and then sieved through 100-400 mesh fine sieves to remove particle size effect. Then all the pressed samples were prepared in the same form with a thickness of 13 mm by applying a pressure of 10 tons equally to each sample with a pressing machine. Any losses that might occur during sample preparation and error to minimize tools are used. Samples were prepared in the form of pellets of mass 0.6g. The advantage of making these pellets is that interelement enhancement effects in the sample are minimized. Counting time for each sample has been set 10800s. Manufactured by Rigaku Company ZSX 1000e WDXRF instrument was used. The data received by the WDXRF system is transferred to the origin pro 7.5 of the program and element spectra have been drawn. Representatively, the spectrum of 0.6g Cr sample is showed in Fig 1.

Detection limits of the elements were calculated from using Eq (2). Calculated results are shown in the table 1, table 2, table 3, table 4 and table 5.

kcps
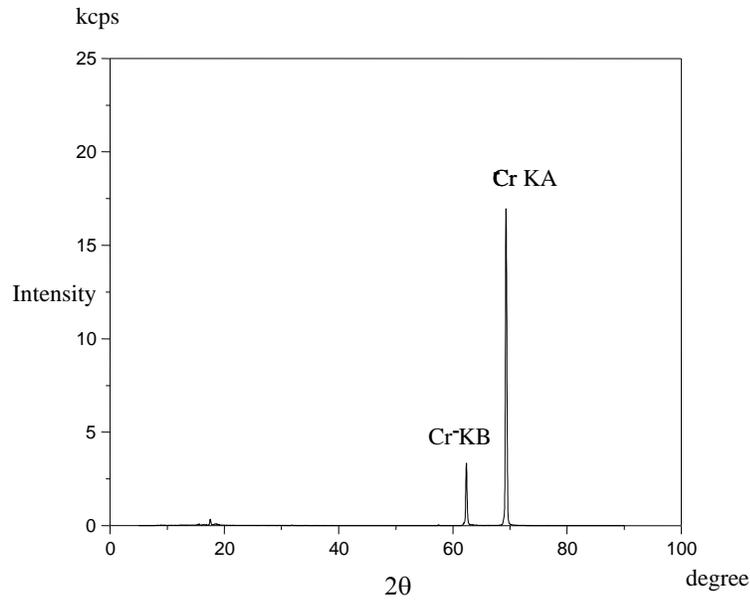
Figure 1. 0.6g Cr sample of X-ray spectrum of K_α and K_β.

Table 1. The C_{DL} has been calculated for Ti, Cr, V elements and binary and triple combination of these elements.

Sample	Analyte	C_{DL} (ppm)
Ti		8,21683
Cr		6,24160
V		5,71532
0,5Ti 0,1V		
	Ti	6,18057
	V	1,34397
0,4Ti 0,2V		
	Ti	5,05238
	V	2,19541
0,3Ti 0,3V		
	Ti	4,89362
	V	2,95654
0,5V 0,1Cr		
	V	5,55337
	Cr	1,09310
0,4V 0,2Cr		
	V	5,04408
0,3V 0,3Cr	Cr	1,43912
	V	4,63893
	Cr	2,61159
0,5Ti 0,1Cr		
	Ti	7,83066
	Cr	0, 80172
0,4Ti 0,2Cr		
	Ti	5,51336
	Cr	2,22325
0,3Ti0,3Cr		
	Ti	4,82093
	Cr	3,08829

0,4Ti 0,1V 0,1Cr	Ti	3, 92613
	V	1,17492
	Cr	2,13014
0,3Ti 0,2V 0,1Cr	Ti	3,24820
	V	2,22665
	Cr	1,28536
0,3Mn 0,1Fe 0,2Ni	Ti	2,83310
	V	2,31355
	Cr	1,45261
0,2Mn 0,2Fe 0,2Ni	Ti	2,50904
	V	1,64086
	Cr	2,56115

Table 2. The C_{DL} has been calculated for As, Y, Zr, Nb, Mo elements.

Sample	C_{DL} (ppm)
As	5,15022
Y	7,35368
Zr	7,50342
Nb	7,94702
Mo	8,02405

Table 3. The C_{DL} has been calculated for Fe, Mn, Ni elements and binary and triple combination of these elements.

Sample	Analyte	C_{DL} (ppm)
Fe		5,69786
Mn		5,26947
Ni		5,14553
0,5Mn 0,1Fe		
	Mn	3,14869
	Fe	0,38061
0,4Mn 0,2Fe		
	Mn	4,62920
	Fe	0,55162
0,3Mn 0,3Fe		
	Mn	4,93372
	Fe	2,16401
0,5Mn 0,1Ni		
	Mn	3,64869
	Ni	2,96533
0,4Mn 0,2Ni		
	Mn	2,72444
0,3Mn 0,3Ni	Ni	4,14291
	Mn	2,17375
	Ni	5,40387
0,5Fe 0,1Ni		
	Fe	5,38086
	Ni	1, 74123
0,4Fe 0,2Ni		

Sample	Analyte	Value
	Fe	4,79443
	Ni	2,37291
0,3Fe 0,3Ni		
	Fe	4,19142
	Ni	4,61387
0,4Mn 0,1Fe 0,1Ni	Mn	3, 61961
	Fe	0,24320
	Ni	1,65356
0,3Mn 0,2Fe 0,1Ni	Mn	2,84615
	Fe	0,61279
	Ni	1,81125
0,3Mn 0,1Fe 0,2Ni	Mn	2,14044
	Fe	0,25263
	Ni	2,78491
0,2Mn 0,2Fe 0,2Ni	Mn	1,88106
	Fe	0,51117
	Ni	2,82660

Table 4. The C_{DL} has been calculated for Ag, Cd, Sb elements and binary and triple combination of these elements.

Sample	Analyte	C_{DL} (ppm)
Ag		8,12247
Cd		9,22396
Sb		10,0217
0,5Ag0,1Cd		
	Ag	7,65784
	Cd	0,54496
0,4Ag0,2Cd		
	Ag	6,44775
	Cd	1,82913
0,3Ag0,3Cd		
	Ag	3,92228
	Cd	4,78321
0,5Cd0,1Sb		
	Cd	7,78526
	Sb	1,58377
0,4Cd0,2Sb		
	Cd	6,41392
	Sb	3,04778
0,3Cd0,3Sb		
	Cd	4,93237
	Sb	4,61682
0,5Ag 0,1Sb		
	Ag	5,75317
	Sb	1,93770
0,4Ag0,2Sb		
	Ag	4,72392
	Sb	2,94944
0,3Ag0,3Sb		
	Ag	3,90539
	Sb	4,85898
0,4Ag0,1Cd0,1Sb		

	Ag	5,52481
	Cd	1,26692
	Sb	1,68731
0,3Ag 0,2Cd 0,1Sb		
	Ag	5,03097
	Cd	2,35657
	Sb	1,71835
0,3Ag 0,1Cd 0,2Sb		
	Ag	4,61418
	Cd	1,51606
	Sb	2,84283
0,2Ag 0,2Cd 0,2Sb		
	Ag	3,25696
	Cd	2,43185
	Sb	3,21256

Table 5. The C_{DL} has been calculated for Nd, Er, Sb elements and binary and triple combination of these elements.

Sample	Analyte	C_{DL} (ppm)
Nd		15,1860
Gd		17,8293
Er		18,6608
0,5Nd0.1Gd		
	Nd	14,1688
	Gd	1,26718
0,4Nd0,2Gd		
	Nd	12,2619
	Gd	3,64456
0,3Nd0,3Gd		
	Nd	1,12522
	Gd	16,2169
0,5Gd0,1Er		
	Gd	16,0117
	Er	1,89313
0,4Gd0,2Er		
	Gd	13,9736
	Er	4,17825
0,3Gd0,3Er		
	Gd	9,84345
	Er	9,14732
0,5Nd 0,1Er		
	Nd	10,0412
	Er	3,65477
0,4Nd 0,2Er		
	Nd	9,31480
	Er	6,24224
0,3Nd 0,3Er		
	Nd	5,87458
	Er	9,56043
0,4Nd 0,1Gd 0,1Er		

	Nd	11,2636
	Gd	1,05750
	Er	2,03146
0,3Nd 0,2Gd 0,1Er		
	Nd	11,1478
	Gd	3,51325
	Er	2,58146
0,3Nd 0,1Gd 0,2Er		
	Nd	9,65643
	Gd	1,27062
	Er	2,62759
0,2Nd 0,2Gd 0,2Er		
	Nd	2,17820
	Gd	4,45414
	Er	9,15146

4. Result and Discussion

In this study, mixtures of various ratios of elements on the C_{DL} are used to observe the effects of matrix. To investigate the analyte mass concentration on detection limits, in the present study, Ti, V, Cr, Mn, Fe, Ni, Cu, Zn, As, Y, Zr, Nb, Mo, Ag, Cd, Sb, Nd, Gd, Er elements and binary and triple combination of these elements were chosen as test samples. Tables 1, 2, 3, 4 and 5 demonstrate the detection limit values of these samples. As a result, it was found that the detection limit for the low analyte concentration was more affected than the high analyte concentration. If the analyte concentration is reduced, the background significantly decreases as the fluorescence peak increases the tail width. Decreasing the analyte concentration causes the analyte peak to weaken and causes the detection limit value to be smaller than the appropriate value.
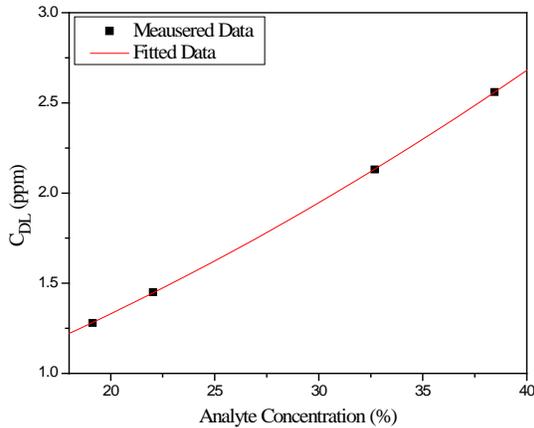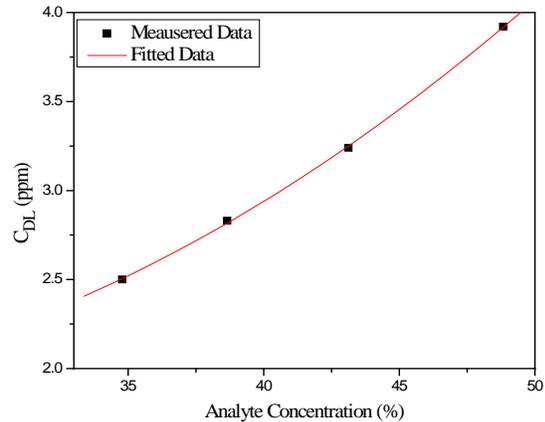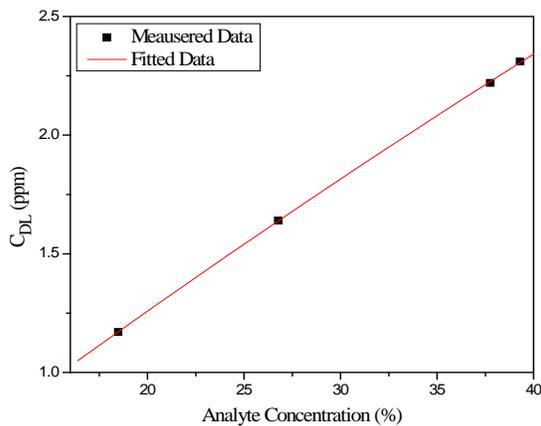
Figure 2. (a) Variation of Ti detection limits with analyte concentration in the sample of TiVCr. (b) Variation of V detection limits with analyte concentration in the sample of TiVCr. (c) Variation of Cr detection limits with analyte concentration in the sample of TiVCr.

As shown in figure 2 (a) drawn for the TiVCr sample, the minimum detectable limit for Ti analysis is equal to the analyte concentration of 2,509 ppm to 34,78 ppm (about 14 times). As shown in Figure 2 (b), the minimum detectable limit value for V analytics is equal to the analyte concentration of 1,175 ppm to 18,48 ppm (about 16 times). As shown in Figure 2 (b), the minimum detection limit for Cr analysis is equal to the analyte concentration of 1,285 ppm to 19,13 ppm (about 15 times).

We have also taken into account the total errors contributed in detection limits measurement as well as in preparation of analyte concentration. Since the detection limit depends linearly on analyte concentration, the net error in these two parameters has been calculated partially. The total error contributed to detection limit measurement has been found to vary from 1-8%.

One of the biggest problems encountered in XRF analyzes is the matrix absorption enhancement effects. The intensity of the secondary X-ray given by the quantitative element is influenced by the other elements in the sample, either positively or negatively. As a result of this influence, the analyte intensity may be greater or less than predicted. For the K lines of consecutive element pairs from the periodic table atomic number 22 titanium to the atomic number 72 hafnium from the atomic order, absorption-enhancing effects occur at the middle level. In this study, if the atomic number of Ti is 22, the atomic number of 23 is V, and the atomic number of 24 is Cr, For the TiV mixture, K_α of the V excites the Ti. For the VCr mixture, K_α of the Cr excites the V. For the TiCr mixture, K_α of the Cr excites the Ti. For the TiVCr mixture, K_α of the V excites the Ti, K_α of the Cr excites Ti, K_α of the Cr excites V and K_α of the V excites Ti The contributions to the intensity of Ti from the primary beam excitation are directly enhancement by the K_α of V, direct enhancement by the K_α of Cr and the third element enhancement by the K_α of V. All of the angular spectrometers and devices that select the pulse height cannot distinguish these lines. For this reason, the K_α and K_β lines of some elements are overlaid.

In conclusion, our study shows that the detection limit tends to be dependent on the analyte concentration. The results from this systematic study are given in order to get the best detection limit value under the experimental conditions that can help us on what should be required of the mass concentration of the analyte. The results obtained indicate that the optimum value of detection limit will correspond to analyte mass concentration 5-25 times of the best detection limit. It is clear from this that the limit of detection is dependent on the analyte mass concentration.

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