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Algorithm Method for Chemical Analysis Elemental by WDXRF Technique

M. A. Scapin[1], M. C. Tessari-Zampieri[1], and M. E. B. Cotrim[1]

[1] *mascapin@ipen.br, Instituto de Pesquisas Energéticas e Nucleares,*
IPEN–CNEN-SP, CEP 05508-000
São Paulo – SP – Brasil

1. Introduction

X-ray fluorescence spectrometry (XRFS) is an instrumental analytical technique used to identify and quantify elements in geological, nuclear, environmental, forensic samples and others [1-6]. The quantitative results in terms precision and accuracy are satisfactory by calibration curve method using certified reference materials (CRMs). The calibration curve method is used to minimize inter-element effects (the matrix effect), but is often expensive. [7-8]. Mathematical methods have been proposed to minimize these costs, e.g., the Fundamental Parameters Method and the Algorithms Method [9]. Currently, mathematical models such as Back Propagation (BP), Radial Basis Function (RBF), Self-Generator Neural Network (SGNN) and Network Hopfield are being used in artificial intelligence for chemical analysis. The models show nonlinear data processing efficiency; however, improvements are needed for X-ray fluorescence spectrometry applications [10].

Therefore, this study aimed to measure the continuous spectrum for the element's boron (^{5}B) to uranium (^{92}U) using a wavelength dispersive X-ray fluorescence spectrometer (WDXRF). Furthermore, evaluate through mathematical fitting the area of continuous spectra and relate them to the respective elements. Subsequently, to relate the area values obtained for each element with the tabulated physical parameters (fluorescence yield, attenuation coefficient, among others), and finally, to build an instrumental sensitivity curve to quantify major and minor elements without using a calibration curve.

2. Methodology

The experiments were carried out using a Rigaku Co. (Tokyo, Japan) wavelength dispersive X-ray fluorescence spectrometer (WDXRF) model RIX 3000, with an Rh-anode X-ray tube, 75 µm Be windows, a 60 kV maximum acceleration voltage generator, NaI (Tl) scintillation detectors, and a gas-flow proportional counter.

The 2-theta-scan mode was used with a sample holder of 20 mm Ø area. The spectrum of each element was obtained by compounds and metals of analytical grade measuring, e.g, H_3BO_3, C_3H_6, Na_2CO_3, Mg^0, Al^0, SiO_2, $Ca_3(PO_4)_2$, Ti^0, Ni^0, Cu^0, Zn^0, Ag^0, Pb^0 ... U_3O_8. The software coupled to WDXRF was used to subtract background (BG) from the original spectrum.

Thus, were obtained two spectra: spectrum A with the characteristic lines and BG and spectrum B with the characteristic lines without BG.
The count rate (kcps) versus 2-theta (for 4,250 points) were transferred to a spreadsheet (Microsoft Excel 2013). Afterward, spectrum A was subtracted from spectrum B, resulting in spectrum C (continuous spectrum).

The Gauss-Amp fit model was applied in spectrum C (kcps versus 2-theta) for area calculation using Origin Pro 8 software.

The area of continuous spectrum of each element were related to their respective atomic numbers. Two fitting models were used to evaluate the correlation: second-degree polynomial fitting and third-degree polynomial fitting using Origin Pro 8 software.

The certified reference material (CRM) stainless steel 304 L (British Chemical Standards - BCS. 463) was analyzed to assess the method, using Eq. 1.

$$C_i = \frac{AP_i * AC_i * CF_i}{\sum CS_i}\ x\ 100 \qquad (1)$$

Where: Ci = concentration element (i); APi = peak area element (i); ACi = area of continuous spectrum calculated of element (i); CFI = sum following parameters: fluorescence yield, X-Ray mass attenuation coefficients, and Edge absorption element (i); ∑ CSi = sum of APi, Aci, and CFi for all elements analyzed.

3. Results and Discussion

The Fig. 1 (A) show continuous spectrum by WDXRF and Fig. 1(B) the continuous spectrum after GaussAmp fitting for ^{12} Mg, ^{14}Si, ^{20}Ca, ^{26}Fe, ^{40}Zr, and ^{92}U. The increase in X-rays absorption is observed in both cases.

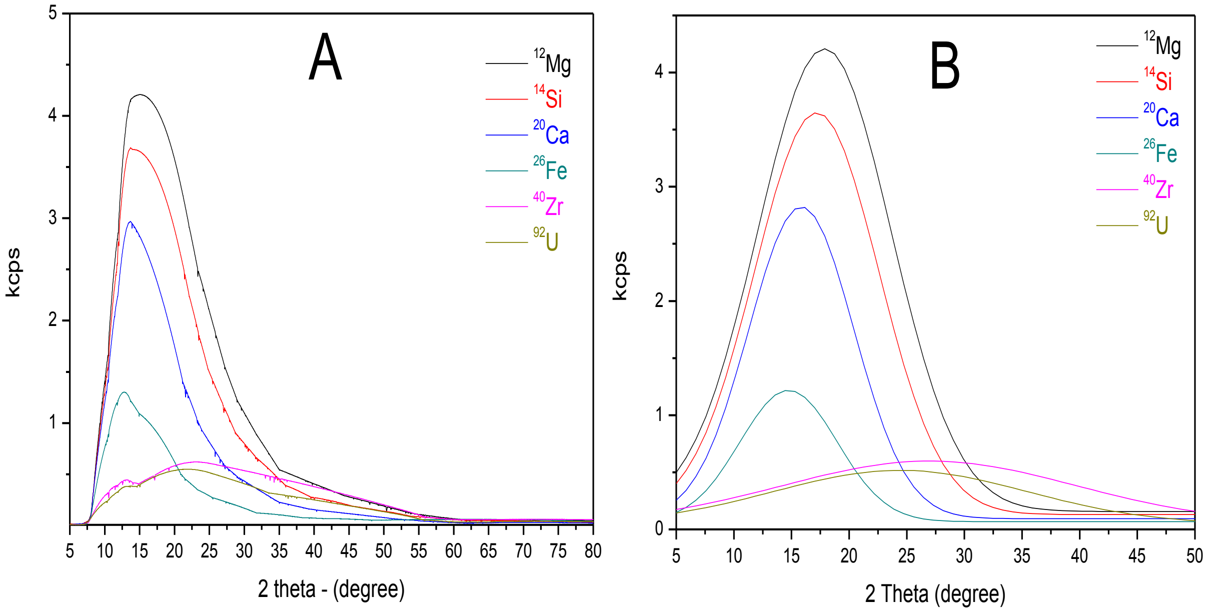
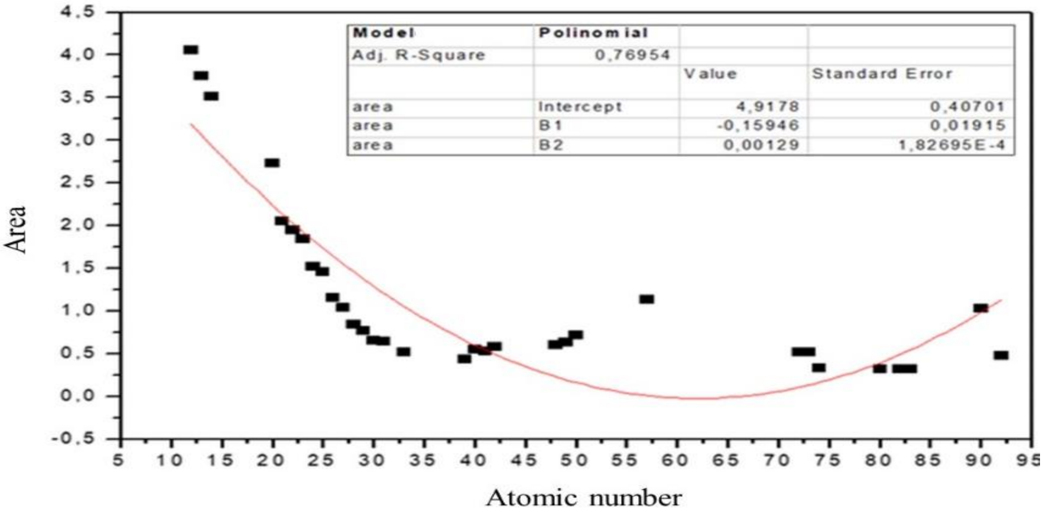


Figure 1: continuous spectrum for WDXRF (A) and continuous spectrum after GaussAmp fitting (B).

The Fig. 2 shows area (kcps - GaussAmp fitting) versus elements (Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Y, Zr, Nb, Mo, Cd, In, Sn, La, Hf, Ta, Hg, Pb, Bi, Th and U) by second-degree polynomial fitting;. Correlation ($R^2 \approx 0.77$).

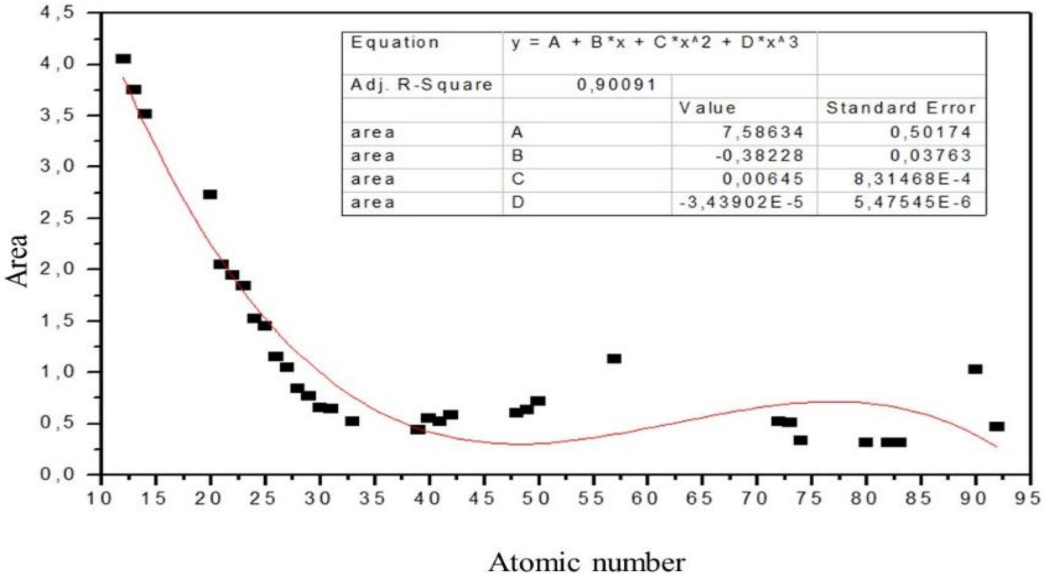
The Fig. 3 shows area (kcps - GaussAmp fitting) versus elements (Mg, Al, Si, Ca, Sc, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Ga, As, Y, Zr, Nb, Mo, Cd, In, Sn, La, Hf, Ta, Hg, Pb, Bi, Th and U) by third-degree polynomial fitting;. Correlation ($R^2 \approx 0.90$).

Figure 2: area versus elements - second-degree polynomial fitting



Model	Polinomial		
Adj. R-Square	0,76954		
		Value	Standard Error
area	Intercept	4,9178	0,40701
area	B1	-0,15946	0,01915
area	B2	0,00129	1,82695E-4

Figure 3: area versus elements - third-degree polynomial fitting



Equation	y = A + B*x + C*x^2 + D*x^3		
Adj. R-Square	0,90091		
		Value	Standard Error
area	A	7,58634	0,50174
area	B	-0,38228	0,03763
area	C	0,00645	8,31468E-4
area	D	-3,43902E-5	5,47545E-6

The certified ($\bar{X} \pm \sigma$) and determined content using Eq. 1 and ($\bar{D}$), relative error (RE%), Z-score test (Z-score) and tabulated values for fluorescence yield (φ), X-Ray mass attenuation coefficients (μ_m), Edge absorption (μE) are presented in Table I.

Table I: Parameters certified and determined for MCR 463 (WDRFX).

Elemento	$\bar{X} \pm \sigma$ (%)	$\bar{D}$ (%)	$RE\%$	$Z-Score$	φ	μ_m	μ_E
Fe	70.7±0.1	73±2	3.2	1.1	0.340	0.408	7.111
Cr	18.29±0.05	17±1	7	1.3	0.283	0.598	5.989
Ni	9.65±0.05	9.3±0.3	4	1.2	0.410	0.329	8.332
Mn	0.77±0.02	0.54±0.02	43	8.1	0.313	0.452	6.538
Si	0.51±0.01	0.020±0.001	2892	48.8	0.043	0.003	1.840
P	0.015±0.001	0.0070±0.0002	124	7.8	0.060	0.002	24

Accuracy in terms RE% is satisfactory since the Z-Score values <2 for Fe, Cr, and Ni (major contents). Z-Score for Mn, Si and P (minor contents) unsatisfactory since Z-Score >2.

Conclusions

The quantitative analysis model for stainless steel 304 L without calibration curve showed in this work it's appropriate. The proposing methodology is a promising way to collaborating with improvement of nonlinear data processing efficiency applied artificial intelligence for chemical analysis.

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