REDUCING MATRIX EFFECT ERROR IN EDXRF: COMPARATIVE STUDY OF USING STANDARD AND STANDARDLESS METHODS FOR STAINLESS STEEL SAMPLES

MEOR YUSOFF M.S.[a], **MASLIANA M.**[b] and **WILFRED P.**[c]

[1]*Material Technology Group, Industrial Technology Group, Malaysian Nuclear Agency, Bangi, 43000 Kajang, Selangor*

[a]*meor@nuclearmalaysia.gov.my,* [b]*masliana@nuclearmalaysia.gov.my,* [c]*wilfred@nuclearmalaysia.gov.my*

ABSTRACT

Even though EDXRF analysis has major advantages in the analysis of stainless steel samples such as simultaneous determination of the minor elements, analysis can be done without sample preparation and non-destructive analysis, the matrix issue arised from the inter element interaction can make the the final quantitative result to be in accurate. The paper relates a comparative quantitative analysis using standard and standardless methods in the determination of these elements. Standard method was done by plotting regression calibration graphs of the interested elements using BCS certified stainless steel standards. Different calibration plots were developed based on the available certified standards and these stainless steel grades include low alloy steel, austentic, ferritic and high speed. The standardless method on the other hand uses a mathematical modelling with matrix effect correction derived from Lucas-Tooth and Price model. Further improvement on the accuracy of the standardless method was done by inclusion of pure elements into the development of the model. Discrepancy tests were then carried out for these quantitative methods on different certified samples and the results show that the high speed method is most reliable for determining of Ni and the standardless method for Mn.

ABSTRAK

Walaupun analisis EDXRF mempunyai beberapa kelebihan didalam menganalisis keluli seperti boleh menentukan unsur surihan secara spontan, analisis boleh dibuat tanpa penyediaan sampel dan teknik analisis tanpa rosak, isu matriks dari interaksi antara unsur boleh menyebabkan analisis akhir kuantitatif menjadi tidak tepat. Kertas kerja ini menerangkan satu kajian kuantitatif perbandingan mengguna piawai dan tanpa piawai bagi menentukan unsur-unsur ini. Kaedah piawai dilakukan dengan melakar geraf kalibrasi secara regression bagi unsur-unsur yang dikehendaki menggunakan piawai keluli dari BCS. Geraf-geraf kalibrasi bagi keluli jenis low alloy steel, austentic, ferritic dan high speed telah dibangunkan melalui kaedah ini. Kaedah tanpa piawai pula melibatkan penggunaan model mathematik yang menggurangkan kesan matriks menggunakan model Lucas-Tooth and Price. Penambaikkan bagi model ini dilakukan melalui penggunaan unsur-unsur tulen bagi meningkatkan ketepatan analisis. Ujian perbezaan kemudiaannya dilakukan bagi berapa sampel piawai dan hasil darinya didapati kaedah high speed adalah terbaik bagi unsur Ni manakala kaedah tanpa piawai adalah terbaik bagi unsur Mn.

Keywords: EDXRF, minor elements, stainless steel, standard and standardless methods

INTRODUCTION

Stainless steel is presently one of the widely used structural metals. The two most common categories of stainless steel are the 300 and 400 series. Each of these series can be further reclassified into different grades (Tiwari et al, 2001). Stainless steel 300 series and in particular the SS 304 and SS 316 grades are the most widely used metal. The SS 304 is used in sanitary, cryogenic applications as well as tank structural parts and processing equipments. While SS 316 is more resistance to corrosive and it is used in applications like handling of hot organic and fatty acids, boat rails and hardware and facades of buildings near the ocean. One of the important method of identifying type and grade of stainless steel is from their elemental content. Generally in stainless steel samples besides Fe, other alloying elements like C, Mn, Cr, Mo and Ni are also present to improve the strength and properties of the metal. One of the methods that had been approved to analysed the elemental content of stainless steel is energy dispersive x-ray flourescence (EDXRF). As an example, E1085-95(2000) is a ASTM standard test method for the determination of stainless steel using the EDXRF method.

Even though EDXRF is known to be a modern technique for fast and non-destructive elemental analysis, the accuracy of the technique is much depended on the availability of standard reference material with the chemical content as the sample. Matrix effect is term as the inter element effect resulted from the characteristic x-ray produced from the element that can further result in the enhancement or absorption of the energy release. The effect is much depended on the binding energy value of the different atoms present. Reduction of matrix effect can be done either by the standard or standardless methods. In the standard method, calibration graphs of the interested elements are plotted and from this graphs the concentration of the elements in the sample will be obtained.

Matrix effect correction of stainless steel samples can also be done using the standardless method. The standardless method involves methematical calculation to reduce the absorption and enhancement effects or also known as matrix effect from the characteristic x-ray of the different elements present in the samples [5]. Standardless method is a cheaper and faster method is determine these elements as it does not requires the need of plotting of interested elements from standard reference samples. However, the standarless method has a lower accuracy than the standard method where some past papers have put it as 20-50% less accurate compared to the standard method [2,3,5,6]. A modified standardless method was used by our group whereby pure elements were incorporated into the matematical model to further helps in eliminating the matrix effect.

In this study we will do a comparative study to determine the error of using the standard as well as a modified standardless method on stainless steel. The accuracy is determine by using the discrepancy test where the elements present in the certified value of stainless steel standard was compared the standard and standardless methods.

EXPERIMENTAL METHODS

EDXRF analysis was carried out using Thermo-Fisher Quant X at Malaysian Nuclear Agency, Bangi. Four different sets of stainless steel standards (low alloy steel, austentic, ferritic and high speed) obtained from British Certified Standard (BCS) were used for the analysis. The interested elements of Cr, Mn, Ni and Mo with different concentrations were used for the plotting of the calibration graphs. Each sample was run in triplicate and the mean of the result was plotted in the calibration graph together with their error bars. X-ray tube serves as the source for X-ray beams in EDXRF and this will results to the development of an absorption process. The transition of a higher energy level electron to its lower level will produce characteristics X-ray that will be channeled to the detector [6]. The presence of a multi-channel analyzer card in the computer enables the identification of the elements present through their energy spectrum. The percentage of element present in the standard was determined both by standard and standardless methods.

RESULTS AND DISCUSSION

When an X-ray strikes an electron from the inner orbit of an atom, the determinant factor for the electron to be released from its orbit is binding energy. The electron will be released if the x-ray energy is greater than the binding energy and this will eventually resulted to the electron from the outer orbit to replace the empty position of the inner orbit. As the electron in ther outer orbit has a higher energy than that of posses by electron in the inner orbit, the different in energy will be released as characteristic x-ray. Characteristic x-ray produced from the different atoms could resulted in either it can initiate further charateristic x-ray of other atoms or is also known as the enhancement effect. This happen for atoms that lower binding energy than the produced characteristic x-ray [3,5,7]. However in cases where the binding energy for the electron is higher than the emitted characteristic x-ray, the atom will absorbed the x-ray and eventually resulted to a reduction in the characteristic x-ray. Thus, matrix effect involves the error obtained for the different elements present in the sample due to the absorption and enhancement effects.

The matrix effect can be corrected by using standard reference material of the same matrix such as the stainless steel reference standards as had been done in this study. The method involves the construction of calibration graphs of each of these elements and this was done by measuring the intensities of the different elements found in the reference standards. The reference standards were then then analysed under these two different conditions to acquire all the interested elements. The energy spectral intensity data from these standards were then processed by least-square regression analysis with statistcal evaluation carried out after repeating each analysis 3 times. The resulting regression equation is of the form [5,7];

$$C_i = K_i \,.\, I_i \,.\, F_i \qquad (1)$$

where

C_i = concentration of element I

K_i = a calibration constant, for the measurement conditions used

I_i = net peak intensity of element i

F_i = some function correcting matrix (= 1, if no correction is used)

The intensities of the characteristics energies for the different elements were then plotted with the certified reference standards used in the analysis and calibration graphs of the elements were obtained. Calibrations graphs were for plotted for Si, Cr, Mn and Ni using low alloy steel, austentic, ferritic and high speed types of stainless steels.

Straight-line calibration graphs were obtained for all the elements with the correlation coefficients values ranges from 0.914 to 0.999 (Table 1) for low alloy steel, 0.812 to 0.995 for ferritic, 0.590 to 0.989 for austentic and 0.691 to 1.000 for high speed tool. The correlation coefficients values obtained are important as they indicate the accuracy of the method whereby the larger is the value the more accurate is the calibration.

Table 1: Correlation coefficient values of calibration graphs of minor elements in different stainless steel

Element	Correlation coefficient, R^2			
	Low alloy Steel	Ferritic	Austentic	High speed
Cr	0.999	0.990	0.989	0.937
Mn	0.984	-	-	1.000
Ni	0.992	0.995	0.958	0.691
Si	0.914	0.812	0.590	-

Matrix effect correction can also be done by the standardless method. The absorption and enhancement effect is also known as the matrix effect and some function had to introduce into F_i value of Eq. (1) to correct for this matrix effect [5,8]. A Lucas-Tooth and Price model as shown in the following equation using the mathematical model to calculate the absorption and enhancement effects by [5]:

$$F_i = 1+\Sigma\alpha_{ij}\, R_i/100 \qquad (2)$$

where:

α_{ij} = absorption and enhancement coefficient

R_{ij} = peak intensities ratio

This equation is used as part of the standardless method to calculate the concentration of the interested elements present. Advantage of this method includes cost and time savings from the used of no reference standard and also there is no need of calibration graph plotting. However a major disadvantage of this method is high error reportly in range of 30-50% of this method with the regression method. To reduce this error we have included different pure elements spectrum in the analysis for better absorption and enhancement correction.

Discrepancy tests were then performed between the different standard methods and standardless method. Table 2 below shows result for Ni discrepancy test of these methods using three different reference standards. BCS 475 is a stainless steel standard containing 5.660% Ni and of the different analysis standard methods of analysis, the calibration method using high speed has the smallest discrepancy with value of 1.050%. The ferritic method come closest next with 5.430% while low alloy and austentic have almost similar discrepancy value of 6.070% and 6.080% respectively. Analysis of Ni in the next two standards BCS 494/1 and BCS 495/1 also show similar discrepancy result for the standard methods with high speed as the most reliable followed by ferritic and the last position occupied by low alloy and austentic methods. Using the standardless method for the analysis of Ni in these three reference standards places the method a surprise second to the high speed tool standard method. This shows that the incorporation of pure metal into the mathematical model has tremendously improved the accuracy of the method.

Table 2: Comparative study of discrepancy test for Ni in different stainless steel reference standard using different standard and standardless methods

Reference standards	Discrepancy value for different methods (%)					
	Certified value for Ni (%)	Low Alloy	High speed tool	Austentic	Ferritic	Standardless
BCS 475	5.660	6.070	1.050	6.080	5.430	3.890
BCS 494/1	0.730	0.660	0.110	0.660	0.590	0.490
BCS 495/1	1.130	1.020	0.180	1.020	0.910	0.730

The next element determined is Mn and for the standard method only low alloy and high speed tool methods has the capability to determine Mn (Table 3). This is due to the present of Mn in this type of stainless steel and hence able to plot the Mn calibration graph. Results obtained from Table 3 also shows that the discrepancy value is related to content of Mn in the reference standard where the higher the content will resulted higher discrepancy. Comparing the two standard methods show that the low alloy method gives more reliable result than the high speed tool with a lower discrepancy range of 0.520 – 5.660% for the former compared to 0.550 – 6.040% for the latter. Discrepancy test results for the standardless method shows that it has the smallest discrepancy for Mn analysis in all the three different reference standards. The range of discrepancy of 0.060 – 1.160 is better than the two standard methods mentioned earlier.

Table 3: Comparative study of discrepancy test for Mn in different stainless steel reference standard using different standard and standardless methods

Reference standards	Discrepancy value for different methods (%)			
	Certified value for Mn (%)	Low alloy	High speed tool	Standardless
BCS 363/1	1.260	0.520	0.550	-0.060
BCS 494/1	14.830	5.660	6.040	1.160
BCS 495/1	13.100	4.080	5.200	1.040

The discrepancy test of Cr involves all the developed standard and standardless methods. Three different stainless steel reference standards were used with Cr content ranging from 1.930 to 14.140%. The austentic and ferritic methods shows more accurate analysis results compared to the high speed and low alloy methods. Austentic method for example have a lower range of dicrepancy value of 0.040 to 2.670% compared to low alloy method of having higher range of 0.190 to 3.460%. The standardless method has a reasonably reliable result of having a discrepancy range of 0.410 to 2.590% better than the standard high speed and low alloy methods.

Table 4: Comparative study of discrepancy test for Cr in different stainless steel reference standard using different standard and standardless methods

Reference standards	Discrepancy value for different methods (%)					
	Certified value for Cr (%)	Low Alloy	High speed tool	Austentic	Ferritic	Standardless
BCS 387	12.460	3.460	0.880	2.670	2.790	2.590
BCS 475	14.140	0.810	-3.020	-0.360	-0.180	2.590
BCS 495/1	1.930	0.190	-0.310	0.040	0.060	0.410

CONCLUSION

The study involves development of four different stainless steel regression methods namely low alloy steel, austentic, ferritic and high speed. Standardless method was improved by incorporating pure metal standards into the mathematical model. A comparative discrepancy test was perform for determine the accuracy of determining Ni, Mn and Cr in both standard and standardless methods. The result shows that high speed tool method is highly accurate in determine of Ni while the austentic method is best for the analysis of Cr. The improved standardless method however is relatively highly accurate with being the best method in determine of Mn.

ACKNOWLEDGEMENT

The authors would like to thanks MTEC supporting staff and the management of Malaysian Nuclear Agency for their help and support for this project.

REFERENCES

[1] Tiwari M.K., et al., 2001, Analysis of stainless steel sample by EDXRF spectrometry, Bull. Mater. Sci., 24(6), p. 633-638.

[2] Goldstein S.J. and Sivils L.D., 2002, A non-destructive XRF method for analysis of metal alloy wire samples, Advances in X-ray Analysis, 45, p.457-462, ICDD, Philadelphia.

[3] E.P. Bertin: Principles and practices of X-ray spectrometric analysis, (2nd Ed., Plenum Press, New York 1975).

[4] B. Yokhin and R.C. Tisdale,1993, High-sensitivity energy-dispersive XRF technology Part 1: Overview of XRF technique, Am. Lab., 36G.

[5] V. Thomsen, 2007, Basic Fundamental Parameter in X-ray Flourescence, Spectroscopy, 22(5), p46-50.

[6] ASTM E1085-95(2000) Standard Test Method for X-Ray Emission Spectrometric Analysis of Low-Alloy Steels

[7] R. Tertian and F. Claisse, 1982, Principles of Quantitative X-Ray Fluorescence Analysis, Heyden, London.

[8] V. Thomsen, D. Schatzlein, and D. Mercuro, 2005, Spectroscopy 20(9), p.22–25.