Automated peak interpretation in low resolution SIMS spectra; a comparison of two algorithms

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Low mass resolution secondary ion mass spectra from solid samples frequently exhibit multiple line interferences at integer mass numbers due to extensive clustering and molecule formation between constituent sample atoms. Two computer algorithms are described which try to address the problem of spectrum interpretation, i.e. the assignment of isotopic and molecular ion species (and their total specific ion currents) to the peaks observed in the mass spectrum. The algorithms are applied to a positive SIMS spectrum, a negative SIMS spectrum and a mass spectrum emitted from a liquid metal ion source; interpreted results are compared.

1. Introduction

It is the goal of quantitative constitutional analysis of solid samples to identify the elements present in the sample and to determine their absolute or fractional concentrations in a selected sampling volume. In secondary ion mass spectrometry (SIMS) the raw data for such an analysis generally are acquired in the form of a mass scan, i.e. a record of the spectrometer detector current as a function of scanning time (in spectrometers) or of the blackening of a photoplate as a function of distance (in mass spectrographs). In automated SIMS analysis a mass scan generally is sampled at intervals corresponding to a fraction of an atomic mass unit. Three steps of data reduction have to be performed before elemental concentration values are obtained:

(a) Peak search; this step locates the peaks in the sampled mass scan and generates a list of peak heights (areas) vs mass number in low resolution mass scans. This list, frequently called 'mass spectrum', may also include peaks at non-integer mass numbers originating from doubly or triply charged atomic or molecular ions.

(b) Peak interpretation; in this step, the peaks of a mass spectrum are interpreted in terms of contributions from monatomic ions, isoelemental clusters and heteroatomic molecular ions, taking into account isotopic and molecular overlap at integer mass numbers. This step generates a list of identified ionic species and corresponding ion currents (summed over all possible isotopic combinations of each species).

(c) Elemental quantification; this final step generates a list of identified elements and corresponding fractional or absolute atomic concentrations [at cm^{-3}] from the list of identified ionic species.

In an analytical laboratory it is desirable to automate this total procedure, requiring operator interference only when absolutely necessary. It is imaginable that the operator only specifies the operating parameters of the mass spectrometer (viz. mass range, scan speed, analytical area) and a computer is taking over instrument control and data evaluation, providing the operator with the quantitative analysis quasi-on-line with the data acquisition. Algorithms for peak search and elemental quantification are available in the program libraries of many SIMS laboratories although, particularly in the quantification step, fundamental physical questions remain to be solved[1-3]. Peak interpretation however so far has escaped a routine treatment, at least where wide mass range, low mass resolution survey spectra are concerned. It is generally done 'manually' and therefore frequently is suceptible to human error, quantitative inaccuracy and subjective interpretation. A large amount of information contained in a secondary ion mass spectrum thus may be left unused. Nevertheless, only few attempts of computerizing peak interpretation in secondary ion mass spectra have been described in the literature[4-8].

2. Peak interpretation

The main problems in the interpretation of low resolution SIMS spectra can be listed as follows:

(a) Ion bombardment of a multielement sample not only results in the emission of monatomic (elemental) ions $(A^+, B^+, \ldots)$ but also of 'isoelemental clusters' $(A_n^+, B_n^+, \ldots)$, heterogeneous 'hybrid molecules' $(A_j B_k C_l^+, \ldots)$ and multiply charged elemental ions $(A^{u+}, B^{v+}, \ldots)$; in the molecular ions (clusters or hydrids) the respective isotopes of the constituent atoms combine to give a mass spectrum of extreme complexity, frequently with multiple overlap of molecular peaks at integer mass numbers.

(b) There is, at present, no model available which predicts the relative abundances of iso-elemental cluster lines with different numbers of atoms. Also, the cluster spectra of multi-element samples generally are not linear superpositions of the cluster

spectra of pure elements. The relative abundances of cluster lines therefore have to be treated as 'free variables' in any interpretation scheme.

(c) There is no model existent which predicts the relative abundances of heterogeneous hybrid clusters in a multi-element system; these abundances therefore have also to be treated as free variables.

(d) Abundances of clusters and hybrids have a strong 'matrix effect', i.e. they depend on the physicochemical state of the target and on the presence of third elements. Therefore, in the general case the idea of generating an atlas of 'fingerprint spectra' for each element and then linearly superimposing fingerprint spectra in a multielement sample will not be successful. In special cases however, such as in a system of oxides with the same cation, fingerprinting has been used to obtain information on the stoichiometry of a mixture of oxides[9].

All the effects mentioned above may contribute to make the number of ionic species to be identified (= number of 'variables') larger than the number of independent equations (= measured peak currents at integer mass numbers) available. In this case there will be no physically founded solution to the problem, although there are numerical methods available to find solutions satisfying certain optimization criteria (e.g. linear programming).

Naturally, many of the problems connected with overlapping mass numbers can be avoided when using a high mass resolution spectrometer. The advantage of (generally) unambiguous peak interpretation however can be offset by increased instrument cost and analysis time and by reduced analytical sensitivity. Computer interpretation of low mass resolution spectra naturally is of particular interest to the increasing number of users of quadrupole-based SIMS instruments.

3. Computer interpretation of low resolution spectra

We want to describe here two different algorithms developed to approach the problem of interpretation of wide mass range, low mass resolution SIMS spectra; we further will compare results when both algorithms are applied to the same experimentally measured SIMS spectra. In addition, the same interpretation algorithms are tested on the mass spectrum emitted from an electrohydrodynamic liquid metal ion source.

3.1. Repetitive spectrum stripping. This algorithm was developed by Steiger and Ruedenauer[4,5] and implemented in the computer code SIP (Spectrum Identification Program). It approaches spectrum interpretation in a heuristic way, i.e. much as a human operator would. SIP first looks for prominent peaks in the mass spectrum and tries to ascribe to these peaks as much elemental ion current as is in accordance with natural isotropic abundances and measured peak currents.

The highest possible values of isotopic currents are subtracted (stripped) at the proper mass numbers from the original spectrum, yielding a 'residual' spectrum. In this residual spectrum the elemental stripping is repeated iteratively. Following the identification of a predetermined number of elements, SIP looks for clusters, oxides and hydroxides of these elements, stripping again the maximum possible isotopic currents from the residual spectrum. In addition, molecules of type A_iB_j (A, B being previously identified elements) and selected types of ternary and four-element hybrids may be stripped. When all clusters and hybrids of the first k identified elements have been processed (k being a free control parameter), the program looks for the highest

peak in the residual spectrum and the elemental and molecular stripping procedure is started again, now skipping all previously identified ionic species. This procedure is repeated until a predetermined number of peaks has been classified 'unidentifiable' (i.e. all elements and allowed types of molecules have been stripped from the respective peaks). Finally, two figures of merit are computed: (a) the 'matching factor' (MF), i.e. the ratio of identified current and original current, averaged over all mass numbers inside a predetermined 'matching interval'; (b) the 'identified current fraction' (ICF), i.e. the sum of identified ion currents divided by the sum of original peak currents (the summation again being carried out inside the same matching interval). Further details of the algorithm have been described in the literature.

This straightforward method obviously contains a great amount of arbitrariness since the solution can be influenced by the choice of the following initial conditions and control parameters: (a) the sequence in which the first few elements are identified; (b) the degree of clustering and oxide formation which is taken into account; (c) the number of elements which have to be identified before clusters and oxides of these elements are stripped; (d) the number of initial elements for which hybridization with all further identified elements is permitted. Still, the results are remarkably good when the solution 'suggested' by the computer is compared against human 'intuition'.

3.2. The matrix method. This method, developed by Antal *et al*[6,7] and implemented in the computer code MATRIX tries to put the identification process on a mathematically sound basis. The input spectrum is considered to be a column vector $\mathfrak{C} = (c_1, c_2, \ldots, c_E)^T$, where the components c_i are the ion counts (currents) at mass number i. A list of 'variables' ($V_1, V_2, \ldots V_N$) is set up, each variable corresponding to an ionic species (element, molecule, cluster, hybrid). The isotopic abundances of any variable V_j are considered as another column vector $\mathbf{G}_j = (G_{j1}, G_{j2}, \ldots G_{jN})^T$. The total specific detected current (summed over all isotopes) of variable V_j is denoted X_j. The X_j can be arranged into a third column vector $\mathscr{X} = (X_1, X_2, \ldots X_N)^T$.

Obviously, the detected current c_j at each mass number can be considered as a linear superposition of all isotopic contributions G_{ij} of those variable V_j having an isotope at mass number i. Therefore, a matrix equation can be formulated

$$\mathbf{G} \cdot \mathscr{X} = \mathfrak{C} \tag{1}$$

where the columns of the matrix $\mathbf{G}$ are the 'abundance vectors' $\mathscr{G}_i^T$ of the variable V_j

$$\mathbf{G} = [\mathscr{G}_1^T, \mathscr{G}_2^T, \ldots, \mathscr{G}_N^T] \tag{2}$$

From the measured 'spectral vector $\mathfrak{C}$ and the tabulated abundance vectors' $\mathbf{G}_i^T$, equation (1) allows to estimate the desired total specific currents X_j of the ionic species V_j present in the (secondary) ion beam analysed. In (1), $\dim(X) = N$, i.e. the number of permitted variables; $\dim(\mathfrak{C}) = E$, i.e. the number of different mass peaks in the range of the input spectrum; $\dim(\mathbf{G}) = [E, N]$.

In the first step of spectrum interpretation those variables V_i have to be selected which possibly can give a higher than background contribution to the original spectrum ('tentative' variables). Once these variables are identified, the determination of their corresponding total intensities X_j is a mathematically straightforward solution of the matrix equation (1). If (1) is overdetermined, i.e. if there are less variables V_j than mass peaks

$(N < E)$, a positive definite solution can be found by minimizing, in the least square sense, the differences between computed and measured peak counts. If there are more variables than mass peaks $(N > E)$, linear programming techniques have to be used for the solution of (1).

A variable V_j is tentatively accepted to occur in the mass spectrum if the peak count at the position of its highest abundance isotope is higher than the background count and if the abundance-scaled other isotopes of that variable also have higher than background peak counts. Up to three-fold charged monatomic ions, isoelemental clusters (up to three-atomic) and hybrid molecules of previously accepted atomic species may be tentatively accepted as variables. In addition there are 'preferred' variables (e.g. H_2, O_2, H_2O, C, CO, hydrocarbons) which, at this preliminary stage, are automatically accepted because they are assumed to occur in the residual gas background of the mass spectrometer. After the list of tentative variables has been compiled, it frequently turns out that the large (E, N)–matrix $\mathbf{G}$ decomposes into a number of smaller, non-overlapping sub-matrices. Equation (1) therefore splits up into a number of independent matrix equations which can be solved individually (least square or linear programming, according to the number of variables and lines in each sub-matrix). If, in the solution of any of the sub-equations of (1), the total current X_j of any variable V_j comes out negative, this variable is removed from the list and the individual sub-equation is solved with the reduced number of variables. In the final solution of (1) it frequently turns out that some of the tentatively accepted variables are assigned total ion currents X_j less than the spectral background (assumed to be independent of mass number). Such variables are tagged 'not identified' and removed from the final list of identified ionic species.

Finally, the mass spectrum is 'reconstructed' from the computed solution of (1) and the difference D between the summed identified and the summed original peak currents (counts) is calculated as a figure of merit for the particular spectrum identification run.

In MATRIX there are also a number of free control parameters which, to some extent, allow the operator to influence the outcome of the interpretation. There is (a) the 'background limit' (BGL): a variable will only be identified when the measured ion count at the main isotope of the respective variable exceeds $10 \times$ BGL; (b) the 'cluster limit' (CL): isoelemental clusters of elements, already tentatively accepted as variables, are accepted as additional variables only when the ion count at their main isotope exceeds the 'CL'; and (c) 'Cluster background limit' (CBGL): a similar limit as CL, operative for the acceptance of hybrid molecules.

4. Results and discussion

The two identification algorithms MATRIX and SIP have been tested by applying them to experimentally recorded mass spectra (see Table 1 and Figures 1–3). Spectrum SCH-2 is a positive SIMS spectrum of stainless steel, recorded on a quadrupole ion microprobe previously described[10,11]. Bombardment conditions were: 10 keV O_2^+, no oxygen jet, current density 0.3 mA cm^{-2}. Spectrum INVEW is a negative SIMS spectrum of another type of stainless steel, recorded on the same ion microprobe. Bombardment conditions in this case were: 10 keV In$^+$ primary ions, current density 0.1 mA cm^{-2}, no oxygen jet. Spectrum EHD is a mass spectrum of the ion beam emitted from a liquid metal ion source of the capillary type with 99.99% purity indium as charge

Table 1. Peak counts vs mass number for mass spectra SCH-2, INVEW and EHD

amu SCH-2	Peak count	amu INVEW1	Peak count	amu EHD	Peak count	amu EHD	Peak count (contd)
11	9	1	100	54	2.00 E1	116	9.00 E2
12	5	11	4	56	9.00 E2	117	1.80 E2
16	88	12	59	56.5	1.05 E3	118	1.30 E3
20	5	13	82	57	8.50 E1	119	3.20 E2
23	516	16	4514	57.5	2.20 E4	120	1.80 E3
24	219	17	759	58	1.00 E4	121	3.30 E1
25	29	18	7	58.5	2.40 E3	122	1.30 E2
26	35	19	26	59	8.70 E3	123	4.20 E1
27	782	21	4	59.5	2.60 E3	124	1.70 E2
28	1269	22	8	60	1.30 E4	125	3.00 E0
29	66	23	7	61	7.50 E2	126	1.70 E2
30	41	24	108	62	1.10 E3	128	1.50 E2
32	8	25	93	63	1.10 E5	130	4.40 E1
39	468	26	218	64	2.80 E1	171	2.00 E0
40	262	27	375	65	5.00 E4	173	4.30 E1
41	43	32	103	66	1.50 E1	175	1.90 E1
44	27	33	13	67	3.00 E0	176	9.10 E1
46	8	35	704	68	8.00 E0	178	3.60 E3
47	7	36	10	88	2.00 E0	180	8.70 E2
48	56	37	201	89	3.00 E0	183	6.00 E0
50	491	38	4	90	4.00 E0	188	2.00 E0
51	88	40	7	91	2.00 E0	189	2.20 E1
52	8931	41	6	96	3.00 E0	191	2.50 E1
53	1020	42	87	97	3.00 E0	193	1.70 E1
54	638	43	332	98	1.00 E0	195	2.00 E0
55	2044	45	6	99	3.00 E0	203	1.50 E2
56	5684	48	20	100	4.00 E0	204	3.20 E1
57	140	49	7	101	3.00 E0	205	3.10 E2
58	250	51	4	102	2.00 E1	206	5.60 E2
59	17	59	12	103	9.50 E2	207	3.90 E2
60	98	60	14	103.5	6.00 E2	208	1.10 E3
61	7	61	4	104	2.10 E3	226	8.00 E0
62	15	68	4	106	1.20 E1	227	4.00 E0
63	6	72	27	107	1.20 E1	228	8.80 E2
64	6	76	12	108	8.00 E0	230	1.50 E4
66	5	79	4	109	3.00 E0	233	3.00 E0
67	5	84	15	110	1.10 E2	234	3.00 E0
68	84	88	25	111	1.20 E2	235	3.00 E0
69	12	100	19	112	5.50 E2	241	1.20 E1
70	6	101	6	113	3.00 E7	243	1.10 E1
71	14	104	5	114	6.50 E2	245	2.00 E0
72	29	115	115	6	6.70 E8		
92	16	119	3				
94	12	129	7				
95	13	131	110				
96	17	146	4				
97	10	148	7				
98	16						
100	6	50	4				
106	4	52	84				
108	16	53	10				
110	5	54	8				
112	17	56	92				
113	3						
114	7						

material[12]. This source is part of a microfocus primary ion gun, mounted in the ion microprobe referred to above[13] and also was used to record spectrum INVEW. Spectrum EHD itself was recorded on a double focusing tandem mass spectrometer[14,15]. Peaks were located and measured 'manually' in spectrum EHD but were located and measured fully under computer control in spectra SCH-2 and INVEW.
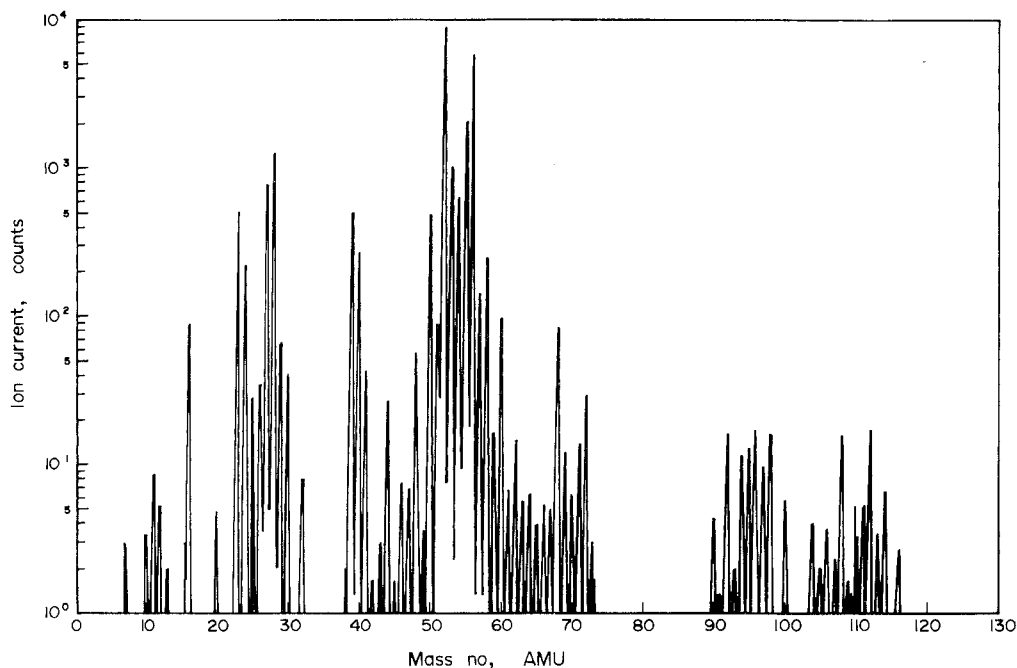
Figure 1. Positive SIMS spectrum (SCH-2) of stainless steel sample, recorded on a quadrupole ion microprobe.

The identification results on spectrum SCH-2 are very similar for SIP and MATRIX, at least for the species with large identified count numbers and generally agree within the confidence limits (1 standard deviation σ) computed by SIP (see Table 2). The elements C, Ne, Cu, Zn, Pd are not identified by SIP because of the particular choice of background count (5 cts peak^{-1}); the MATRIX-results are not in contradiction to these data, although the presence of elements such as Ne and Pd is highly unlikely in this type of steel. O_2 is not identified by SIP because, at such low
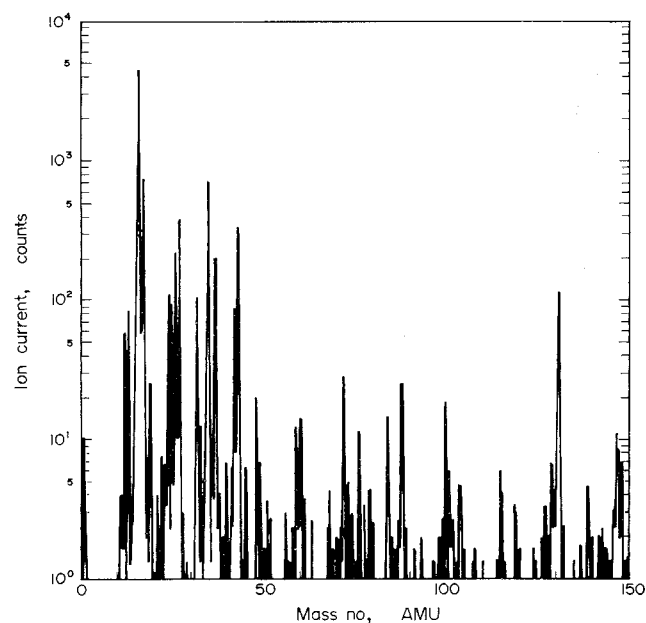

Figure 2. Negative SIMS spectrum (INVEW) of stainless steel sample, recorded on quadrupole ion microprobe.

ion count values, the program has already switched into the highest peak count mode which preferentially looks for elements (in this case S is identified at $M = 32$); O_2 obviously is the better choice. Argon has not been identified by SIP which ascribes the current at $M = 40$ to ^{40}Ca doubtlessly this is a better choice than Ar in this sample because Ar is very unlikely to occur either in the vacuum or in the sample. The occurrence of Ca in positive SIMS spectra of steel however is frequently observed. MATRIX ascribes only a small portion of the peak count at $M = 40$ to Ca, the other strong Ca-isotope at $M = 44$ being interpreted as a superposition of SiO and CO_2. SIP leaves 21.8 counts at $M = 44$ 'unidentified'. Cr^{++} is not identified by SIP because, at the present stage, multiply charged ions cannot be handled. A disagreement also occurs for Mo and Zr which have overlapping isotopes; the Zr-count identified by SIP (5.8 counts) however is insignificant and the total Mo-current identified by MATRIX is higher than the total isotope counts in the original spectrum by about the same amount. SiAl is found by MATRIX as a residual contribution to $M = 55$ where the main contribution is ^{55}Mn in both algorithms; SIP is deleting search for SiAl because of the smallness of Al^+. Note that the statistical uncertainty at $M = 55$ ($\sigma = 182$) is larger than the SiAl contribution identified by MATRIX. MnO is left 'unidentified' in SIP because of its smallness. The overall quality of fit (ICF and MF respectively) is good for both algorithms in this spectrum; obviously, on the average 84% of each peak count in SIP and even 95% in MATRIX can be assigned to specific ion species.

Negative SIMS spectra such as INVEW are posing a great problem to any interpretation routine because of the large amount of clustering and hybrid formation observable, particularly in the hydrocarbon fractionization peaks $C_mH_n^-$. It should be noted that, in the present stage of development, both algorithms cannot identify hydrocarbon species with $n > 2$ when $m > 2$. Control parameters for these clusterings are difficult to choose and may strongly influence interpretation results. The
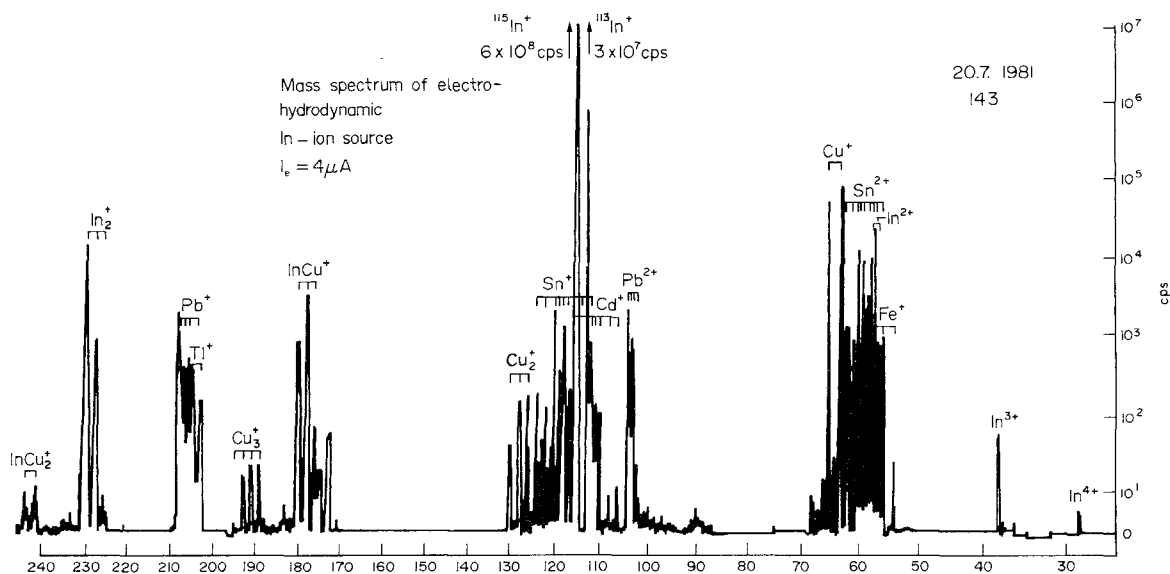
Figure 3. Mass spectrum of ion beam emitted from liquid metal indium ion source; recorded on double focusing tandem mass spectrometer.

Table 2. Identification results for spectrum SCH-2

Element (molecule)	SIP Counts	$\pm\sigma$ counts	MATRIX counts
B	10.8	3.2	11.0
C			5.0
O	87.9	4.5	88.0
Ne			5.0
Na	516.0	24.0	516.0
Mg	278.0	8.0	279.0
Al	782.0	34.0	782.0
Si	1340.0	31.0	1375.0
S	8.1	3.1	
K	503.0	13.0	503.0
Ar			212.0
Ca	270.0	6.0	52.0
Ti	54.4	3.5	79.0
V	88.5	5.1	88.0
Cr	10700.0	182.0	10665.0
Cr^{2+}			4.0
Mn	2040.0	85.0	1944.0
Fe	6200.0	116.0	6196.0
Co	16.7	3.7	17.0
Ni	338.0	6.7	345.0
Cu			7.0
Ga	5.0	3.0	4.0
Zn			4.0
Zr	5.8	3.1	
Mo	58.8	3.3	86.0
Pd			5.0
Ru	9.5	3.1	
Cd	12.5	3.1	19.0
FeO	32.0		32.0
Fe_2	20.6		15.0
CrO	100.0		100.0
FeCr	20.3		19.0
O_2			8.0
CO_2			11.0
SiO			17.0
SiAl			108.0
MnO			12.0
MF	0.843		0.949
ICF	0.987		0.997

quality of fit therefore is much lower in a negative than in a positive SIMS spectrum (see Table 3).

The liquid metal mass spectrum EHD is remarkable due to its high dynamic range in peak intensities ($7 \times 10^8 : 1$). To make numbers manageable for MATRIX, the contributions at $M = 113$ and 115 (assumed to be solely In^+) have both been reduced by a factor of 10^2. The interpretation of mass spectra from liquid metal ion sources is of great practical interest with respect to the potential use of this source type in microelectronic fabrication[16] and microbeam SIMS analysis[13]. In the latter application, even trace amounts of impurities emitted by the source would contaminate the analytical sample when an ion gun without mass separation is used; in microelectronic fabrication, an excess fraction of molecular and cluster species would unduly increase energy spread in the beam[17] and thereby reduce spatial resolution[18].

A large degree of clustering is apparent in spectrum EHD from the results of both programs. SIP obviously suffers from its present (not principal) inability to handle multiply charged ions (see Table 4). This has the effect that SIP cannot properly interpret peaks at the mass positions of odd mass number isotopes of doubly charged atomic ions and tends to ascribe doubly charged peaks of even isotopes (appearing at integer mass numbers) to other elements (viz. the interference between $^{59}Co^+$ and $^{118}Sn^{++}$). Discrepancies in the identification of Ni^+ are largely due to the least square fit algorithm of MATRIX which ascribes approximately twice the current actually measured at $M = 61, 62, 64$ to elemental Ni. The least square fit method may however also prove to be beneficial as is demonstrated, e.g. in the case of In_2^+. SIP limits the total identified current of this species according to the (statistically inaccurate) current of 10 cps at the low abundance $^{113}In_2^+$ molecular isotope; MATRIX however constructs a best fit to all In_2^+ isotopes (at $M = 226, 228, 230$), thereby overestimating the current at $M = 226$ compared to the actually measured count at this mass number; because of that fact however MATRIX is able to interpret a larger fraction of the actually measured In_2^+ current. The inability of MATRIX to find molecular combinations like SnCu, SnNi, etc. is due to the clustering limits chosen in that particular interpretation run. Note

Table 3. Identification results for spectrum INVEW

Element (molecule)	Counts	SIP $\pm\sigma$ counts	MATRIX Counts
H	100.0	5.4	100.0
B			5.0
C	59.3	4.3	60.0
O	3430.0	80.3	3237.0
F	26.0	4.0	24.0
Na	6.7	3.3	7.0
Mg			168.0
Al	375.0	18.0	361.0
Cl	821.0	21.2	920.0
Ca	6.9	3.1	
Sc			5.0
Cr	100.0	4.2	100.0
Fe	100.0	4.3	100.0
Co	12.0	3.5	
In	6.3	3.1	6.0
O_2	104.0		104.0
OH	759.0		742.0
O_2H	12.7		
O_3	20.1		20.0
O_3H	7.0		
C_2	111.0		
CH	82.6		82.0
CO_2H	6.4		
CH_4			930.0
FO	84.1		
FOH	10.3		
MgH			127.0
Mg_2H			10.0
MgAl			3.0
MgCl			21.0
MgCr			16.0
CrO_2	18.0		18.0
CrO_3			23.0
CrAl			4.0
FeO	29.9		29.0
FeO_2	27.8		27.0
FeO_3			5.0
FeC			4.0
InO			
MF	0.669		0.73
ICF	0.763		0.93

Table 4. Identification results for spectrum EHD

Element (molecule)	Counts	SIP $\pm\sigma$ counts	MATRIX counts
Fe	344.0	7.6	648.0
Co	8700.0	350.0	1076.0
Ni	2590.0	35.1	8189.0
Cu	159000.0	3410.0	159627.0
Sr			2.0
Y			3.0
Zr			7.0
Ru	17.6	2.1	66.0
Rh	950.0	40.0	58.0
Ag			15.0
Cd	888.0	7.2	4348.0
In	700000000.0	19000000.0	699000000.0
Sn	2370.0	15.0	4884.0
Sb			72.0
Te	6.3	2.0	
Lu			1.0
Hf	10.8	2.1	
Ir			6.0
Tl	440.0	11.4	450.0
Pb	1730.0	22.9	2092.0
In_2	4370.0		16312.0
Cu_2	351.0		356.0
Cu_3	56.6		58.0
Sn_2	11.1		
Ni_2	540.0		
Co_2			127.0
Sn^{2+}			31755.0
In^{2+}			22863.0
Pb^{2+}			3779.0
InCu	2860.0		4937.0
$InCu_2$			26.0
InNi	56.3		64.0
InSn	7.3		10.0
SnCu	9.5		
SnNi	20.2		
SnCd	11.4		
NiCu	26.9		
NiFe	120.0		
$NiCo_2$			23.0
CuFe	49.7		
MF	0.657		0.719
ICF	0.9999		1.0000

however, that the currents identified by SIP for these species are very low, particularly considering the fact that they have to be distributed approximately amongst 10 molecular isotopes.

Finally, Table 5 compares characteristic technical data for SIP and MATRIX in their respective present state of development and implementation.

5. Conclusion

The two identification algorithms presented above yield comparable results in the identification of SIMS and liquid metal ion source mass spectra. For simple positive SIMS spectra (such as shown in Table 1) the quality of fit is generally of the order of 98% (ICF) or 65–100% (MF) respectively. MATRIX generally gives marginally better quality of fit, probably due to the use of more types of molecules to fit small peaks, to the possibility of accepting higher identified than measured isotopic peak counts and to the capability of accepting multiply charged isotopic species at non-integer mass numbers. In the spectra presented above however,

the main differences occur for very low ion count species where statistical accuracy of peak measurement starts to play a role. Obviously, more efficient schemes have to be investigated which can take into account the precision of peak measurement and which therefore can avoid the identification of spurious ion species. The heuristic structure of SIP may, in extreme cases, lead to misinterpretations of more abundant ion peaks, although this has not been observed in spectra of similar complexity than those listed in Table 1. This disadvantage of SIP is partially offset by its higher computational speed, at least in the present stage of development and computer implementation of both programs; a comparison of computing speeds on the same machine would be interesting and is planned for the near future.

Negative SIMS spectra present a demanding task to any interpretation algorithm because of the possibility of formation of large hydrocarbon molecules which cannot be readily handled by the algorithms described. Accordingly, the quality of fit is lower in negative than in positive SIMS spectra.

Liquid metal mass spectra can be reasonably well interpreted,

Table 5. Technical data for spectrum interpretation algorithms SIP and MATRIX

	SIP	MATRIX
Computer implemented on	PDP 11/34	HP-9825A
Language	FORTRAN IV	HPL
Operating system	RSX 11-M(V3.2)	HP
Memory (kwords)	112	12
Approx. program size (kwords)	24	12
Typical running times		
Input file/element file	60 s	3–20 min
Input file/full molecule printout	3 min	3–20 min
Maximum number of input peaks	250	200
Highest possible mass number	250	3000
Maximum number of variables	no lim	200

probably indicating some fundamental similarities in cluster formation mechanisms for both types of emission processes.

A fundamental difficulty, inherent to low resolution mass spectrum interpretation, is the necessity to rely on natural isotopic abundances for the identification of an element or molecule. Measured isotopic abundances may deviate from natural abundances owing to actual isotopic fractionization in the sample previous to analysis (e.g. in extra-terrestrial materials[19,20], irradiated materials[21] and artificially enriched isotopes). For these types of samples, SIMS spectrum interpretation will be extremely difficult indeed, particularly when a complicated matrix is crowding the mass spectrum and no further information concerning the fractionization process is available. Further deviations arise from isotopic discrimination in the measurement process; the sputtering process itself[22], the ionization process of the sputtered atoms[23,24] and instrumental mass discrimination (mass analyser and ion detector) have all been identified as possible sources for isotope discrimination. Discrimination effects in ionization have been reported which are of the order of a few % per mass unit at medium masses[20,24]; instrumental mass discrimination effects, particularly in quadrupole mass spectrometers can be expected to be of the same order[25]. Note that, for a multi-isotope element even at moderate peak counts (10^3–10^4), the peak height discrimination due to mass discrimination may be considerably larger than the statistical accuracy of peak height determination and detector background; large fractions of (generally the heavier) isotopes may be underestimated, the residual counts at the lighter isotopes being ascribed to isotopically overlapping elements or molecules. Therefore in crowded sections of a mass spectrum, identification of ionic species below a current level of a few % of the highest peaks may

be of questionable value. Improvements of the present algorithms are feasible which avoid many of the difficulties and pitfalls described above, possibly at the cost of losing identification sensitivity. A decisive increase in identification accuracy may however only be expected when more physical information on the processes of ion formation, analysis and detection are fed into the interpretation algorithms.

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