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UNCERTAINTY ESTIMATION FOR SDAR-OES INTERNAL STANDARD METHOD

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Spectrometria de emisie optică cu descărcare electrică prin scânteie în argon (SDARis theOES) este cea mai utilizată tehnică pentru analiza elementală a aliajelor metalice deoarece are cel mai mare raport eficienţă/cost. In conformitate cu standardul SR EN 13005/2005, normele europene EA 4/16is the EA guidelines on the expression of uncertainty in quantitative testing, EURACHEM /CITAC Guide CG 4, Quantifying Uncertainty in Analytical Measurement (second edition) 2000 şi alte reglemetări specifice raportarea concentraţiilor elementelor trebuie însoţită de incertitudinea extinsă calculată pentru un nivel de încredere dat. De asemenea, normativele respective cer ca incertitudinile extinse să fie estimate pe baze fundamentate teoretic şi tehnic. In acest sens, lucrarea prezintă un model avansat de estimare a contribuţiei metodei standardului intern la bugetul de incertitudine al incercării spectrochimice SDARis theOES. Astfel, autorii propun un nou mod de estimare a deviaţiilor standard ale rapoartelor intensităţilor liniilor spectrale şi ale rapoartelor concentraţiilor masice. De asemenea, lucrarea prezintă un mod de calcul al incertituidinii standard compuse.

The spark discharge in argon optical emission spectrometry (SDARis theOES) is the most used technique for elemental analysis of metallic alloys due to its highest efficiency/cost ratio. In this field the SR EN 13005/2005 standard and other European documents as EA 4/16is the EA guidelines on the expression of uncertainty in quantitative testing, EURACHEM /CITAC Guide CG 4, Quantifying Uncertainty in Analytical Measurement (second edition) 2000, etc. require that the uncertainty estimation to be done on the fundamental basics as much as possible. In this sense, the paper addresses mainly an advanced theoretical model for estimation of SDARis theOES internal standard method contribution to the spectrochemical uncertainty budget. In this regard, the authors have introduced new ways of estimation of the standard deviations of the spectral line intensity ratios, mass concentration ratios and finally were given a route of computation of compound standard uncertainties for dozed concentrations.

Key words: uncertainty, standard deviations, SDARis theOES, spectrochemical analysis, internal standard method

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1. Introduction

Spark discharge in argon optical emission spectrometry (SDAR-OES) is the most used technique for elemental analysis of metallic alloys due to its highest efficiency ratio [1÷7]. The working principle of SDAR-OES analysis is the measurement of intensity of characteristic spectral lines emitted by atoms during sparking.

Generally, the intensity ratio of the analysis channel and a suitable reference channel shows a better reproducibility than the single channel result of the analytical element. That is why to calibrate the channels are often use instead of raw intensities [3].

The relation between vaporization, excitation, intensity yield and measured variable is known only qualitatively, which is why spectrometers need to be calibrated. There is no calibration curve theory which can be used for entire operating practice. The most used method for OES spectrochemical analysis is the internal standard method (ISM). The ISM assumes a polynomial relationship between concentration ratio and the intensity ratio of the spectral lines emitted by the alloying elements in the sample and the internal standard of the form [1, 3]:

$$\frac{C_i}{C_s} = a_0 + a_1\frac{I_i}{I_s} + a_2\left(\frac{I_i}{I_s}\right)^2 + a_3\left(\frac{I_i}{I_s}\right)^3 + a_4\left(\frac{I_i}{I_s}\right)^4 \tag{1}$$

where: C_i is the mass concentration of the element “i”; C_s is the mass concentration of the internal standard which is, generally, the matrix concentration, i.e. base concentration; I_i is the intensity of analytical line of the i-th alloying element; I_s is the intensity of the analytical line of the chosen internal standard; a_k is the coefficients determined by the least squares regression method, k=1…4.

Note 1: The a_2, a_3 and a_4 coefficients are frequently disregarded.

Spectrometry usually adjust the spectrometer parameters through linearization of eq. (1), i.e. disregarding the a_2, a_3 and a_4 coefficients.

The ISM is applied with the hypothesis that all alloying elements into the sample are dozed with the exception of trace elements, whose concentration do not exceed 0.5(%) [1, 3]. In this sense, the trace elements are disregarded and the sum of the dozed elements is considered 100(%):

$$\sum_{i=1}^{n} C_i + C_s = 100(\%) \tag{2}$$

where: n is the is the number of the alloying elements.

The eq. (2) is equivalent to:

$$\sum_{i=1}^{n}\frac{C_i}{C_s}+1=\frac{100}{C_s} \tag{3}$$

In the case of routine analysis, on the abscissa we find the ratios of intensities $x_i=\frac{I_i}{I_s}$ while the ordinate the $y_i=\frac{C_i}{C_s}$ quotients (fig.1) [3]. Thus, the $\frac{C_i}{C_s}$ quotients are estimated by the y_i, which are calculated values based on calibration method.

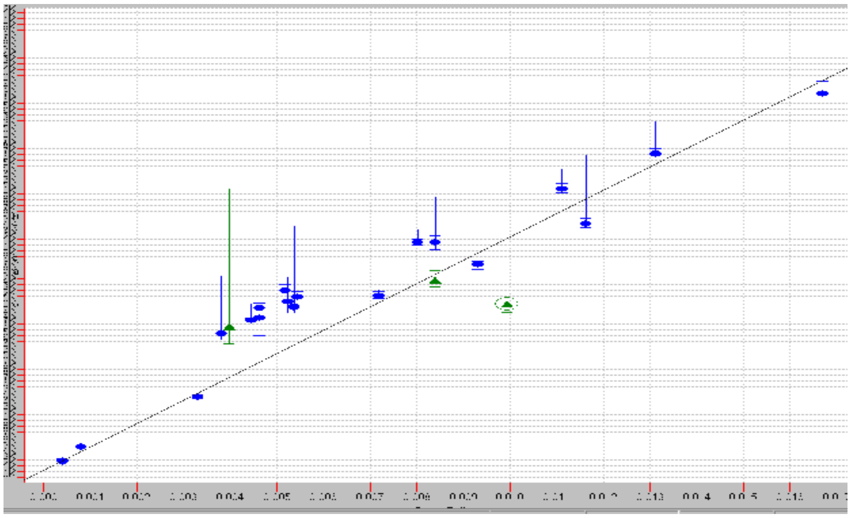

Fig. 1. An example of calibration curve with intensity ratios on OX axis and concentration ratios on OY axis [3].

Fig.1 shows the intensities ratio plotted on the OX axis and the concentrations quotients on OY axis. This might be somehow up-down at first glance, as the concentration quotients would be as the "known" variable. But, for routine analyses the intensity ratio are known and the concentration quotients can be calculated.

On the other hand, from the statistical point of view, the independent variable for a least square regression of a set $\{x_i, y_i\}$, $i=\overline{1,n}$, the used data should be the variable with the smaller relative standard deviation (RSD). Thus, for a low alloyed Certified Reference Material (CRM) the RSDs of the y_i quotients are of 1…2 % order (see Table 1) while the RSDs of the x_i, may be of 2…10 % as it is shown in eq. (4)[1, 2, 4].

$$RSD_{x_i} = \sqrt{\frac{1}{I_S} + \frac{1}{I_E}} \cdot 100(\%) = \sqrt{10^{-3} + 10^{-5}} \cdot 100 > 3.0(\%) \tag{4}$$

When the uncertainties of the concentrations are critical for the mechanical or chemical properties of a grade and should be kept as low as possible then the RSDs could be minimized by increasing I_S and I_E. Thus, for a modern spectrometer which provides $I_S > 5 \cdot 10^5$ cps and $I_E > 2 \cdot 10^4$ cps the RSD_X is brought down to about 1%. Nevertheless, when $C_E \leq 0.1\%$ then $I_E < 10^3$ and $RSD_{XE} > 3\%$. Comparing the RSDs for x_i and y_i (Table 1) it results that choosing I_i/I_s as independent variable is consistent when I_s is greater, but more important, when I_E exceeds 10^4 cps.

2. Concentration computation for Internal Standard Method

Supposing that all y_i have been estimated on the basis of functional dependence on x_i e.g. on the basis of calibration curves then, the C_S is calculated easily using the following relation:

$$C_S = \frac{100}{1 + \sum_{i=1}^{n} y_i} \tag{5}$$

Once the C_s is find then, the concentrations of the alloying elements can be easily calculated as:

$$C_i = C_s \cdot y_i = 100 y_i \Big/ (1 + \sum_{j=1}^{n} y_j) = C_i(y_1, ..., y_i, ..., y_n) \tag{6}$$

where: y_j is the estimation of C_j/C_s on the base of its calibration curve for the I element.

It is generally accepted that y_j, $j=\overline{1,n}$, are independent indirect variables which are affected only by random errors [1, 2, 8].

Table 1.

The main data of a CRM for a low alloyed steel grade

Element	**C**	**Si**	**S**	**P**	**Mn**	**Ni**	**Cr**	**Mo**	**Cu**	**Al**	**Fe**
C, % mass	0,257	0,498	0,131	0,074	0,533	0,38	0,348	0,242	0,162	0,09	96.7
U (95%)	0,005	0,01	0,005	0,003	0,011	0,007	0,005	0,006	0,004	0,004	0.2
RSDc(%)	0,97	1,00	1,91	2,03	1,03	0,92	0,72	1,24	1,23	2,22	0.22

3. Estimation of type B standard uncertainties of the concentrations for ISM

Based on the above hypotheses and on the error propagation law, the standard deviation of the concentration of the element *i*, is expressed as:

$$S^2_{C_i} = \frac{10^4 y_i^2}{(1+\sum_{j=1}^{n} y_j)^4} \cdot \sum_{\substack{j=1\\ j\neq 1}}^{n} S^2_{y_j} + \frac{10^4[(1+\sum_{j=1}^{n} y_j) - y_i]^2 \cdot S^2_{y_i}}{(1+\sum_{j=1}^{n} y_j)^4}$$

$$= C_i^2 \left[\frac{\sum_{\substack{j=1\\ j\neq 1}}^{n} S^2_{y_j}}{(1+\sum_{i=1}^{n} y_i)^2} + (1 - \frac{y_i}{1+\sum_{i=1}^{n} y_i})^2 \cdot \frac{S^2_{y_i}}{y_i^2} \right] \tag{7}$$

$$= \frac{C_i^2}{10^4}\left[C_s^2 \cdot \sum_{j=1}^{n} S^2_{yj} + (100 - C_i)^2 \frac{S^2_{y_i}}{y_i^2} \right]$$

The eq. (7) can be expressed as:

$$RSD_{C_i}(\%) = \left[\left(\frac{C_s^2}{100}\right)^2 \cdot \sum_{\substack{j=1\\ j\neq 1}}^{n} S^2_{y_i} + \left(\frac{100-C_i}{100}\right)^2 \frac{S^2_{y_i}}{y_i^2} \right]^{\frac{1}{2}} * 100 \tag{8}$$

where RSD_{Ci} is the relative standard deviation *per cent* of the i-th element concentration.

The expression of $RSD^2_{C_i}$ could be put in a more significant form if one takes into account the expression of the standard deviation of the inner standard that is:

$$S^2_{C_s} = \frac{10^4}{\left(1+\sum_{i=1}^{n} y_i\right)^4} \sum_{j=1}^{n} S^2_{y_j} = \frac{C_S^4}{10^4} \sum_{j=1}^{n} S^2_{y_j} \tag{9}$$

The relative standard deviation of the inner standard concentration is:

$$RSD^2_{C_S} = \left(\frac{C_S}{100}\right)^2 \sum_{j=1}^{n} S^2_{y_i} \tag{10}$$

If the first term in eq. (8) is replaced by RSD_{C_S} in eq. (10) then the RSD_{C_i} gets a more consistent expression, respectively:

$$RSD_{C_i}{}^2 = \left[RSD^2_{C_S} + \left[\left(\frac{100-C_i}{100}\right)^2 - \left(\frac{C_S}{100}\right)^2 \right] * RSD^2_{y_i} \right] \tag{11}$$

The eq. (10) reveals that the *Achilles' heel* of ISM is the summation of dispersions for each dozed concentration and the critical value of internal standard RSDs determines the all other RSDs as it is shown in Fig. 2. When RSDs represent 1% of RSDs of the alloying elements, are quite similar with the calculated ones from the CRM's Certificate but when RSD_S increase to 6%, than the whole RSDs increase beyond 6%. From the SR EN 13005:2005 point of view, the S_{CS} and S_{Ci}

represent the standard uncertainties of type B that are compound uncertainties[9÷11].

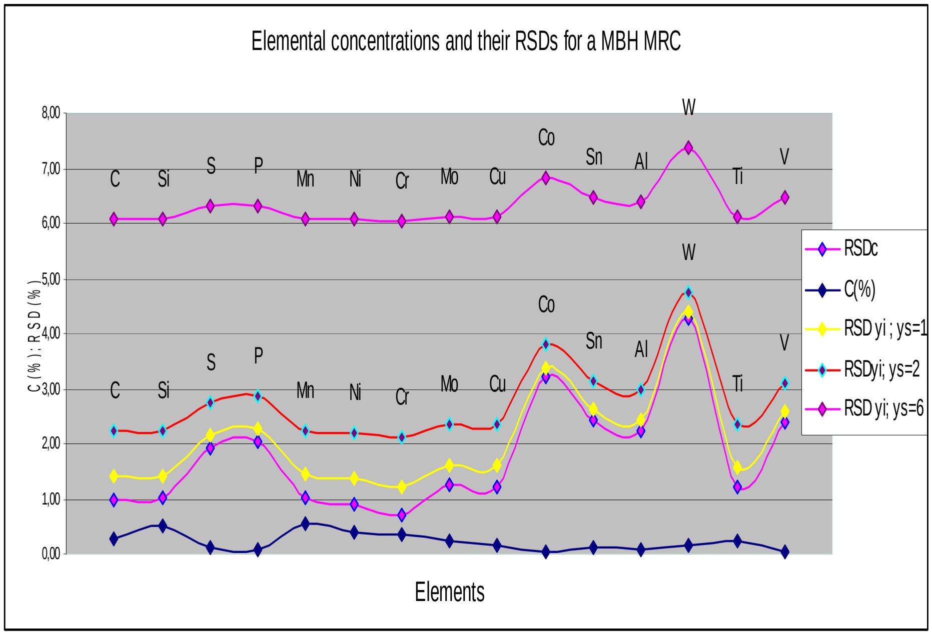

Fig. 2. CRM's concentrations and their RSDs depending on internal standard RSD (%)

4. Contribution estimation of the calibration process to the spectrochemical uncertainty budget

The calibration practice consists in the sparking of dozen of CRMs for each calibration curve, i.e. obtaining the data (y_{ik}, x_{ik}), $k = \overline{1, N_i}$ for element *i.*

In this paper we will consider the case of linear relationship between y_i and x_i for all dozed elements because this is the case of spectrochemical routine analyses.

Applying the least square linear regression method (LSLRM) to the (y_{ik}, x_{ik}), $k=1\ldots N_i$, data one obtains a relationship of the form:

$$x_i = A_i \cdot y_i + B_i \tag{12}$$

where A_i and B_i are well known regression coefficients [12÷15]:

$$A_i = \frac{\sum_{k=1}^{N_i}\left(x_{ik} - \langle x_i \rangle\right)\left(y_{ik} - \langle y_i \rangle\right)}{\sum_{k=1}^{N_i}\left(y_{ik} - \langle y_i \rangle\right)^2} \tag{13}$$

where: N$_i$ is the number of CRMs used for calibration; y_{ik} is the known quotient (C$_i$/C$_s$) of the *k*-th CRM; x_{ik} is the measured intensity ratio associated to y_{ik}; $\langle y_i \rangle$ is the average of the calibration "known" values y_{ik}, i.e. :

$$\langle y_i \rangle = \frac{1}{N_i} \sum_{k=1}^{N_i} y_{ik} \tag{14}$$

$\langle x_i \rangle$ is the average of the x_{ik} measured values, i.e.

$$\langle x_i \rangle = \frac{1}{N_i} \sum_{k=1}^{N_i} x_{ik} \tag{15}$$

As it can be noticed from eq. (7), eq. (9) and eq. (11), the calibration is among the most significant contributor to the uncertainty budget of the ISM. In this sense, the estimation of the standard deviation S_{y_i} of y_i, i = $\overline{1,n}$ is unavoidable.

It is often used by the spectrometrists the functional eq. $y_i = a_i x_i + b_i$ for a routine analysis that complicates the $S^2_{y_i}$ estimation, while the calibration is done backwards, e.g. $x'_{i,k} = A_i y_{ik} + B_i$. In this respect, the only way to estimate $S^2_{y_i}$ is to consider the calibration curve residue $S^2_{O_i}$ as a measure of the dispersion of the Xi variable [15], respectively:

$$S^2_{O_i} = \sum_{k=1}^{N_i} \left(x_{ik} - x'_{ik} \right)^2 / Ni - 2 \tag{16}$$

where: $x_{ik}, k = \overline{1, N_i}$ is the measured values; $x'_{i,k}$ is the calculated values LSLRM, i.e

$$x'_{i,k} = A_i y_{ik} + B_i \tag{17}$$

According to LSRLM and to error propagation law the standard deviation of A_i is [13, 15]:

$$S^2_{A_i} = {S^2_{O_i}}\big/{V_i^2} \tag{18}$$

where:

$$V_i = \sum_{k=1}^{N_i} \left(y'_{ik} - \langle y'_i \rangle \right)^2 \tag{19}$$

where: y'_{ik} is the "known" y_{ik} of the k^{th} CRM used for calibration; $\langle y'_i \rangle$ is the average value of the y'_{ik}, $k = \overline{1, N_i}$.

The derived expression of the standard deviation of a x^m_i which was determined by interpolation using the calibration curve and the measured value y_i^m is:

$$S_{x_i}^{2m} = S_{oi}^2 \cdot \left[\frac{1}{N_i} + \frac{\left(y_i^m - \langle y'_i \rangle\right)^2}{V_i^2} \right] \tag{20}$$

According to eq. (20) and LSLRM theory the derived expression of the standard deviation of B_i is:

$$S_{B_i}^2 = S_{oi}^2 \cdot \left(\frac{1}{N_i} + \frac{\langle y'_i \rangle^2}{V_i^2} \right) \tag{21}$$

The expression of the standard deviation of the y_i^m was deduced on the basis of the above derived relations as:

$$S_{yi}^{2m} = \frac{S_{oi}^2}{A_i^2 V_i^2} \left[y_i^{2m} + \left(y_i^m - \langle y'_i \rangle\right)^2 + 2\langle \tilde{y}_i \rangle^2 \right] + \frac{2S_{oi}^2}{N_i A_i^2} \tag{22}$$

Note 2. The quantity y_i^m is identical with y_i used in eq. (5) and specifies that y_i^m was estimated ones only from measured data.

The eq. (22) shows that the standard deviation of measured y_i^m (y_i) quotient depends on its value, but mainly on the calibration parameters as the number of CRM used for calibration N_i, on distribution of y_i' into analytical range which is estimated by V_i and on the slope of regression line (A_i).

As it is generally accepted, the minimum value of S^2_{yi} is reached when y_i^m is closed to $<y_i'>$ [10, 15], but from eq. (22) it results that S^2_{yi} is minimum for $y_m = \langle \tilde{y}_i \rangle / 2$ that is a surprising result.

From our derivation of the standard deviation $S^2_{y_i^m}$ [see eq. (22)] it results that it could be decreased to an accepted value mainly by reducing the residue of LSLR procedure. This implies an accurate calibration with a large number (N_i) of adequate CRMs and, the last but not the least, using a good “radiation measure machine” which is the spectrometer. Thus, a precise and accurate measurement of spectral line intensities depends on many factors such as: sample parameters (chemical homogeneity, microstructure, cleanness, etc.), optic parameters (transmittance of the lens and glass fiber; dispersion of diffraction lattice and other aberrations etc.), electronic parameters (CCD’s efficiency, electronic noise, etc.).

From the above it results that the estimation of the RSD_i implies at least two steps:

1- calculation of RSD_{C_S} using eq. (10);

2- calculation of RSD_{C_i} using eq. (11);

The estimation of RSD_{C_S} and RSD_{C_s} implies knowing the values of N_i, V_i, S_{O_i} for all dozed elements, i.e. $i=\overline{1,n}$.

The $y_i^m \equiv y_i, i=\overline{1,n}$ values are not directly accessible to the spectrometrist but they could be replaced with the C_i/C_s values that are values displayed by the spectrometer.

Using an appropriate software, RSD_{C_S} and subsequently RSD_{C_s} could be calculated, but the data of ISM calibration of a spectrometer is a matter of know-how that is protected. Thus, the issue of the calibration contribution to the uncertainty budget of SDAR-OES ISM remains, for a while, to the theoretical level that is, anyhow, a big breakthrough. Once we have the validation of the correctness of eq. (22), it will be quite easier to estimate $RSD_{Ci,}$ i=1…n.

The authors will search for calibration data that could be brought in public paper in the next couple of month and will perform computations and simulations of the SDAR-OES ISM contribution to the uncertainty budget of spectrochemical analysis.

5. Conclusions

The paper addresses a very sensitive and important subject concerning the contribution of the calibration to the uncertainty budget of SDARis theOES internal standard method.

There were theoretically estimations of the standard deviations and relative standard deviations for all dozed elements.

Two of the most striking results of this issue are:

1. The relative standard deviation of an alloying element *i* (RSD^2_{Ci}) consists of two terms, one which is the same for all alloying elements and one that, somehow in a complicate manner, depends on element *i* (see eq. (10)). This fact shows that the RSD^2_{Ci} could not be decreased down to $(C_S/100)^2 \cdot RSD^2_{Cs}$.

2. The standard deviation of the quotient y_i, $S^2_{yi,}$ reaches its minimum value when y_i is one half of the average value of the quotient used to fit the calibration line, i.e. $y_i = \langle y_i' \rangle /2$.

The authors found an adequate approach to match the way of spectrometer calibration to the manner the spectrometer is operated, which consists in the way of S^2_{yi} calculation using the calibration based on parameter setting $\{Ni, S^2_{oi}, V_i\}, i=\overline{1,n}$.

The paper specifies the possibility of computing RSD_{C_s} and subsequently, RSD_{ci} but their application to a real case of uncertainty estimation are hindered, for a while, because the calibration data are classified for available commercial spectrometers.

Anyhow, from the authors' knowledge, it is for the first time when a thoroughly theoretical estimation of the SDAR-OES ISM contribution to the spectrochemical uncertainty budget was done.

The results presented in the paper as well as other expected in this field will be used to develop a more reliable procedure for uncertainty estimation of spectrochemical analyses that will comply better with the EA 04/16 and SR EN 13005: 2005 requirements.

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