

# Checking of the Equivalency of One-Standard and Multistandard Calibration Methods in Solid-Sampling Atomic Spectroscopy\*

<sup>a</sup>K. FLÓRIÁN\*\*, <sup>b</sup>J. HASSLER, <sup>c</sup>P. RUTAROVÁ, and <sup>d</sup>GY. ZÁRAY

<sup>a</sup>Department of Chemistry, Faculty of Metallurgy, Technical University Košice, SK-042 00 Košice  
e-mail: Karol.Florian@tuke.sk

<sup>b</sup>Wacker Ceramics Kempten, D-87471 Kempten, Germany

<sup>c</sup>Institute of Chemistry, Faculty of Natural Sciences, P. J. Šafárik University, SK-041 57 Košice

<sup>d</sup>Research Group of Environmental and Macromolecular Chemistry, Hungarian Academy of Sciences, H-1518 Budapest, Hungary

Received 16 October 2002

The common problem of all solid-sampling spectrochemical methods is the adequate calibration. Mostly only a limited number of adequate certified reference materials, or laboratory reference materials is available. Therefore besides the use of solution standards some other calibration procedures were proposed as the so-called one-standard methods. Here the change of independent variable – content is achieved by applying different masses of one standard.

The classical calibration with a set of calibration samples has been compared with the above-mentioned method in the present work. Some validation characteristics as concentration range, goodness of fit, precision of the method, *etc.* were calculated in spectrochemical analysis of typical solid samples as boron carbide and boron nitride.

The calibration is the most important process of each dependent analytical procedure. This is true also in solid-sample spectrochemical analysis, where the calibration has its special background. While in classical solution analysis the preparation of calibration standards is only a routine operation, in solid-sample analysis it could be a serious problem, caused by the lack of suitable reference (CRMs) or at least laboratory reference (LRMs) materials. Therefore, a complex study of different calibration procedures and throughout them of some validation characteristics is needed.

It is one of the difficulties of direct solid-sampling spectrochemical methods to find a suitable analytical calibration, though many procedures were reported. All of them have some advantages but also disadvantages to mention – without a wide discussion – just these of compared two methods:

*a)* Certified reference materials (CRMs): correct way of calibration if the matrices are similar, possibility of correct statistical evaluation (normality and homoscedasticity of repeated data); but mostly a lack of suitable CRMs, if they exist in needed number then

inadequate content range for analytes, differences in homogeneity and particle size;

*b)* Only 1 CRM with variable masses of sample: a possible way of calibration, no differences in matrix, economic factor; but content range limited by upper content (CRM) and lower content (mass), risk of change in experimental conditions due to changes in the mass of the sample.

It is not certain, whether in both procedures the independence of calibration, the linearity and the normality of calibration data will be ensured. The different calibration procedures could produce different validation results, therefore a complex comparative study is needed.

## EXPERIMENTAL

All of the experiments were carried out by using the so-called Laboratory Reference Materials (LRMs, Wacker Ceramics, Kempten, Germany) [1]. The instrumentation was the LECO-750 (former LECO – Germany) GD-OES multichannel spectrometer, modified for the use with DC arc, connection to spectrometer by quartz-fibre optics, using two each to other in 90° angle oriented independent collection lenses [2]. The computer-controlled modernized DCA-301 (Spectral Systems, Fürstenfeldbruck, Germany) DC-arc source [3] enabled the total evaporation and destruction of the solid sample, without need of any

\*Presented at the XVIth Slovak Spectroscopic Conference, Košice, 23–27 June 2002.

\*\*The author to whom the correspondence should be addressed.

**Table 1a.** Characteristics of 10 Repeated Measurements of 5 Boron Nitride LRMs for Analytes Ca and Si

Parameter LRM	Element									
	Ca					Si				
	$\bar{y}$	$s_y$	$\tilde{y}$	$R$	$RSD_i$	$\bar{y}$	$s_y$	$\tilde{y}$	$R$	$RSD_i$
83/2	36.9	1.5	36.6	3.97	4.1	14.1	0.61	14.2	1.51	4.3
86/2	29.6	1.4	29.6	3.83	4.7	9.83	0.60	9.77	1.65	6.1
420	10.4	0.82	10.4	2.11	7.9	22.1	1.62	22.0	3.83	7.3
1305	55.7	3.9	54.8	9.80	7.0	14.5	0.88	14.7	2.10	6.1
362	5.11	0.28	5.06	0.73	5.5	9.73	0.53	9.38	1.10	5.5
RSD <sub>a</sub>					5.8					5.9

Remarks:  $\bar{y}$  – arithmetical mean,  $s_y$  – standard deviation,  $\tilde{y}$  – median,  $R$  – range,  $RSD_i$  – relative standard deviation expressed in %,  $RSD_a$  – average relative standard deviation [5] expressed in %.

**Table 1b.** Characteristics of 5 Repeated Measurements of 4 Boron Carbide LRMs for Analytes Al and Fe

Parameter LRM	Element									
	Al					Fe				
	$\bar{y}$	$s_y$	$\tilde{y}$	$R$	$RSD_i$	$\bar{y}$	$s_y$	$\tilde{y}$	$R$	$RSD_i$
St.1	10.8	0.94	11.4	1.66	8.7	50.9	0.66	50.9	1.30	1.3
St. 2	14.0	1.90	13.9	3.80	13.6	52.0	4.52	51.4	9.00	8.7
B-13	9.1	0.39	9.0	1.57	4.3	55.2	5.08	58.0	8.70	9.2
St. 5	9.1	0.92	9.0	1.97	10.1	65.5	3.67	65.4	8.90	5.6
RSD <sub>a</sub>					9.2					6.2

spectrochemical additive. The sample mass weighted into the high-resistance carbon carrier electrode (Elektrokarbon – Topoľčany, Slovakia) was either ( $4 \pm 0.05$ ) mg using a set of boron nitride LRMs, or the individual sample masses varied between 1–5 mg. The sample mass of boron carbide LRMs was ( $5 \pm 0.05$ ) mg, the individual sample masses varied in the range 1–7 mg.

Using the commercial software of the spectrometer the integrated spectral-line intensities of chosen analytes were obtained as an analytical signal (consequently  $y = \Sigma I$  in arbitrary units).

Two sets of data were achieved:

a) Results of 10 repeated measurements of 5 applied LRMs (with constant sample mass): arithmetical mean and variance, resp. median and range (see Tables 1a and 1b).

b) Independent results of 25 single measurements of 5 BN LRMs with variable mass of the sample (all measurements normalized on 4 mg average mass), resp. of 15 single measurements of 2 B<sub>4</sub>C LRMs with variable sample mass (all measurements normalized on 4 mg average mass), calculation of arithmetical mean and variance, resp. median and range (Tables 2a and 2b).

## RESULTS AND DISCUSSION

Using the data sets described above, the parameters of calibration functions (linear regression, least-squares method)

$$y = a + b \cdot w \quad (1)$$

were calculated.

From the most important validation characteristics [4] the following were chosen:

- range;
- precision, calculated as average relative standard deviation ( $RSD_a$ ) [5], the average of  $RSD_i$  values characterizing each of individual calibration samples (Tables 1a and 1b); or as RSD of normalized signal data of one sample (Tables 2a and 2b);
- correlation coefficient ( $r$ ) commonly used for the assessing of linearity in validation procedure, graph with  $r > 0.995$  are considered to be linear. It should be mentioned that it was declared by several authors that  $r$  might not be a useful indicator of linearity and other procedures were proposed [6];
- residual variance – one of the most important comparative characteristics [7], calculated as

$$s_{\text{res}} = \sqrt{\frac{1}{N-2} \sum_{i=1}^N (\bar{y}_i - \hat{y}_i)^2} \quad (2)$$

( $\bar{y}_i$  are the mean of signal values, *i.e.* integrated intensities,  $\hat{y}_i$  are the calculated values);

– the in the German norm [8] defined precision of the method

$$RSD_{\text{method}} = \frac{1}{b} \times \frac{s_{\text{res}}}{\bar{w}} \quad (3)$$

**Table 2a.** Characteristics of 25 Single Measurements of 5 Boron Nitride LRMs Calculated after Normalizing the Data on 4 mg Average Sample Mass – Analytes Ca and Si

Parameter LRM	Element									
	Ca					Si				
	$\bar{y}$	$s_y$	$\hat{y}$	$R$	$RSD_i$	$\bar{y}$	$s_y$	$\hat{y}$	$R$	$RSD_i$
83/2	41.2	6.0	37.7	21.3	14.6	17.8	7.4	14.9	18.4	41.5 !
<i>corr.</i>	37.6	2.7	37.3	6.6	7.3	14.6	2.0	14.5	4.9	13.9
86/2	34.5	8.2	30.2	17.2	23.7	12.6	4.6	11.0	11.0	36.4
<i>corr.</i>						10.6	0.63	10.6	1.4	6.0
420	13.2	4.7	10.4	10.1	35.4	23.8	4.0	22.1	9.9	16.8
<i>corr.</i>						22.3	2.4	21.7	5.5	10.5
1305	61.2	12.3	55.7	28.7	20.1	16.9	4.4	15.3	20.6	26.2
<i>corr.</i>	55.7	1.34	55.5	3.2	2.4	15.0	0.77	14.9	1.7	5.2
362						15.2	10.1	10.3	5.6	66.7 !
<i>corr.</i>						10.8	2.45	10.0	5.6	22.7
RSD <sub>a</sub>					23.5					37.5
<i>corr.</i>					17.2					11.7

Remarks: *corr.* – reduced (corrected) data set without data with the value of  $\Delta > 3.0$ .

**Table 2b.** Characteristics of 15 Single Measurements of 2 Boron Carbide LRMs Calculated after Normalizing the Data on 6 mg Average Sample Mass – Analytes Al and Fe

Parameter LRM	Element									
	Al					Fe				
	$\bar{y}$	$s_y$	$\hat{y}$	$R$	$RSD_i$	$\bar{y}$	$s_y$	$\hat{y}$	$R$	$RSD_i$
St.1	21.8	11.7	18.5	34.2	53.7 !	74.7	25.5	64.3	73.0	34.1 !
<i>corr.</i>	16.4	2.87	15.4	7.2	17.5	62.6	3.91	62.7	10.6	6.3
St. 2	17.1	5.97	14.5	17.0	34.9 !	89.0	9.36	87.2	21.1	10.5
<i>corr.</i>	14.1	1.62	13.7	4.6	11.5	84.2	3.39	83.8	6.4	4.0
RSD <sub>a</sub>					44.3					22.3
<i>corr.</i>					14.5					5.2

This figure of merit, expressed as a percentage relative standard deviation, should also serve as a comparative characteristic;

– linearity – besides the correlation coefficient  $r$ , discussed above, the well known characteristic is the quality coefficient QC [6, 9], calculated as

$$QC = 100 \% \times \sqrt{\frac{\left(\sum_{i=1}^n \frac{y_i - \hat{y}_i}{\bar{y}}\right)^2}{n - 1}} \quad (4)$$

where the value of  $QC < 5 \%$  should characterize the suitable calibration [6]. Another possibility offers the use of the so-called goodness-of-fit, or linearity test, based on testing of residual variance (2) vs. variance of repeated measurements [4, 7]. Of course, if there are no repeated measurements (one-standard method), the modified [9] statistical test allows only a relative comparison of the calibration efficiency.

The obtained results allow the following conclusions:

i) The data in data sets of multistandard calibration are near to symmetric distribution (mostly equal

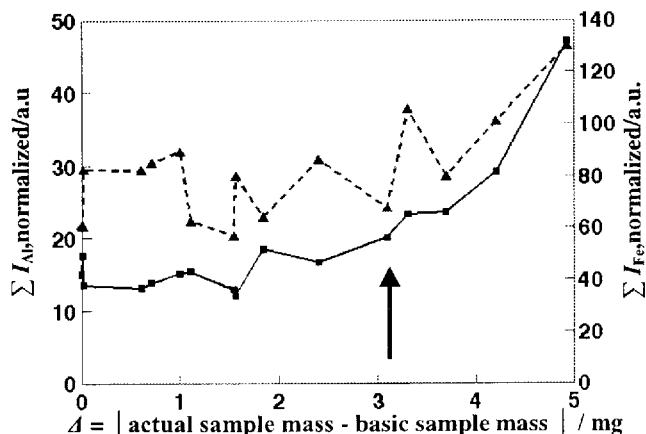


Fig. 1. Dependence of normalized intensity values upon the difference  $\Delta = |\text{actual sample mass} - \text{basic sample mass}| / \text{mg}$ . ■ Al in  $B_4C$ ; ▲ Fe in  $B_4C$ ; basic sample mass = 4 mg.

values of mean and median), the RSDs with few exceptions (at Al, Fe in  $B_4C$ ) are acceptable for this type of analysis (Table 1).

**Table 3a.** The Main Characteristics of Calibration Functions of Ca and Si in BN

Calibration parameter	Ca		Si	
	5 LRM	Single measur. $n = 25$	5 LRM	Single measur. $n = 25$
Content range/ $(\mu\text{g g}^{-1})$	20–295	7–355	18–75	3–88
$r$	0.998	0.999	0.999	0.983
$s_{\text{res}}$	1.1	2.41	0.23	0.86
QC/%	3.32	8.65	1.67	7.20
RSD <sub>method</sub> /%	4.8	8.5	3.7	9.7
$a$	$6.44 \pm 0.950$	$6.71 \pm 0.896$	$5.55 \pm 0.180$	$5.63 \pm 0.299$
$b$	$0.166 \pm 0.0056$	$0.163 \pm 0.0056$	$0.220 \pm 0.0051$	$0.213 \pm 0.0080$

**Table 3b.** The Main Characteristics of Calibration Functions of Al and Fe in B<sub>4</sub>C

Calibration parameter	Al		Fe	
	4 LRM	Single measur. $n = 15$	4 LRM	Single measur. $n = 15$
Content range/ $(\mu\text{g g}^{-1})$	35–100	6.8–100	580–1200	108–1500
$r$	0.994	0.929	0.999	0.971
$s_{\text{res}}$	0.251	0.973	0.237	5.65
QC/%	1.2	8.18	0.42	9.63
RSD <sub>method</sub> /%	5.7	17.8	1.3	14.3
$a$	$6.36 \pm 0.372$	$7.59 \pm 0.512$	$37.7 \pm 0.167$	$19.2 \pm 2.98$
$b$	$0.074 \pm 0.0047$	$0.140 \pm 0.0115$	$0.023 \pm 0.0005$	$0.055 \pm 0.0036$

ii) The data sets of single measurements (variable sample masses) give another picture. The normalized data are distributed asymmetrically (differences in mean vs. median), some RSDs are hardly acceptable (Table 2). This fact is illustrated by Fig. 1, showing the dependence of normalized intensities upon the difference ( $\Delta$ ) between actual sample mass and average sample mass. It is evident that over the value  $\Delta = 3.0$  the normalized intensities increase inadequately, which gives the explanation of asymmetric character of data sets. This statement is confirmed by results of reduced (corrected) data sets, where the values with  $\Delta > 3.0$  have been rejected.

iii) The comparison of both studied calibration procedures shows their matrix dependence. While the results of BN matrix (Table 3a) illustrate a good agreement in calibration parameters ( $a$ ,  $b$ ,  $r$ ), in matrix B<sub>4</sub>C (Table 3b) are these quite different, in some cases more as one order of magnitude.

## CONCLUSION

The presented number of examples prevents one from giving general conclusions. Some further experiments with various matrices, more analytes, and variable excitation conditions (to avoid the influence of excitation process) are needed. At least it is possible to declare the one-standard method as a possible alternative of calibration if no other ways are disposable. It should be mentioned that the observed dependence

of output signals on sample mass gives some limits for the applicability of this calibration method.

*Acknowledgements.* The Slovak Grant Project No. 1/7418, 2000 and the Slovak-German International Cooperation Project No. SVK-01/021 supported this work. The authors are obliged to express their gratitude for these supports.

## REFERENCES

1. Quevauviller, Ph., Bennink, D., and Bøwadt, S., *Fresenius' J. Anal. Chem.* 370, 11 (2001).
2. Hassler, J. and Perzl, P. R., *GIT Lab. Fachz.* 40, 98 (1996).
3. Flórián, K., Hassler, J., and Marquardt, D., *GIT Lab. Fachz.* 46, 1144 (2002).
4. Kromidas, S., *Validierung in der Analytik*. Wiley-VCH, Weinheim, 1999.
5. Záray, Gy. and Kántor, T., *Spectrochim. Acta* 50B, 48 (1995).
6. Van Luco, L., Elskens, M., Croux, Ch., and Beernaert H., *Accred. Qual. Assur.* 7, 281 (2002).
7. Danzer, K. and Currie, L. A., *Pure Appl. Chem.* 70, 993 (1998).
8. Damman, V., Donnevert, G., and Funk, W., *Qualit Assurance in Analytical Chemistry*. VCH, Weinheim 1995.
9. Massart, D. L., Dijkstra, A., and Kaufman, L., *Evaluation and Optimization of Laboratory Methods and Analytical Procedures*. Elsevier, New York, 1978.