

PAPER • OPEN ACCESS

Comparative study between EDXRF and ASTM E572 methods using two-way ANOVA

To cite this article: A Krummenauer *et al* 2018 *J. Phys.: Conf. Ser.* **975** 012004

View the [article online](#) for updates and enhancements.

Related content

- [Advanced Secure Optical Image Processing for Communications: A comparative study of CFs, LBP, HOG, SIFT, SURF, and BRIEF for security and face recognition](#)
A Al Falou
- [The comparative study for the isotropic and orthotropic circular plates](#)
C Popa and G Tomescu
- [Vaccination Strategies: a comparative study in an epidemic scenario](#)
D. B. Prates, C. L. T. F. Jardim, L. A. F. Ferreira et al.



IOP | ebooks™

Bringing you innovative digital publishing with leading voices to create your essential collection of books in STEM research.

Start exploring the collection - download the first chapter of every title for free.

Comparative study between EDXRF and ASTM E572 methods using two-way ANOVA

A Krummenauer, H M Veit and J Zoppas-Ferreira

Programa de Pós-Graduação em Engenharia de Minas, Metalúrgica e de Materiais (PPGE3M), Universidade Federal do Rio Grande do Sul (UFRGS), Av. Bento Gonçalves, 9500, Porto Alegre, RS, Brazil.

alex_krum@yahoo.com.br

Abstract. Comparison with reference method is one of the necessary requirements for the validation of non-standard methods. This comparison was made using the experiment planning technique with two-way ANOVA. In ANOVA, the results obtained using the EDXRF method, to be validated, were compared with the results obtained using the ASTM E572-13 standard test method. Fisher's tests (F -test) were used to comparative study between of the elements: molybdenum, niobium, copper, nickel, manganese, chromium and vanadium. All F -tests of the elements indicate that the null hypothesis (H_0) has not been rejected. As a result, there is no significant difference between the methods compared. Therefore, according to this study, it is concluded that the EDXRF method was approved in this method comparison requirement.

1. Introduction

In Brazil, the laboratories of RBLE (Brazilian Network of Testing Laboratories), accredited by CGCRE/INMETRO, according to ABNT NBR ISO/IEC 17025:2005 standard [1] must comply, among other things, the following requirements: non-standard methods (item 5.4.4), and validation of methods (item 5.4.5), described in this standard. To assist in this task, INMETRO provides document DOQ-CGCRE-08 - Guidance for validation of analytical methods [2] which guides laboratories in the validation process of a non-standard method, i.e., that is not described in a national or international standard.

The LACOR (Laboratory of Corrosion, Protection and Recycling of Materials), at UFRGS, is accredited by CGCRE/INMETRO (RBLE 1139) and uses the Thermo Scientific Niton XL3t GOLDD+ portable EDXRF analyzer to perform metal determination tests in steel samples, by energy dispersive X-ray fluorescence spectrometry (EDXRF). However, the EDXRF method is a non-standard method and therefore it must be validated. One of the requirements for validation, as determined by item 8.2.6.3.4 of document DOQ-CGCRE-08 [2], is the comparison with a reference method. The purpose of this comparison is to evaluate the accuracy of method to be validated by analyzing samples with concentrations through the entire range in which the method should be validated. Samples were analyzed, with six measurements, by using the two methods separately [2].

There are several techniques that can be used to compare the results obtained by two test methods. In this sense, document DOQ-CGCRE-08 [2] suggests: hypothesis tests and planning of experiment. In this comparison, it was decided to use the two-way factorial experiment (two-way ANOVA) described in the experiment planning technique [3, 4, 5]. In order to obtain the results of the method to be validated, the NITON analyzer was used to analyze the samples 2Q15S1 [6], 2Q15S2 [6], 4Q15S1



[7], and 4Q15S2 [7]. These samples were measured by ASTM E572-13 reference method [8], with the wavelength dispersive X-ray fluorescence spectrometry (WDXRF) method, in the Inter-Laboratory Analysis Programs (ILAP), performed by ASTM International [6, 7], in which LACOR laboratory participated. The term ED "energy dispersive" in EDXRF refers to the technique of detecting X-rays emitted, which is affected by a detector which generates an intensity spectrum as a function of energy [9]. While the term WD "wavelength dispersive" in WDXRF refers to the use of single crystal or synthetic multilayer Bragg diffraction to disperse characteristic X-rays [9]. Figure 1 shows a comparison between the detection techniques used in EDXRF and WDXRF.

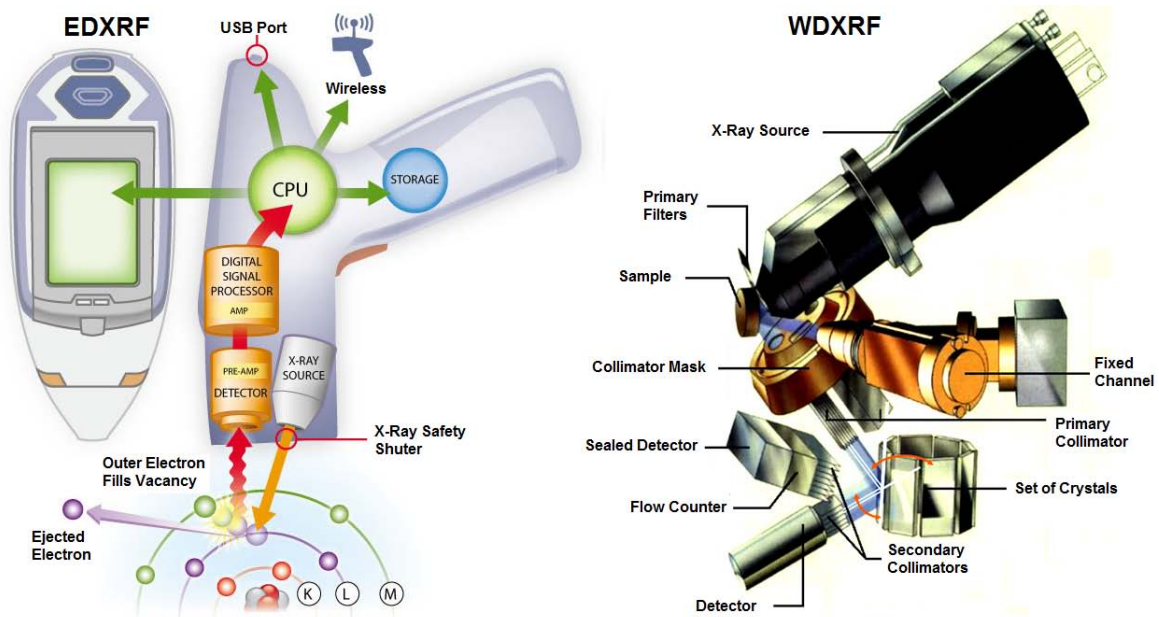


Figure 1. Comparison between the detection techniques used in EDXRF and WDXRF [9, 10].

In this study, the results of the following chemical elements were analysed: molybdenum (Mo), niobium (Nb), copper (Cu), nickel (Ni), manganese (Mn), chromium (Cr), and vanadium (V). Comparison of the results for tungsten (W) and cobalt (Co) was also obtained, but with other methods, outside the scope of this paper. Therefore, these results are not mentioned in this article.

2. Objective

This study performs a comparative study between the non-standard EDXRF method and the ASTM E572 reference method (WDXRF), by using the two-way ANOVA. The objective is to validate the EDXRF method and maintain the accreditation by CGCRE/INMETRO of the metal determination testing by FRX.

3. Materials and methods

In this study, the four samples, used in interlaboratory comparisons [6, 7], were measured with six measurements, under repeatability conditions, by using the NITON analyzer along with the Mobile Test Stand accessory. NITON has been configured with: calibration curve (table 1), general metals analysis from the main menu, two filters – main range (20s) and low range (20s), disable AI, and autoswitch ON [10]. All measurements were taken by using the following procedure quoted in the NITON manual: 1 - preparation of the sample; 2 - clean with isopropyl alcohol and lint-free paper; 3 - perform a system check once every working day; 4 - warm up for ten minutes after start up [10].

Results with six measurements ($n = 6$), in each sample, were compared with six randomly selected results from other laboratories that participated in interlaboratory comparisons [4, 5]. Two-way ANOVA was used for each chemical element: factor A – concentration – with four levels ($a = 4$) and factor B – method – with two levels ($b = 2$).

Table 1. Parameters of the calibration curve and coefficient of determination (R^2).

Chemical element	Intercept (a)	Slope (b)	R^2
Mo	-0.0054	1.0219	0.9999
Nb	0.0033	0.8916	0.9999
Cu	-0.0148	1.1157	0.9993
Ni	0.0021	1.0096	1.0000
Mn	-0.0258	0.9803	0.9997
Cr	-0.0932	0.9758	0.9995
V	0.0019	0.9116	0.9996

3.1. Factorial experiment (two-way ANOVA)

According to Ribeiro and ten Caten [3] and Montgomery [4, 5], the statistical model of two-way ANOVA is equation (1).

$$y_{ijk} = \mu + \tau_i + \beta_j + (\tau\beta)_{ij} + \varepsilon_{ijk} \quad (1)$$

Where μ is the population mean; τ_i is the effect of the i -th level of “concentration”; β_j is the effect of the j -th level of “method”; $\tau\beta_{ij}$ is the effect of the “concentration·method” interaction; ε_{ijk} is the random error, with $i = 1, a$; $j = 1, b$ and $k = 1, n$. Assumption: $\varepsilon_{ijk} \rightarrow N(\mu = 0, \sigma)$.

Thus, there are three hypothesis tests to be performed [3, 4, 5]:

- For the factor “concentration”: $H_0: \tau_i = 0$ and $H_1: \tau_i \neq 0$ for some $i, i = 1, a$.
- For the factor “method”: $H_0: \beta_j = 0$ and $H_1: \beta_j \neq 0$ for some $j, j = 1, b$.
- For the factor “concentration·method”: $H_0: \tau\beta_{ij} = 0$ and $H_1: \tau\beta_{ij} \neq 0$ for some ij .

For each hypothesis tests, it was computed F tabulated (F_{tab}) of the Fisher distribution (F -distribution) and compared with the F calculated (F_{calc}). If $F_{calc} > F_{tab}$ then the null hypothesis is rejected and therefore the change in levels of the factor analyzed has a significant effect on the mean response [3, 4, 5].

The value of F_{calc} is obtained from equation (2) and F_{tab} is calculated by equation (3).

$$F_{calc} = \frac{\text{Variance between groups}}{\text{Variance within the groups}} = \frac{MQ(\text{factor})}{MQR} \quad (2)$$

$$F_{tab} = F_{\alpha; GL \text{ numerator}; GL \text{ denominator}} \quad (3)$$

Where $MQ(\text{factor})$ is mean square or variance, MQR is mean square of error, α is significance level, $GL_{\text{numerator}}$ is degrees of freedom of numerator and $GL_{\text{denominator}}$ is degrees of freedom of denominator [3, 4, 5].

If $F_{calc} > F_{tab}$, or $p\text{-value} < 0.05$ ($\alpha = 5\%$), the effect studied is significant for a confidence level of 95% [3, 4, 5]. According to Ribeiro and ten Caten [3] and Montgomery [4, 5], the formulas for calculations are described below.

$$TC = \frac{(T \dots)^2}{abn} \quad (4)$$

$$SQA = \sum_{i=1}^a \frac{(T_{i..})^2}{bn} - TC \quad (5)$$

$$SQB = \sum_{j=1}^b \frac{(T_{j\cdot})^2}{an} - TC \quad (6) \quad SQAB = \sum_{i=1}^a \sum_{j=1}^b \frac{(T_{ij\cdot})^2}{n} - TC - SQA - SQB \quad (7)$$

$$SQR = \sum_{i=1}^a \sum_{j=1}^b \sum_{k=1}^n y_{ijk}^2 - \sum_{i=1}^a \sum_{j=1}^b \frac{(T_{ij\cdot})^2}{n} \quad (8) \quad SQT = \sum_{i=1}^a \sum_{j=1}^b \sum_{k=1}^n y_{ijk}^2 - TC \quad (9)$$

The verification of equation (9) can be done by equation (10).

$$SQT = SQA + SQB + SQAB + SQR \quad (10)$$

Where TC is the correction term, SQ(factor) is the sum of squares of each factor, MQ(factor) is the calculation of the mean square, equation (11), and GDL are the degrees of freedom of each factor. Table 2 presents these calculations.

$$MQ(factor) = \frac{SQ(factor)}{GDL} \quad (11)$$

Table 2. Calculations for two-way ANOVA.

Factor	Sum of squares	GDL	Mean square	Fcalc	Ftab
A	SQA	(a - 1)	MQA	MQA/MQR	$F_{\alpha;GLA;GLT}$
B	SQB	(b - 1)	MQB	MQB/MQR	$F_{\alpha;GLB;GLT}$
AB	SQAB	(a - 1)*(b - 1)	MQAB	$MQAB/MQR$	$F_{\alpha;GLAB;GLT}$
Error	SQR	ab(n - 1)	MQR		
Total	SQT	abn - 1			

4. Results and discussion

The six results obtained with NITON, in the four samples for Mo, and also the six sample means of these samples from laboratories that participated in ILAP of the ASTM [6, 7], method E572, are presented in table 3. Results of the other chemical elements were obtained by using the same methodology. By using the methods and calculations described in item 2 of this article, with the data from table 3, the following values were obtained for Mo: $a = 4$, $b = 2$, $n = 6$, $TC = 53.129788$, $SQA = 45.504863$, $SQB = 0.000199$, $SQAB = 0.000051$, $SQR = 0.003461$ e $SQT = 45.508574$. Table 4 presents the values of two-way ANOVA calculations for Mo.

Table 3. Values obtained with NITON (EDXRF) and ASTM E572 (WDXRF) for Mo.

Concentration	Values measured with NITON (%)			Sample means obtained with E572 (%)		
0.051 % (2Q15S2)	0.049	0.050	0.052	0.058	0.050	0.052
	0.050	0.051	0.049	0.055	0.054	0.051
0.102 % (2Q15S1)	0.102	0.104	0.101	0.110	0.106	0.110
	0.101	0.105	0.104	0.108	0.107	0.109
2.003 % (4Q15S1)	2.020	2.002	2.008	2.020	2.003	2.020
	2.003	2.008	2.011	2.008	2.007	2.001
2.058 % (4Q15S2)	2.044	2.052	2.011	2.046	2.076	2.033
	2.043	2.046	2.035	2.056	2.035	2.024

Table 4. ANOVA two-way calculations for Mo.

Factor	Sum of squares	GDL	Mean square	Fcalc	Ftab
Concentration (A)	45.504863	3	15.168288	175298	2.8
Method (B)	0.000199	1	0.000199	2.3	4.1
Interaction (AB)	0.000051	3	0.000017	0.2	2.8
Error	0.003461	40	0.000087		
Total	45.508574	47			

As mentioned previously, the studied effect is significant for $F_{calc} > F_{tab}$. Table 4 shows that the factor “concentration” was significant and the factor “method” and the interaction were not significant. This result shows that the concentrations had great variation between the samples, but this was expected, since each sample actually had a very different value of concentration of Mo in relation to the others. However, most importantly, the methods do not have significant differences and therefore for Mo the EDXRF method is approved in requirement 8.2.6.3.4 of document DOQ-CGCRE-08 [2], for a confidence level of 95 %. That was the purpose of this study. Figure 2 shows the analysis of the factor method using the F -distribution of Fisher.

Figure 3 shows the comparison between the means of measurements made for Mo, with the EDXRF method and the means obtained with the ASTM E572 method (WDXRF) and it can be observed that there is no difference between the values.

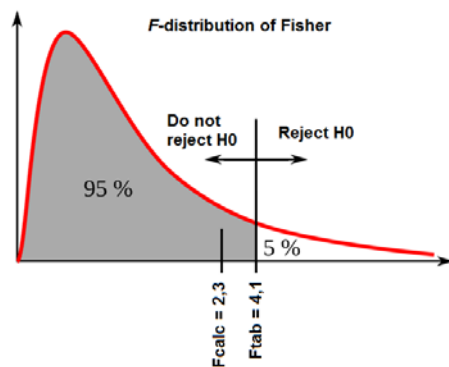


Figure 2. Analysis factor method using F -distribution of Fisher.

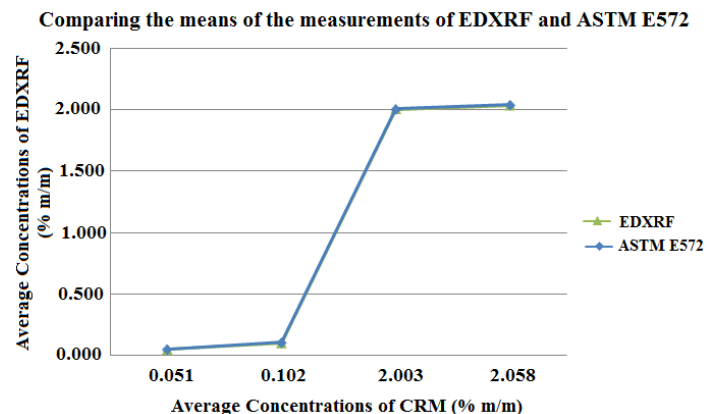


Figure 3. Comparing the sample means of the measurements of EDXRF and ASTM E572.

As for the other elements that followed the same methodology of Mo, table 5 presents a summary of two-way ANOVA calculations of each of the chemical elements.

Analyzing the data in table 5, it is concluded that all chemical elements that have been analyzed and compared with the E572 method [8] are approved for requirement 8.2.6.3.4 of document DOQ-CGCRE-08 [2], for a confidence level of 95 %. There was no significant difference between the methods because no F_{calc} was greater than F_{tab} (see table 5).

Table 5. Summary of two-way ANOVA calculations for the factor “method” of chemical elements.

Chemical element	Sum of squares	GDL	Mean square	Fcalc	Ftab
Mo	0.000199	1	0.000199	2.3	4.1
Nb	0.000006	1	0.000006	4.0	4.1
Cu	0.000284	1	0.000284	4.0	4.1
Ni	0.001349	1	0.001349	1.0	4.1
Mn	0.000524	1	0.000524	1.0	4.1
Cr	0.003485	1	0.003485	1.0	4.1
V	0.000003	1	0.000003	0.2	4.1

5. Conclusion

The comparison of the EDXRF method with the ASTM E572 reference method (WDXRF), using the two-way ANOVA technique, resulted in the approval of the method for measuring Mo, Nb, Cu, Ni, Mn, Cr, and V, in the alloy steels analysis. However, it should be noted that this alone does not characterize the complete validation of the analytical method, since many other requirements have to be approved, as described, for example, in DOQ-CGCRE-08 [2], for final definitive approval of the EDXRF method.

Acknowledgments

The authors thank CAPES for the support with the masters scholarship program; UFRGS, PPGE3M and LACOR by technical and instrumental support; FINEP, for the resources obtained, through the SIBRATEC - Technological Services Provision Networks, for the acquisition, by LACOR, of the portable EDXRF analyzer.

References

- [1] ABNT 2005 *NBR ISO/IEC 17025:2005 General Requirements for the Competence of Testing and Calibration Laboratories* (Rio de Janeiro: ABNT)
- [2] INMETRO 2016 *DOQ-CGCRE-008 Orientação sobre Validação de Métodos Analíticos* (Rio de Janeiro: INMETRO)
- [3] Ribeiro J L D and ten Caten C S 2014 *Projeto de Experimentos* (Porto Alegre: UFRGS)
- [4] Montgomery D C 2009 *Introduction to Statistical Quality* (New York: Wiley & Sons)
- [5] Montgomery D C 1997 *Design and Analysis of Experiments* (New York: Wiley & Sons)
- [6] ASTM International 2015 *Proficiency Test Program: Chemical Analysis of Stainless Steel Second Quarter 2015* (West Conshohocken: ASTM International)
- [7] ASTM International 2016 *Proficiency Test Program: Chemical Analysis of Stainless Steel Fourth Quarter 2015* (West Conshohocken: ASTM International)
- [8] ASTM International 2016 E572-13 – *Standard Test Method for Analysis of Stainless and Alloy Steels by Wavelength Dispersive X-Ray Fluorescence Spectrometry* (West Conshohocken: ASTM International)
- [9] Santos E S 2012 *Determinação de Cobre, Ferro, Níquel e Zinco em Matrizes Etanólicas por Espectrometria de Fluorescência de Raios-X com Energia Dispersiva após Pré-Concentração em Papel Cromatográfico*, Ph.D. dissertation (Salvador: UFBA)
- [10] Thermo Fisher Scientific 2010 *Niton XL3 Analyzer User's Guide Revision C*