

INTERNATIONAL ROUND-ROBIN EXPERIMENT FOR SIMS-QUANTIFICATION*

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Abstract

Cross Calibration is an attempt to make relative sensitivity factors (RSFs) transferable between SIMS instruments and also usable by the same instrument at different times. The method relies on adjustment of carefully selected operating conditions and instrument tuning parameters, so that closely corresponding raw peak height ratios are obtained from the same sample by different instruments. The transferability of RSFs can be characterised by the factors 1.68 and 2.40 for metallic glass and semiconductor matrices, respectively. Quantitative analysis of "unknown" samples resulted in an overall error factor of 1.31.

Introduction and history

The relative sensitivity factor (RSF) algorithm is widely applied for quantitative analysis of SIMS data. For high analytical accuracy RSFs have to be determined on each individual SIMS instrument and for each individual analysis immediately before analyses of an unknown sample with the use of standard samples (on site standardization, OSS). OSS essentially has been

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practiced for a long time [1, 2], recently a detailed round-robin study on inter-laboratory correlation of analytical results has been published [3] reporting 10% agreement among 9 laboratories. OSS, however, requires the presence of the appropriate standards in each laboratory. The task of producing such a large number of standards is truly formidable, the accurate calibration of the instrument in each case for each element by this standards is also really time consumable work. It would therefore be a great help if laboratories could exchange RSFs and still be able to produce analyses of reasonable accuracy. Thus the load of determining RSFs could be split between laboratories.

It is the dilemma of SIMS analysis that peak height ratios, obtained on different instruments (in different laboratories) from the same sample may differ by a factor of up to 50, and that quantitative concentrations, derived from measured peak heights by some quantification procedure still may differ by a factor of about 10 [1, 4]. Consequently the RSFs are generally not transferable between instruments.

During the SIMS III Conference in Budapest (1981) a group of SIMS experts from 4 countries decided to perform an interlaboratory experiment, called Cross Calibration Experiment (CCE), aiming to elaborate and check a new quantification method based on transfer and use of RSFs. Later more laboratories joined to the runs of the CCE. 11 laboratories took part in the CCE so far, supplying a big number of experimental results. Detailed philosophy of the cross calibration, results of the sections of CCE from 1981 to 1988 have been published elsewhere [5, 6]. Here we outline the basic idea of cross calibration and report on quantitative analysis of "unknown" alloys by the CCE method.

Cross calibration method

Obviously, in all instruments wishing to exchange RSFs for a particular sample, the sample environment and the bombarding conditions must be set to basically arbitrary but well specified common standard operating conditions (SOC). It is much more difficult to achieve coincidence in energy and directional windows, because in many types of SIMS instruments mechanical or electrical adjustments for these parameters are either not calibrated or interdependent. Therefore an empirical instrument tuning procedure — cross calibration — must be followed.

The cross calibration hypothesis means the following. If two SIMS instruments give identical peak height ratios from any sample analyzed under standard operating conditions, they are tuned to the same energy (and directional) window. If two SIMS instruments are tuned by the proper way to the some energy (and directional) window, they produce identical peak

height ratios (RSFs) from all samples, analyzed under standard operating conditions. Consequently, the tuned instruments will produce identical analytical results from any sample when the concentration is calculated from peak heights using the Data Catalogue compiled previously by laboratories having tuned their SIMS by the same way.

For tuning the instruments a sample has to be selected with at least three suitably chosen elements (primary calibration standard PCS). In the CCE experiments a particular choice was made for the PCS on the basis of previous studies of sensitivity factors and energy distribution of amorphous alloys (metallic glasses) [7, 8]. As PCS the amorphous $\text{Fe}_{75}\text{B}_{15}\text{W}_{10}$ alloy was used produced at the KFKI, Budapest [9]. The composition of the PCS is well certified, its components are of broad mass range, their secondary energy spectra are shifted with respect to each other.

The cross calibration strategy outlined above requires closely corresponding bombarding and sample environmental conditions in all participating instruments. The data in *Table 1* appeared to be accessible to all participating instruments and can therefore be considered as standard operating conditions. They also should be the guideline for operating parameters in any "newcomer" instrument having not participated in the CCE experiment so far but wanting to use the RSFs of the Cross Calibration Data Catalogue. When environmental and operating parameters are adjusted according to *Table 1* (or close to them), there still remains a large degree of freedom in instrumental parameter settings in the secondary ion analysis section. They can serve as tuning parameters.

When the tuning parameter is varied, practical sensitivities vary according to the energy distribution of the particular element. In case of the FeBW primary calibration standard for each value of the tuning parameter one obtains three practical sensitivities (for Fe, B and W), and two relative sensitivity factors (for B and W with respect to Fe). Individual instruments

Table 1

Suggested standard operating conditions (SOC) in the Cross Calibration Experiment

Primary ions	O_2^+
Primary energy	10 keV
Target angle	varies according to instrument
Oxygen partial pressure	up to saturation of Fe^+ at analytical raster conditions, after precleaning (or as high as possible)
Primary current for analysis	20 nA
Primary spot size	50 μm
Average primary current density for analysis	$2 \cdot 10^{-4}$ A/cm ²
Precleaning raster	200 × 200 μm^2
Precleaning sputter depth	50 nm
Analytical raster	100 × 100 μm^2

show different behaviour of the RSFs as the tuning parameter is varied. In the first run of the CCE it could be seen that there exists no set of values for the tuning parameters for which both RSF(B) and RSF(W) are identical for all instruments. There exists, however, a so called virtual operating point (VOP) with the coordinates

$$\text{RSF(B)}=0.250 \text{ and } \text{RSF(W)}=0.0335$$

which could be approached by all instruments the best. These values were accepted by the participants also for the forthcoming round-robins.

Each individual instrument tuning has a point of minimum distance (PMD) and the individual tuning error (TUE), the distance between the VOP and PMD which can be defined by the equation:

$$\lg^2 \text{TUE} = \lg^2 \frac{\text{RSF(B, PMD)}}{\text{RSF(B, VOP)}} + \lg^2 \frac{\text{RSF(W, PMD)}}{\text{RSF(W, VOP)}}$$

The TUE can be considered as a measure of the tuning of the instrument and it also serves as the basis of the prediction of the error of the measured unknown concentration.

Quantification by CCE method

Table 2 shows the laboratories and instruments having participated in the Cross Calibration Experiment so far.

The first independent test on the feasibility of the cross-calibration strategy was performed by round-robin experiments on series of metallic glasses and semiconductors. The laboratories determined the RSFs of the components of the binary and ternary homogeneous samples under CCE conditions. For each laboratory combination the ratio of elemental RSFs was calculated and averaged over all measured elements and laboratories, resulting the global transfer error (GTE). The GTE can be considered as the mean agreement factor between RSFs determined under CCE conditions in different laboratories. The GTE is also the basis of the error estimation of analytical results for a particular group of samples (metallic glass alloys, semiconductors etc.) *Table 3* shows the GTE values for the two groups of samples studied in course of the CCE round-robins.

Two samples with compositions unknown to the laboratories were distributed among 8 laboratories. It only was made known that these samples were of the FeBX-type metallic glasses containing X=Ni or Cr. The laboratories were asked to analyse the samples under CCE-conditions and to use appropriate RSFs from the Data Catalogue of the CCE. The concentration figures thus obtained (c_m) were compared to the nominal values

Table 2
Laboratories participating in the Cross Calibration Experiment

Acronym	Laboratory	Instrument	Contribution			
			1.	2.	3.	4.
AWP	Univ. of Antwerp	Cameca ISM 3f	N	Y	Y	Y
BLE	Humboldt Univ., Berlin	Unitra QMS 500	Y	Y	Y	Y
BUD	Techn. Univ., Budapest	Balzers QMG 311	Y	N	N	N
GTB	Chalmers Univ., Göteborg	Cameca IMS 3f	N	N	N	Y
JUE	Kernforsch. anlage, Jülich	ARL IMMA	Y	Y	N	Y
MOS	Inst. GIREDMET, Moskow	Cameca IMS 3f	N	N	N	Y
SEI	Austr. Forsch. Ctr Seibersdorf	Riber SQ 156	Y	Y	Y	Y
WFB	Werk f. Fernseh., Berlin	Cameca IMS 3f	Y	Y	Y	Y
WIE	Techn. Univ., Vienna	Cameca IMS 3f	Y	Y	N	N
ZFG	Ctr. Inst. Mater. Res. Dresden	ARL IMMA	Y	Y	Y	Y

1. original tuning experiment (1982)
 2. round-robin on metallic glasses (1983–84)
 3. round-robin on semiconductors (1985–89)
 4. quantification of unknown samples (1986–89)
- Y yes
N no

Table 3
Global transfer error (GTE) of RSF when transferred between different SIMS instruments

Sample	Number of samples	Number of laboratory combinations	GTE
Metallic glasses	6	15	1.68
Semiconductors	11	15	2.40

which were obtained by atomic absorption analysis (c_r). The error factor of the measurement (F_m) is defined by

$$F_m = c_m/c_r \quad \text{if } c_m > c_r$$

or

$$F_m = c_r/c_m \quad \text{if } c_m < c_r$$

Also the predicted error factor was calculated for each measurement from the global transfer error of the matrix [6] and averaged over all data. The results are presented in *Table 4*. The quantification error factor averaged over all elements and laboratories (42 values) resulted in

$$\bar{F}_m = 1.31$$

Table 4
Results of quantification of "unknown" metallic glass samples

	Laboratory								Sample			
	FeBNi								FeBCr			
	c_r		c_r		c_r		c_r		c_r		c_r	
	10.0	18.0	72.0	77.0	20.0	3.0						
	c_m	F_m	c_m	F_m	c_m	F_m	c_m	F_m	c_m	F_m	c_m	F_m
AWP	10.3	1.03	25.7	1.43	64.1	1.12	68.7	1.12	29.3	1.47	2.0	1.52
BLE	20.1	2.01	31.3	1.74	48.6	1.48	58.1	1.32	39.5	1.98	2.1	1.43
GTB	8.7	1.15	17.9	1.01	73.3	1.02	74.3	1.04	23.2	1.16	2.4	1.25
JUE	9.3	1.08	11.8	1.53	79.0	1.10	82.3	1.07	13.0	1.54	4.8	1.58
MOS	11.0	1.10	37.0	2.06	52.0	1.38	76.0	1.01	21.0	1.05	3.0	1.00
SEI	15.3	1.53	36.9	2.05	47.8	1.51	81.1	1.05	13.7	1.46	5.1	1.70
WFB	10.4	1.04	29.1	1.62	60.5	1.19	75.7	1.02	20.5	1.03	3.8	1.27
ZFB	8.7	1.15	17.1	1.05	74.2	1.03	80.6	1.05	15.9	1.26	3.5	1.16
mean	11.7	1.26	25.9	1.56	66.4	1.23	74.6	1.09	22.0	1.37	3.3	1.36

c concentration, in atomic %

c_m concentration measured by CCE method, in atomic %

F_m error factor

Table 5
Comparison of the CCE and LTE method measured by GTB

Sample	Element	CCE		LTE	
		c_m	F_m	c_m	F_m
FeBNi	Fe	8.7	1.15	10.9	1.09
	B	17.9	1.01	23.8	1.32
	Ni	73.3	1.02	65.3	1.10
FeBCr	Fe	74.3	1.04	84.1	1.09
	B	23.2	1.16	14.2	1.41
	Cr	2.4	1.25	1.7	1.76
mean			1.11		1.30

c_m concentration measured, in atomic %

F_m error factor

Two other opportunities for checking the quantification by CCE method emerged when

- GTB as a newcomer analysed the samples by the CCE method and also by the LTE quantification procedure using empirical T and n_e values;

Table 6
Comparison of the CCE and OSS method measured by
MOS

Sample	Element	CCE		LTE	
		c_m	F_m	c_m	F_m
FeBW	B	27	2.14	10	1.26
	Fe	68	1.18	83	1.04
	W	5	1.46	7	1.04
mean			1.59		1.11

c_m concentration measured, in atomic %

- MOS as a newcomer analysed the same FeBW “unknown” sample by CCE method with two sets of RSFs: 1. values taken from the Data Catalogue of CCE [6], 2. with the method of the OSS using RSFs determined in the same laboratory on the same day. The results are presented in *Table 5* and *Table 6*, respectively.

Conclusions

The results above show that cross calibration allows to achieve semiquantitative results. It can not be compared in accuracy with the on-site-standardization method, where each laboratory has to determine their own RSFs using a set of standard samples. Whenever a standard is not physically available in a particular laboratory, but the required RSFs have been determined under CCE conditions, cross calibration method allows to obtain at least semiquantitative concentration values for unknown multicomponent samples especially if not trace analysis but an overlook analysis is required.

The CCE an “open method”: laboratories so far have not yet participated in the round-robins still may use of the RSFs already existing in the Data Catalogue or can contribute new data to it. The reader is asked to join to the international CCE group.

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