Estimation of measurement uncertainty in the EDXRF spectrometry of stainless steel

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Abstract. The uncertainty in the analysis of nine elements in stainless steels performed with the NITON spectrometer was estimated. Initially, an Ishikawa diagram was used to describe the main sources of uncertainty. After calculating the standard uncertainties of these sources, they were combined to determine the combined standard uncertainty and the expanded uncertainty for each element. An uncertainty contribution graph was developed to assist in analyzing the influences of uncertainty sources on the final value of combined standard uncertainty. A simple uncertainty can be attributed to each element and the calibration curve is a very significant uncertainty source.

1. Introduction

Whenever reporting the measurement result, it becomes mandatory that some quantitative indication of the accuracy of result is provided. This way, whoever uses it can evaluate its confidence interval. The measurement uncertainty expresses, quantitatively, the value of the accuracy of the measurement result [1, 2].

The estimation of uncertainty of this study followed the guidelines outlined in the GUM [1], in the QUAM [2], in the NIT-DICLA-021 [3], in the RM-68 [4] and in the DOQ-CGCRE-019 [5], a bottom-up approach, which consists of identifying the Type A and Type B sources of uncertainties; quantifying them; transforming them into standard uncertainties; combining them to obtain combined standard uncertainty; determining the effective degrees of freedom and corresponding coverage factor— that defines an interval corresponding to a confidence level of approximately 95 percent - in order to finally calculate the expanded uncertainty.

The objective of this study was to determine the uncertainty in the analysis of stainless steel specimens using the Thermo Fisher Scientific NITON XL3t GOLDD+ spectrometer in the premises of Laboratório de Corrosão, Proteção e Reciclagem de Materiais (LACOR) – UFRGS. In this study, measurement results of only of the following elements were analyzed: molybdenum (Mo), niobium (Nb), tungsten (W), copper (Cu), nickel (Ni), cobalt (Co), manganese (Mn), chromium (Cr) and vanadium (V). This limitation is due to the fact that there were at least five certified reference materials (CRMs) only for these elements, with iron-based alloys matrix, to determine a calibration curve for each element. Consequently, it is possible to guarantee a metrological traceability to the measurement result of only these chemical elements. Thus, the calibration curve of each chemical element obtained within...
a metrological traceability chain is the key point for determining a measurement result with a reliable measurement uncertainty. Since corrections from the calibration curve is applied directly during the measurements by NITON software, the measurement bias is not applied in the expanded uncertainty calculation, but it uses a standard uncertainty of calibration curve [1, 2, 3, 4].

2. Materials and methods
This study used a portable energy dispersive X-ray fluorescence (EDXRF) spectrometer (Thermo Fisher Scientific, model NITON XL3t GOLDD+) coupled to its mobile test stand accessory [6]. Fifteen certified reference materials (CRMs) were used to determine a calibration curve for each chemical element, with at least five calibration points, in order to guarantee the metrological traceability of the results. Table 1 lists CRMs, their traceability and which CRM were used specifically in the calibration curve of each chemical element [7].

Table 1. Lists CRMs, their traceabilities and applications in each chemical element.

| Identification | Certificate | Certificate date* | Traceability | Calibrated chemical element |
|----------------|-------------|-------------------|--------------|----------------------------|
| IARM 35KN     | 35KN-10112011-IARM-P | 10/11/2011       | NISTb        | Mo, Nb, Cu, Cr             |
| C1153a        | C1153a      | 12/09/1990        | NIST         | Nb, Ni, Co, Cr, V          |
| SS 421        | SS-CRM No. 421 | Jul/2016         | BASd         | W                          |
| SS 422        | SS-CRM No. 422 | Jul/2016         | BAS          | W                          |
| SS 423        | SS-CRM No. 423 | Jul/2016         | BAS          | W                          |
| SS 424        | SS-CRM No. 424 | Jul/2016         | BAS          | W                          |
| SS 474        | SS-CRM No. 474 | Sep/2010         | BAS          | Ni, Cr, V                  |
| SS 483/1      | SS-CRM No. 483/1 | Nov/2013        | BAS          | Mo, W, Co                  |
| SS 485/1      | SS-CRM No. 485/1 | Nov/2013        | BAS          | Co, V                      |
| SS 486/1      | SS-CRM No. 486/1 | Nov/2013        | BAS          | Co, Mn, V                  |
| SS 487/1      | SS-CRM No. 487/1 | Nov/2013        | BAS          | Co, Mn, V                  |
| 2Q15S1        | 2Q15S1      | 02/07/2015       | ASTMd        | Mo, Nb, Cu, Ni, Mn, Cr     |
| 2Q15S2        | 2Q15S2      | 02/07/2015       | ASTM         | Mo, Nb, Cu, Ni, Mn, Cr, V  |
| 4Q15S1        | 4Q15S1      | 31/12/2015       | ASTM         | Mo, Nb, W, Cu, Ni, Mn, Cr, V|
| 4Q15S2        | 4Q15S2      | 31/12/2015       | ASTM         | Mo, Nb, W, Cu, Ni, Mn, Cr  |

a) Expiration of certification – valid indefinitely.
b) NIST: National Institute of Standards and Technology.
c) BAS: Bureau of Analyzed Samples Ltd.
d) ASTM: American Society for Testing & Materials.

NITON was configured using the calibration curves obtained from the CRMs listed in table 1. Table 2 presents a summary of the values obtained from the intercept of axis (a) and the slope (b) for each calibration curve and the value of the R² for each chemical element [7].

The measurements were performed on the three stainless steel specimens, using the NITON analyzer coupled to the Mobile Test Stand. The three samples - AISI 304, 316 and 430 - were measured five times at different positions on their surfaces. NITON has been configured for the general metals analysis from the main menu using three filters – main range (20 s) and high range (20 s) and light range (20 s), disable Al, and autoswitch ON. All measurements were taken by using the following procedure quoted in the NITON manual: 1 – sample preparation – cleaning using isopropyl alcohol and lint-free paper; 2 – perform a system check once every working day; 3 – warm up for ten minutes after start up [6, 7].
Table 2. 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  |
| W                | 0.0108         | 0.9989      | 1.0000  |
| Cu               | -0.0148        | 1.1157      | 0.9993  |
| Ni               | 0.0021         | 1.0096      | 1.0000  |
| Co               | -0.0026        | 1.0013      | 0.9997  |
| Mn               | -0.0258        | 0.9803      | 0.9997  |
| Cr               | -0.0932        | 0.9758      | 0.9995  |
| V                | 0.0019         | 0.9116      | 0.9996  |

3. Results and discussion

The statistical results of the measurements of the three stainless steel samples are presented in table 3. The means ($\bar{y}$), standard deviations of samples $s(x_i)$, and standard deviations of the means $s(\bar{x}_i)$ were calculated using equation (1), where $n$ is the number of measurements [1, 2, 3, 4, 5, 7].

$$s(\bar{x}_i) = \frac{s(x_i)}{\sqrt{n}}$$  \hfill (1)

Table 3. Statistical parameters for stainless steel samples AISI 304, 316 and 430.

| Chemical element | AISI 304 | AISI 316 | AISI 430 |
|------------------|----------|----------|----------|
|                  | $\bar{y}$ | $s(x_i)$ | $s(\bar{x}_i)$ | $\bar{y}$ | $s(x_i)$ | $s(\bar{x}_i)$ | $\bar{y}$ | $s(x_i)$ | $s(\bar{x}_i)$ |
| Mo               | 0.3064   | 0.0028   | 0.0012   | 1.9890   | 0.0110   | 0.0049   | 0.4622   | 0.0019   | 0.0009   |
| Nb               | 0.0038   | 0.0008   | 0.0004   | 0.0108   | 0.0004   | 0.0002   | 0.0102   | 0.0004   | 0.0002   |
| W                | 0.0402   | 0.0016   | 0.0007   | <LOD     | <LOD     | <LOD     | <LOD     | <LOD     | <LOD     |
| Cu               | 0.3668   | 0.0093   | 0.0041   | 0.0530   | 0.0039   | 0.0018   | 0.0218   | 0.0039   | 0.0020   |
| Ni               | 8.2386   | 0.0529   | 0.0236   | 10.0022  | 0.0450   | 0.0201   | 0.2230   | 0.0132   | 0.0059   |
| Co               | 0.2176   | 0.0109   | 0.0049   | <LOD     | <LOD     | <LOD     | <LOD     | <LOD     | <LOD     |
| Mn               | 1.9466   | 0.0208   | 0.0093   | 1.3370   | 0.0079   | 0.0035   | 0.9496   | 0.0258   | 0.0115   |
| Cr               | 18.2752  | 0.0087   | 0.0039   | 16.6364  | 0.0188   | 0.0084   | 16.3446  | 0.0639   | 0.0286   |
| V                | 0.0254   | 0.0025   | 0.0011   | 0.0496   | 0.0039   | 0.0017   | 0.0474   | 0.0117   | 0.0052   |

*<LOD indicate the measurements were below the limit of detection (LOD). All values are expressed in % m/m.

3.1 Measurement uncertainty sources for the analysis of steel by EDXRF

The calculation of the measurement uncertainty for steel analysis by EDXRF begins with the analysis of uncertainty sources according to the Ishikawa diagram (figure 1). The sources of uncertainty may be of Type A or Type B. The Type A source is a component of statistics methods, and in this study is related to the repeatability standard deviations. The sources of uncertainty Type B, however, are components evaluated by methods other than the series of observations. In the case of the EDXRF method, the following were considered as Type B components: intermediate precision uncertainty, CRM value uncertainty, calibration curve uncertainty and NITON digital resolution uncertainty [1, 2, 3, 4, 5, 7].
3.1.1. Repeatability standard deviation. The repeatability standard deviation of each element is defined as \( s(sp_i) \) - calculated by equation (1) - and is presented in table 3. It is a source of uncertainty Type A determined by \( n \) repeated and independent observations (in this study \( n = 5 \)), where the standard uncertainty Type A is \( u(sp_i) = s(sp_i) \) and the degrees of freedom are \( \nu = n - 1 \), for all elements in each sample [1, 2, 3, 4, 5, 7]. The calculated values of standard uncertainties \( u(sp_i) \), of each sample and each element, are presented in table 3.

\[
\begin{align*}
\text{Figure 1. Ishikawa diagram of uncertainties for EDXRF [7].}

3.1.2. Intermediate precision. In this study, the standard deviation of the intermediate precision denoted by \( s_i(TO) \) was calculated for each chemical element according to ISO 5725-3 [8]. Among the four changeable factors in the intermediate measurement conditions, only two of them - namely time \( (T) \) and operator \( (O) \) - were changed. For this case, the standard deviation of the intermediate precision is denoted by \( s_i(TO) \). The number of samples tested \( (t) \) in each chemical element ranged from eight to sixteen, always having eight replicates per sample \( (m) \). The equation (2) presents how to calculate a two-factor \( s_i(TO) \), according to ISO 5725-3 [7, 8]. The standard uncertainty of the intermediate precision \( u(s_i) \) was calculated using equation (3), and the degrees of freedom calculated using \( \nu = t - 1 \).

\[
\begin{align*}
s_i(TO) &= \sqrt{ \frac{1}{t(m-1)} \sum_{j=1}^{m} \sum_{i=1}^{t} (y_{ij} - \bar{y}_j)^2 } \quad (2) \\
u(s_i) &= \frac{S_i(TO)}{\sqrt{t}} \quad (3)
\end{align*}
\]

Table 4 presents a summary of the calculated values for the standard deviations of the intermediate precision \( s_i(TO) \), the number of samples tested \( (t) \), the standard uncertainties of the intermediate precision \( u(s_i) \) and the degrees of freedom for each chemical element. In these calculations, the CRMs listed in table 1 were used to carry out the measurements with three different operators.

3.1.3. CRM value. The standard uncertainty relating to the CRM value, \( u(CRM) \), is calculated based on the expanded uncertainty found in the CRM certificate. Because the calibration of each element was done with at least five CRMs, the largest uncertainty value among the CRMs was used in the calculation for each element. This value was then divided by its coverage factor. The highest values of \( u(CRM) \) and their degrees of freedom are presented in table 4 for each element [1, 2, 3, 4, 5, 7].

3.1.4. Calibration curve. The standard uncertainty for the calibration curve, \( u(curve) \), considers the correlation between the intercept of axis \( (a) \) and the slope \( (b) \) of the linear equation \( (y = a + b \cdot x) \), and is estimated using equation (4). The \( u(curve) \) values for all elements are shown in table 4. Since \( w \) independent observations were used to determine both the slope and the intersection of a straight line
by linear regression, the degrees of freedom can be calculated using \( v_i = w - 2 \), where \( w \) is the amount of CRMs used in each calibration curve [1, 2, 3, 4, 5, 7].

\[
u(\text{curve}) = \sqrt{c_a^2 u^2(a) + c_b^2 u^2(b) + 2 c_a c_b u(a) u(b) r(a, b)}
\]  

(4)

Where \( c_a \), equation (5), is the sensitivity coefficient \((c_i)\) for \( a \) and \( c_b \) is the sensitivity coefficient for \( b \), equation (6).

\[
c_a = \frac{\partial f}{\partial a} = \frac{\partial [(y - a)/b]}{\partial a} = \frac{-1}{b}
\]  

(5)

\[
c_b = \frac{\partial f}{\partial b} = \frac{\partial [(y - a)/b]}{\partial b} = \frac{a - y}{b^2}
\]  

(6)

The standard uncertainty \( u(a) \) was obtained using equation (7) and the standard uncertainty \( u(b) \) using equation (8).

\[
u(a) = \sqrt{\frac{S^2 \sum x_i^2}{n \sum x_i^2 - (\sum x_i)^2}}
\]  

(7)

\[
u(b) = \sqrt{\frac{S^2}{n \sum x_i^2 - (\sum x_i)^2}}
\]  

(8)

Where the correlation coefficient \( r(a, b) \) was calculated using equation (9) and the residual variance \((S^2)\) was calculated using equation (10).

\[
r(a, b) = -\frac{\sum x_i}{\sqrt{n \sum x_i^2}}
\]  

(9)

\[
S^2 = \frac{\sum w_i (y_{\text{calc}_i} - y_{\text{real}_i})^2}{w - 2}
\]  

(10)

| Table 4. Values of standard uncertainties and degrees of freedom for intermediate precision, CRM value and calibration curve. |
|---|---|---|---|---|---|---|
| Chemical element | \( s_i (\text{TO}) \) | \( t \) | \( u(s_i) \) | \( v_i \) | \( u(\text{CRM}) \) | \( v_i \) | \( u(\text{curve}) \) | \( v_i \) |
| Mo | 0.001617 | 13 | 0.000448 | 12 | 0.005089 | 20 | 0.006206 | 4 |
| Nb | 0.00728 | 12 | 0.000210 | 11 | 0.003536 | 4 | 0.002638 | 4 |
| W | 0.006339 | 10 | 0.002005 | 9 | 0.007892 | 7 | 0.002336 | 5 |
| Cu | 0.005843 | 15 | 0.001509 | 14 | 0.002821 | 21 | 0.002975 | 3 |
| Ni | 0.025826 | 12 | 0.007299 | 11 | 0.03128 | 5 | 0.016082 | 4 |
| Co | 0.027006 | 8 | 0.009548 | 7 | 0.047796 | 5 | 0.061659 | 3 |
| Mn | 0.015968 | 18 | 0.003764 | 17 | 0.007752 | 21 | 0.009759 | 4 |
| Cr | 0.025386 | 16 | 0.006347 | 15 | 0.031566 | 7 | 0.153061 | 5 |
| V | 0.004531 | 15 | 0.001170 | 14 | 0.007752 | 5 | 0.009759 | 5 |
3.1.5. **NITON digital resolution.** The NITON equipment resolution is 0.001 %m/m. The standard uncertainty of the digital resolution, $u_{\text{res}}$, was calculated using equation (11). The $u_{\text{res}}$ is a rectangular distribution and it is assumed that the degrees of freedom tend towards infinity for this distribution [1, 2, 3, 4, 5, 7].

$$u_{\text{res}} = \frac{\text{resolution}}{\sqrt{12}} = \frac{0.001}{\sqrt{12}} = 0.000289 \%m/m$$  

3.2. **Combined standard uncertainty calculations for steel analysis using the EDXRF method**

After transforming all the uncertainties (Type A and Type B) into standard uncertainties $u(x_i)$, they can be combined using equation (12), which renders the combined standard uncertainty $u_c(y)$. Since all the sensitivity coefficient ($c_i$) for the $u(x_i)$ in this study are equal to 1 (because their contributions are given in %m/m), equation (12) can be simplified into equation (13). The calculated values for $u_c(y)$ for each element, per sample, are shown in table 6.

$$u_c(y) = \sqrt{\sum_{i=1}^{n} [c_i]^2 u^2(x_i)}$$  

$$u_c(y) = \sqrt{u(s_x)^2 + u(s_t)^2 + u(CRM)^2 + u(curve)^2 + u(res)^2}$$  

3.3. **Expanded uncertainty calculations**

Firstly, the effective degrees of freedom $\nu_{\text{eff}}$ are calculated using the Welch-Satterthwaite formula, equation (14), rounding the integer values downwards. Later, the coverage factor $k_p$ is calculated using equation (15), where $t_p$ is obtained from the bilateral $t$-distribution (Student's distribution) [1, 2, 3, 4, 5, 7].

$$\nu_{\text{eff}} = \frac{u_c^2(y)}{\sum_{i=1}^{N} \frac{u_i^2(y)}{\nu_i}} \text{ com } \nu_{\text{eff}} \leq \sum_{i=1}^{N} \nu_i$$  

$$k_p = t_p(\nu_{\text{eff}})$$

Finally, the uncertainty of measurement or expanded uncertainty ($U_p$) is obtained by multiplying the combined standard uncertainty $u_c(y)$ by the coverage factor ($k_p$), according to equation (16) [1, 2, 3, 4, 5, 7].

$$U_p = k_p \cdot u_c(y)$$

Whenever possible, measurement uncertainty calculations should be shown, in an organized fashion, in a measurement uncertainty spreadsheet [1, 2, 3, 4, 5, 7]. As this study deals with nine elements measured in three samples, this requests 27 uncertainty calculation spreadsheets. Therefore, table 5 presents only the worksheet of the uncertainty values calculated for Cr in AISI 304 steel. The calculations of the other elements follow the same methodology. All calculated values for $u_c(y)$, $k_p$ and $U_p$ are presented in table 6, for an interval with a confidence level of approximately 95.45 %. The exception is for W and Co in AISI 316 and 430 steels, where the measured values were below the limit of detection (LOD).
Table 5. Calculations of $U_p$ of Cr in stainless steel AISI 304.

| Input quantity          | Estimate $x_i$ (%) m/m | Probability distribution | Standard uncertainty $u(x_i)$ (%) m/m | Dividing factor | Sensitivity coefficient $c_i$ | Contribution to standard uncertainty $u(y) = u(x_i) \cdot c_i$ | Degrees of freedom $v_i$ |
|-------------------------|------------------------|--------------------------|--------------------------------------|----------------|-----------------------------|--------------------------------------------------------------------------------|---------------------------|
| Repeatability           | $s(\bar{x})$           | normal                   | $u(s_{x})$                           | $\sqrt{n}$    | 1                           | $u_i(y) = \frac{u(s_{x})}{\sqrt{n}}$                                        | $v_i = n - 1$             |
| Intermediate precision  | $s_T(\bar{T})$         | normal                   | $u(s_{x})$                           | $\sqrt{t}$    | 1                           | $u_i(y) = \frac{u(s_{x})}{\sqrt{t}}$                                        | $v_i = t - 1$             |
| CRM value               | 0.068                  | normal                   | $u(\text{CRM})$                      | $k$            | 1                           | $u_i(y) = \frac{u(\text{CRM})}{k}$                                           | $v_i = 7$                 |
| Calibration curve       | ---                    | normal                   | $u(\text{curve})$                    | ---            | 1                           | $u_i(y) = \frac{u(\text{curve})}{k}$                                          | $v_i = w - 2$             |
| NITON digital resolution| 0.001                  | rectangular              | $u(\text{res})$                      | $\sqrt{12}$   | 1                           | $u_i(y) = \frac{u(\text{res})}{\sqrt{12}}$                                    | $v_i = \infty$            |
|                         |                        |                          |                                      |                |                             |                                                                                  |                           |

$U_p = 0.41\%$ m/m $k_p = 2.65$ $u(y) = 0.156460$ $v_{eff} = 5$

Table 6. Uncertainty measurement calculated for AISI 304, 316 and 430 stainless steel sample.

| Chemical element | $u_i(y)$   | $k_p$ | $U_p$  | $u_i(y)$   | $k_p$ | $U_p$  | $u_i(y)$   | $k_p$ | $U_p$  |
|------------------|------------|-------|--------|------------|-------|--------|------------|-------|--------|
| Mo               | 0.008132   | 2.28  | 0.019  | 0.009418   | 2.20  | 0.021  | 0.008094   | 2.28  | 0.018  |
| Nb               | 0.004444   | 2.43  | 0.011  | 0.004431   | 2.43  | 0.011  | 0.004431   | 2.43  | 0.011  |
| W                | 0.008505   | 2.32  | 0.020  | ---        | ---   | ---    | ---        | ---   | ---    |
| Cu               | 0.005998   | 2.23  | 0.013  | 0.004734   | 2.18  | 0.010  | 0.004813   | 2.17  | 0.010  |
| Ni               | 0.042980   | 2.25  | 0.097  | 0.041162   | 2.25  | 0.093  | 0.036402   | 2.37  | 0.086  |
| Co               | 0.007875   | 2.52  | 0.20   | ---        | ---   | ---    | ---        | ---   | ---    |
| Mn               | 0.016002   | 2.18  | 0.035  | 0.013485   | 2.21  | 0.030  | 0.017373   | 2.21  | 0.038  |
| Cr               | 0.156460   | 2.65  | 0.41   | 0.156637   | 2.65  | 0.42   | 0.159004   | 2.65  | 0.42   |
| V                | 0.012570   | 2.32  | 0.029  | 0.012636   | 2.28  | 0.029  | 0.013558   | 2.23  | 0.030  |

* All values are expressed in % m/m.

By analyzing the data obtained in table 6, it was identified that the expanded uncertainties $U_p$ are of the same order of magnitude, for the same element, in the three different steels samples. For example, the smallest $U_p$ are for Cu: 0.013 %m/m – AISI 304; 0.010 %m/m – AISI 316; 0.010 %m/m – AISI 430; and the highest $U_p$ are for Cr: 0.41 %m/m – AISI 304; 0.42 %m/m – AISI 316; 0.42 %m/m – AISI 430. However, the expanded uncertainty values have very different orders of magnitude among the elements, since the highest $U_p$ (0.42 %m/m for Cr) is about 40 times greater than the lowest uncertainty (0.010 %m/m for Cu). This can be explained by studying the uncertainty contribution graph. When calculating any measurement uncertainty, uncertainty contribution graph should be compiled. This
graph allows a fast, clear and objective way of observing the sources that predominate in the measurement uncertainty of a given studied measure [2, 5, 7].

Figure 2 displays the uncertainty contributions for Cu and Cr in the AISI 304 steel sample. The sources of uncertainty can be seen to have different relative weights in the composition of the combined standard uncertainty value. For Cu, the greatest contributor is repeatability. For Cr, on the other hand, the repeatability has almost no influence and the major contributor is the calibration curve. This is because four of the five analyzed variables - repeatability, intermediate precision, calibration curve and CRM value - are independent and very distinct among the nine measured elements.

![Contributions to uncertainty](image)

**Figure 2.** Contributions to uncertainty.

Since the purpose of this article is to express the final measurement with its corresponding measurement uncertainty in the analysis of chemical elements for steel samples, table 7 shows these values already rounded and with two significant digits for the uncertainty.

**Table 7.** Final measurement results for AISI 304, 316 and 430 samples.

| Chemical element | AISI 304 $\left( \bar{x} \pm U_p \right)$ | AISI 316 $\left( \bar{x} \pm U_p \right)$ | AISI 430 $\left( \bar{x} \pm U_p \right)$ |
|------------------|---------------------------------|---------------------------------|---------------------------------|
| Mo               | 0.306 ± 0.019                   | 1.989 ± 0.021                   | 0.462 ± 0.018                   |
| Nb               | 0.004 ± 0.011                   | 0.011 ± 0.011                   | 0.010 ± 0.011                   |
| W                | 0.040 ± 0.020                   | <LOD                           | <LOD                           |
| Cu               | 0.367 ± 0.013                   | 0.053 ± 0.010                   | 0.022 ± 0.010                   |
| Ni               | 8.239 ± 0.097                   | 10.002 ± 0.093                  | 0.223 ± 0.086                   |
| Co               | 0.22 ± 0.20                     | <LOD                           | <LOD                           |
| Mn               | 1.946 ± 0.035                   | 1.337 ± 0.030                   | 0.950 ± 0.038                   |
| Cr               | 18.28 ± 0.41                    | 16.64 ± 0.42                    | 16.34 ± 0.42                    |
| V                | 0.025 ± 0.029                   | 0.050 ± 0.029                   | 0.047 ± 0.030                   |

*<LOD indicate the measurements were below the limit of detection (LOD). All values are expressed in % m/m.*
4. Conclusion

Upon the evaluation of the calculated measurement uncertainties, it is possible to conclude that the measurement uncertainty has different values for each chemical element analyzed by the NITON spectrometer using the EDXRF method. Therefore, a single measurement uncertainty value cannot be assigned to the whole instrument. A single calibration uncertainty, however, can be assigned for every calibration range in each chemical element – as shown in the Ni measurement results. When comparing the Ni results for the AISI 304 and AISI 430 steel, it is observed that the two means are very different in the measurement range, but the uncertainty values are not statistically different. This also occurs in the measurements of Mo, Cu and Mn.

Another conclusion concerns the uncertainty contribution graph, since it is important to be able to quickly and easily identify the main contributors to the final uncertainty value and whether it needs to be optimized to reduce the expanded uncertainty or not. Its presentation is vital in studies that calculate measurement uncertainty.

Regarding the sources of uncertainty, it is concluded that the calibration curves are very significant sources of uncertainty in the estimation of the final uncertainty, thus the use of these in the NITON software is essential to minimize errors and to ensure the calculations are more robust and reliable.

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