**Investigation of Quantification of SIMS Data:
Analysis of NBS Glass and Iron Standards**

David H. Smith
W. H. Christie

OAK RIDGE NATIONAL LABORATORY

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INVESTIGATION OF QUANTIFICATION OF SIMS DATA:

ANALYSIS OF NBS GLASS AND IRON STANDARDS

David H. Smith

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ABSTRACT

Thirteen NBS glass and five NBS iron standards have been analyzed by the ion microprobe mass analyzer (IMMA) in the authors' laboratory. Data from all standards have been processed via a theoretical model and a pragmatic comparative approach (sensitivity factor). Results from the two approaches are compared, and detailed charts and plots are presented to assist in interpretation and to serve as guides in future work.

CHAPTER 1. INTRODUCTION

The development of ion microprobe mass analysis (IMMA) — also known as secondary ion mass spectrometry (SIMS) — has introduced a powerful new analytical tool for surface characterization into the armory of the physical scientist. It offers unparalleled sensitivity for most elements and has the ability to return spatial information regarding the surface distribution of the species being monitored.

The genealogy of ion microprobe instrumentation and prospects for future developments have been discussed by Liebl.¹ IMMA is a surface analytical technique. Analysis is accomplished by impinging a finely focused beam of ions onto the surface to be examined. These energetic bombarding ions dislodge or sputter from the surface material that is characteristic of it. An appreciable fraction of this sputtered material is in the form of charged particles (ions). It is these ions with which IMMA is concerned because they can be electrically extracted from the region of the surface and directed into a mass spectrometer where mass analysis is accomplished.

The bombarding ions can be moved about on the surface in a controlled fashion. This allows one to correlate the observed ion signals with specific locations on the sample surface. In this manner, ion micrographs can be prepared that show the distribution of an element on a surface. IMMA is an elemental analysis technique. The bombarding ions are energetic enough to destroy the compounds present on a surface. Therefore, little information is gained concerning chemical state or molecular structure. In principle, all elements can be detected by IMMA, but in practice wide variations in sensitivity are observed. The sensitivity for various elements is determined more by their ionization potentials than by any other physical property. Thus, the alkali metals show the greatest sensitivities with limits of detectability extending to the low parts per billion. The inert gases, on the other hand, are essentially undetectable.

A recent review article by Evans² compares IMMA with other commonly used surface analytical techniques. The ion probe is clearly the most sensitive surface technique available for most elements.

Thus, in many aspects of qualitative analysis, IMMA is without peer. There are many problems, however, in which quantitative information would be extremely useful, and here IMMA encounters numerous problems. The ionization process is extremely complex, the result of which is that sensitivities for different elements vary over six orders of magnitude. Figure 1 is a plot showing sensitivities of many of the elements taken from Storms et al.³

Fig. 1. Elemental sensitivities in IMMA.

Among the problems encountered are inhomogeneities, such as metallic precipitates in an alloy and segregation of elements along grain boundaries, that cause no trouble in larger scale analyses: IMMA's sensitivity and spatial resolution are disadvantages rather than advantages when quantitative data are required. Another problem occurring in metals is the effect known as channeling: the ionization efficiency of a given crystallite is a function of its orientation with respect to the impinging primary beam. If the crystal is oriented in such a way that it presents a high density of lattice points to the beam, many collisions occur near the surface, and sputtering and secondary ion formation are relatively efficient. If, on the other hand, the crystal presents a low density of lattice points to the beam, a substantial fraction of the impinging species can penetrate the lattice to such depths that neither sputtering nor ionization will occur. A recent report⁴ indicates that the relative numbers of ions formed from different species is not constant from one orientation to the next; i.e., the ratio of ions formed from two elements will vary. This further complicates an already complicated situation. All the analyst can do to combat these problems is to raster a large enough area so that inhomogeneities and lattice effects present an "average" result that can be made quantitatively representative of the sample as a whole.

Two approaches seem possible in attacking the problem of quantifying data from IMMA: The first is to develop a model that accurately reflects the ionization process and allows one to calculate concentrations on theoretical grounds; the second is to use an empirical approach and develop a suite of sensitivity factors, such as has been used successfully in spark source mass spectrometry,⁵⁻⁷ from which concentrations are calculated directly from ratios of ion counting rates. The problems with either approach are manifold. The complexities of the ionization process present a formidable challenge to the theoretician in the development of a model; and the fact that different matrices have different ionization efficiencies for all elements implies a prodigious number of measurements — one set for each matrix to be studied — in the sensitivity factor approach. The thorny question of just what it takes to make one matrix enough different from another to require determination of a new

set of sensitivity factors has not yet been answered. It is well known, for instance, that conducting and non-conducting matrices require different sets of sensitivity factors, but just how much of a given element needs to be added to an alloy, for example, before a new set is required has not yet been defined.

This report summarizes the results we have obtained from investigating both quantification techniques on the same sets of data from five iron and thirteen glass standards, all obtained from NBS.

CHAPTER 2. EXPERIMENTAL CONSIDERATIONS

The quantitative model selected was that developed by Andersen,⁸ based on the assumption of local thermal equilibrium (LTE), an assumption that is open to doubt. Other models have been suggested,⁹⁻¹² but have not yet been tested on real data, as Andersen's has.⁸ Also tested was Simons' LTE model,¹³ which is basically a simplified version of Andersen's, omitting corrections for oxide and negative ion formation and other refinements. Andersen's model has been encoded for a computer, and is available as a copyrighted program, CARISMA. It requires as input the counting rates for each element for which an analysis is desired and the counting rate for one oxide peak. In addition, the concentrations for up to six constituents of the samples are required for use as internal standards. Because of the mathematical complexity of the model, analytical solutions to the various equations are not possible, and the program searches a grid of values of two parameters called temperature and electron density for the best fit to the data. It is questionable, however, that these parameters have the physical meaning their names imply (temperatures can range from 3000 to 19,000 degrees Kelvin); it is safer to consider them as fitting parameters for the mathematical model. The best fit to the data is defined as the minimum in the sum of the differences between the theoretical (input) and calculated values of the internal standards. This implies that the more standards are used, the more closely the calculated results will approach the real values. Our experience has been that this is not necessarily so; and to reflect the real world where, after all, the whole idea is to determine concentrations and not to input them, we decided to use only the two most abundant constituents as internal standards. In addition, experimenting to compare the results obtained from using various different standards is extremely time consuming and can quickly degenerate into mere game playing. Our opinion is that such an approach most accurately reflects the circumstances likeliest to occur in the laboratory. A scientist is much more likely to know (or be readily able to measure) the major components of a sample than he is to

know the concentrations of several minor constituents. The precision of the results makes it unnecessary for the concentrations of the internal standards to be known to any great accuracy.

Simons' simplified LTE model, which we adapted for use on our IBM 1130 computer (CARISMA requires too much core to be readily usable on our 8 k system), requires essentially the same input information as CARISMA, except that no oxide peak is required and initial values for the two fitting parameters are. The range and increment size has been made constant in our adaptation to facilitate automatic handling of many analyses.

Sensitivity factors are defined as:

$$S_i = \frac{I_{ij}/(C_i f_{ij})}{I_R/(C_R f_R)}$$

where

S_i = sensitivity factor of element i;

I_{ij} = ion count rate of isotope j of element i, corrected for counting loss and background;

C_i = atomic concentration of element i;

f_{ij} = isotopic fraction of isotope j of element i.

Subscript R refers to the relevant property of the reference element, which was Si for glass standards and Fe for iron standards. Sensitivity factors thus calculated can be used to compute concentrations in atom percent from the following formula:

$$C_i = \frac{I_{ij}/(S_i f_{ij})}{\sum_i I_{ij}/(S_i f_{ij})} * 100$$

where the terms have the same meaning as in the preceding equation.

To test the sensitivity factor method (frequently abbreviated SF in the text), we first determined individual sensitivity factors on several replicate runs of each standard and then averaged them over all determinations. The sensitivity factors thus calculated were then used to determine the concentrations of each element in each analysis. This seems rather like a dog chasing its tail, but we feel that the test is valid and gives a good idea of the results one can reasonably expect. Of course, an unknown sample must have a matrix similar enough to the standards from which the sensitivity factors were calculated to make valid the application of those factors.

We wrote all the programs involved with sensitivity factors to run on this laboratory's IBM 1130 computer. Listings of all computer programs we wrote are available upon request; inquiries concerning CARISMA and the simplified LTE model should be directed to their respective authors.

A measure of the accuracy of a determination can be obtained by dividing the calculated value by the theoretical value:

$$F = \frac{C_i(\text{calculated})}{C_i(\text{theoretical})}$$

To avoid plotting complexity when F is less than 1, 1/F is plotted; thus

$$R = F \text{ for } F \geq 1 \text{ (overestimate)}$$

$$R = 1/F \text{ for } F < 1 \text{ (underestimate)}$$

Bar graphs of R covering various ranges of values are given in the appendices and at various places in the text. Underestimates of the true value fall to the left on the plots and overestimates to the right. Calculated values with $R > 5$ are not shown linearly on the plots, but are lumped together under the label "GT 5" (greater than 5). The assumption here is that values of $R > 5$ represent complete failures of the method to estimate the true concentration of the element in question, and the actual values of R are of only academic interest, if that. This treatment of the data is patterned after Newbury.¹⁴

It is generally conceded by experienced IMMA operators that determinations within a factor of two of the theoretical value (i.e., $0.5 \leq F \leq 2$) are perfectly acceptable; for purposes of this report, we have assumed that determinations to within 20% of the theoretical ($R \leq 1.2$) can be considered to be exact in this context. Under no conditions can IMMA be considered to be as accurate as, for example, spark source mass spectrometry. But frequently factors of two estimates are of great value to the investigator when coupled with the detailed spatial information concurrently obtainable from IMMA.

In the data presented on the following pages, analyses for only CARISMA and sensitivity factor calculations are usually given; the simplified LTE model was found, as might be expected, to give results qualitatively similar to CARISMA, but not as accurate.

CHAPTER 3. DATA FROM GLASS STANDARDS

At a workshop concerning quantification of IMMA data held at the National Bureau of Standards in January, 1976, it was decided that it was necessary to define "standard" operating conditions to facilitate comparison of data from different instruments, all of which were manufactured by ARL. The conditions decided upon are listed in Table 1. We used these conditions to analyze 13 NBS glass standards. The standards and their compositions in atom percent are given in Table 2. Data were not taken until the primary beam had been on for at least an hour so that it would be as stable as possible. Periodic checks of beam current showed no significant deviation (i.e., <10%) from the 1 na norm. The data consist of two sets of two replicate runs of each standard; thus, each standard was analyzed a total of four times, except NBS 489, which has been analyzed in duplicate several days previously and is represented by six analyses.

Table 1. Standard Operating Conditions for ARL IMMA's

Primary beam accelerating voltage	15 kV
Primary beam current	1 na
α slit width	0.64 cm
β slit width	0.64 cm
Secondary collector slit width	0.05 cm
Focus on peak	$^{28}\text{Si}^+$ for glasses $^{56}\text{Fe}^+$ for irons
Data-taking raster size	50 μm x 50 μm
Primary beam	$^{16}\text{O}^-$ for glasses $^{16}\text{O}_2^+$ for irons

Problems are sometimes encountered in trying to obtain a mass representative of an element that is free of interferences. For example, the major isotope of Zn is at mass 64 (48.9%). If titanium is in the sample, ^{48}TiO falls at mass 64 and thus renders it necessary either to make a correction based on a different TiO peak (62, 63, 65, 66) or to

Table 2. Composition of NBS Glass Standards, Atom Percent

Element	230	240	249	251	252	253	309	326	489	490	491	493	497
Li									0.0043	4.773	0.0039	0.0032	0.0014
B								15.602	0.184	30.696	0.186	0.193	0.090
Na								1.169					
Mg		3.741						13.522					4.453
Al	3.957		4.026	2.118			7.483		0.182	5.595	0.185	0.188	4.451
Si	20.141	20.141	20.461	21.607	21.262	20.979	16.930	9.011	24.906	0.107	0.187	22.196	0.093
P													22.259
Ca							6.801	2.583					
Ti		3.769							0.184	0.105	0.192	0.192	0.091
Mn					1.837	3.525							
Fe							4.778		0.184	0.105	0.192	0.192	0.091
Co					2.213	1.053							
Cu					2.005	0.992							
Zn	2.479	1.851			3.922	3.369			1.463	0.105			
Ge											21.419		
Zr		2.810							0.182	0.105	0.192	0.190	0.091
Ba	2.632	5.852	2.674	2.824	7.290	7.193	2.489		5.161				
Ce									0.182	0.106	0.192	0.189	0.092
Ta	0.913		1.855	0.978					0.183	0.106	0.192	0.191	0.092
Pb	8.134		7.805	9.212					0.184	0.106	15.684	14.801	0.092
Bi			0.439	0.928									
O	61.744	61.756	62.740	62.333	61.555	62.290	61.521	58.113	63.001	58.091	61.375	61.665	68.104

measure a different Zn peak (66 or 68). However, the problems have only started. If copper is present, it interferes as masses 63 and 65. We realized too late that if Ba is present in large enough concentrations, Ba^{+2} falls at 66 and 68. All these problems are exacerbated by the fact that Zn does not ionize very well. However, corrections were made, and the results were not too bad when mass 64 was being monitored.

The glass standards are made up of mixtures of various oxides and consequently consist of about 60 atom percent oxygen. Table 2 presents the compositions of the 13 glass standards analyzed.

Table 3 lists the sensitivity factors found for 20 elements, using Si as the reference. The values range from 0.06 for P to 10.45 for Ba.

Matrix Effects

Bar graphs of the results of the accuracy of measurements from each standard are given in Appendix 1 for both CARISMA and sensitivity factor calculations. Figure 2 is a bar graph of the composite data for all analyses of glass standards for both CARISMA and sensitivity factor methods. A similar plot for data from the simplified LTE model is given in Figure 3.

Several standards have similar matrices: 230, 251, and 493 are predominantly Si-Pb; 240, 249, 252, 253, and 489 are predominantly Si-Ba. The other five standards have unique matrices: 309, Si-Al-Ca; 326, B-Mg; 490, B-Al-Li; 491, Ge-Pb; 497, P-Mg-Al.

Table 4 presents the percentage of the analyses of each glass standard that falls within the given range for CARISMA, simplified LTE, and sensitivity factors. Composite results are also given.

The worst results in each case were obtained for NBS-491. This standard is the only one with a Ge-Pb matrix. It is probably valid to infer that it is a matrix sufficiently different from the others to make the application of average sensitivity factors to it questionable; in addition, it seems to cause problems for the two LTE models, although CARISMA is markedly more successful than the simplified version. The other matrices all seem to be similar enough in ionization characteristics to be considered identical for application of sensitivity factors. In nearly every case, calculations using sensitivity factors gave more accurate results than either of the LTE methods; in the composite

Table 3

Elemental Sensitivity Factors for Glass Standards
(based on Si = 1.00)

<u>Element</u>	<u>No. of Analyses</u>	<u>Sensitivity Factor</u>
Li	22	3.92
B	26	0.35
Na	4	2.84
Mg	12	2.84
Al	38	3.73
Si	52	1.00
P	4	0.06
Ca	8	9.51
Ti	26	3.61
Mn	8	3.27
Fe	26	1.90
Co	8	1.94
Cu	8	1.13
Zn	12	0.18
Ge	4	0.44
Zr	25	1.71
Ba	34	10.45
Ce	22	2.56
Ta	34	0.21
Pb	34	0.64

results, sensitivity factors gave nearly 45% "exact" (within $\pm 20\%$) results, while the two model methods gave about 30%. Using the factor of 2 criterion for a "good" analysis, we find that 87% of the results from sensitivity factors fall within this range, while the other techniques yielded about 60%.

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Fig. 2. Composite results of all glass standards from CARISMA and sensitivity factor calculations.

Fig. 3. Composite results from glass standards for Simons' simplified LTE model.

Table 5 lists the average sensitivity factors found for each element in each standard. All averages result from four replicate runs except for NBS 489, where there are six replicates. It is obvious that in general NBS 491 gave much higher sensitivity factors than the other matrices, indicating that ionization from it is more efficient for most elements with respect to silicon; otherwise, most elements gave reasonable reproducibility from sample to sample, with a few exceptions. Ba varied from 6.5 to 15.5; it seems to be very sensitive to small changes

Table 4. Distribution of Accuracies for Glass Standards

	Total Anal.		R								
			≤1.2	≤1.5	≤2.0	≤2.5	≤3.0	≤3.5	≤4.0	≤4.5	≤5.0
230	24	CARISMA	16.7	50.0	50.0	58.3	66.7	66.7	66.7	66.7	66.7
		Sim.LTE	16.7	16.7	41.7	50.0	50.0	54.2	66.7	66.7	66.7
		SF	41.7	79.2	83.3	83.3	83.3	83.3	91.7	100.0	
240	24	CARISMA	41.7	50.0	66.7	75.0	87.5	91.7	95.8	100.0	
		Sim.LTE	33.3	50.0	66.7	66.7	75.0	100.0			
		SF	83.3	83.3	91.7	100.0					
249	20	CARISMA	20.0	30.0	50.0	80.0	80.0	80.0	80.0	80.0	80.0
		Sim.LTE	25.0	50.0	60.0	60.0	60.0	65.0	80.0	80.0	80.0
		SF	60.0	90.0	100.0						
251	20	CARISMA	20.0	20.0	50.0	80.0	80.0	80.0	80.0	80.0	80.0
		Sim.LTE	10.0	15.0	50.0	60.0	60.0	70.0	80.0	80.0	80.0
		SF	45.0	95.0	100.0						
252	24	CARISMA	37.5	66.7	83.3	83.3	83.3	87.5	87.5	91.7	100.0
		Sim.LTE	58.3	79.2	91.7	95.8	100.0				
		SF	45.8	66.7	83.3	87.5	87.5	100.0			
253	24	CARISMA	33.3	70.8	87.5	87.5	87.5	87.5	87.5	95.8	100.0
		Sim.LTE	50.0	70.8	83.3	83.3	87.5	95.8	95.8	100.0	
		SF	50.0	79.2	83.3	83.3	87.5	100.0			

Table 4 - Continued

	Total Anal.		R								
			≤1.2	≤1.5	≤2.0	≤2.5	≤3.0	≤3.5	≤4.0	≤4.5	≤5.0
309	20	CARISMA	80.0	100.0							
		Sim.LTE	70.0	100.0							
		SF	80.0	100.0							
326	20	CARISMA	65.0	80.0	85.0	100.0					
		Sim.LTE	65.0	80.0	90.0	100.0					
		SF	60.0	100.0							
489	71	CARISMA	23.9	39.4	57.8	66.2	71.8	76.1	83.1	87.3	90.1
		Sim.LTE	25.4	39.4	49.3	59.2	69.0	78.9	83.1	83.1	84.5
		SF	36.6	63.4	78.9	87.3	88.7	93.0	94.4	95.8	97.2
490	40	CARISMA	30.0	42.5	70.0	75.0	80.0	85.0	85.0	85.0	85.0
		Sim.LTE	30.0	50.0	57.5	70.0	75.0	80.0	80.0	80.0	80.0
		SF	52.5	82.5	95.0	95.0	95.0	95.0	95.0	95.0	95.0
491	44	CARISMA	11.4	20.5	57.5	70.5	79.6	81.8	81.8	81.8	81.8
		Sim.LTE	18.2	20.5	22.7	25.0	31.8	31.8	36.4	40.9	45.5
		SF	15.9	40.9	59.1	70.5	77.3	88.6	90.9	93.2	95.5
493	40	CARISMA	30.0	45.0	60.0	65.0	77.5	80.0	85.0	95.0	95.0
		Sim.LTE	27.5	42.5	57.5	60.0	72.5	80.0	87.5	90.0	95.0
		SF	30.0	67.5	100.0						

Table 4 — Continued

			R								
Total Anal.			≤1.2	≤1.5	≤2.0	≤2.5	≤3.0	≤3.5	≤4.0	≤4.5	≤5.0
497	46	CARISMA	21.7	32.6	41.3	52.2	52.2	54.4	54.4	58.7	65.2
		Sim.LTE	21.7	30.4	34.8	52.2	60.1	65.2	71.7	73.9	73.9
		SF	39.1	67.4	91.3	93.5	97.8	100.0			
Composite	417	CARISMA	29.7	45.6	62.6	72.7	77.5	80.0	81.8	84.9	86.8
		Sim.LTE	31.4	45.3	56.3	63.3	69.3	75.5	80.1	81.1	82.5
		SF	44.6	73.1	86.8	90.4	92.6	96.2	97.1	98.1	98.6

Table 5. Sensitivity Factors for the Various Elements from Each Glass Standard

	<u>230</u>	<u>240</u>	<u>249</u>	<u>251</u>	<u>252</u>	<u>253</u>	<u>309</u>	<u>326</u>	<u>489</u>	<u>490</u>	<u>491</u>	<u>493</u>	<u>497</u>	<u>Max/Min</u>
Li									3.24	2.18	13.79*	3.67	4.88	2.24
B								0.28	0.73	0.28	0.35*	0.35	0.32	2.61
Mg		3.57						2.17					3.02	1.65
Al	2.88		2.50	3.17			5.07		4.78	2.35	11.04*	4.18	2.10	2.41
Si	1.00	1.00	1.00	1.03	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00	1.00
Ca							12.55	6.47						1.94
Ti		4.00							4.35	2.34	7.81*	2.70	2.49	1.86
Mn					2.37	4.21								1.78
Fe							2.72		1.95	1.29	4.73*	1.43	2.11	2.11
Co					2.30	0.99								2.32
Cu					1.57	0.69								2.28
Zn	0.17	1.79*			0.24	0.19			0.11					1.41
Zr		2.02							1.75	1.11	2.64*	1.52	1.32	1.82
Ba	6.50	11.29	7.24	6.65	15.53	12.28	22.79		10.38					2.39
Ce									3.47	1.33	3.96*	1.56	1.70	2.61
Ta	0.22		0.24	0.19					0.62	0.15	0.12*	0.18	0.13	1.85
Pb	0.89		0.83	0.86					0.29	0.09*	6.17*	1.05	0.37	2.84

in the matrix. Zn gave a spuriously high result for NBS 240 because of Ba^{+2} interference. This value is included only to show the magnitude of the effect and was ignored for averaging purposes.

The last column of Table 5 lists the ratio of the maximum sensitivity factor found for a given element to the minimum; numbers marked with an asterisk were ignored in this calculation. All elements gave ratios of less than 3.0, which we interpret as further evidence that, except for NBS 491, all of the glass matrices are similar enough to be considered identical for our purposes.

Elemental Effects

Table 6 presents data on an element by element rather than on a matrix basis. Only those elements are included which had 20 or more analyses. Appendix 2 is comprised of bar graphs depicting the accuracy of the measurements for each element via CARISMA and sensitivity factor. A brief discussion of the difficulties involved in the analysis of each element follows.

Lithium

Li would be expected to be very difficult to determine accurately by either technique, since it is well known that mobile ionized species will migrate in electrically insulating solids. The primary ion beam creates electric fields in the solid, and these electric fields usually cause motion of the mobile ionized species. Hughes, Baxter and Phillips have demonstrated the severity of this problem.¹⁵

SF data indicate that a reasonably good steady state can be reached, and reasonably accurate results obtained. LTE results, which tend to be low, as would be expected (see Appendix 2), indicate that an empirical correction factor might successfully be applied to the count rate before performing the calculations.

Boron

In general, both methods have more difficulty with elements having low sensitivity factors — those that are more difficult to ionize than Si. The SF for B is 0.35, one of the lowest obtained. Appendix 2 shows a reasonable distribution for SF data, but a disproportionate number of

Table 6. Distribution of Accuracies for Various Elements in the Glass Standards

Element	Total Anal.	Method	R								
			≤1.2	≤1.5	≤2.0	≤2.5	≤3.0	≤3.5	≤4.0	≤4.5	≤5.0
Li	22	CARISMA	9.1	18.2	45.5	68.2	86.4	90.9	95.5	95.5	100.0
		Sim.LTE	9.1	13.6	22.7	36.4	59.1	63.6	77.3	77.3	77.3
		SF	50.0	81.8	100.0						
B	26	CARISMA	26.9	46.2	46.2	46.2	53.9	57.7	61.5	69.2	76.9
		Sim.LTE	42.3	42.3	50.0	57.7	65.4	73.1	80.8	80.8	84.6
		SF	42.3	50.0	76.9	84.6	88.5	92.3	92.3	96.2	100.0
Al	38	CARISMA	31.6	57.9	81.6	86.8	89.5	89.5	94.7	100.0	
		Sim.LTE	29.0	55.3	81.6	84.2	84.2	86.8	92.1	94.7	94.7
		SF	50.0	84.2	100.0						
Si	52	CARISMA	65.4	82.7	86.5	86.5	88.5	88.5	88.5	88.5	88.5
		Sim.LTE	75.0	88.5	88.5	92.3	92.3	92.3	92.3	92.3	96.2
		SF	67.3	86.5	94.2	94.2	96.2	98.1	100.0		
Ti	26	CARISMA	3.9	30.8	61.5	80.8	92.3	92.3	96.2	100.0	
		Sim.LTE	7.7	23.1	46.2	73.1	84.6	92.3	92.3	92.3	92.3
		SF	19.2	61.5	100.0						
Fe	26	CARISMA	34.6	61.5	88.5	92.3	96.2	96.2	96.2	96.2	100.0
		Sim.LTE	11.5	69.2	80.8	84.6	92.3	92.3	100.0		
		SF	42.3	96.2	100.0						

Table 6 — Continued

Element	Total Anal.	Method	R								
			≤1.2	≤1.5	≤2.0	≤2.5	≤3.0	≤3.5	≤4.0	≤4.5	≤5.0
Zn	22	CARISMA	9.1	22.7	31.8	31.8	40.9	45.5	45.5	59.1	72.7
		Sim.LTE	4.6	9.1	22.7	27.3	45.5	68.2	68.2	68.2	72.7
		SF	0.0	0.0	9.1	31.8	45.5	72.7	81.8	90.9	90.9
Zr	25	CARISMA	4.0	12.0	36.0	48.0	52.0	68.0	80.0	88.0	88.0
		Sim.LTE	8.0	8.0	16.0	24.0	40.0	76.0	76.0	84.0	84.0
		SF	64.0	88.0	92.0	92.0	100.0				
Ba	34	CARISMA	64.7	76.5	76.5	100.0					
		Sim.LTE	64.7	70.6	70.6	70.6	70.6	79.4	100.0		
		SF	44.1	79.4	100.0						
Ce	22	CARISMA	9.1	9.1	54.6	68.2	72.7	81.8	86.4	86.4	86.4
		Sim.LTE	4.6	9.1	18.2	40.9	54.6	63.6	63.6	63.6	63.6
		SF	22.7	63.6	86.4	100.0					
Ta	34	CARISMA	5.9	8.8	14.7	29.4	32.4	35.3	38.2	47.1	47.1
		Sim.LTE	0.0	0.0	0.0	0.0	5.9	5.9	8.8	8.8	14.7
		SF	38.2	64.7	76.5	79.4	82.4	94.1	94.1	94.1	94.1
Pb	34	CARISMA	20.6	23.5	35.3	50.0	58.8	58.8	58.8	61.8	61.8
		Sim.LTE	20.6	23.5	44.1	52.9	52.9	55.9	61.8	64.7	64.7
		SF	26.5	58.8	70.6	76.5	85.3	88.2	88.2	91.2	94.1

Table 6 — Continued

Element	Total Anal.	Method	R								
			≤1.2	≤1.5	≤2.0	≤2.5	≤3.0	≤3.5	≤4.0	≤4.5	≤5.0
Composite	405	CARISMA	29.9	45.2	61.5	71.4	76.3	78.8	81.0	84.4	86.4
		Sin.LTE	29.6	43.7	55.1	62.0	68.2	74.8	79.5	80.5	82.0
		SF	44.4	73.3	87.2	90.4	93.1	96.3	97.0	98.0	98.5

overestimates for LTE. A relatively difficult element to obtain decent results for; 30% of the LTE results were from cases where B was used as an internal standard.

Aluminum

Al, for which IMMA is very sensitive, gave good results.

Silicon

Excellent results from SF. The data for LTE are skewed by the fact that, since it was a common matrix element, it was frequently used as an internal standard and thus forced to a good fit. Nearly three quarters (38/52) of the Si results are thus affected; of the remainder, 43% (6/14) are gross overestimates. Si is thus probably a bad actor unless used as an internal standard.

Titanium

Ti behaved relatively well, although more analyses fell out of the factor of 2 range on the LTE method than one would like.

Iron

One of the best of all elements.

Zinc

The data misrepresent the situation due to spuriously high count rates having been measured at masses 66 and 68 for standards NBS 240 and 489. This is due to Ba^{+2} peaks. The plot in Appendix 2 clearly shows the bi-nodal results; the correct results are on the underestimate (left) side of the plot. The data for NBS 230, 252, and 253 are valid, and for these the LTE models fail miserably, while the SF technique is merely adequate. The sensitivity factor is 0.18 — very low. It seems that Zn in glass matrices is not amenable to the LTE approach.

Zirconium

Zr yields gracefully to the SF approach, but presents problems for LTE. The plot of LTE data in Appendix 2 shows a distinct bias on the underestimate side, and an envelope of very low profile. Proceed with caution here, perhaps applying a small correction factor to shift the envelope to the right.

Barium

Ba was another common internal standard, being used thus in 65% (22/34) of the analyses. Hence, its LTE plot in Appendix 2 is somewhat misleading, but seems to be reasonable. Ba had the highest sensitivity factor, 10.45, and gives fine results with the SF technique.

Cerium

Ce gave trouble to the LTE calculations, presenting a very low profile envelope in the plot in Appendix 2. In addition, 15% of the results were overestimates larger than a factor of 5.

Tantalum

An unequivocal failure for LTE: nearly half (16/34) of the results were underestimates by greater than a factor of 5, and another pair were overestimates. Ta also gave one of the poorest results for SF. The problems involved here were undoubtedly the result of Ta's proclivity to form molecular ions. TaH^+ was frequently equal to or greater than Ta^+ in intensity. TaO^+ and $TaOH^+$ were also very large, the former often equal to Ta^+ . The ratios of the molecular peaks to Ta^+ were quite variable, particularly TaH^+ and $TaOH^+$. The safest approach might well be to determine a sensitivity factor for Ta by summing all four peaks (Ta^+ , TaH^+ , TaO^+ , $TaOH^+$). For LTE calculations, it is obviously necessary to include the TaH^+ count rate along with the Ta^+ . The results should then improve, but it is doubtful that really good ones would ever be obtained.

Lead

Another serious problem. Nearly half (16/34) of the analyses plotted in Appendix 2 for CARISMA are the results of internal standards, and the plot is abysmally bad. Clearly, LTE fails for Pb. It is much better for SF, but still relatively poor, with a tendency to underestimate. Pb has a low sensitivity factor, and sometimes seems to refuse to ionize. We observed no molecular ion problems similar to those described for Ta while analyzing Pb.

Bismuth

Although Bi is a constituent of two standards, it is not reported because our IMMA did not have sufficient resolving power to separate it

from ²⁰⁸Pb at the slit settings determined by the committee. Our experience leads us to believe that its behavior would be rather similar to that of Pb.

CHAPTER 4. DATA FROM IRON STANDARDS

Data were taken from five NBS iron standards: 661, 662, 663, 664, and 665. The compositions of these standards in atom percent are given in Table 7. Two problems complicated the acquisition of data from these standards. One was the inhomogeneous distribution of Ti, Zr, and Nb. Figure 4 reproduces ion micrographs for Ti^+ , Zr^+ , Nb^+ , and Co^+ . The micrographs represent an area of approximately $70\text{ }\mu\text{m} \times 60\text{ }\mu\text{m}$. It is readily apparent that, on this scale, the first three elements are inhomogeneously distributed, due to the formation of precipitates (they all have roughly the same distribution), and Co is uniformly distributed. Other elements, such as Mn and Cr, also exhibited inhomogeneities, but on small enough scales to allow satisfactory integration over the $50\text{ }\mu\text{m} \times 50\text{ }\mu\text{m}$ raster from which we collected data.

The second problem encountered in taking data from the iron standards was the low concentration levels of many of the constituents, particularly in NBS 665. The data from both LTE and SF show that results tend to be unreliable below about 60 ppm. Results from NBS 665 were not used in the calculation of sensitivity factors. Elements with concentrations below 10 ppm were not measured. In addition, carbon and phosphorus had such low sensitivity factors ($<10^{-2}$) that, although data were collected for them, they were not included in the tabulations and bar graphs. (Carbon, with concentrations in the 1-4% range, frequently gave concentrations of 60-70% when calculated by CARISMA.) Sulfur, at mass 32, is completely obscured by the impinging primary beam, O_2^+ , and not measurable under these conditions. Arsenic, a mononuclidic element with mass 75, falls right on top of $^{59}\text{CoO}^+$, also mononuclidic. Since no correction was possible, data were not included. Nickel was sometimes monitored at mass 58, where correction for ^{58}Fe was necessary, and sometimes at mass 60. Better results were obtained from the latter peak.

Sensitivity factors and number of analyses for the various elements from the iron standards are given in Table 8.

Table 7
Composition of NBS Iron Standards, Atom Percent

<u>Element</u>	<u>661</u>	<u>662</u>	<u>663</u>	<u>664</u>	<u>665</u>
B		0.013	0.0045	0.055	0.0007
C	1.750	0.740	2.570	3.932	0.031
Al	0.043	0.196	0.482		0.0014
Si	0.437	0.771	1.427	0.130	0.016
P	0.027	0.075	0.051	0.032	0.0054
S	0.029	0.066	0.014	0.047	0.010
Ti	0.023	0.097	0.056	0.272	0.0006
V	0.012	0.045	0.329	0.112	0.0006
Cr	0.730	0.320	1.364	0.068	0.0078
Mn	0.661	1.051	1.478	0.252	0.0058
Fe	94.216	94.813	91.705	94.102	99.866
Ni	1.866	0.559	0.295	0.131	0.039
Co	0.028	0.283	0.044	0.138	0.0066
Cu	0.036	0.437	0.084	0.213	0.0050
As	0.0088	0.068	0.0072	0.038	0.0001
Zr	0.0048	0.116	0.029	0.040	
Nb	0.013	0.173	0.029	0.092	
Mo	0.109	0.039	0.017	0.277	0.0029
Sn	0.0050	0.0074			
Sb	0.0018	0.0054	0.0007		
La		0.0001	0.0002		
Ce	0.0005				
Ta		0.061		0.033	
W		0.063	0.013	0.030	
Pb		0.0001	0.0005	0.0062

Fig. 4. Ion micrographs showing the distribution of (a) Ti, (b) Zr, (c) Nb, and (d) Co in NBS 661.

Table 8
Sensitivity Factors for Iron Standards
(Fe = 1.00)

<u>Element</u>	<u>No. of Analyses</u>	<u>Sensitivity Factor</u>
B	21	0.15
C	36	<0.001
Al	25	6.64
Si	36	0.16
P	32	0.005
Ti	32	5.83
V	36	2.94
Cr	36	3.85
Mn	36	2.33
Fe	36	1.00
Ni	24	0.24
Co	36	0.64
Cu	26	0.35
Zr	34	0.80
Nb	30	0.71
Mo	28	0.28
Sn	18	0.74
Sb	19	0.81
Ta	14	0.04
W	17	0.18
Pb	12	0.43

Matrix Effects

A bar graph of the results obtained from each iron standard is given in Appendix 3 for CARISMA and sensitivity factor determinations; Appendix 4 contains bar graphs of the accuracies obtained for each element in the iron standards. Figure 5 is bar graphs representing the composite results of all analyses of iron standards for CARISMA and SF. Table 9 tabulates the accuracies obtained by the two methods from each

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Fig. 5. Composite results of all iron standards from CARISMA and sensitivity factor calculations.

Table 9
Distribution of Accuracies for Iron Standards

	Total Anal.	Method	R								
			≤1.2	≤1.5	≤2.0	≤2.5	≤3.0	≤3.5	≤4.0	≤4.5	≤5.0
661	126	CARISMA	30.2	43.7	56.3	66.7	73.0	78.6	81.0	81.7	81.7
	145	SF	50.3	69.0	82.8	89.7	91.7	93.1	93.1	94.5	95.9
662	123	CARISMA	17.1	37.4	51.2	62.6	63.4	66.7	70.7	74.0	76.4
	136	SF	47.1	77.9	86.0	91.2	95.6	97.1	97.1	98.5	98.5
663	106	CARISMA	9.4	24.5	40.6	62.3	74.5	82.1	86.8	89.7	94.3
	115	SF	52.2	69.6	88.7	94.8	96.5	97.4	97.4	98.3	99.1
664	101	CARISMA	15.8	34.7	45.5	53.5	58.4	61.3	67.3	69.3	71.3
	112	SF	47.3	71.4	86.6	89.3	90.2	92.0	93.8	96.4	98.2
665	57	CARISMA	19.3	26.3	31.6	40.3	43.9	45.6	47.4	49.1	50.9
	53	SF	39.6	45.3	62.2	69.8	79.2	83.0	84.9	84.9	84.9
Composite	513	CARISMA	18.7	34.5	47.0	59.3	64.9	71.2	73.3	75.2	77.6
	561	SF	48.3	69.5	83.6	89.1	92.2	93.8	94.3	95.7	96.6

standard by showing the cumulative percent of the results that fall closer to one than a given calculated true ratio. Table 10 presents similar data by element rather than matrix.

Comparison of the composite accuracies listed in Tables 4 and 9 for the glass and iron standards, respectively, shows that CARISMA is somewhat more accurate on the former (63% within a factor of two as opposed to 47%). This is probably due to the higher concentrations of minor constituents in the glasses. Sensitivity factor calculations are virtually the same on both sets: 87% vs 84% within a factor of 2.

The sensitivity factor results indicate that all five standards may be considered to be the same matrix. If this had not been the case with matrices so similar, quantification of IMMA results would be even more difficult than it is now. Accuracy is poorest on NBS 665 by both techniques, as would be predicted on the basis of the low concentrations of minor constituents in this standard. The results from CARISMA for NBS 663, the iron standard with the highest concentration of minor constituents, are a little lower than might be expected, but probably not low enough to be statistically meaningful.

Table 11 lists the sensitivity factors obtained from each standard for each element. The individual values are in quite good agreement, with only a few exceptions. Cu and Mo gave spuriously high results on NBS 664 for reasons unknown to us. Because of low concentrations, values for NBS 665 are unreliable, and were not used in calculating averages. Zr and Nb, known to be inhomogeneous (see Figure 4), gave widely scattered results to which no particular attention should be paid. The other element with inhomogeneous distribution, Ti, gave more consistent results; we have no explanation for this fact.

The maximum/minimum ratio is tabulated in the last column of Table 11. These values in general are less than 2 and show better consistency than the results from the glass standards (Table 5). There are two obvious contributing factors to explain this. One is purely statistical: since there are 12 glass standards considered and only 4 iron standards, it is only to be expected that the range of individual values in the former will exceed that of the latter. The second factor is that the iron standards are chemically very close to being pure iron, and

Table 10. Distribution of Accuracies for Various Elements in the Iron Standards

Element	Total Anal.	Method	R								
			≤1.2	≤1.5	≤2.0	≤2.5	≤3.0	≤3.5	≤4.0	≤4.5	≤5.0
B	19	CARISMA	0.0	5.3	5.3	15.8	21.1	26.3	47.4	52.6	63.2
	21	SF	14.3	38.1	76.2	81.0	90.5	95.2	95.2	95.2	95.2
Al	22	CARISMA	9.1	13.6	18.2	18.2	18.2	18.2	18.2	27.3	54.5
	25	SF	72.0	84.0	92.0	96.0	100.0				
Si	34	CARISMA	8.8	17.6	47.1	58.8	67.6	67.6	70.6	73.5	73.5
	36	SF	66.7	77.8	88.9	88.9	97.2	100.0			
Ti	30	CARISMA	6.7	6.7	13.3	33.3	43.3	50.0	53.3	60.0	60.0
	32	SF	25.0	56.3	78.1	84.4	84.4	84.4	84.4	84.4	84.4
V	34	CARISMA	41.2	67.6	85.3	97.1	100.0				
	36	SF	33.3	77.8	97.2	97.2	100.0				
Cr	34	CARISMA	11.8	26.5	50.0	79.4	85.3	91.2	94.1	94.1	94.1
	36	SF	100.0								
Mn	34	CARISMA	29.4	64.7	73.5	82.4	88.2	88.2	88.2	88.2	88.2
	36	SF	83.3	83.3	88.9	100.0					
Fe	34	CARISMA	64.7	79.4	94.1	94.1	94.1	94.1	94.1	94.1	94.1
	36	SF	100.0								
Ni	27	CARISMA	33.3	77.8	81.5	92.6	100.0				
	26	SF	15.4	57.7	84.6	92.3	96.2	96.2	96.2	96.2	100.0

Table 10 — Continued

Element	Total Anal.	Method	R								
			≤1.2	≤1.5	≤2.0	≤2.5	≤3.0	≤3.5	≤4.0	≤4.5	≤5.0
Co	34	CARISMA	17.6	50.0	52.9	88.2	94.1	94.1	94.1	94.1	94.1
	36	SF	100.0								
Cu	33	CARISMA	6.1	12.1	45.5	60.6	69.7	78.8	84.8	90.9	93.9
	35	SF	34.3	82.9	88.6	88.6	88.6	88.6	88.6	88.6	88.6
Zr	30	CARISMA	23.3	46.7	63.3	70.0	73.3	73.3	83.3	83.3	86.7
	29	SF	24.1	58.6	65.5	79.3	86.2	86.2	89.7	89.7	89.7
Nb	30	CARISMA	6.7	36.7	53.3	70.0	76.7	93.3	93.3	93.3	93.3
	30	SF	30.0	50.0	80.0	86.7	86.7	93.3	93.3	100.0	
Mo	32	CARISMA	0.0	0.0	0.0	0.0	6.3	15.6	37.5	46.9	46.9
	30	SF	50.0	77.8	94.4	94.4	100.0				
Sn	16	CARISMA	18.8	43.8	75.0	87.5	87.5	100.0			
	18	SF	50.0	77.8	94.4	94.4	100.0				
Sb	19	CARISMA	5.3	21.1	26.3	31.6	31.6	42.1	42.1	42.1	42.1
	19	SF	31.6	36.8	57.8	78.9	89.5	94.7	94.7	94.7	100.0
Ta	14	CARISMA	0.0	0.0	7.1	21.4	35.7	35.7	35.7	35.7	35.7
	14	SF	14.3	28.6	50.0	50.0	64.3	71.4	71.4	85.7	92.9
W	20	CARISMA	15.0	15.0	30.0	45.0	60.0	65.0	65.0	65.0	65.0
	17	SF	23.5	47.1	58.8	82.4	83.2	94.1	94.1	100.0	

Table 10 — Continued

Element	Total Anal.	Method	R								
			≤1.2	≤1.5	≤2.0	≤2.5	≤3.0	≤3.5	≤4.0	≤4.5	≤5.0
Pb	13	CARISMA	0.0	23.1	23.1	23.1	23.1	23.1	30.8	38.5	46.2
	12	SF	16.7	41.7	50.0	58.3	58.3	58.3	58.3	66.7	75.0

Table 11
Sensitivity Factors for Various Elements
from Each Iron Standard

<u>Element</u>	<u>661</u>	<u>662</u>	<u>663</u>	<u>664</u>	<u>665</u>	<u>Max/Min.</u>
B		0.21	0.14	0.11		1.91
Al	7.32	6.82	6.31			1.16
Si	0.22	0.15	0.15	0.19	0.36*	1.47
Ti	5.40	7.93	4.33	4.56		1.83
V	2.22	2.24	3.60	3.91	2.76*	1.76
Cr	3.50	3.75	3.72	4.16	3.99*	1.19
Mn	2.20	2.23	2.25	2.60	5.12*	1.18
Fe	1.00	1.00	1.00	1.00	1.00*	1.00
Ni	0.32	0.27	0.20	0.44	0.49*	2.20
Co	0.67	0.62	0.61	0.40	0.71*	1.68
Cu	0.43	0.28	0.42	2.11*	2.49*	1.54
Zr	6.09	1.56	1.10	0.43		14.16
Nb	1.10	1.02	0.54	0.17		6.47
Mo	0.15	0.22	0.49	2.90*		3.27
Sn	1.26	0.80				1.58
Sb	1.10	0.82				1.34
Ta		0.04		0.03		1.33
W		0.05	0.20	0.30		6.00
Pb				0.43		

differ from each other only in the average concentrations of the minor constituents. Thus, the suite of iron standards is collectively much closer to a single chemical matrix than the glass standards. This undoubtedly contributes to there being more scatter in the data from the latter.

Elemental Effects

CARISMA did very well calculating the concentrations of some elements (see Table 9). These tended to be transition metals lying close to iron in the periodic table; results for V, Mn, and Ni fall within a

factor of two about 80% of the time. Cr, Co, and Cu are somewhat worse (about 50%). Most of the other elements gave less accurate results than these. A brief discussion of each element follows.

Boron

Boron gave results that were uniformly too high with CARISMA (see bar graph, Appendix 4), which could be indicative of contamination. Over one third of the results were too large by greater than a factor of 5. Contaminants at mass 11 other than boron itself are not easy to think of, and perhaps it is just a difficult element for CARISMA to deal with. CARISMA usually has trouble with elements of low sensitivity factor; boron's SF is 0.13.

Sensitivity factor results give a reasonably good distribution of accuracies.

Carbon

Carbon results were so erratic that they are not included in tables and graphs. Neither technique was able to cope satisfactorily with carbon. It had an extremely low SF: <0.001 .

Aluminum

Aluminum gave CARISMA trouble, with nearly half the results being more than a factor of 5 too high. Results from SF calculations were good. Aluminum is a frequent contaminant because many polishing compounds contain it; this tends to lead to surface contamination and accumulation of Al in cracks. However, it is unlikely that the CARISMA problems are due to contamination because of the long raster times and the consistency of the SF results. Our feeling is that IMMA is unusually sensitive for Al (SF = 6.6), more so than would be predicted from its chemical properties.

Silicon

Silicon gave good results with SF calculations and mediocre ones from CARISMA. The distribution envelope of the latter is quite low, and about one-fourth of the results were too great by more than a factor of 5. Silicon is a common contaminant for the same reason Al is, and

the same arguments apply to it being unlikely that contamination is the cause of the high results. Silicon has a low SF (0.16), and CARISMA consistently has trouble with such elements.

Titanium

Considering that titanium is demonstrably inhomogeneous in its distribution (See Figure 4), the results from SF calculations are surprisingly good, with only about 15% being out by greater than a factor of 5 and 78% being within a factor of 2. CARISMA had trouble: 40% of the results are more than a factor of 5 too high, and the remaining results give a distribution shifted to the high side of the plot (See Appendix 4). Ti was concentrated in hot spots where it had precipitated rather than being uniformly distributed. The CARISMA results perhaps imply that Ti ionizes more efficiently out of the precipitate matrix than out of the iron matrix. It is difficult to explain the high results otherwise, since statistically we should have studied regions of high and low concentration with equal frequency.

Vanadium

A successful element by both techniques.

Chromium

Very fine results from SF calculations. A little disappointing from CARISMA: 50% of the results were within a factor of 2, but one would hope for success on the order of vanadium here (85% within a factor of 2). We have no explanation for this discrepancy.

Manganese

A very successful element by both techniques, although it should be pointed out that it was used as an internal standard for CARISMA about two thirds (21/34) of the time.

Iron

Excellent results from both techniques; it was always an internal standard for CARISMA.

Nickel

CARISMA results were a little better here than for SF calculations, but analyses were quite successful by both techniques, with over 80% being within a factor of 2 of theoretical in each case.

Cobalt

Excellent with SF calculations; somewhat disappointing with CARISMA with less than half the results giving $R < 2$, largely due to a high population in the $-2.5 < R < -2.0$ range.

Copper

CARISMA results tended to be low for copper; another case of a low sensitivity factor (0.35). SF calculations were quite good.

Zirconium

Zirconium gave surprisingly good results considering its inhomogeneous distribution (see Figure 4). Both techniques gave results that yielded quite reasonable distribution envelopes, and about 65% of the results gave $R < 2$, and only 10-15% with $R > 5$.

Niobium

The results for niobium are not too bad considering that it is also inhomogeneously distributed. The envelopes tend to consist of bars of equal height, but this is perhaps not surprising for elements with inhomogeneous distribution.

Molybdenum

An unmitigated failure for CARISMA, as Andersen has previously discussed.⁸ Every result is too low, and over half of them have $F < 0.2$. SF results are quite good. Mo is incompatible with the present CARISMA model. Andersen suggests multiplying the Mo^+ counting rate by 6.25.⁸ Doing so vastly improves our results, giving an average F of 1.30.

Tin

Good results were obtained by both techniques.

Antimony

A problem element. Over half the CARISMA results were too high by greater than a factor of 5. SF calculations were more successful, but

still not too good. The relatively low concentrations of Sb undoubtedly contributed heavily to the difficulties.

Tantalum

Another tough one. CARISMA results gave $F > 5$ on over 60% of the analyses and $F < 0.2$ on about 8%. A dismal failure. SF results were also poor, with only 50% having $R < 2$. Ta is tough to analyze in any matrix, apparently. It has a very low sensitivity factor (0.04). TaH^+ was not observed from iron standards, as it was from glasses.

Tungsten

CARISMA gave results which tended to be low, and 35% yielded $F < 0.2$. Clearly the results as a whole were untrustworthy. SF results were better, but still not too good; only about 60% gave $F < 2.0$. A low sensitivity factor (0.05) contributed to the problems.

Lead

Poor results from each technique, but its concentrations are so low that the results are not too meaningful. Nearly 50% of CARISMA results have $F < 0.2$.

CHAPTER 5. DISCUSSION

From the data we have collected, it is clear that the use of sensitivity factors is a more reliable approach for quantifying IMMA results than CARISMA. This presupposes, however, the existence of a valid set of sensitivity factors for the matrix in question. More work needs to be done on various matrices to establish the range over which a given set of sensitivity factors is applicable. It seems evident from our data that all the iron standards can be considered a single matrix and all but one of the glasses as a single different matrix.

Figures 6-11 are plots of theoretical *vs* calculated values for CARISMA and sensitivity factor results; plots of all samples and those for glass and iron standards separately are given. Only averages for each element in each standard are plotted to reduce clutter in the graphs. The central 45-degree line represents $F = 1$, and the two other lines represent $F = 0.5$ and $F = 2.0$. Thus, the points in the area between the last two lines are those for which the calculated value is within a factor of two of the theoretical. While these presentations are in a sense redundant with the bar graphs of Figures 2 and 5, additional information is available, such as how accuracy varies as a function of concentration. It is clearly apparent that accuracy declines with concentration for each technique, as would be expected. The CARISMA results show more scatter than the SF, and the points a considerable distance from the $F = 1$ line on the former plots represent those elements that give CARISMA particular trouble.

Indiscriminate use of sensitivity factors can easily lead to grief, however. Interference ions, such as CoO^+ with As^+ and Ba^{+2} with Zn^+ , can give rise to reproducible ion currents and cause spuriously high counting rates which can easily mask variations in the element of interest. Contaminants such as Al^+ and Si^+ are frequently difficult both to detect and remove.

CARISMA results can presently be said to give only a skeleton description of the actual sample. Many elements give woefully inaccurate results. Mo, Ta, W, B, Al, Ti, and Sb all had better than 35% of their results with $R > 5$ in analyses of iron standards. Sometimes corrections to CARISMA data can be made by multiplying the ion counting rates

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Fig. 6. Plot of theoretical vs calculated values for CARISMA results from all standards.

ORNL-DWG 77-7144

Fig. 7. Plot of theoretical vs calculated values for CARISMA results from glass standards.

ORNL-DWG 77-7145

Fig. 8. Plot of theoretical vs calculated values for CARISMA results from iron standards.

ORNL-DWG 77-7146

Fig. 9. Plot of theoretical vs calculated values for sensitivity factor results from all standards.

ORNL-DWG 77-7147

Fig. 10. Plot of theoretical vs calculated values for sensitivity factor results from glass standards.

ORNL-DWG 77-7148

Fig. 11. Plot of theoretical vs calculated values for sensitivity factor results from iron standards.

by an appropriate correction factor, as Andersen has suggested.⁸ However, our data lead us to view this approach with a jaundiced eye. With Mo, for example, where Andersen suggests multiplying the counting rate by 6.25, this technique vastly improves the results as a whole; but the consistency of individual values for each standard suggest that a different correction is needed for each. Table 12 lists individual values of F obtained after the counting rate had been multiplied by 6.25. As can be seen in the Table, 6.25 is correct only for NBS 662; NBS 661 requires a factor of 9.2, and NBS 663 and 664 require a factor of about 3.5. Andersen also suggests correction factors of 2.5 for Zr and 5.7 for Nb, which would make the results obtained from our data too high for these elements, especially Nb. Such an approach for Ta leads to disaster: 60% of the analyses of Ta in iron standards were too high by greater than a factor of 5, and nearly 50% of the Ta analyses in glasses were too low by more than the same factor.

Table 12
Values of F for Mo After Correction of Counting Rate

Standard	F*					Theoretical Correction Factor
					Avg.	
661	0.67	0.62	0.61	0.83	0.68	9.2
662	0.69	1.00	1.23	1.10	1.01	6.2
663	1.65	1.53	1.82	1.88	1.72	3.6
664	1.84	1.77	1.78	1.74	1.78	3.5

*Calculated after multiplying count rates of Mo⁺ by a correction factor of 6.25.

It seems clear that this correction factor approach to CARISMA is very dangerous because the value of the factor required for a given element varies with the matrix. It would thus be necessary to determine such a factor for each element in each matrix, making the technique equivalent to the sensitivity factor approach; correction factors are essentially sensitivity factors in any case.

Trying to correlate inaccurate CARISMA results with poorly known partition functions has not been successful. Mo and Ta, for instance, seem to have reasonably well-known partition functions.

Newbury has compiled sensitivity factors obtained from three NBS glass standards by five laboratories;¹⁴ the data were presented at the NBS workshop in January, 1976. Also included in his tables are the maximum to minimum ratio of sensitivity factors for each element. The largest values of this ratio are 10.2 for Ta, 8.01 for Zn, and 7.95 for B (all in NBS 489). These three elements are among the most difficult for IMMA to analyze, so it is not surprising that the results for them showed the largest variations. The average for all maximum/minimum ratios is 3.30; it was 2.49 when the three largest values are excluded.

Storms and Brown have reported analyses of NBS glass fiber standards,^{16,17} including data on some of the same standards we have analyzed. Even though their data were, in general, not taken under "standard" conditions (as defined in Table 1), there should be reasonable agreement between their results and ours. Table 13 lists sensitivity factors obtained for elements analyzed in each laboratory. We feel that overall agreement between the sets of results is quite good. Ta, Co, and Cu gave the poorest agreement, but in all cases the two values are well within a factor of two of each other. Thus, in this case at least, either laboratory could use the other's sensitivity factor values in semiquantitative determinations.

The point at issue here is whether or not a single set of sensitivity factors for a given matrix is applicable to all ion microprobes (at least those with the same manufacturer). If it is not, then each probist will have to determine his own sensitivity factors for each matrix, a truly formidable task. The data don't seem to us to be as discouraging as might be indicated at a quick glance; each set of data was taken under somewhat different operating conditions, which will necessarily affect the results; and in several cases, a single high result caused a maximum/minimum ratio not truly representative of the consistency of the results. More data are needed covering more samples before a final decision on this question can be made. Our feeling is

Table 13
Sensitivity Factors for Glass Standards:
Comparison of Two Laboratories

<u>Element</u>	<u>ORNL Value</u>	<u>VAL Values*</u>	<u>ORNL/VAL</u>
Mg	2.84	4.03	0.70
Al	3.73	3.52	1.06
Ca	9.51	8.10	1.17
Ti	3.61	4.26	0.85
Mn	3.27	2.93	1.12
Fe	1.90	2.06	0.92
Co	1.94	1.25	1.55
Cu	1.13	0.73	1.55
Zn	0.18	0.18	1.00
Zr	1.71	2.35	0.73
Ba	10.45	7.54	1.39
Ta	0.21	0.34	0.62
Pb	0.64	0.51	1.25
Average			1.07

*Taken from work done at the General Electric Company Laboratories at Vallecitos Nuclear Center. See reference 17.

optimistic: we feel that sensitivity factors generated by one laboratory will be usable by another for a similar matrix, at least for educated guesses on a semiquantitative basis. The relatively good agreement between our data and those of Storms and Brown¹⁷ seems to be a reasonably solid base for our optimism.

Storms et al., in their impressive collection of plots and tables relating to CARISMA,¹⁸ have shown the temperature dependence of sensitivity factors in that program. The apparent temperatures for replicate analyses can vary by more than a factor of 2 (e.g., two replicate runs taken consecutively on NBS 662 gave "temperatures" of 11560°K and 5100°K, with the electron densities being about four orders of magnitude different).

It thus seems possible that an improved "initial value" attack might lead to better results: the individual ion counting rates did not seem to be different enough to explain such radical variation in the results.

However, the major flaw in CARISMA seems to us to be in the model itself. Even though it is highly questionable that local thermal equilibrium exists, CARISMA does seem to come reasonably close a good deal of the time. What seems to be required is for CARISMA to be refined to improve its accuracy or an entirely new model be programmed and made generally available to the analyst. We await the efforts of the theoreticians.

CHAPTER 6. CONCLUSIONS

Our final recommendation is to use sensitivity factors where possible. Our experience has been that an enlightened guess, based on the knowledge of sensitivity factors for the elements in question in a similar matrix, is nearly always within a factor of two of the true concentrations. The need for internal standards is frequently fatal to the application of CARISMA, and in any case, the results are often untrustworthy.

IMMA, with its unmatched sensitivity for many elements, yields qualitative and spatial information frequently unobtainable in any other way. From the quantitative point of view, it yields results that are at best semiquantitative, and the outlook for improvement on that front is not hopeful, at least in the near future.

CAVEAT EMPTOR!

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Appendix 1

Bar Graphs of the Accuracy of LTE and Sensitivity Factor Calculations for Each Glass Standard. Data are arranged in increasing numerical order of the standards' identifying numbers.

ORNL-DWG 77-7149

Fig. A1-1

ORNL-DWG 77-7150

Fig. A1-2

ORNL-DWG 77-7151

Fig. A1-3

ORNL-DWG 77-7152

Fig. A1-4

ORNL-DWG 77-7153

Fig. A1-5

ORNL-DWG 77-7154

Fig. A1-6

ORNL-DWG 77-7155

Fig. A1-7

ORNL-DWG 77-7156

Fig. A1-8

ORNL-DWG 77-7157

Fig. A1-9

ORNL-DWG 77-7158

Fig. A1-10

ORNL-DWG 77-7159

Fig. A1-11

ORNL-DWG 77-7160

Fig. A1-12

ORNL-DWG 77-7161

Fig. A1-13

Appendix 2

Bar graphs of the Accuracy of LTE and Sensitivity Factor Calculations for Various Elements in the Glass Standards. Plots are in order or increasing atomic number.

ORNL-DWG 77-7162

R

Fig. A2-1

ORNL-DWG 77-7163

Fig. A2-2

ORNL-DWG 77-7164

Fig. A2-3

ORNL-DWG 77-7165

Fig. A2-4

ORNL-DWG 77-7166

Fig. A2-5

ORNL-DWG 77-7167

Fig. A2-6

ORNL-DWG 77-7168

Fig. A2-7

ORNL-DWG 77-7169

Fig. A2-8

ORNL-DWG 77-7170

Fig. A2-9

ORNL-DWG 77-7171

Fig. A2-10

ORNL-DWG 77-7172

Fig. A2-11

ORNL-DWG 77-7173

Fig. A2-12

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Appendix 3

Bar Graphs of the Accuracy of LTE and Sensitivity Factor Calculations for Each Iron Standard. Plots are in increasing numerical order of the standards' identifying numbers.

ORNL-DWG 77-7174

Fig. A3-1

ORNL-DWG 77-7175

Fig. A3-2

ORNL-DWG 77-7176

Fig. A3-3

ORNL-DWG 77-7177

Fig. A3-4

ORNL-DWG 77-7178

Fig. A3-5

Appendix 4

Bar Graphs of the Accuracy of LTE and Sensitivity Factor Calculations for Various Elements in the Iron Standards. Plots are in order of increasing atomic number.

ORNL-DWG 77-7179

R
Fig. A4-1

ORNL DWG 77-7180

Fig. A4-2

ORNL DWG 77-7181

Fig. A4-3

ORNL DWG 77-7182

Fig. A4-4

ORNL DWG 77-7183

Fig. A4-5

ORNL DWG 77-7184

Fig. A4-6

ORNL DWG 77-7185

Fig. A4-7

ORNL DWG 77-7186

Fig. A4-8

ORNL DWG 77-7187

Fig. A4-9

ORNL DWG 77-7188

Fig. A4-10

ORNL DWG 77-7189

Fig. A4-11

ORNL DWG 77-7190

Fig. A4-12

ORNL DWG 77-7191

Fig. A4-13

ORNL-DWG 77-7192

Fig. A4-14

ORNL-DWG 77-7193

Fig. A4-15

ORNL-DWG 77-7194

Fig. A4-16

ORNL-DWG 77-7195

Fig. A4-17

ORNL-DWG 77-7196

Fig. A4-18

ORNL-DWG 77-7197

Fig. A4-19

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