

# Problems on computer processing of SIMS spectra\*

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*The main problems of the interpretation of low resolution secondary ion mass spectra are treated and an evaluation program is presented for SIMS spectra. The programme searches automatically for monoatomic single and double charged ions as well as isoatomic and heteroatomic single charged cluster ions which are the most typical for SIMS spectra and provides also the total ionic current of these species.*

## Introduction

In quantitative constitutional analysis of solid surfaces one has to determine the different elemental constituents and their concentration in a given target. Applying secondary ion mass spectrometry (SIMS) the measurement itself containing all information results in a mass scan, i.e. the current of the spectrometer detector vs scanning time.

There are two main problems in SIMS analysis:

(a) decomposition of the measured mass spectrum for the contributing ionic species (e.g. by computer processing of mass spectra);

(b) determination of the equivalent concentration to all contributing ionic species (using the ionization probabilities).

In this paper only the first problem will be treated. This problem, decomposition, involves two further problems:

(a1) identification of contributing ionic species;

(a2) determination of total ionic currents in consistency with the measured spectrum (quantification).

There is a strong need for computer identification of low resolution SIMS spectra not only to save time but also to improve the accuracy, sensitivity and reliability of the interpretation. A convenient method should work as far as possible without human intervention during the computation. The identification of measured mass spectra is currently carried out 'manually' in most cases. This means the possibility of human errors, subjective interpretation, and the requirement of a great amount of time. Accordingly, very often only the highest easy-to-find peaks will be taken into account wasting quite a lot of information contained by the spectra. Only a few attempts at computer aided peak interpretation have been reported in the literature<sup>1-4</sup>.

In the present paper the basic problems are treated first then a new computer program is described for identification and quantification of constituents. The input of the program is the

measured mass spectrum in counts s<sup>-1</sup> (CPS list); while the output is the constituent ionic species found and their total ionic currents (in CPS). Investigating the consistency and reliability of results obtained a reconstruction of mass spectrum and a guess of probable errors are also given.

## Basic problems

In mass spectrometers of moderate or low resolution (mostly used in practice), the different isotopic contributions can result in a very complex mass spectrum with multiple overlapping in different mass numbers.

In an ideal case an incoming flux of different ionic species produces a mass spectrum (see Figure 1) according to the following expression:

$$C_j(M_j) = \sum_{i=1}^n V_{ji} X_i \quad (1)$$

$$j = 1, \dots, m$$

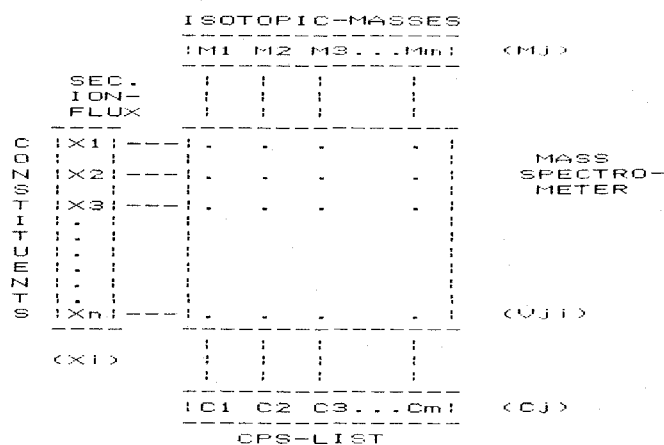


Figure 1. Ideal mass spectrometer.

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where  $C_j(M_i)$  is the CPS value belonging to mass number  $M_i$  in a CPS list having  $m$  peaks. There are  $n$  constituent ionic species, each having a total flux  $X_i$  and  $V_{ji}$  is the isotopic abundance matrix of the constituents. In the general case of spectrum identification only the vector  $C_j(M_i)$  is given and one has to search:

(1) for proper constituents, i.e. for being consistent relating to their isotopic masses and abundances given by the proper column of  $V_{ji}$  matrix;

(2) for their total ionic fluxes  $X_i$  which contribute to the mass spectrum;

i.e. relations (1) have to be solved providing consistent  $V_{ji}$  and  $X_i$  at the same time.

In choosing the possible constituents the column of the matrix  $V_{ji}$  will be determined and if there is a solution one gets the total ionic currents for the constituents  $X_i$  too. In most cases the possible constituents can be:

- (a) monoatomic ions:  $A^+$ ,  $B^+$ ;
- (b) isoatomic cluster ions:  $(A_s)^+$ ,  $(B_t)^+$  ( $s, t$  low integers, e.g.: 2, 3...);
- (c) multiply charged monoatomic ions:  $A^{++}$ ,  $B^{+++}$ ;
- (d) heteroatomic (molecular) cluster ions:  $(A_s B_t C_u)^+$  (to mention only the most frequently occurring ones).

Serious problems can arise, however, in collecting the list of possible constituents:

(i) Heteroatomic ions can be expected in the normal case only for constituents when their monoatomic components can also be found in the spectrum in a reasonable quantity. Though these clusters and their monoatomic 'parent' ions are connected by physical processes, unfortunately there is no general model available at present predicting the relative occurrence of the isoatomic or heteroatomic clusters as well as multiply charged ions in the presence of the related monoatomic ions. It is worth mentioning, however, that some special results have been reported in this field: an empirical formula of secondary ion yields for metal-oxygen systems  $[Me_xO_y]^{\pm}$  based on experimental evidence<sup>5,6</sup>, but there is, as yet, no generally applicable theory.

(ii) At least partial information loss can hinder the peak interpretation when the measurements are not carried out in the proper ion current range. The abundances vary by 4-5 orders of magnitude and therefore the measured contributions of different species are scaled over by the contributing partial fluxes. A compressed range of magnitude in measurements can result in the multi-isotopic constituents becoming virtually mono-isotopic ones and they can even have the same mass number at their biggest isotopic abundances overlapping each other and even some mono-isotopic ones, allowing no further possibility to determine their ratio in the target. The group shown in Figure 2 is typical. The different constituents can be identified only through the peaks at their isotopic masses. But in measuring a given target at low current rate some peaks may 'disappear'.

Having a list of possible constituents (i.e. their isotopic masses and abundances) one can try to solve equation (1) by some adequate mathematical methods. Because of inevitable errors in measurements and loss of information due to the problems mentioned above, one cannot expect a system of linear equations like equation (1) to be valid in general but only for an ideal case. A possible method<sup>4,7</sup> which we used previously is the least-squares-fitting-method (LSF). A limiting condition in this case is that the number of possible constituents must be lower than the number of measured peaks while a more serious problem can result from LSF, that even physically meaningless negative current values might appear. One can try to eliminate these by some adequate

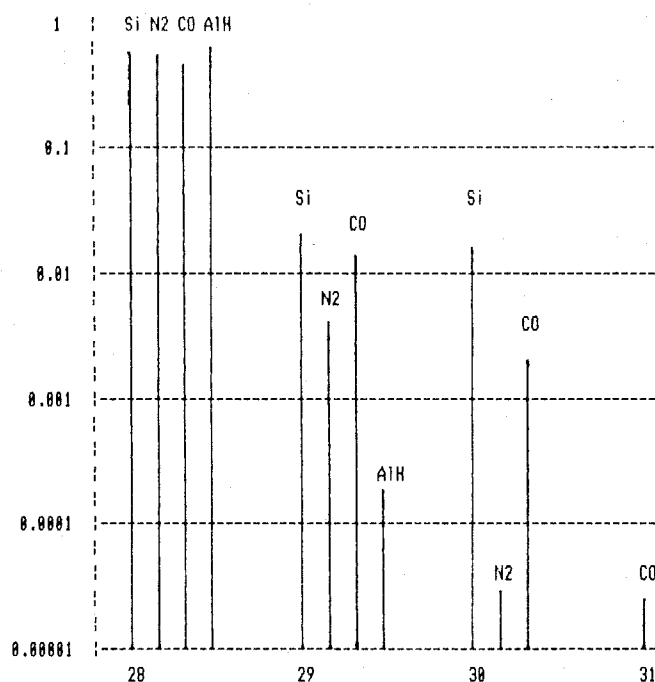


Figure 2. Isotopes of different constituents at a few overlapping mass numbers.

strategy by deleting improper variables from the list and repeating the calculational process until all values are non-negative. Our final results using this method<sup>7</sup> were rather good, but the strategy to be used itself was somewhat heuristic and the calculations were very time-consuming.

The investigation for the consistency of the results to the measured spectra can be done, for example by reconstructing the mass spectra using the total ionic currents found and the isotopic abundance matrix of the constituents. This is a sort of simulation for the CPS list itself. The LSF method producing the least fitting error can result, of course, in the simulated CPS list peaks of higher or even lower values than the measured data.

One can start however instead of (1) using a system of linear inequalities

$$\begin{aligned} \bar{C} &\geq \bar{V}\bar{X} \\ \bar{X} &\geq 0 \end{aligned} \tag{2}$$

where the relations were written in matrix form for solution by the linear-programming-method (LP) and searching for the maximum of the sum of total ionic current ( $\text{Max}[\sum_i X_i]$ ), i.e. for minimum deviation between the measured and simulated spectra. In this case positive definite results are guaranteed. The program described in the following uses the LP method.

Finally, a problem of more general nature is the question of uniqueness of the solution. Do two or more different targets exist providing the same mass spectrum? Unfortunately the answer is, in general yes<sup>4</sup>, but the authors hope that it happens rather seldom and only in special cases which are not very common in everyday practice.

**Program**

**1. List of variables.** The program consists effectively of two main parts. The first one provides a list of tentative constituents (called

variables). To have a list one has to find variables taking into account all possible combinations of atoms whose mass spectra are consistent with the input CPS list. Because of the enormous number of possibilities it is necessary to eliminate as many of them as possible by means of some logical conditions.

The variables are classified as *basic* or *derived* ones. The basic variables are chosen by the program according to a condition described later, taking the related data from the so-called basic library consisting of all atoms with their isotopic masses and natural abundancies. They are divided further into noble, metallic and other (so-called component) types.

Derived variables are proposed and chosen—also automatically—according to a built-in logic (explained later) among the previously found metallic type basic constituents. They can be isoatomic metallic clusters  $Me_2$ ,  $Me_3$ , double charged metallic ions  $Me^{++}$ , or heteroatomic (molecule-like) cluster ions. The first member of heteroatomic clusters is always a metallic atom. The second constituent is either also atomic (metallic or component type) or an isoatomic cluster of metallic atoms. All the constituents are always chosen from the list of previously found variables. The built-in logic prohibits clusters made of noble type atoms.

To start the program, 3 control parameters have to be set or optional values can be used. They are:

BGLT (background limit);

CLT (the cluster limit for metals);

ACLT (auxiliary cluster limit for second part of clusters).

For inserting a variable into the tentative list of constituents the following logical conditions are used:

(a) The CPS value in mass spectra at the mass line of the highest isotopic abundance of the constituent cannot be lower than BGLT.

(b) A preliminary guess is made for the maximum possible value of the constituent using all other isotopic masses and abundancies, too. It can happen, of course, that the final guessed value will be lower than BGLT or even that some of the mass lines in the input are absent. In this case the corresponding isotopes will be deleted and the variable will be termed as a reduced one.

Derived variables (clusters) will be proposed by the program automatically combining basic variables, whose guessed total value is higher than CLT or ACLT respectively. Because only the natural isotopic abundancies of atoms are known, the abundancies of clusters will be calculated using the natural atomic ones.

For inserting derived variables to the list again, conditions (a) and (b) are used.

After selecting the variables the unknown values for the total ionic currents will be determined.

**2. Linear programming.** Having a complete list of possible constituents one has to solve inequality (2) by LP providing only positive definite solutions.

The present version uses the so-called Simplex algorithm and provides  $\max(\sum_i X_i)$ , i.e. the LP can only underestimate the measured data.

### Implementation

The program has been developed on a normal 8 bit micro-computer with 64 K RAM and floppy disks. It allows for an input of maximum 200 mass lines and searches up to a maximum 200 constituents. The algorithm was developed in FORTRAN under CP/M compatible operating system. Typical running time is a few

(3-10) minutes depending on the complexity of the mass spectrum input. The program is capable of running on a mainframe as well.

### Application

For illustration two examples are shown. (The spectra were recorded by F G Ruedenauer in Vienna.) The first spectrum [1-SCH] is a simple positive SIMS spectrum of a stainless steel target having only a few lines recording on a quadrupole ion microprobe (Table 1)<sup>8</sup>. In Table 2 we have collected the results of evaluation given by LSF and LP using the measured data as an upper limit (LP1) and the other possibility (2)

$$\bar{C} \leq \bar{V}\bar{X} \quad (3)$$

$$\bar{X} \geq 0$$

$$\text{Min} \left[ \sum_i X_i \right]$$

**Table 1.** Positive SIMS spectrum (1-SCH) recorded on a quadrupole ion microprobe

Mass	CPS
12	6
16	48
23	181
24	21
27	103
28	43
29	3
32	6
39	122
40	131
41	12
48	11
50	313
51	21
52	5527
53	627
54	544
55	300
56	5819
57	168
58	238
59	17
60	85
62	12
68	36
69	5
72	27
108	11
112	11
Total	14448

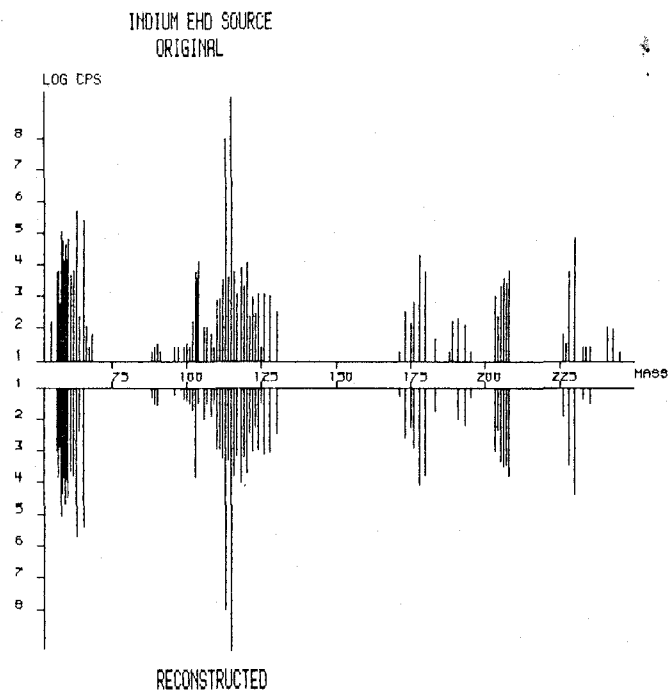
Thus the program LP2 overestimates the input data. Differences between the three methods were found at Ca and at Ar. The other results were practically the same.

Generally, not all the variables found are the same in these cases. The right interpretation should be somewhere between. However relations (2) provide more reliable results and generally the use of (2) is proposed.

The second example<sup>7</sup> is a more complicated spectrum because of the occurrence of non-integer mass numbers. It is a mass spectrum of an ion gun using a liquid metal indium ion source

**Table 2.** Identification results for spectrum I-SCH using different methods

El	LSF	LPI	LP2
C	6	6	6
O	48	48	48
Na	181	181	181
Mg	26	27	27
Al	103	103	103
Si	41	47	63
CO	5		
O <sub>2</sub>	6	6	6
Ar	129		131
K	131	131	174
Ca	2	135	
Ti	17	15	15
Cr	6600	6595	7261
V	21	21	21
Fe	6349	6346	7636
Mn	300	300	300
Ni	322	322	324
Co	17	17	17
CrO	43	43	53
FeO	29	29	30
CrFe	14	14	14
Fe <sub>2</sub>	13	13	13
	14403	14399	16423



**Figure 3.** Original computer graphics showing the measured and reconstructed mass spectrum.

**Table 3.** Original computer listing of identification result for spectrum of an ion gun using liquid metal indium ion source

No	Var	Mass	CPS	No	Var	Mass	CPS
1	In <sup>+</sup>	(57.5)	22925	17	Co <sub>2</sub>	(118.0)	418
2	Ni	(58.0)	2414	18	Sn	(120.0)	1835
3	Co	(59.0)	5560	19	CuNi	(121.0)	25
4	Sn <sup>+</sup>	(60.0)	13077	20	Sb	(121.0)	19
5	Cu	(63.0)	159190	21	Cu <sub>2</sub>	(126.0)	351
6	Sr	(88.0)	2	22	InNi	(173.0)	65
7	Y	(89.0)	3	23	Lu	(175.0)	1
8	Zr	(90.0)	8	24	InCu	(178.0)	2926
9	Mo	(98.0)	3	25	NiSn	(178.0)	23
10	Ru	(102.0)	18	16	CuSn	(183.0)	20
11	Rh	(103.0)	950	27	Ir	(193.0)	28
12	Ag	(107.0)	6	28	Pt	(195.0)	6
13	Cd	(114.0)	888	29	Tl	(205.0)	440
14	In	(115.0)	699592768	30	Pb	(208.0)	1726
15	Ni <sub>2</sub>	(116.0)	1244	31	In <sub>2</sub>	(230.0)	4471
16	CoNi	(117.0)	61	32	InSn	(235.0)	9

Conditions: CLT=1800. ACLT=1800. BGLT=1. Line=83 CPS ·SUM=700256192. RCPS SUM=699811392. RCPS. Err.=0.064%.

recorded on a double focussing tandem mass spectrometer. Table 3 shows the original computer listing containing the variables, their main isotope mass number, and their total specific ionic current in CPS. The original spectrum containing 83 mass lines and the reconstructed one are shown in Figure 3. There are 9 unidentified mass lines. Two double charged constituents were found.

**Conclusion**

The method described is able to choose and to handle the constituents of a SIMS spectrum automatically without any human intervention. With a full list of variables quantification is possible in a general way in order to avoid the error propagation due to the stripping method<sup>2,7</sup>.

However, since no iteration steps are required, to eliminating

the incorrect values the calculation time is shorter than that of the other methods.

The program was developed to serve as a powerful tool in quantitative constitutional analysis of SIMS measurements, but it is applicable for other cases of mass spectroscopy, too.

#### Acknowledgements

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