Chemometric Evaluation of Direct Spectrochemical Methods in the Determination of Elements in the SiC Matrices*

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The chemometric evaluation of the achievement of direct spectrochemical methods for SiC matrices, and the judgement of fulfillment of the defined analytical order is based on the fundamental parameters of the information theory. These parameters, the value of information content, as well as the corresponding measure value were computed from the theoretical tolerance parameters of the analytical order. The computation was repeated for the set of parameters derived from experimental metrological characteristics. This valuation should be extended to complex determination of the degree of accuracy of the tested methods. The testing is based on the analysis of standards with certified mass fraction values by the methods in question. On the basis of determined accuracy values it is possible to calculate the information content values related to the accuracy values.

Generally, for a critical chemometric evaluation of the fulfillment of analytical order of the given analytical method it is first necessary to determine its theoretical tolerance (index T) performance parameter. The analytical order is mainly suggested with regard to the chemical character of the analyzed matrices, and must incorporate the list of analytical elements, and chosen parameters. These are: the lower required mass fraction content level $w(\mathrm{X}_{\mathrm{min,T}})$, the upper required mass fraction level $w(\mathrm{X}_{\mathrm{max,T}})$, and the required standard deviation $s(w_{\mathrm{X,T}})$ of the content determination, usually given as a general relative precision of the content determination $s(w_{\mathrm{X,r,T}})$. The value $s(w_{\mathrm{X,T}})$ is related to the value $s(w_{\mathrm{X,r,T}})$ and is given by the following equation

$$s(w_{\mathrm{X,T}}) = s(w_{\mathrm{X,r,T}})\ \ w(X)\ \ (1/100) \qquad (1)$$

For the mentioned evaluation of the fulfillment of analytical order it is also necessary to derive the performance parameters from the experiments, the metrological characteristics of the applied method [1]. These are: the lower content value $w(\mathrm{X}_{\mathrm{min}})$ expressed mainly as the limit of detection $w(\mathrm{X_L})$ or the rigorous level given by the limit of guarantee of purity $w(\mathrm{X_G})$, the highest content level $w(\mathrm{X}_{\mathrm{max}})$ expressed mainly as the highest used content value of the analytical calibration, and the value of standard deviation $s(w_{\mathrm{X}})$ of the content determination.

From the theoretical tolerance parameters and from the values of metrological characteristics it is first necessary to calculate [2—4] the following fundamental parameters of the information theory: the value of the information content $\hat{I}(p, p_{\mathrm{o}})_{\mathrm{X}}$ and the corresponding measure of the information content $\widehat{\mathrm{MI}}(p, p_{\mathrm{o}})$.

THEORETICAL

In the previous paper [5] the sequence of the applied computation of fundamental parameters of the information theory was defined. Special attention has been paid to the problem of the influence of accuracy upon the mentioned fundamental parameters.

The information content [1] value $\hat{I}(p, p_{\mathrm{o}})_{\mathrm{X}}$ was calculated according to the relationship

$$\hat{I}(p, p_{\mathrm{o}})_{\mathrm{X}} = \frac{w(X_{\mathrm{max}}) - w(X_{\mathrm{min}})}{s(w_{\mathrm{X}})} \quad \frac{\sqrt{N}}{2t(\alpha, F)} \qquad (2)$$

for $\alpha = 0.04$ and the degree of freedom $F = N - 1$; N represents the number of measurements in determination of the standard deviations of content determination $s(w_{\mathrm{X}})$. For calculation of the value of information content measure $\widehat{\mathrm{MI}}(p, p_{\mathrm{o}})$ the simplifying assumption was adopted that either no correlation existed between the content values of the individual elements (X) or the measure of correlation was significantly lower than 50 % [2]

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$$\widehat{\mathrm{MI}}(p, p_o) = \sum_{j}^{Q} (I(p, p_o)_X)_j \qquad (3)$$

$j = 1, . . ., Q$, Q represents the maximum number of analytical elements determined.

The information content value as well as further parameters of the information theory are influenced also by the measure of accuracy of the used analytical technique [6, 7]. This is evaluated as an identity between the experimentally observed content value $w(X_{st,exp})$ and the declared value $w(X_{st})$ of a certified standard

$$\delta = |w(X_{st,exp}) - w(X_{st})| \qquad (4)$$

The condition required for application of the formula (4) is the fulfillment of unequality

$$\delta \ll s(w_X) \;\; 2t(\alpha^*, F)/\sqrt{N^*} \qquad (5)$$

The information content value is then calculated from the transformed equation

$$\hat{I}(r; p, p_o) = \ln \left(\frac{(w(X_{max}) - w(X_{min}))\sqrt{N}}{s(w_X) \;\; 2t(\alpha, F)} \right) - \frac{N^*}{4} \left(\frac{\delta}{s(w_{X,st}) \;\; t(\alpha^*, F)} \right)^2 \qquad (6)$$

$\alpha^* = 0.01$ and N^* is the number of independent measurements in the determination of standard deviation value $s(w_{X,st})$. For the final evaluation of the valuated analytical methods the most important values are the differences

$$\Delta I = \hat{I}(p, p_o)_X - \hat{I}(r; p, p_o)_X \qquad (7)$$

$$\Delta \mathrm{MI} = \widehat{\mathrm{MI}}(p, p_o) - \widehat{\mathrm{MI}}(r; p, p_o) \qquad (8)$$

EXPERIMENTAL

The complete set of experiments was realized consequently by the DC arc excitation [8]. Two spectrochemically active additives were used: the spectrochemically pure graphite powder SU-602 and the mixture of $CaF_2 + Ba(NO_3)_2$ in a mass ratio 1 1. The silicon carbide ground matrix was excited with graphite powder and with a combined mixture of additives with fluorizing character. In the SiC matrix two minor elements (Al, Fe) and two trace elements (Ti, V) were observed. For all combinations, the analytical calibration for the concentration range $w(X) \in \langle 3.16, 0.00316 \rangle$ was realized, and simultaneously, the value of standard deviation $s(w_X)$, the values of limits of detection $w(X_L)$, and guarantee of purity $w(X_G)$ were determined.

The experimental conditions were identical with the conditions listed in Ref. [9]. For the experiments five typical matrices were used: a SiC standard matrix (SiC_{st}), an internal standard from Elektroschmelzwerk Kempten (SiC_{ARR-3}), the equimolar mixture of the elements Si and C (Si + C), and SiO_2 powder of high purity with graphite powder of spectrochemical purity (SiO_2 + C). To these matrices the following minor and trace elements were successively added in the oxide form: Al, Fe, Ti, and V in the scale from 3.16 % to 0.00316 %. These mixtures were used as calibration matrices for construction of the analytical functions. In the experimentally obtained spectra first the blackening values (S) of the chosen spectral lines were measured. Following this basic operation, the S values were transformed by the I-transformation procedure [10] into proportional I values which allowed calculation of the ΔY values. This numerical matrix of experimental values was then used as input data for all evaluation procedures of content determination and in the calculation of parameters of information theory.

RESULTS AND DISCUSSION

The evaluation of the performance of the developed analytical method is based on one hand on the comparison of information content and the measure of information content values of tolerance parameters with the experimentally obtained information parameters for the given matrices and two additives. After this fundamental evaluation procedure the influence of the accuracy on the parameters of information theory is followed.

Influence of the Spectrochemical Character of the Additives

In the case of using the graphite additives (Table 1) it was possible to verify that the experimentally obtained values $\hat{I}(p, p_o)_X$ for the elements X = Al and Fe were in all cases higher than the corresponding tolerance values $I(p, p_o)_{X,T}$ Since the elements Al

Table 1. The Values of the Information Content $\hat{I}(p, p_o)_X$, the Measures of the Information Content $\widehat{\mathrm{MI}}(p, p_o)$, and their Corresponding Tolerance Values for the Graphite Additive

X	Matrix			$I(p, p_o)_{X,T}$ MI $(p, p_o)_T$
	SiC_{st} + C	Si + C	SiO_2 + C	
	$\hat{I}(p, p_o)_X$			
$\hat{I}(p, p_o)_{Al}$	3.08	3.13	2.77	2.61
$\hat{I}(p, p_o)_{Fe}$	3.00	3.44	3.04	2.66
$\hat{I}p, p_o)_{Ti}$	2.18	2.53	3.11	3.01
$\hat{I}(p, p_o)_V$	2.62	2.64	2.85	2.85
$\widehat{\mathrm{MI}}(p, p_o)$	10.88	11.74	11.76	11.13

Table 2. The Values of the Information Content $\hat{I}(p,p_o)_X$, the Measures of the Information Content $\widehat{MI}(p,p_o)$, and their Corresponding Tolerance Values for the Fluorizing Additive

X	Matrix: SiC_{st} + C	SiC_{ARR-3} + C	Si + C	SiO_2 + C	$I(p,p_o)_{X,T}$ $MI(p,p_o)_T$
	$\hat{I}(p,p_o)_X$				
$\hat{I}(p,p_o)_{Al}$	2.53	2.65	2.03	2.70	2.65	2.61
$\hat{I}(p,p_o)_{Fe}$	2.41	2.86	2.59	2.58	2.29	2.66
$\hat{I}(p,p_o)_{Ti}$	1.98	2.83	1.89	2.48	2.17	3.01
$\hat{I}(p,p_o)_V$	1.93	2.34	2.28	2.42	2.54	2.85
$\widehat{MI}(p,p_o)$	8.85	10.68	8.79	10.18	9.65	11.13

and Fe are the most important from the standpoint of the judgement of chemical quality of SiC matrices the above-mentioned statement confirms the fulfillment of the analytical order. The fact that the values $\hat{I}(p,p_o)_X$ for the elements X = Ti and V are lower than the tolerance values $I(p,p_o)_{X,T}$ is not significant from the analytical point of view, because they are chemically less important elements of the SiC matrices. On the contrary, the fact that the experimentally obtained values $\widehat{MI}(p,p_o)$ of the matrices Si + C and SiO_2 + C are higher than the tolerance values $MI(p,p_o)_T$, is very important.

In the cases of applying complex fluorizing additive (Table 2), higher values $\hat{I}(p,p_o)_X$ than the corresponding tolerance values $I(p,p_o)_{X,T}$ were found only rarely. By comparing the experimentally obtained values of the measures of information content $\widehat{MI}(p,p_o)$ with the corresponding tolerance values $MI(p,p_o)_T$ the required tolerance value has never been reached, which indicates that the interaction of fluorizing reactions in the given plasma, under the simultaneous presence of Ba atoms and suitable Ba thermoions, does not afford a desirable plasma stability. Both the detectability and the precision of the content determination of analytical elements are therefore worsened.

Influence of the Correction for Accuracy

Decrease of the experimentally obtained values $\hat{I}(p,p_o)_X$ corrected for the determined accuracy of the content determination, and the derived values of the measures of information content $\widehat{MI}(r;p,p_o)$ was remarkably different for the excitation of the SiC matrices with two chemically different efficient additives (Tables 3 and 4).

Application of the graphite additive (Table 3) caused remarkably lower decrease of the values $\hat{I}(r;p,p_o)_X$ in comparison with the values $\hat{I}(p,p_o)_X$. Simultaneously, the application of the graphite additive reduced the values of information content only

Table 3. The Uncorrected, and for the Accuracy Corrected Values of Information Content and Measures of Information Content for the Graphite Additive

X		Matrix: SiC_{st} + C	Si + C	SiO_2 + C
Values of Information Content $\hat{I}(p,p_o)_X$				
Al	(1)	3.08	3.13	2.77
	(2)	2.39	3.07	2.67
	(3)	0.69	0.06	0.10
Fe	(1)	3.00	3.44	3.04
	(2)	2.65	3.41	2.96
	(3)	0.35	0.03	0.08
Ti	(1)	2.18	2.53	3.11
	(2)	2.63	2.44	3.06
	(3)	0.45	0.09	0.05
V	(1)	2.62	2.64	2.85
	(2)	2.69	2.56	2.65
	(3)	0.07	0.08	0.20
Values of Measures of Information Content $\widehat{MI}(p,p_o)$				
	(1)	10.88	11.74	11.76
	(2)	10.36	11.48	11.34
	(3)	0.52	0.26	0.42
	(4)	− 4.78 %	− 2.22 %	− 3.57 %

(1) $\hat{I}(p,p_o)_X$ resp. $\widehat{MI}(p,p_o)$,
(2) $\hat{I}(r;p,p_o)_X$ resp. $\widehat{MI}(r;p,p_o)$,
(3) $\hat{I}(p,p_o)_X - \hat{I}(r;p,p_o)_X$ resp. $\widehat{MI}(p,p_o) - \widehat{MI}(r;p,p_o)$,
(4) $(\widehat{MI}(p,p_o) - \widehat{MI}(r;p,p_o))/\widehat{MI}(p,p_o)$.

Table 4. The Uncorrected and for the Accuracy Corrected Values of Information Content and Measures of Information Content for the Combined Additive with Fluorizing Character

X		Matrix: SiC_{st} + C	SiC_{ARR-3} + C	Si + C	SiO_2 + C
Values of Information Content $\hat{I}(p,p_o)_X$					
Al	(1)	2.53	2.65	2.70	2.65
	(2)	1.62	2.33	2.45	2.02
	(3)	0.91	0.32	0.25	0.63
Fe	(1)	2.41	2.86	2.58	2.29
	(2)	1.11	2.42	2.56	2.00
	(3)	1.30	0.41	0.02	0.29
Ti	(1)	1.98	2.83	2.48	2.17
	(2)	1.55	2.76	1.19	2.16
	(3)	0.43	0.07	1.38	0.01
V	(1)	1.93	2.34	2.42	2.54
	(2)	1.90	2.18	2.22	2.34
	(3)	0.03	0.16	0.20	0.20
Measures of Information Content $\widehat{MI}(p,p_o)$					
	(1)	8.85	10.68	10.18	9.65
	(2)	6.18	9.69	8.33	8.52
	(3)	2.67	0.99	1.85	1.13
	(4)	− 30.17 %	− 9.36 %	− 18.17 %	− 11.71 %

The same comment as in Table 3.

by about −2 %. This advantage is expressively seen on the values of measures of information content $\widehat{\mathrm{MI}}(r; p, p_o)$. The average decrease of these values for three partially different SiC matrices was only −3.5 %. On the contrary, when applying the complex additive with fluorizing character remarkably worse results (Table 4) were obtained. In case of the determination of Fe (SiC_{st} matrix), the value of information content decreased by about −54 %. The average decrease of the value of measure of information content by applying complex additive with fluorizing character was −17.4 %.

CONCLUSION

The correction of the values of information content and therefore also of the corresponding values of the measures of information content for the accuracy of analytical determination always causes a decrease in all evaluated parameters of the information theory. This decrease is element-specific, but it is also dependent on the excited matrix and its crystallochemical character and also on the spectrochemical behaviour of applied additives.

In the given case, the application of graphite additive was more efficient than that of the complex additive with fluorizing character. The difference in efficiencies was nearly one order of magnitude.

SYMBOLS

$w(X_{\mathrm{min,T}})$ the lowest required mass fraction tolerance level

$w(X_{\mathrm{max,T}})$ the highest required mass fraction tolerance level

$w(X_{\mathrm{T}})$ arithmetical mean of the mass fraction range

$s(w_{\mathrm{X,T}})$ required tolerance standard deviation of the mass fraction value $w(X_{\mathrm{T}})$

$s(w_{\mathrm{X,r,T}})$ required tolerance level of relative precision of the mass fraction determination

$w(X_{\mathrm{min}})$ the lowest level of the real mass fraction determination

$w(X_{\mathrm{max}})$ the highest level of the real mass fraction determination

$w(X_{\mathrm{L}})$ limit of detection of the element (X)

$w(X_{\mathrm{G}})$ limit of the guarantee of purity of the element (X)

$s(w_{\mathrm{X}})$ standard deviation of the mass fraction value $w(X)$

$w(X_{\mathrm{st}})$ mass fraction level of the used standard reference material

$s(w_{\mathrm{X,st}})$ standard deviation of determination of the mass fraction level of the standard reference material

$I(p, p_o)_{\mathrm{X,T}}$ tolerance value of the information content

$\hat{I}(p, p_o)_{\mathrm{X}}$ information content value derived from the experimental data

$\hat{I}(r; p, p_o)_{\mathrm{X}}$ information content corrected for the accuracy of the determination of the element (X)

$\mathrm{MI}(p, p_o)_{\mathrm{T}}$ tolerance value of the measure of information content

$\widehat{\mathrm{MI}}(p, p_o)$ value of the measure of information content derived from the experimental data

$\widehat{\mathrm{MI}}(r; p, p_o)$ value of the measure of information content corrected for the accuracy

N number of measurements for the determination of standard deviation value $s(w)$

N^* number of measurements for the determination of standard deviation $s(w_{\mathrm{X,st}})$

Q maximum number of used analytical elements (X)

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