# STATISTICAL TESTS FOR 302 AND 304 SERIES STAINLESS STEEL ALLOYS ANALYSIS BY XRF SPECTROMETRY

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**Abstract** – *Stainless steal alloys play an important role for different kinds of technologies, their application ranging from the automotive and aerospace to building industries. Therefore, chemical composition specifications assurance of these materials has become of great importance. Among contemporary analytical techniques such as Atomic Absorption (AAS) and Inductively Coupled Plasma Optical Emission (ICP-OES), the X-ray Fluorescence Spectrometry (XRFS) distinguishes for its condition of a non-destructive and multi-elemental analysis. Usually, the metallic samples analysis does not require chemical treatments, mainly the dissolution process; consequently, the propagation of error is minimized. This paper presents the validation of the method for stainless steel alloys (302 and 304 series) analysis by wavelength-dispersive X-ray fluorescence spectrometry (WDXRF). The fundamental parameters method was used for matrix effect correction. Certificated reference materials from BAS (stainless steel 474 and 475), BCS (austenitic stainless steel 462 to 468) and Electrometal (stainless steel E-304) were used to obtain the calibration curves for Si, P, V, Cr, Mn, Ni and Mo elements. Measurement uncertainty was determined using statistical tools according to ISO 17025.*

## Introduction

Nowadays the stainless steel is one of the most versatile materials in use. Some applications are visible such as kitchenware, building and automotive and anothers more subtle like power generation, food production and chemicals manufacture. It also features benefits like heat and corrosion resistance, long-term value and ease of fabrication [1]. Chemical composition assurance has become an important quality standard seal for many worldwide stainless steel producers.

Current analytical methods like Instrumental neutron activation analysis (INAA), Atomic absorption spectrometry (AAS) and Inductively coupled plasma optical emission spectrometry (ICP-OES) are often used to perform elemental

analysis. The X-ray fluorescence spectrometry (XRF) distinguishes for a non-destructive and multi-elemental analysis characteristics. It has been extensively used for the analysis of metals, alloys, minerals, ores, ceramics, archaeological samples, catalysts, forensic and environmental science samples and for small samples analysis [2].

For any materials analysis by any analytical techniques, the method assessment is the most important pre-requisite for analytical results assurance. According to ISO/IEC 17025, 2001, the validation of a method is the confirmation by examination and the provision of objective evidence that the particular requirements for a specific intended use are fulfilled.

In this work, the validation of the method for stainless steel alloys (302 and 304 series) analysis by wavelength-dispersive X-ray fluorescence spectrometry (WDXRF) was performed. Statistical tests were calculated according to ISO IEC 17025 [3].

## Materials and methods

A FPL Fortel polishing machine and a Fortel sandpaper polisher, 400 mm, were used to perform a simple polishing on the certificated reference materials British Chemical Standards, BCS (austenitic stainless steel Ns. 462, 463, 464, 465, 466, 467 and 468), Bureau of Analyzed Samples, BAS (stainless steel Ns. 474 and 475) and Eletrometal (stainless steel E 304). This procedure is necessary to assure the physical effects elimination, such as scratches, shielding and scattering from the metallic surface.

Instrumental parameters (line emission, collimator, analyzing crystal, detector and fixed time counting), Table 1, were established.

Si, P, V, Cr, Mn, Ni and Mo individual calibration curves were obtained by means of three measurements made in the BCS and BAS CRM's. The calibration curves parameters, the intercept (a), the slope (b) and the linear regression coefficient ($R^2$) were obtained by the linear regression method and limits of quantification (LQ) were calculated according to Eq. 1, presented in Table 2.

$$LQ = I + \frac{10 \cdot \sigma}{a} \qquad (1)$$

$\sigma$ – standard deviation
I – background counting rate (cps)
a – intercept

Ten measurements were performed on the CRM Eletrometal E 304 sample using the RIX 3000 Rigaku, Co., X-ray fluorescence spectrometer, coupled with fundamental parameters method software.

The uncertainty of measurement was calculated according to Eq. 2.

$$U = t_{n-1(\alpha/2)} \cdot \frac{\sigma_{det}}{\sqrt{n}} \qquad (2)$$

$\sigma$ – standard deviation
n – number of measurements
$t_{n-1\,(\alpha/2)}$ – (tstandard value: $t_{9,\,0.025}$) = 2,262 [5]

The accuracy of the method was evaluated by relative error (%ER – Eq. 3), Z-score values (Zscore – Eq. 4) and normalized error values (En – Eq. 5). The results are presented on TAB. 3.

$$\% \quad ER = \frac{X_{det} - X_{cert}}{X_{cert}} \cdot 100 \quad (3) \qquad X_{det} = \text{determined values}$$
$$X_{cert} = \text{certificated values}$$

$$Zscore = \frac{(X_{det} - X_{cert})}{s} \quad (4) \qquad s = \text{uncertainty of the CRM}$$

$$\% \quad En = \frac{(X_{det} - X_{cert})}{\sqrt{U^2 + s^2}} \quad (5) \qquad U = \text{uncertainty of the laboratory}$$

## Results

Table 1 – Instrumental parameters of measurements established at WDXRF spectrometer.

| | Rh Tube – 50kV × 50 mA | | | | Fixed Couting Time(s) |
|---|---|---|---|---|---|
| Element | Line of emission [4] | Collimator | Analyzing Crystal | Detector | Peak |
| Si | K-L₃ (K_) | 480 _m | PET (111) | SFP | 40 |
| P | K-L₃ (K_) | 160 _m | PET (111) | SFP | 40 |
| V | K-L₃ (K_) | 160 _m | LiF (200) | SC | 20 |
| Cr | K-L₃ (K_) | 160 _m | LiF (200) | SC | 20 |
| Mn | K-L₃ (K_) | 160 _m | LiF (200) | SC | 20 |
| Fe | K-L₃ (K_) | 160 _m | LiF (200) | SC | 20 |
| Ni | K-L₃ (K_) | 160 _m | LiF (200) | SC | 20 |
| Mo | K-L₃ (K_) | 160 _m | LiF (200) | SC | 20 |

SFP: Proportional detector with gas flux (P10 mixture)
SC: Scintillation detector (NaI (Tl))

Table 2 – Calibration curves parameters and limits of quantification.

| Elements | a | b | $R^2$ | LQ(%) |
|---|---|---|---|---|
| Si | 4.97 | 0.086 | 0.945 | 0.03 |
| P | 8.75 | 0.15 | 0.905 | 0.1 |
| V | 22.5 | 0.028 | 0.903 | 0.3 |
| Cr | 43.4 | 204 | 0.963 | 0.9 |
| Mn | 44.1 | 3.49 | 0.997 | 0.4 |
| Ni | 24.7 | 38.8 | 0.995 | 0.3 |
| Mo | 91.3 | 3.2 | 0.999 | 0.8 |

The XRF technique shows very high repeatability of measurements. The uncertainty of the laboratory values was based on the relative standard deviation

**Table 3** – CRM Eletrometal E 304 sample analyse.

| Elements | $X_{det} \pm U$ (%) | $X_{cent} \pm s$ (%) | Relative error (%) | Z score values | En values |
|----------|----------------------|------------------------|--------------------|----------------|-----------|
| Si | 0.261 ± 0.005 | 0.26 ± 0.01 | 0.54 | 0.14 | 0.13 |
| P | 0.039 ± 0.003 | 0.041 ± 0.002 | 4.63 | 0.95 | 0.55 |
| V | 0.043 ± 0.001 | 0.05 ± 0.01 | 13.80 | 0.69 | 0.49 |
| Cr | 18.94 ± 0.01 | 18.94 ± 0.05 | 0.03 | 0.10 | 0.10 |
| Mn | 1.34 ± 0.01 | 1.34 ± 0.02 | 0.08 | 0.20 | 0.18 |
| Ni | 8.55 ± 0.01 | 8.56 ± 0.05 | 0.8 | 0.14 | 0.14 |
| Mo | 0.183 ± 0.005 | 0.18 v 0.01 | 1.56 | 0.28 | 0.25 |

($n = 10$), which could have caused lower uncertainty values than certified values. In addition, the CRM E 305 from Electrometal is considered a secondary standard and its uncertainty is assured only by few analytical data. Therefore, the calculated uncertainty showed a good agreement with CRMs uncertainty, demonstrating good precision of the method (Table 3).

The relative error of major elements determination (Si – RE: 0.54%, Cr – RE: 0.03%, Mn – RE: 0.08% and Ni – RE: 0.8%) indicated a good agreement between determined and certified values. The minor elements determination (P – RE: 4.63%, V – RE: 13.8% and Mo – RE: 1.56%) showed higher %RE; these values are directly associated with the spectrometer sensibility, which is correlated to instrumental parameters of measurements. Moreover, the accuracy evalution by Z-score test showed satisfactory values (0.10 to 0.95) for all the elements determination; since Z-score values are evaluated as follows: $Z \le 2$ is satisfactory, $2 < Z \le 3$ are questionable and $Z > 3$ are insatrisfactory. The normalized error calculation presented values lower than 1 (0.1 to 0.55); once $En \le 1$ values are accepted, the method presented in this work could be considered apropriated for stainless steel analysis.

## Conclusion

The different statistical tests, recommended by ISO IEC 17025 analytical methodology evaluation, permitted the validation of 302 and 304 series stainless steel alloys analysis method by X-ray fluorescence technique.

## References

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