

**REDUCTION OF MULTIELEMENT
MASS SPECTRA**

PROGRESS REPORT

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ABSTRACT

Even though the spectra obtained by inductively coupled plasma source mass spectrometry (ICP-MS) are relatively simple, their interpretation can be complicated by the presence of molecular and isobaric interferants. To the extent that isotopic abundances are known and constant, one can treat observed spectra as sums of known components. A linear decomposition approach for determining the concentrations of the components in a spectrum and correctly propagating uncertainties is presented. This technique differs from linear regression in that an exact fit is made to a subset of isotopes and goodness-of-fit is evaluated from the deviations between the predicted and measured intensities of the other, unfit isotopes. This technique can be applied to a wide range of spectral fitting problems. In this paper, its applicability to ICP-MS spectra is used to demonstrate the use and utility of the technique.

INTRODUCTION

The utility of any analytical technique is limited by one's ability to interpret the data. This limitation commonly arises in the form of "spectral overlaps" which cause the identification and quantification of peaks to be ambiguous. In the general case, interpreting a spectrum requires a knowledge of the location of peak centers, peak shapes, and peak heights. This paper will be restricted to interpreting inductively coupled plasma source mass spectrometry (ICP-MS) spectra collected using a quadrupole mass filter (Fig. 1). In this case, spectral resolution is low and peaks may be considered to be completely overlapped or completely separated. Furthermore, peaks can be considered to be uniformly spaced at integer values of the mass-to-charge ratio. Peak area is then the only parameter to fit. (A special case of noninteger peaks will be considered below.) While this discussion will be restricted to ICP-MS spectra, the techniques presented were originally developed to interpret noble gas mass spectra and can be applied to other spectra with similar characteristics.

ICP-MS spectra are relatively simple in several senses. The number of naturally occurring isotopes is less than 300. Generally molecular ions are in low abundance compared to atomic ions. The number of molecular ions likely to appear is low, and most elements have at least one isotope which can be considered interference free and used to calculate the element's concentration. Even in these favorable cases, considerable data are wasted because only selected peaks are used. On the other hand, the ability to determine certain elements; e.g., V, Fe, As, and Se, is severely limited by interferences. Furthermore, interferences may be significant in certain types of solutions but not in others. Accurate analysis requires that interferences be recognized and subtracted.

Several approaches have been taken to deal with interferences. One is using a high resolution magnetic-electrostatic mass spectrometer, such as the one being produced by VG Elemental, that can resolve most molecular interferences. Such interferences are thereby removed, but isobaric overlaps can in general not be resolved. Therefore, peaks subject to isobaric interference must be excluded from the analysis.

Alternatively software can be used to correct for interferences. The simplest approach is that used in the software supplied with early ICP-MS's. In this method, peak intensities at selected masses are assumed to be due to a single element and those peak heights are used to calculate elemental concentrations by comparison to calibration curves. To check for interferences on the selected peaks, the concentration for a given element can be calculated from the observed intensities at more than one isotope.

Other software schemes for interference correction range from subtraction routines, that depend on identifying peaks associated with the interferant which are themselves interference free; e.g., EPA method 200.8 (1), to linear regression and principal component schemes (2). Subtraction methods tend to have large compounded uncertainties and can only be used in certain cases. Linear regression requires a knowledge of the components present and forces a fit to those components. An evaluation of goodness-of-fit then depends on a statistical interpretation of deviations. We find this interpretation unsatisfying in terms of not being

"physical".

In this report, we present an alternative approach to spectral decomposition which we call linear decomposition. This approach will be discussed in terms of the method, qualitative descriptions of the software, and results for "real" spectra. The method as implemented can decompose spectra of up to 250 masses.

BACKGROUND INFORMATION

For the linear decomposition calculations, it is assumed that within the resolution of the mass spectrometer, peaks occur only at integer values of charge-to-mass, that the abundance sensitivity is high enough to make mass-to-mass peak overlaps negligible, that peak heights or areas have been previously calculated, and that instrumental drift and sensitivity variations due to matrix effects; e.g., variations in total dissolved salt, have been removed by normalization. These conditions are met using normal instrument tuning and somewhat modified software supplied with the instrument. The data presented here were collected with a PlasmaQuad manufactured by VG Elemental. Only the conversion routine to input VG data into the linear decomposition programs is specific to the VG instrument. This routine, ICP_CONV, will not be described other than to state that it adds counting statistics uncertainties, \sqrt{N} , to the normalized peak areas of spectra and arranges the data in the proper form for use by the decomposition program.

Spectra are transferred as ASCII files from an IBM-PC compatible computer used for the VG data reduction software to a DEC MicroVax II. All decomposition calculations are done on the MicroVax. Output files are stored in ASCII format and can be retrieved by the PC if desired. Because of the large matrices involved in treating a spectrum covering the entire periodic table, no attempt has been made to use the PC for spectral decomposition.

LINEAR DECOMPOSITION

ASSUMPTIONS

The central assumptions of linear decomposition are that each spectrum is the sum of a number of components of unique isotopic composition and that these compositions are known. These components may be elements or compounds, but in all cases their composition is determined by the isotopic abundance patterns found in nature. No special relationship is assumed between the observed intensity of atomic ions and molecular ions containing those elements. These assumptions require some discussion.

First and with certain exceptions, the isotopic compositions of the elements are recognized as being constant throughout nature. The most obvious exception to this rule is caused by mass fractionation effects in nature and mass bias in the mass spectrometer. Both of these are most severe at low masses, and while they may be as large as several percent per mass unit, they can frequently be ignored for concentration calculations where accuracy is generally limited to about one percent by other errors such as sample homogeneity. This is particularly true for minor isotopes which only make small contributions to the total number of ions observed for an element. However, in the case of a low abundance element affected by an interference

from an element of higher concentration, mass bias can not be ignored. Mass bias corrections will be discussed more fully below. Radioactive decay can affect the isotopic composition of the daughter element. In most cases, only one isotope is affected, and the radiogenic contribution can be treated as a separate component. For lead this is not true because three of the four isotopes have radiogenic components. Uranium is another special case because its isotopic composition is frequently altered by nuclear processes.

Generally molecular ions are considered as separate components with no constraint on their concentration relative to atomic ions. If it is desirable to consider a molecular ion to be in a fixed ratio to an atomic ion, a component can be defined which includes the molecular species as if they were isotopes of the element. This can be particularly helpful in the case of essentially monoisotopic oxides which are isobaric with monoisotopic elements.

FORMALISM

For mass M_j , the ion intensity, $I(M_j)$, observed in a spectrum will be

$$I(M_j) = A(Z_1, M_j) * [Z_1] + A(Z_2, M_j) * [Z_2] + \dots + A(Z_n, M_j) * [Z_n]$$

where $[Z_i]$ is the concentration of component Z_i , an element or molecule, and $A(Z_i, M_j)$ is the fractional abundance of the isotope of Z_i occurring at M_j . For a spectrum,

$$\begin{pmatrix} A(Z_1, M_1) & A(Z_2, M_1) & \dots & A(Z_n, M_1) \\ A(Z_1, M_2) & A(Z_2, M_2) & \dots & A(Z_n, M_2) \\ \vdots & \vdots & & \vdots \\ \vdots & \vdots & & \vdots \\ A(Z_1, M_m) & A(Z_2, M_m) & \dots & A(Z_n, M_m) \end{pmatrix} \begin{pmatrix} [Z_1] \\ [Z_2] \\ \vdots \\ \vdots \\ [Z_n] \end{pmatrix} = \begin{pmatrix} I(M_1) \\ I(M_2) \\ \vdots \\ \vdots \\ I(M_m) \end{pmatrix}$$

or

$$M_A V[] = V_I \quad (1)$$

where M_A is a matrix of isotopic abundances, $V[]$ is a vector whose components are chemical concentrations, and V_I is a vector with components corresponding to the observed peak intensities.

The problem is to solve for the components of $V[]$. If there are more components than masses, the system is underdetermined and can not be solved. Fortunately for ICP-MS spectra, this case rarely occurs because of the limited number of molecular species which occur in spectra. Commonly the system is overdetermined. Our approach is to assume that a certain set of components is present in a sample and then exactly fit a subset of masses equal in number to the number of components. Equation 1 then becomes

$$M_A V[] = V_I$$

where M_A is a square matrix and the number of components in the vector $V[]$ is equal to the

number of selected isotopes in V_I . Multiplying by the inverse of M_A , gives

$$V_{[J]} = M_A^{-1} V_I.$$

The resulting concentration vector, $V_{[J]}$, can then be used to calculate a predicted spectrum, $V_I(\text{fit})$ including all the masses; *i.e.*,

$$M_A V_{[J]} = V_I(\text{fit})$$

If the proper set of components, $V_{[J]}$, has been selected, all the masses in the spectrum V_I should be fit or

$$V_I(\text{obs}) - V_I(\text{fit}) \rightarrow 0$$

Throughout the calculations, uncertainties including correlated errors are propagated. The calculated errors on the components of $V_{[J]}$ therefore accurately represent the statistical uncertainties of the individual peaks. These uncertainties and the differences between observed and calculated (fit) peaks are then used to estimate the goodness-of-fit at the masses not included in V_I .

In practice four criteria have been developed for goodness-of-fit. These are all of the "good enough" or "not good enough" type. First, if no "blank" has been subtracted from the spectrum before decomposition, then no component, $[Z_j]$, can have a negative concentration. For this reason blanks are not subtracted before decomposition. Second, if the difference between the calculated and observed intensities at any mass, M_j , is less than a given value, typically 100 counts, then the fit is "good enough" for that mass. In essence this sets a detection limit below which one does not attempt to explain the spectrum. Third, if the difference between the calculated and observed intensities at any mass, M_j , is less than a certain multiple of the calculated standard deviation of the predicted intensity at that mass the fit is good enough. Typically deviations within two standard deviations would be accepted. Finally, if the difference between the calculated and observed intensities at any mass, M_j , is less than a certain fraction of the predicted intensity, typically 0.02, the fit is considered good enough. If no component is predicted to have a negative concentration and every mass meets at least one of the other three criteria, one concludes that the observed peak heights for all masses have been properly partitioned among the components. If the criteria are not met, the fitting process is repeated using a different, usually larger, set of assumed components. Once the criteria are met, one can sum the counts for all the isotopes of a given component and calculate its concentration from a calibration curve for the element. Using all the masses simplifies the calculation and improves sensitivity.

STATUS

All important elements of the principles and software needed for spectral decomposition have been demonstrated, but additional work is needed to make a user-friendly package that will lend itself to routine usage. Each part of the software will be briefly described in this section.

All routines are written in FORTRAN 77 and designed to be portable to other computers. Applications to spectra will be given below.

As discussed above, data are collected with an IBM-PC style computer attached to the ICP-MS. These data in the form of an intensity for each mass in each spectrum are transferred from the PC to the MicroVax using PC-NFS (Sun Microsystems) software via an Ethernet and a Sun server. This software also allows the PC to act as a terminal to the MicroVax. After ICP_CONV is run, decomposition can proceed.

The isotopic compositions of components are stored in a library which includes isotopic abundances, uncertainties, and other supplementary information such as literature references. All the components used for ICP-MS work are stored in the library NEWLIB. NEWLIB currently contains roughly 100 components including oxides, hydroxides, argon molecular species, and a variety of other molecular species as well as all the relevant elements. As additional components are identified, they are added to the library.

The program LIBEDIT is used to enter, delete, view, and edit components in libraries. Appendix 1 contains an annotated printout of an editing session. This program has recently been upgraded to the version illustrated in Appendix 1 and is substantially complete in terms of user interface.

Calculations are made with the program COMDEC. To perform a decomposition, one first identifies the component library to be used (NEWLIB for ICP-MS). One then identifies the masses to be fit exactly; *i.e.*, the vector, V_I , and the elements and molecules whose concentrations are to be calculated; *i.e.*, V_{II} . Whenever possible the selected masses are those of high abundance in a component and with low potential for interference. The program then decomposes the spectrum into the contributions from each of the assumed components and calculates a predicted spectrum. It also calculates the total number of ions present for each component in terms of the total for the component and amounts for each isotope. Finally it tabulates which isotopes have met the criteria described above for goodness-of-fit. If the fit satisfies the criteria, the total number of ions for each component can be used to calculate concentrations. If the criteria are not met, a new set of components can be selected from the library and the process repeated. An example of a COMDEC output is given in Appendix 2. At this time, component and isotope selection must be made individually for each sample. A future version is planned to define sets of isotopes and components for repetitive use, and to provide for analyzing batches of samples.

The program to convert COMDEC output to concentrations has not been written, but should be straightforward. In the meantime, this output is transferred back to the PC where concentrations are calculated with a spreadsheet program such as Symphony (Lotus Development). Spectra for standards and blanks are processed through COMDEC in the same way as those for samples. Blanks due to chemical contamination can be subtracted before or after concentrations are calculated. But as pointed out above, blank subtractions should not be made before running COMDEC.

In addition to blanks resulting from impure reagents and/or contamination, there are background counts in mass spectra due to electronic noise. In our instruments, the background is generally trivial compared to the sample counts. At present no specific correction is made in the decomposition routines for background, but there should be a method for making this correction. Because the background is nearly mass independent, it should be possible to define a component with equal contribution at every mass. Other functional forms could of course be used if appropriate.

Mass bias has until now been ignored in the decomposition programs. In the future, we expect to add routines to mass bias the isotopic compositions of the components when they are selected from the library for use with a particular group of spectra. It is anticipated that the extent of mass bias will be determined by running standards and the measured bias applied to a group of spectra rather than attempting to fit the bias from the information contained in the sample spectra.

EXAMPLES

There are several regions of the mass scale in which interferences are particularly pronounced. Illustrations will be given for two such regions. While the software has been constructed to decompose spectra covering the entire periodic table, the examples given will each be restricted to 30 - 55 mass units.

Spectra of the rare earth region are complicated by several problems. There are many isobaric overlaps. Barium and rare earth oxides (and other molecular species) form relatively easily, and barium and the light rare earth elements (REE's) are generally more abundant than the heavy REE's. Figure 1, a spectrum generated from a geothermal brine, can be used to illustrate several problems arising in this region. Barium ($138/137/136/135/134/132/130 = 71.7/11.2/7.85/6.59/2.41/0.101/0.106$) is obviously the dominant element, and the REE's are generally below the detection limit. Xenon contributes to the peaks at 130, 131, 132, 134, and 136. To this point, the manufacturer-supplied software could be used to interpret this spectrum, but serious difficulties would be encountered in interpreting the other peaks. Using the approach of selecting masses where interferences are least expected, one might well pick 151 and 153 for europium (the only isotopes) and 155 and 157 for gadolinium. In each case, the elemental concentrations calculated for the two isotopes would disagree but not drastically. One might therefore conclude that europium and gadolinium were present. This would be strange in the absence of other REE's but, an operator might interpret these results improperly. (This particular spectrum was in fact initially misinterpreted in our laboratory.) Even without processing this spectrum through COMDEC, it can be seen that the peaks from masses 150 through 154 repeat the barium isotopic pattern. In fact the peaks from 150 through 157 are a superposition of barium oxide, barium hydroxide, and barium fluoride signals. The peak at 139 could be due to either lanthanum or barium hydride. Given the 138 to 139 intensity ratio it is impossible to decide this question with the decomposition technique. One requires prior knowledge of the expected barium to barium hydride ratio. This illustrates a difficulty of setting detection limits. Often signals are clearly detectable but difficult to interpret. The peaks at masses 140 and 142 are presumed to be from cerium. The minor

peaks between 141 and 149 have not been interpreted because of their low intensity. These minor peaks would be significant for the COMDEC fit only if the difference in predicted and measured areas differed by more than the goodness-of-fit criterion of 100 counts, which is greater than their areas. For this rather simple spectrum, a detailed decomposition will not be given. It is shown only as a clear demonstration of some of the types of interferences which can influence the interpretation of spectra and some interpretational limits.

A REE region spectrum for a shale is shown in Figure 2. This spectrum is clearly more complicated than the brine spectrum (Fig. 1). In addition the peak at mass 166 has been distorted by a noise spike. Even though experience had shown that one could expect molecules involving barium to be present, a first pass was made through COMDEC using only the elements from xenon through rhenium. The results of this calculation are shown in Figure 3 and Appendix 2. For this calculation, the following masses were used. The component with which each is principally associated is also given.

132(Xe) 133(Cs) 138(Ba) 139(La) 140(Ce) 141(Pr) 144(Nd) 151(Eu) 152(Sm) 159(Tb)
160(Gd) 164(Dy) 165(Ho) 166(Er) 169(Tm) 174(Yb) 175(Lu) 180(Hf) 181(Ta) 184(W)
185(Re)

Let us examine these results in terms of the goodness-of-fit criteria described earlier. First, though not illustrated, no component is negative so that criterion is met. Several regions of the spectrum have large differences (residuals) between the predicted and measured peak areas. Several regions have significant deviations in terms of the number of standard deviations to which the difference corresponds and/or the fractional deviations. Note that for large peaks the deviation in terms of standard deviations is larger than the fractional deviations, and that the reverse is true for small peaks. This is to be expected statistically. Positive deviations correspond to predicted values exceeding measured. One would guess that the large negative deviations around 155 were due to molecular species of barium. The excess predictions at masses 167 and 168 imply that erbium has been over estimated perhaps as a result of the noise spike.

The spike at 166 was then removed by smoothing the spectrum at the single channel in which the noise occurred, and COMDEC was rerun with BaO^+ , BaOH^+ , BaF^+ , and CeO^+ added to the component list. The results are shown graphically in Figure 4. In terms of counts, there are significant residuals in the mass region around 136 but the percentage difference between predicted and measured is only slightly greater than 2% which would be insignificant in calculating the barium concentration because these are low abundance isotopes. The pattern of the deviations suggests that the effects of mass bias are being observed in barium which is present at a sufficient concentration for the statistical errors to be small. The peaks at masses 145 and 170 have residuals of more than 100 counts and fractional differences for more than 5%, but the fits are within 2 standard deviations and therefore judged "good enough". It is interesting to note that the previous spectrum also had a minor peak at 145. This may be a small XeO^+ peak. Figure 5 illustrates the fraction of each peak between mass 147 and 160 due to each component. Using the manufacturer's software there would be no way to accurately calculate the concentration of europium or gadolinium.

Determinations of selenium and arsenic are complicated by several interferants. These can be inherent to the argon plasma or sample dependent. Monoisotopic arsenic can be overlain by ArCl^+ . All six of the selenium isotopes are subject to interferences from Ar_2^+ , ArCl^+ , and Kr^+ . Figure 6 is the zinc to palladium portion of the spectrum collected from an ancient silver coin. The scan is dominated by the Ar_2^+ peak at mass 80. In addition there are major peaks from zinc and a possible arsenic peak at mass 75. In addition to the elemental peaks and the molecular species already mentioned the high concentration of copper in the sample can lead to the presence of CuAr^+ ions. Doubly charged lead peaks may also be present in the 102 - 104 region.

The possible presence of the latter two molecules illustrates two problems. First, $^{207}\text{Pb}^{2+}$ will appear at mass 103.5, but the model assumes only integer masses. In that the peak areas are calculated by summing the data channels over nearly a full mass unit, the contribution of $^{207}\text{Pb}^{2+}$ was divided between 103 and 104. Because this scan stopped with mass 105, the problem is underdetermined at masses 103 and 104 where there are three components, CuAr^+ , Rh^+ , and Pb^{2+} , but only two masses. Based on the high copper abundance known to be present and the general paucity of rhodium, it was decided to exclude rhodium from the list of components. In retrospect it turned out that Pb^{2+} was not present at a significant level and that the 103 - 105 region could be explained by Pd^+ and CuAr^+ .

Figure 7 shows the fit obtained for the silver coin's spectrum taking the elements excluding rhodium, ArCl^+ , Ar_2^+ , CuAr^+ , and Pb^{2+} . Differences in terms of the number of standard deviations have not been plotted because meeting the criterion of less than 2% difference is adequate for acceptance and all but four peaks meet this test. The peak at 69 is probably caused by ZnH^+ . As with the first spectrum discussed, it is difficult to positively identify a small peak one mass unit above a large one. The over prediction of the fit for masses 74 and 76 appears to reflect a mass bias in the isotopic composition of the argon dimer. This effect was also observed in spectra of "blanks". The observed mass bias may be related to the cryogenic production of the argon rather than a mass spectrometric effect. There is also a suggestion of a bias in the krypton which is believed to be an impurity in the argon. The greatest difference between the predicted and measured spectrum is at 81, and is almost certainly due to Ar_2H^+ .

The main point of interest in this spectrum was identifying the number of ions due to arsenic and selenium. These results are illustrated in Figure 8. The interference of ArCl^+ on arsenic was not severe. For this example, little interference was expected because of the low solubility of silver chloride. In chloride rich samples, the situation could be very different. For selenium there is no isotope without at least a several percent correction. The situation would have been worst if ArCl^+ had been higher, but this example serves to show the usefulness of the decomposition approach.

To this point, only the partitioning of the counts among the components has been discussed and not the uncertainties on the final number of ions attributed to a given component. To test how the predicted uncertainty varied with the fraction of a peak due to the component of

interest, counts were artificially added to masses 75 and 77 of the coin's spectrum. These added counts were set to be in the ratio expected for ArCl^+ . Two artificial cases were submitted to COMDEC. One with ArCl^+ raised to 5% of the total ions at mass 75, and the other to 50%. Figure 9 plots the uncertainty attributed by COMDEC to each of the components at mass 75 for the original and artificial cases. Note that even when a component accounts for only 50% of a peak the uncertainty does not significantly increase above that predicted when the peak is due essentially to that component alone. Even when the component of interest contributes only 5% to the peak, the uncertainty is still only 15% in this example. Of course as the fractional contribution of a component to a peak approaches zero, the fractional uncertainty on the fit of that component becomes very large.

Although not demonstrated in these examples, there is a limitation to linear decomposition which requires comment. This problem takes two forms. A monoisotopic molecular species can not be distinguished from a monoisotopic atomic species of the same nominal mass. For example $^{165}\text{Ho}^{16}\text{O}^+$ would be indistinguishable from $^{181}\text{Ta}^+$. (Tantalum's minor isotope at 180 and oxygen's minor isotopes are sufficiently rare to preclude their being useful.) There are a few cases such as MoO^+ and Cd^+ where two components each have several isotopes, but these occur at the same masses and in nearly the same abundances. The program can in principle fit these multiisotopic cases, but the uncertainty attributed to each of the similar components will be large. Fortunately one can reasonably assume that the ratio of ions from a given element and its molecular species will occur in an approximately known ratio. A single new component can then be constructed with atomic and molecular peaks. In the component library, the uncertainties (including correlated terms) for the molecular peaks in this component can be made as large as necessary to reflect the uncertainty in the ratio of the elemental to molecular ions.

SUMMARY

The examples given show the utility of the decomposition approach for the interpretation of ICP-MS spectra. It can be used to interpret spectra in terms of the elemental and molecular species present and to calculate the fraction of the spectrum due to each component. In doing this, uncertainties are rigorously propagated to assign meaningful error bars to the calculations of the number of ions present from the individual components. A wide variety of problems including those not resolvable by high resolution mass spectrometry can be solved with little expense of time or capital. Although not yet demonstrated, the system can be configured to handle batches of spectra thereby freeing operator time. There appear to be two limitations to the technique. First, it is difficult to positively identify small peaks one mass unit heavier than large peaks when the ratio of these peaks exceeds several hundred. Second, the isotopic patterns of the components must be sufficiently different for the attributions to be distinct.

REFERENCES

1. Long, Stephen E. and Martin, Theodore D. *Method 200.8 Determination of Trace Elements in Water and Wastes by Inductively Coupled Plasma Mass Spectrometry, Version 4.0*, Environmental Monitoring and Systems Laboratory, Office of Research and Development, United States Environmental Protection Agency (1989).
2. Ketterer, Michael E., Reschl, John J., and Peters, Michael J., *Multivariate Calibration in Inductively Coupled Plasma Mass Spectrometry*, Anal. Chem. **61** (1989) 2031-2040.

FIGURE CAPTIONS

Figure 1

Linear and semi-logarithmic plot of the xenon through terbium region of the ICP-MS spectrum of a brine solution. The peaks between mass 150 and 157 could be mistakenly interpreted as being due to rare earth elements when they are in fact molecular ion peaks associated with barium. This plot shows the spectrum as collected in a multichannel analyzer. Before spectra are decomposed by COMDEC the peak areas are determined. The area at each mass is the COMDEC input.

Figure 2

Linear and semi-logarithmic plot of the xenon through rare earth element portion of the spectrum of a dissolved shale. Note the noise spike on the mass 166 peak.

Figure 3

COMDEC results for the first attempt to fit the shale spectrum shown in Figure 2. No molecular ions were included in the component set. The RESIDUAL is the absolute value of the difference between the measured and calculated spectra. For peaks used to obtain the fit and for which this difference is by definition zero, points were plotted at 0 on the log scale.

Figure 4

COMDEC results for the spectrum shown in Figures 2 and 3 with the molecular ions of BaO^+ , BaOH^+ , BaF^+ , and CeO^+ included in the component set and the spike at mass 166 removed. Note the change in ordinate scale from Figure 3.

Figure 5

COMDEC attribution of peak compositions in a portion of the rare earth region for the spectrum in Figures 2 - 4.

Figure 6

Linear and semi-logarithmic plot of the spectral region from zinc to palladium for a dissolved ancient silver coin. This region contains large molecular peaks associated with the argon plasma.

Figure 7

COMDEC results for the spectrum shown in Figure 6 where elemental and molecular species (ArCl^+ , Ar_2^+ , CuAr^+ , and Pb^{2+}) have been included. Note rhodium was

excluded for the reasons discussed in the text.

Figure 8

COMDEC attribution of peaks in the arsenic and selenium region of the spectrum in Figures 6 and 7.

Figure 9

Change of relative uncertainty calculated for a component as a function of the fractional abundance of the component in a peak. The plot is based on the decomposition shown in Figure 8 modified by the addition of various amounts of pseudo- ArCl^+ to the spectrum.

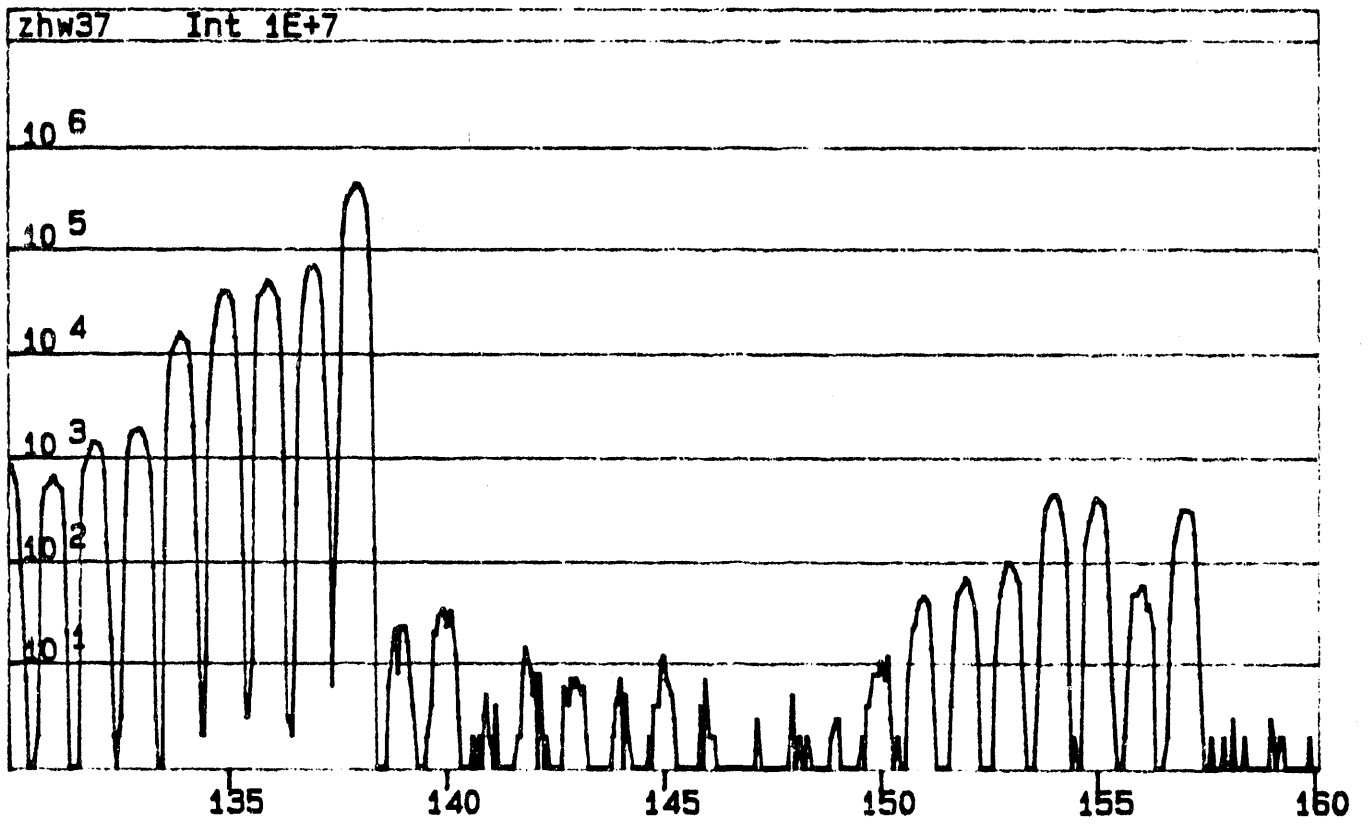
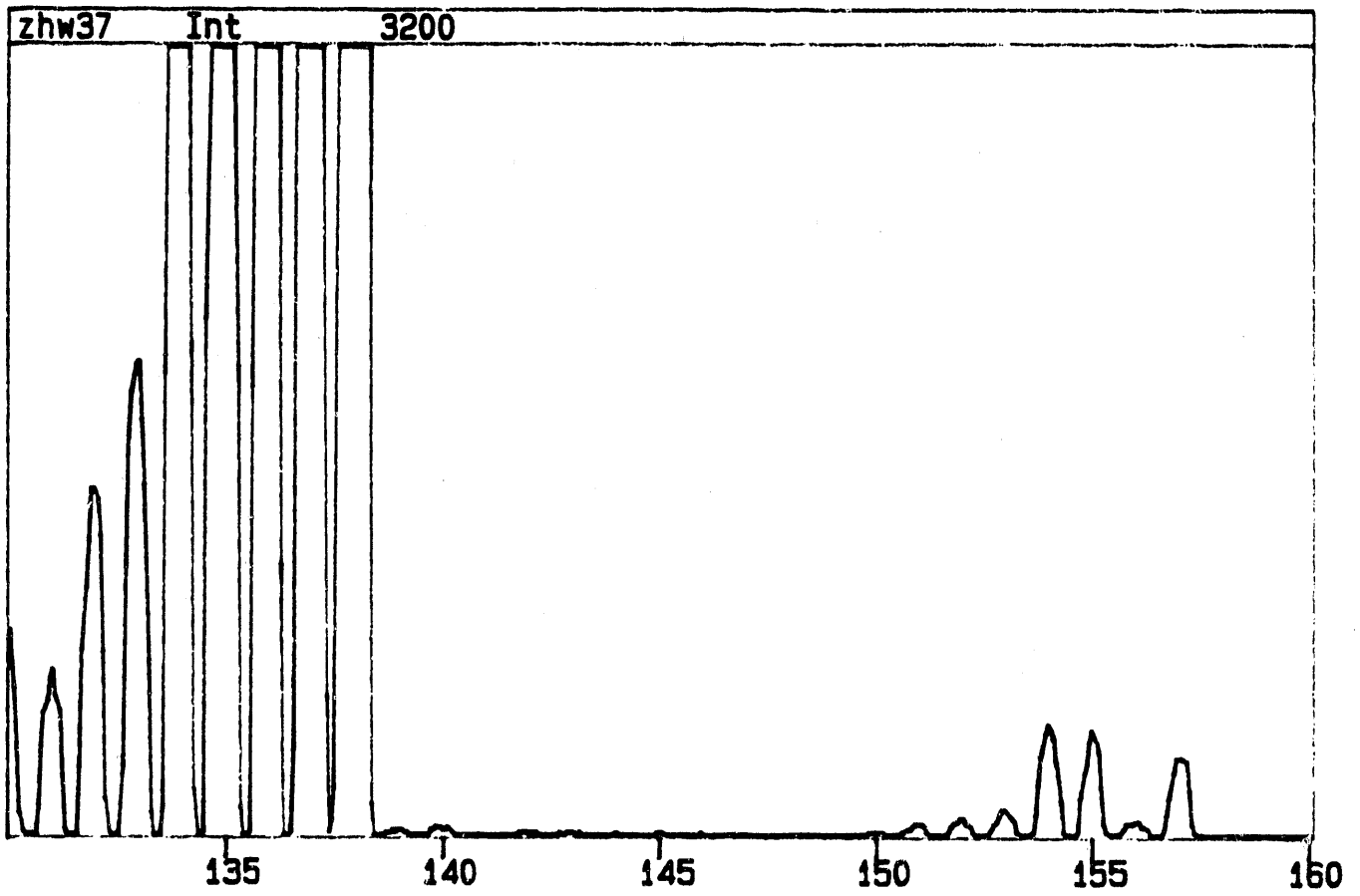


Figure 1

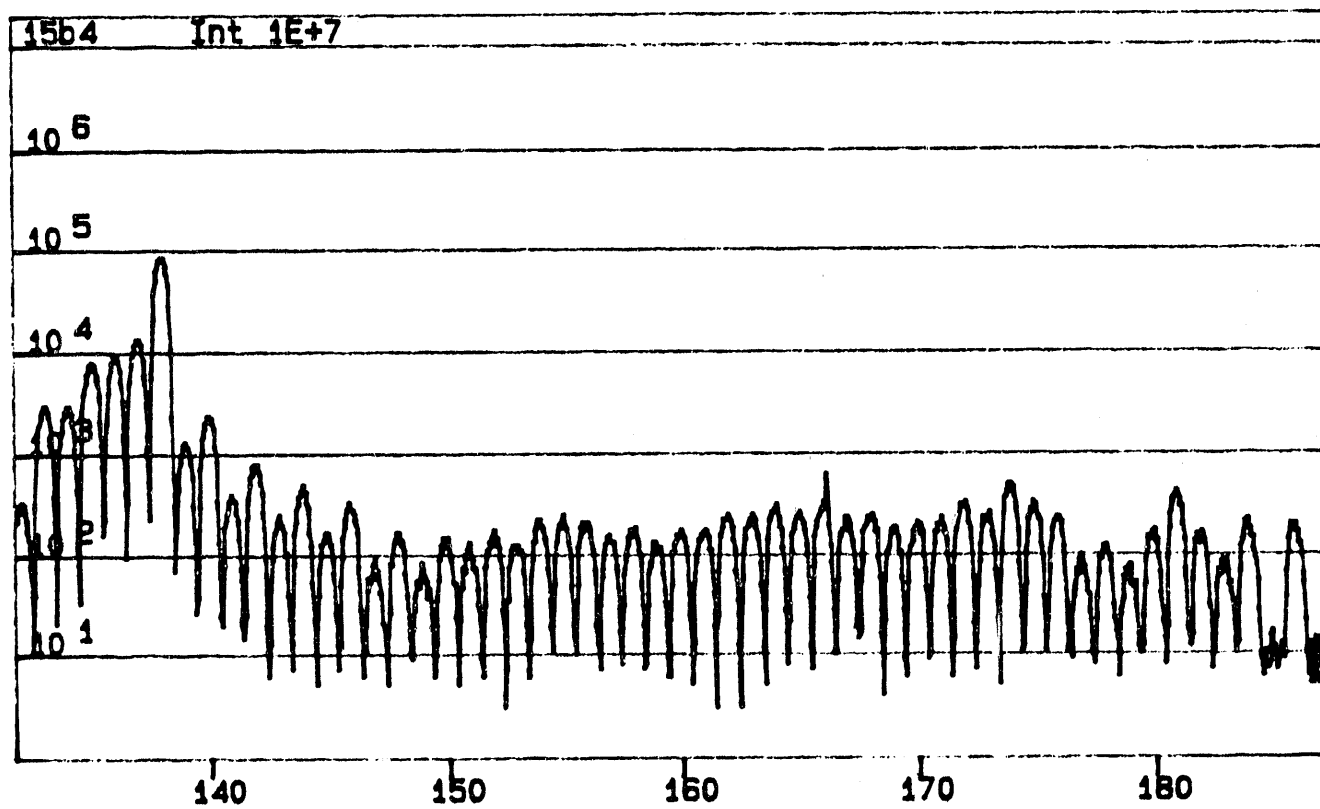
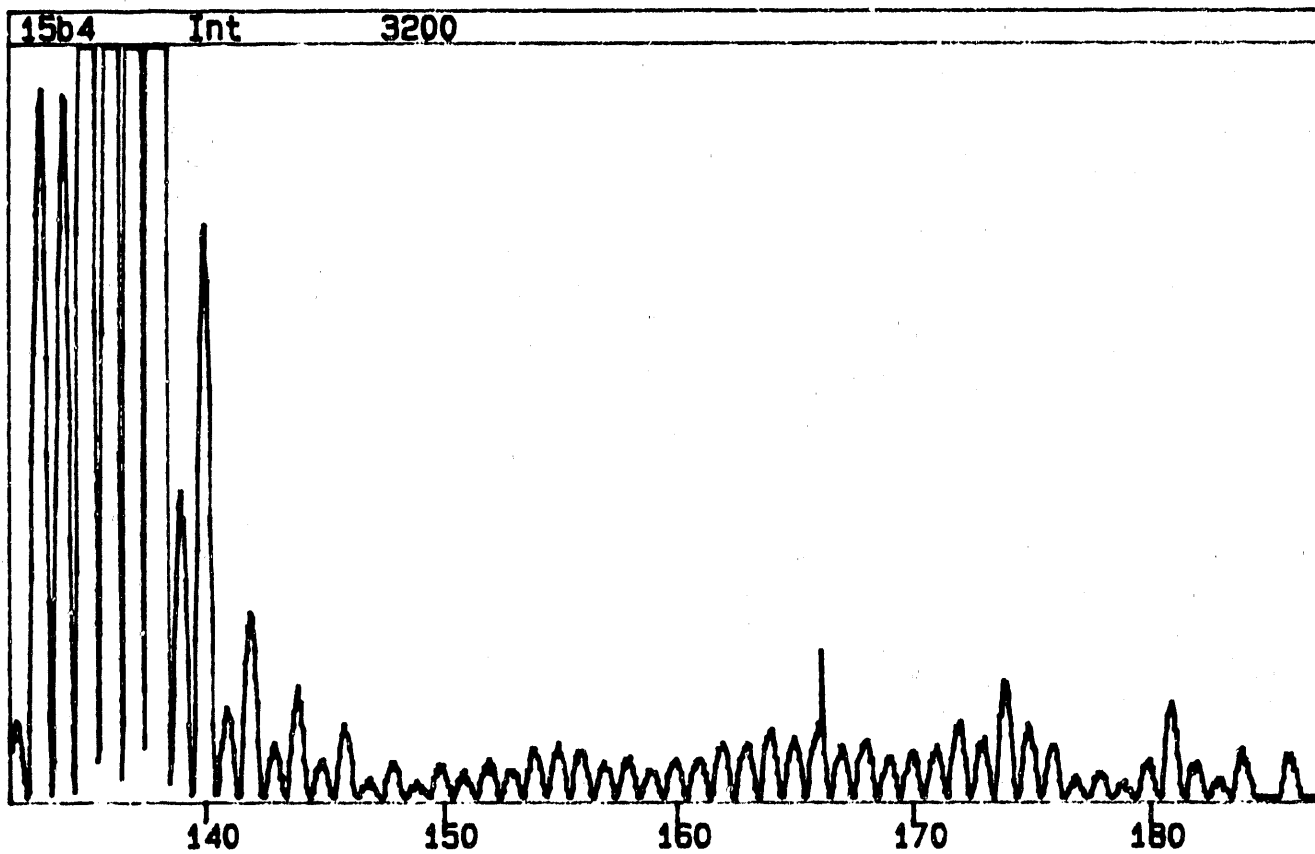


Figure 2

15B4 ELEMENTS ONLY

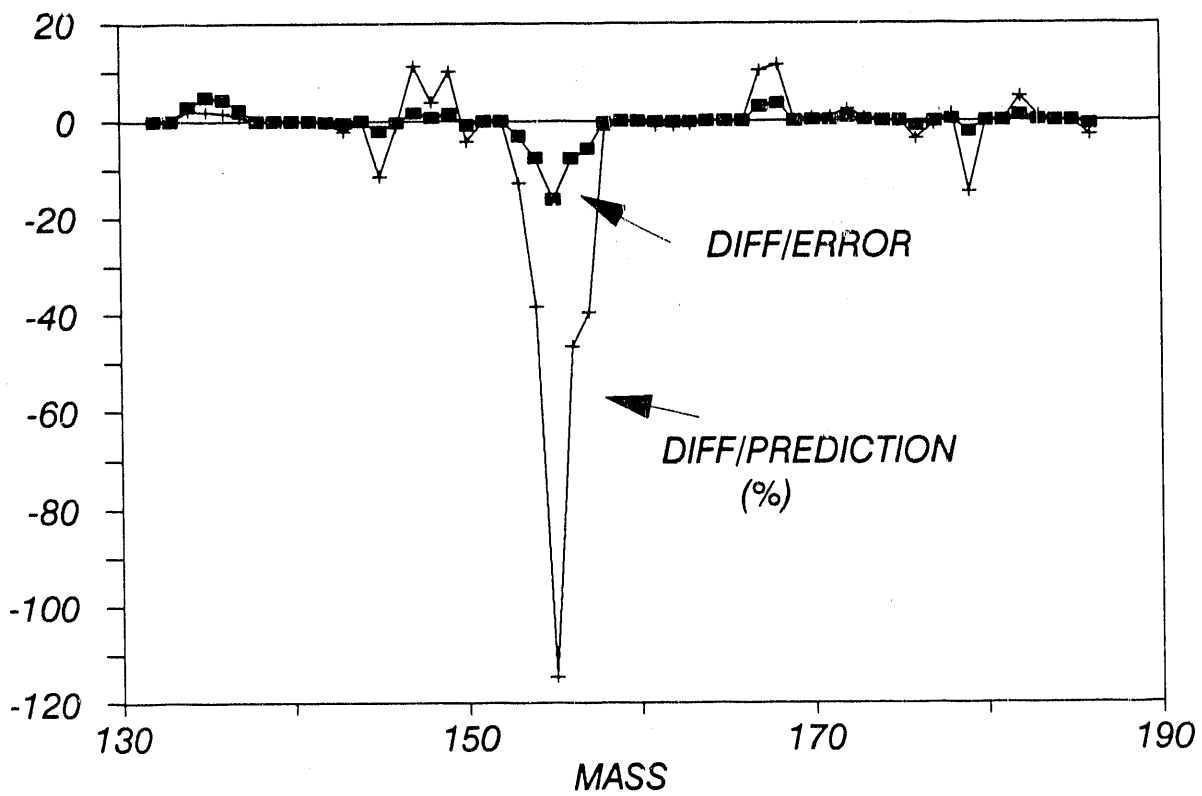
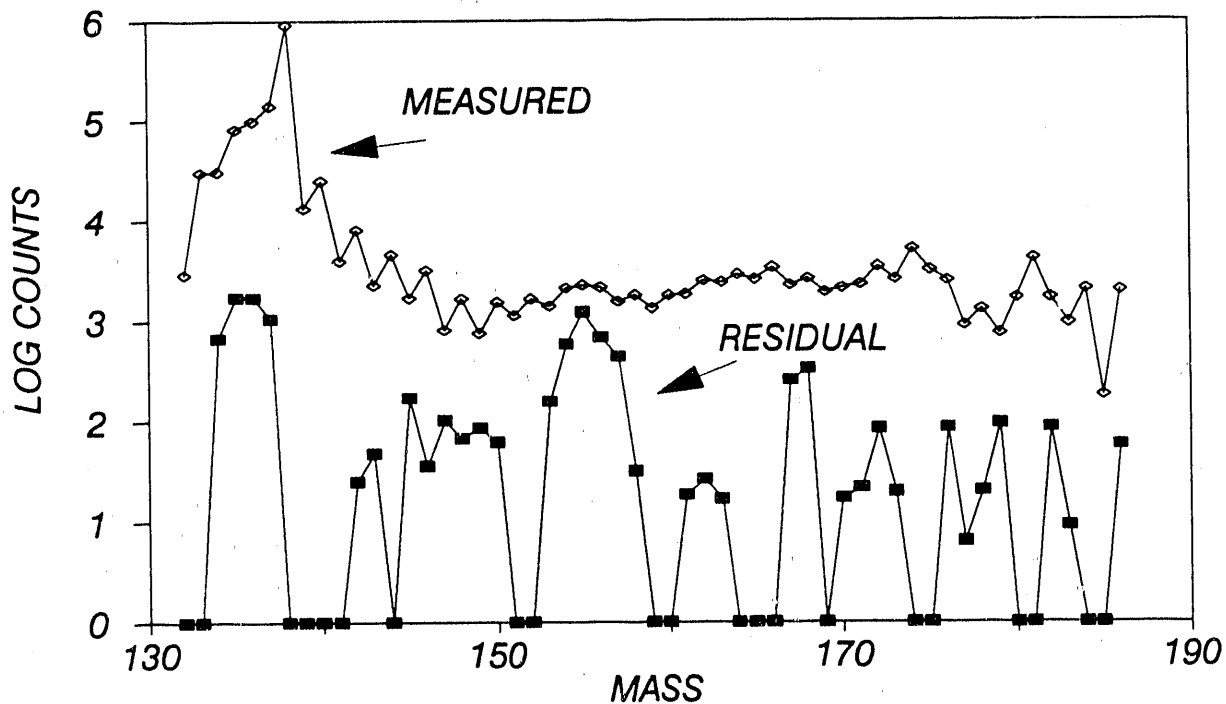


Figure 3

15B4 ELEMENTS, BaO, BaOH, BaF, CeO

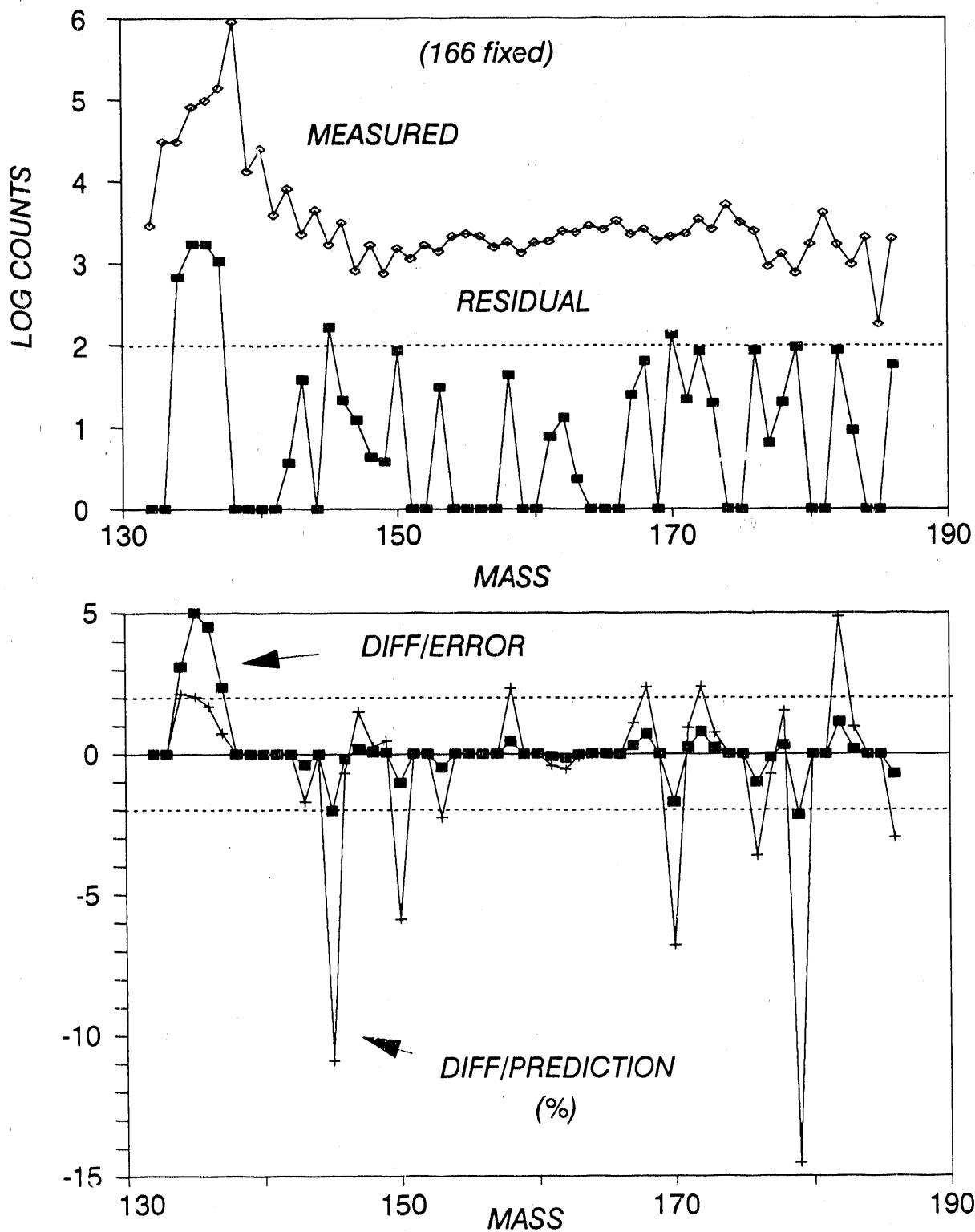


Figure 4

15B4 FINAL

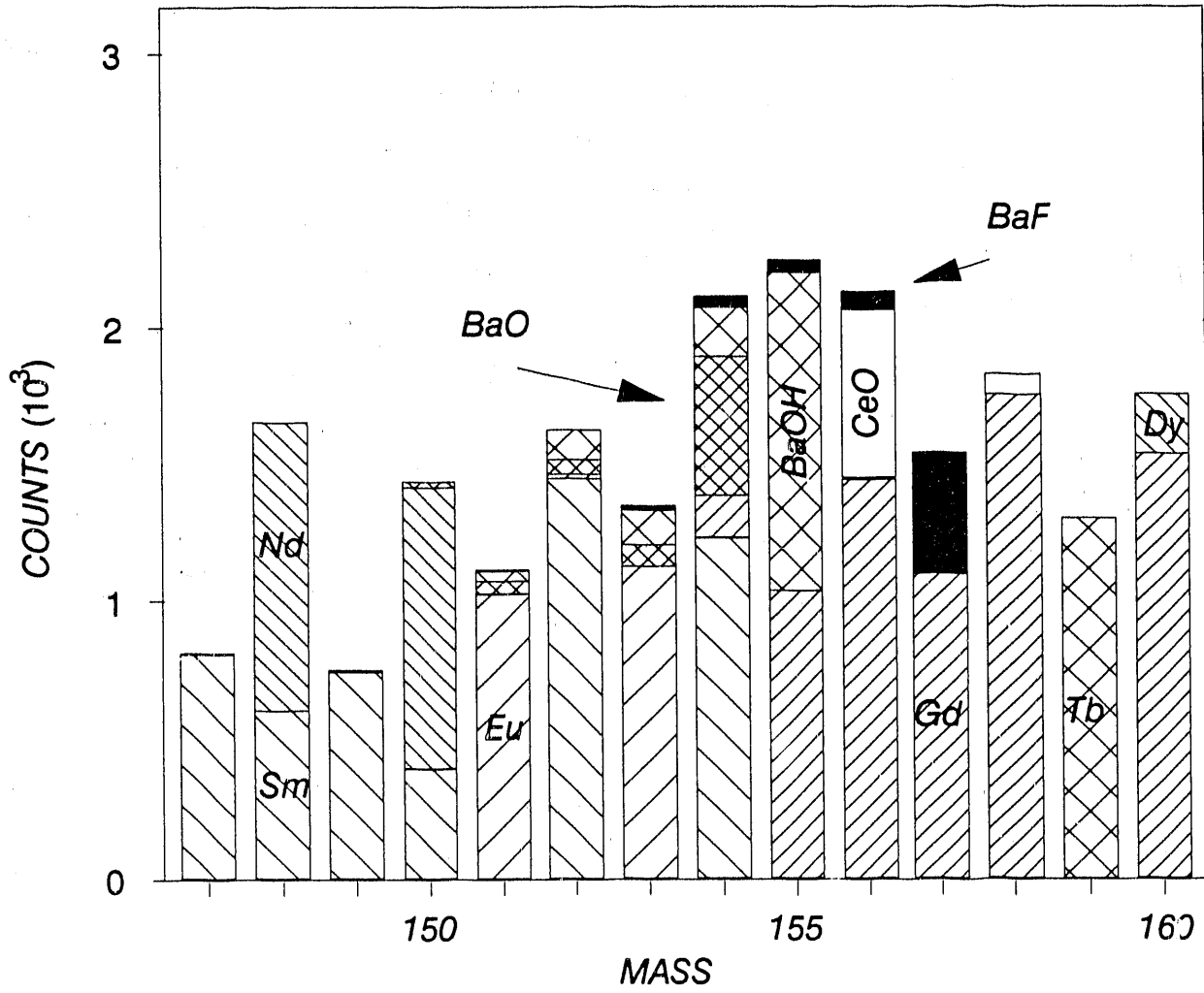


Figure 5

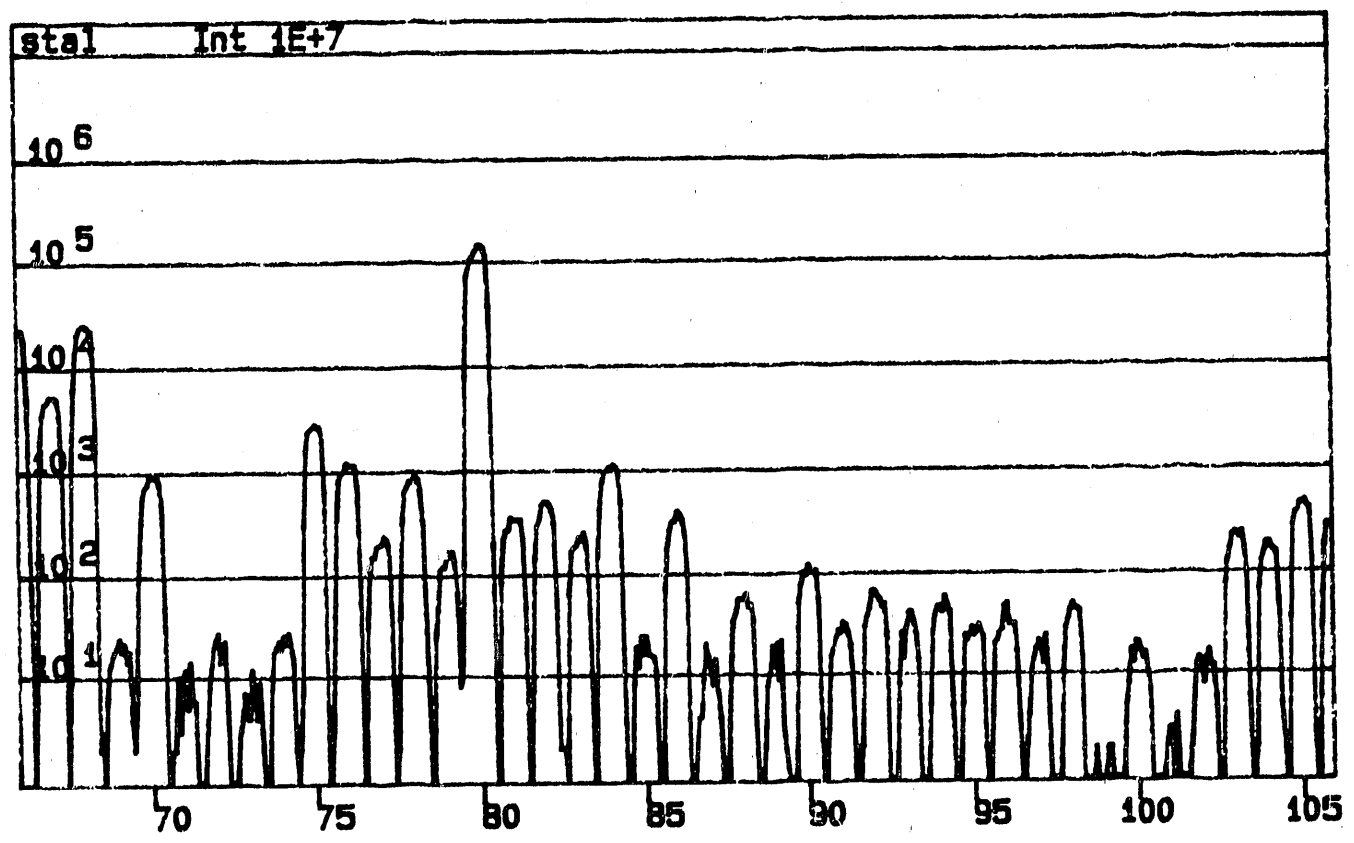
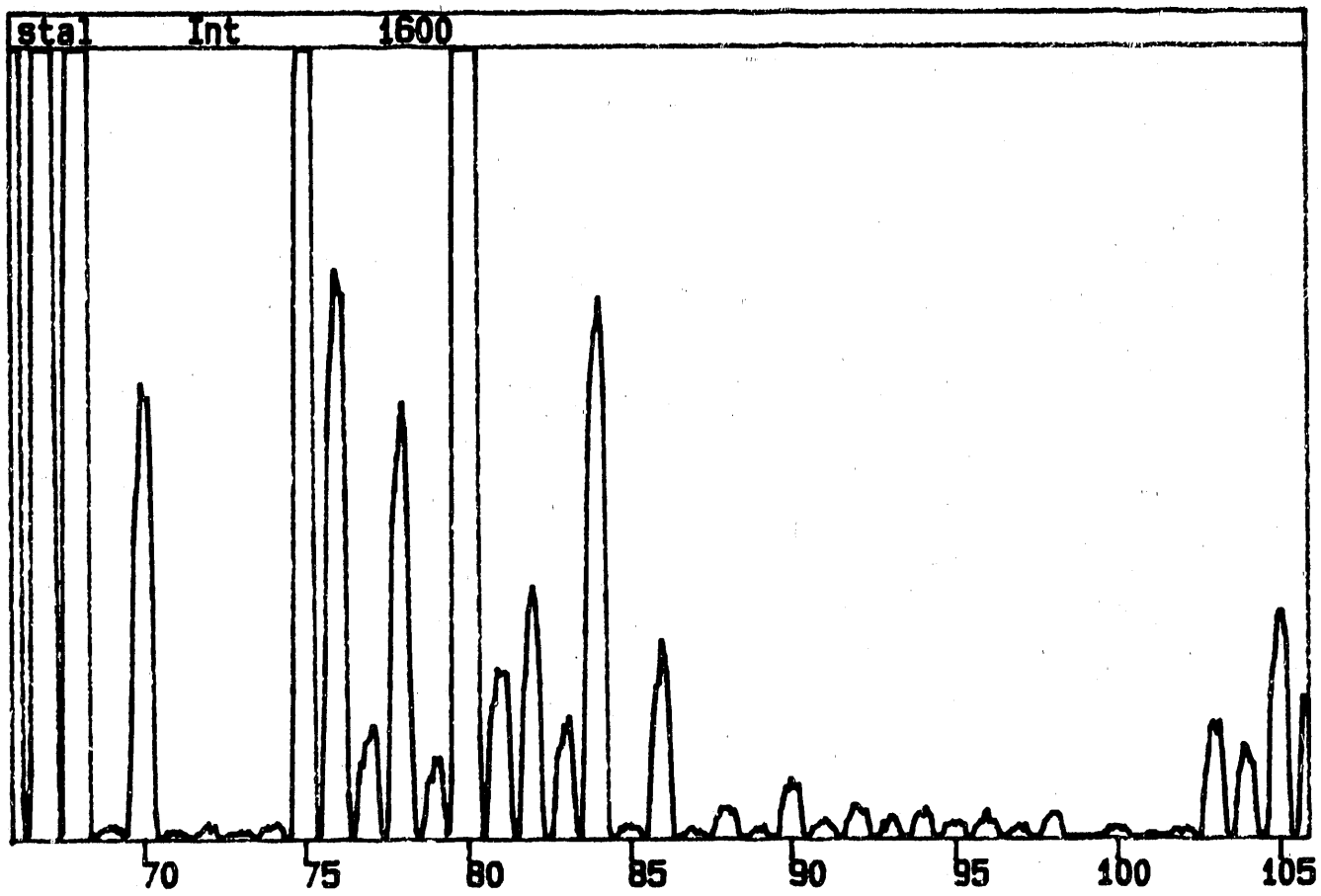


Figure 6

STAL - ELEMENTS, ArCl, ArAr, CuAr, Pb++

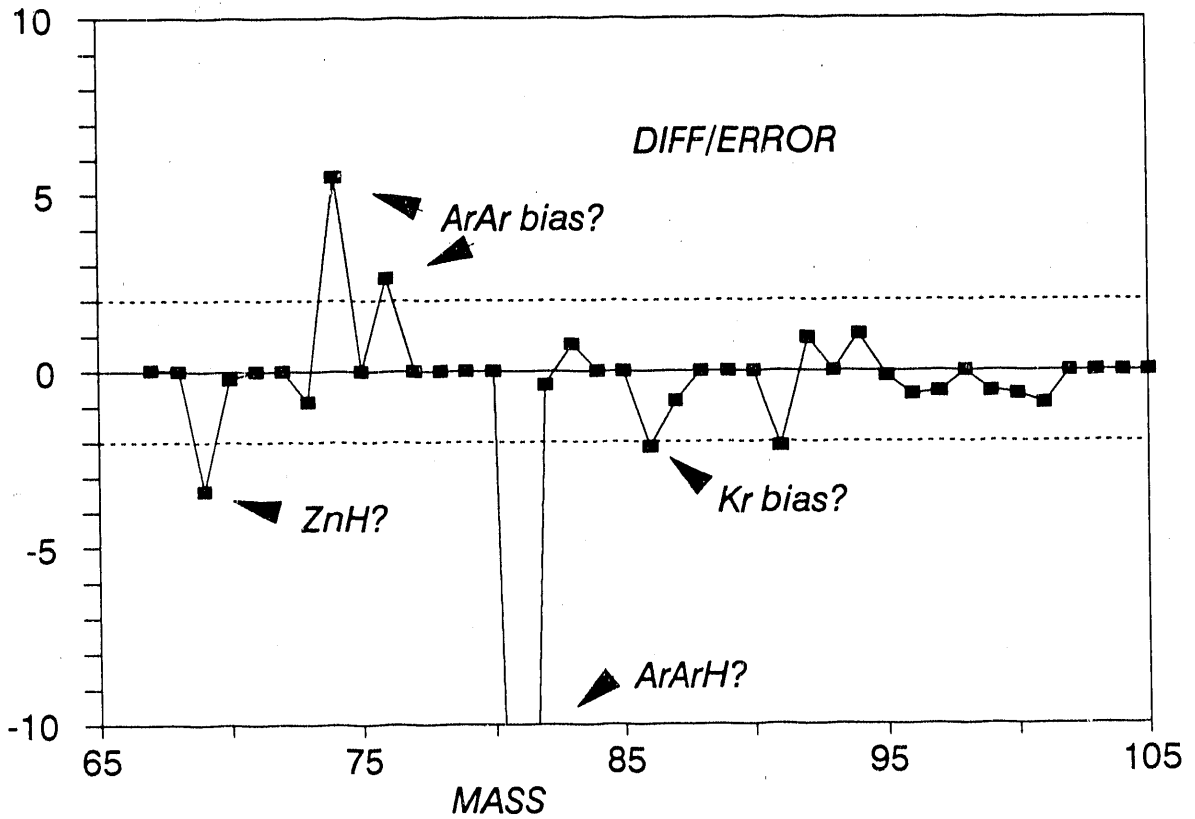
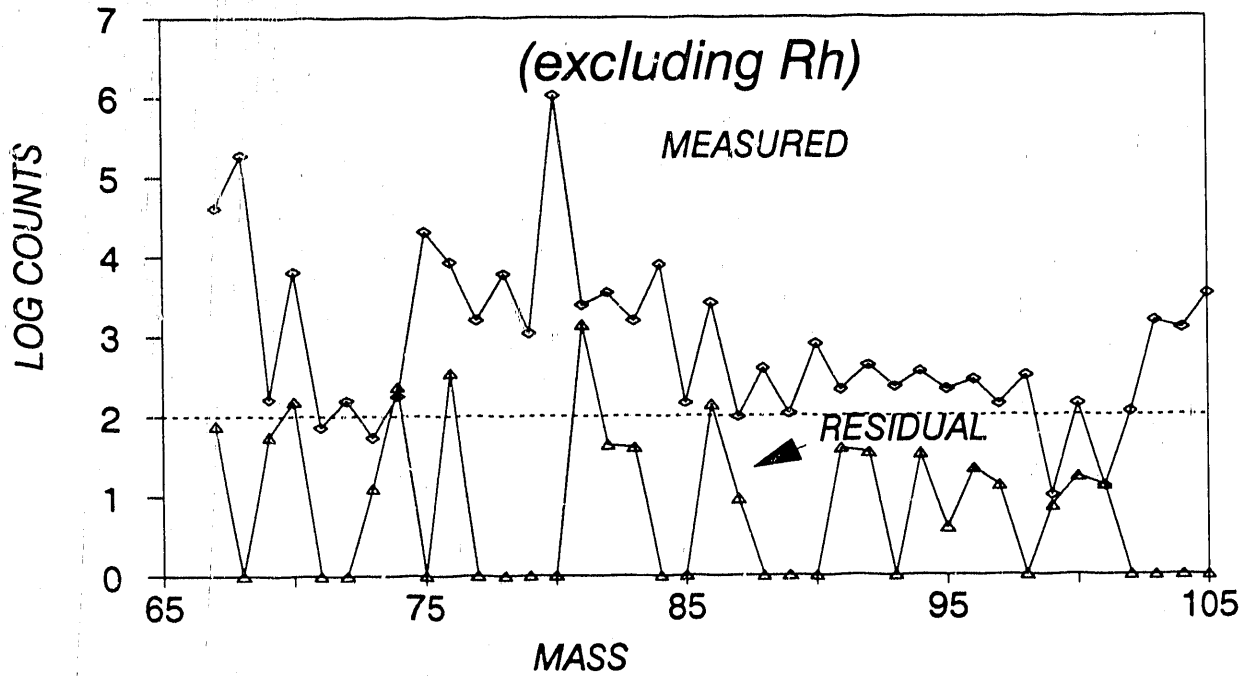


Figure 7

STAL

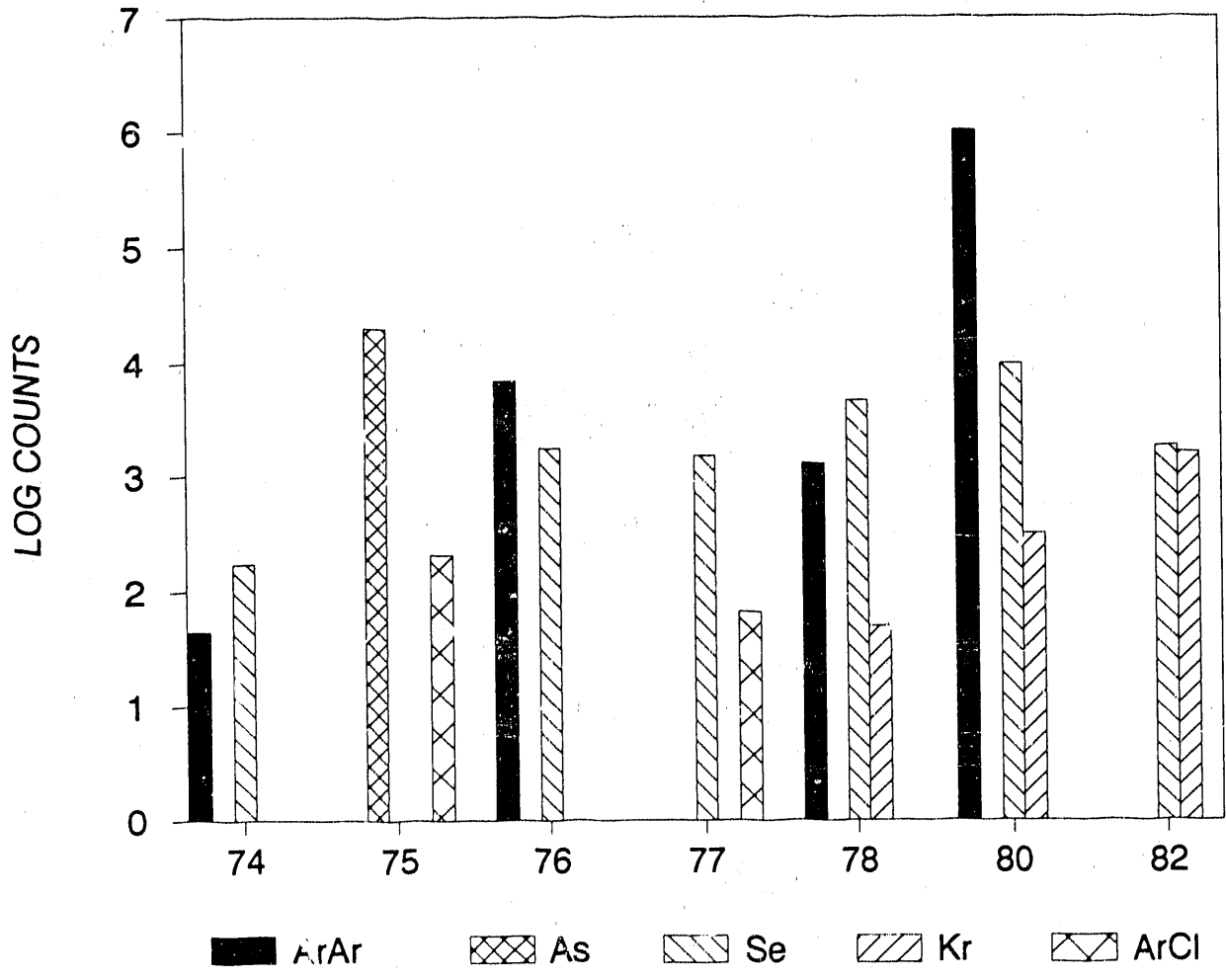


Figure 8

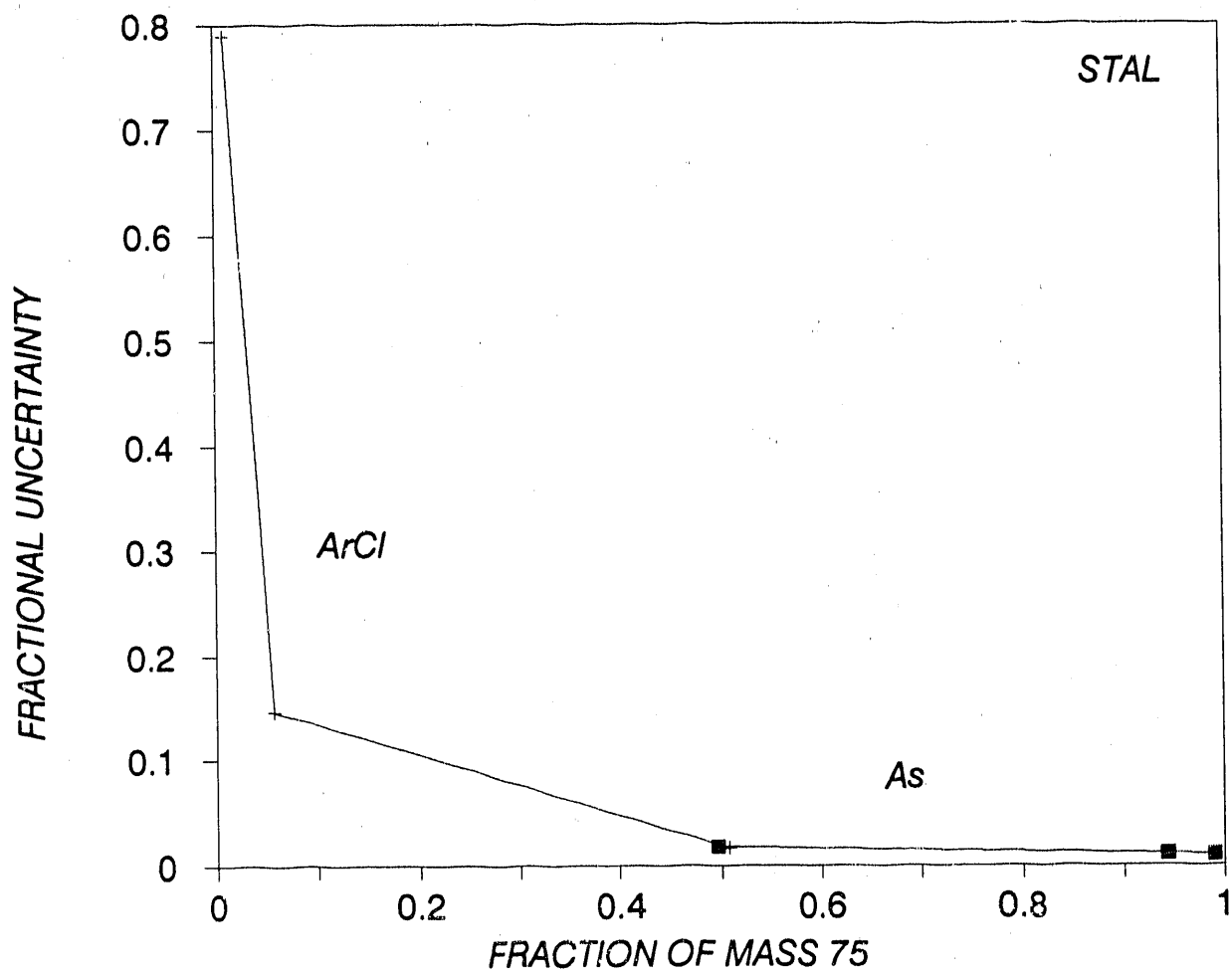


Figure 9

APPENDIX 1 LIBEDIT

The purpose of this appendix is to demonstrate the operation of the component-library editing program LIBEDIT. The Print Scrn key of the PC has been used to capture the information present on the PC's monitor while it is serving as a VAX terminal running LIBEDIT. Each screen ends with the message "1 2 3 4 Sun PC-NFS Telnet..." which is always present when linked to the VAX through the Sun PC-NFS software.

When the command RUN LIBEDIT is given the program responds

Enter the name of the isotope library file :

```
1 2 3 4      Sun PC-NFS Telnet                      F9 for help          NUM RE
```

Upon entering the name of the library, NEWLIB in this case, the program responds with the following menu.

newlib

Please enter menu selection.

```
1...Browse Directory      5...Add Component      7...Change Preferences
2...Examine Component     6...Delete Component   4...Quit
3...Change Component
```

```
1 2 3 4      Sun PC-NFS Telnet                      F9 for help          NUM RE
```

If BROWSE DIRECTORY is selected the response is as follows.

1 barhox	barflo	Li	Be
5 B	Na	Mg	Al
9 Si	P	S	Cl
13 Ca	Sc	Ti	V
17 Cr	Mn	Fe	Co
21 Ni	Cu	Zn	Ga
25 Ge	As	Se	Br
29 Kr	Rb	Sr	Y
33 Zr	Nb	Mo	Ru
37 Rh	Pd	Ag	Cd
41 In	Sn	Sb	Te
45 I	Xe	Cs	Ba
49 La	Ce	Pr	Nd
53 Sm	Eu	Gd	Tb
57 Dy	Ho	Er	Tm
61 Yb	Lu	Hf	Ta
65 W	Re	Os	Ir

```
1...Browse Directory      5...Add Component      7...Change Preferences
2...Examine Component     6...Delete Component   4...Quit
3...Change Component
```

1
Library newlib.OFL contains 99 components.

Do you want to see more? [Y/N (D:N)] :

```
1 2 3 4      Sun PC-NFS Telnet                      F9 for help          NUM RE
```


At this point, one can select to view more of the library than fit into the display window or return to the menu. Note the total number of components in the library is listed even though they can not all be viewed at once. If one selects not to view more and then EXAMINE COMPONENT, the number or name of the component is requested followed by the response below. In this case Zr was requested. Each entry in the component is listed by mass, abundance, variance, and other information such as a literature reference.

25 Ge	As	Se	Br
29 Kr	Rb	Sr	Y
33 Zr	Nb	Mo	Ru
37 Rh	Pd	Ag	Cd
41 In	Sn	Sb	Te
45 I	Xe	Cs	Ba
49 La	Ce	Pr	Nd
53 Sm	Eu	Gd	Tb
57 Dy	Ho	Er	Tm
61 Yb	Lu	Hf	Ta
65 W	Re	Os	Ir

Zr	Type:	Number isotopes: 5	Num extnds: 0	No Ref text
90	0.5145200000000000	e(1):	0.000000008100000	
91	0.1122300000000000	e(1):	0.000000014400000	
92	0.1714600000000000	e(1):	0.000000004900000	
94	0.1738000000000000	e(1):	0.000000014400000	
96	0.0279900000000000	e(1):	0.000000002500000	

Please enter menu selection.

- | | | |
|-----------------------|----------------------|------------------------|
| 1...Browse Directory | 5...Add Component | 7...Change Preferences |
| 2...Examine Component | 6...Delete Component | 4...Quit |
| 3...Change Component | | |

1 2 3 4 Sun PC-NFS Telnet

F9 for help

NUM RE

One then chooses the next operation. If one chooses ADD COMPONENT, one is asked to indicate where in the library the new component should be added, its name, the type of component; e.g., oxide, the mass of the first isotope to be entered, and the fractional isotopic abundance of that isotope. This information appears below. Note that in this case no TYPE was entered. TYPE is not required but can be used indicate the nature of the component; e.g., oxide.

33 Zr	Nb	Mo	Ru
37 Rh	Pd	Ag	Cd
41 In	Sn	Sb	Te
45 I	Xe	Cs	Ba
49 La	Ce	Pr	Nd
53 Sm	Eu	Gd	Tb
57 Dy	Ho	Er	Tm
61 Yb	Lu	Hf	Ta
65 W	Re	Os	Ir
69 Pt	Au	Hg	Tl
73 Pb	Bi	Th	U
77 Rad87	Rad187	CO	NO
81 CO2	NO2	OC1	ArN
85 ArO	ArCl	Ar2	CsO
89 BaO	LaO	CeO	PrO
93 NdO	SmO	EuO	GdO
97 TbO	DyO	HoO	

Enter name or number of the preceding component: 33

Enter name of the new component: ZrZrO

Enter component type:

Setting component type to:

Enter the new isotope number [1:250]: 90

Enter ratio: .51452

1 2 3 4 Sun PC-NFS Telnet

F9 for help

NUM RE

After the abundance is entered the program responds "Setting ratio to:...." One is then prompted to enter the standard deviation of this ratio. The program responds with the variance followed by the question "Do you want to add correlated errors?" This is illustrated in the following screen.

33 Zr	Nb	Mo	Ru
37 Rh	Pd	Ag	Cd
41 In	Sn	Sb	Te
45 I	Xe	Cs	Ba
49 La	Ce	Pr	Nd
53 Sm	Eu	Gd	Tb
57 Dy	Ho	Er	Tm
61 Yb	Lu	Hf	Ta
65 W	Re	Os	Ir
69 Pt	Au	Hg	Tl
73 Pb	Bi	Th	U
77 Rad87	Rad187	CO	NC
81 CO2	NO2	OCl	ArN
85 ArO	ArCl	Ar2	CsO
89 BaO	LaO	CeO	PrO
93 NdO	SmO	EuO	GdO
97 TbO	DyO	HoO	

```

Enter ratio: .51452
Setting ratio to:          0.5145200000000000
Enter std( 1): .00009
Setting std( 1) to:       0.0000900000000000
Setting variance to      0.0000000081000
Do you want to add correlated errors? [Y/N (D:N)] :
1 2 3 4 Sun PC-NFS Telnet          F9 for help          NUM RI

```

If the answer is no, one is returned to the menu.
The other options are self explanatory except CHANGE PREFERENCE which is used to set defaults.

APPENDIX 2 COMDEC OUTPUT

The following material is a copy of the information generated by COMDEC. The first table "Component" gives the amount of each component calculated to be present in the sample. This is the information which would be used to calculate concentrations if the fit passes the "goodness-of-fit" tests. The amount of each isotope in each component follows. The last table compares the measured and predicted spectra and tabulates the results of the goodness-of-fit tests on an isotope by isotope basis.

Decomposition Results For [russ.opf]15b4.opf

Component	Amount	Error
Xe	6032.356	+ - 196.3745
Cs	30567.00	+ - 174.8342
Ba	1263267.	+ - 1319.801
La	13125.68	+ - 114.6184
Ce	28032.78	+ - 178.0011
Pr	3915.000	+ - 62.56996
Nd	18172.73	+ - 326.7749
Sm	6061.051	+ - 133.0216
Eu	2352.941	+ - 70.18235
Gd	7095.146	+ - 164.6998
Tb	1316.000	+ - 36.27671
Dy	9563.595	+ - 77.33659
Ho	2557.000	+ - 50.56679
Er	10877.71	+ - 179.9014
Tm	1895.000	+ - 43.53160
Yb	16117.60	+ - 214.9957
Lu	3240.741	+ - 57.67758
Hf	4792.039	+ - 113.1405
Ta	4125.507	+ - 64.23406
W	6716.710	+ - 148.0587
Re	483.9831	+ - 35.97418

Contributions at each isotope from:

Xe

Isotope	Predicted	Error
124	5.791061	+ - 6.084441
126	5.429120	+ - 5.891235
128	115.7609	+ - 27.20336
129	1594.955	+ - 100.9754
130	246.1201	+ - 39.66570
131	1277.653	+ - 90.37494
132	1622.100	+ - 101.8311
134	629.7779	+ - 63.45054
136	535.0699	+ - 58.48532

Cs

Isotope	Predicted	Error
133	30567.00	+ - 174.8342

Ba

Isotope	Predicted	Error
130	1339.063	+ - 42.96961
132	1275.900	+ - 41.94394
134	30533.16	+ - 205.1856
135	83274.55	+ - 338.8575
136	99204.35	+ - 369.8506
137	141890.1	+ - 442.3205
138	905749.7	+ - 1117.545

La

Isotope	Predicted		Error
138	1.168186	+-	1.081308
139	13114.00	+-	114.5674

Ce

Isotope	Predicted		Error
136	53.37441	+-	7.767053
138	71.09112	+-	8.963908
140	24802.00	+-	167.4299
142	3106.312	+-	59.25326

Pr

Isotope	Predicted		Error
141	3915.000	+-	62.56996

Nd

Isotope	Predicted		Error
142	4935.714	+-	170.2996
143	2213.439	+-	114.0440
144	4330.562	+-	159.5184
145	1508.337	+-	94.14293
146	3120.258	+-	135.4047
148	1043.115	+-	78.28969
150	1021.308	+-	77.46701

Sm

Isotope	Predicted		Error
144	186.4379	+-	23.33004
147	908.8547	+-	51.51046
148	681.3834	+-	44.60094
149	837.5767	+-	49.44934
150	447.3056	+-	36.13686
152	1620.604	+-	68.78388
154	1378.889	+-	63.44727

Eu

Isotope	Predicted		Error
151	1124.000	+-	48.50713
153	1228.941	+-	50.72101

Gd

Isotope	Predicted		Error
152	14.39605	+-	7.418808
154	154.7380	+-	24.32265

155	1050.082	+-	63.36128
156	1452.093	+-	74.50914
157	1110.532	+-	65.15954
158	1762.080	+-	82.07770
160	1551.212	+-	77.01015

Tb

Isotope	Predicted		Error
159	1316.000	+-	36.27671

Dy

Isotope	Predicted		Error
156	5.355613	+-	1.830118
158	9.181052	+-	2.396187
160	223.7881	+-	11.83022
161	1808.476	+-	33.63030
162	2439.673	+-	39.06072
163	2381.335	+-	38.59088
164	2695.978	+-	41.06129

Ho

Isotope	Predicted		Error
165	2557.000	+-	50.56679

Er

Isotope	Predicted		Error
162	14.90247	+-	6.658783
164	175.0224	+-	22.81984
166	3656.000	+-	104.2963
167	2494.260	+-	86.14630
168	2914.140	+-	93.11528
170	1624.043	+-	69.51275

Tm

Isotope	Predicted		Error
169	1895.000	+-	43.53160

Yb

Isotope	Predicted		Error
168	20.46935	+-	7.661813
170	489.9750	+-	37.48578
171	2301.593	+-	81.24447
172	3518.472	+-	100.4515
173	2599.769	+-	86.34693
174	5130.232	+-	121.2964
176	2056.606	+-	76.79891

Lu

Isotope	Predicted	Error
175	3157.000	+ - 56.92750
176	83.74074	+ - 9.271569

Hf

Isotope	Predicted	Error
174	7.767895	+ - 4.555221
176	249.4544	+ - 25.81388
177	891.6067	+ - 48.80277
178	1308.078	+ - 59.11185
179	653.1021	+ - 41.76845
180	1682.030	+ - 67.03083

Ta

Isotope	Predicted	Error
180	0.5074374	+ - 0.7123902
181	4125.000	+ - 64.23011

W

Isotope	Predicted	Error
180	8.463055	+ - 5.255562
182	1767.166	+ - 75.94415
183	959.1462	+ - 55.94973
184	2058.000	+ - 81.95554
186	1923.666	+ - 79.23561

Re

Isotope	Predicted	Error
185	181.0000	+ - 21.99962
187	302.9831	+ - 28.46328

Totals for isotopes:

Fails P/F test if either of the following fail

- 1) Is the difference < 100.00 and the normalized difference < 2.00 and the difference/predicted < 0.020
- or 2) Is the predicted > 0.0 . (Absolute values used)

Iso	Measured	Predicted	Error	Difference	Norm_Diff	Diff/Pred	Tests	P/F
124	0.0	5.8	+ - 0.61E+01	0.58E+01	0.95E+00	0.10E+01	--N-	
126	0.0	5.4	+ - 0.59E+01	0.54E+01	0.92E+00	0.10E+01	--N-	
128	0.0	115.8	+ - 0.27E+02	0.12E+03	0.43E+01	0.10E+01	NNN-	F
129	0.0	1595.0	+ - 0.10E+03	0.16E+04	0.16E+02	0.10E+01	NNN-	F
130	0.0	1585.2	+ - 0.58E+02	0.16E+04	0.27E+02	0.10E+01	NNN-	F
131	0.0	1277.7	+ - 0.90E+02	0.13E+04	0.14E+02	0.10E+01	NNN-	F
132	2898.0	2898.0	+ - 0.11E+03	0.00E+00	0.00E+00	0.00E+00	----	
133	30567.0	30567.0	+ - 0.17E+03	0.00E+00	0.00E+00	0.00E+00	----	
134	30493.0	31162.9	+ - 0.21E+03	0.67E+03	0.24E+01	0.21E-01	NNN-	F
135	81575.0	83274.6	+ - 0.34E+03	0.17E+04	0.38E+01	0.20E-01	NNN-	F
136	98095.0	99792.8	+ - 0.37E+03	0.17E+04	0.35E+01	0.17E-01	NN--	

137	140837.0	141890.1	+-	0.44E+03	0.11E+04	0.18E+01	0.74E-02	N---	
138	905822.0	905822.0	+-	0.11E+04	0.00E+00	0.00E+00	0.00E+00	----	
139	13114.0	13114.0	+-	0.11E+03	0.00E+00	0.00E+00	0.00E+00	----	
140	24802.0	24802.0	+-	0.17E+03	0.00E+00	0.00E+00	0.00E+00	----	
141	3915.0	3915.0	+-	0.63E+02	0.00E+00	0.00E+00	0.00E+00	----	
142	8067.0	8042.0	+-	0.18E+03	-0.25E+02	-0.12E+00	-0.31E-02	----	
143	2261.0	2213.4	+-	0.11E+03	-0.48E+02	-0.38E+00	-0.21E-01	--N-	
144	4517.0	4517.0	+-	0.16E+03	0.00E+00	0.00E+00	0.00E+00	----	
145	1680.0	1508.3	+-	0.94E+02	-0.17E+03	-0.17E+01	-0.11E+00	N-N-	
146	3156.0	3120.3	+-	0.14E+03	-0.36E+02	-0.24E+00	-0.11E-01	----	
147	807.0	908.9	+-	0.52E+02	0.10E+03	0.17E+01	0.11E+00	N-N-	
148	1657.0	1724.5	+-	0.90E+02	0.67E+02	0.68E+00	0.39E-01	--N-	
149	752.0	837.6	+-	0.49E+02	0.86E+02	0.15E+01	0.10E+00	--N-	
150	1530.0	1468.6	+-	0.85E+02	-0.61E+02	-0.65E+00	-0.42E-01	--N-	
151	1124.0	1124.0	+-	0.49E+02	0.00E+00	0.00E+00	0.00E+00	----	
152	1635.0	1635.0	+-	0.69E+02	0.00E+00	0.00E+00	0.00E+00	----	
153	1386.0	1228.9	+-	0.51E+02	-0.16E+03	-0.25E+01	-0.13E+00	NNN-	F
154	2121.0	1533.6	+-	0.68E+02	-0.59E+03	-0.72E+01	-0.38E+00	NNN-	F
155	2254.0	1050.1	+-	0.63E+02	-0.12E+04	-0.15E+02	-0.11E+01	NNN-	F
156	2137.0	1457.4	+-	0.75E+02	-0.68E+03	-0.77E+01	-0.47E+00	NNN-	F
157	1550.0	1110.5	+-	0.65E+02	-0.44E+03	-0.58E+01	-0.40E+00	NNN-	F
158	1803.0	1771.3	+-	0.82E+02	-0.32E+02	-0.34E+00	-0.18E-01	----	
159	1316.0	1316.0	+-	0.36E+02	0.00E+00	0.00E+00	0.00E+00	----	
160	1775.0	1775.0	+-	0.78E+02	0.00E+00	0.00E+00	0.00E+00	----	
161	1827.0	1808.5	+-	0.34E+02	-0.19E+02	-0.34E+00	-0.10E-01	----	
162	2481.0	2454.6	+-	0.40E+02	-0.26E+02	-0.42E+00	-0.11E-01	----	
163	2398.0	2381.3	+-	0.39E+02	-0.17E+02	-0.27E+00	-0.70E-02	----	
164	2871.0	2871.0	+-	0.47E+02	0.00E+00	0.00E+00	0.00E+00	----	
165	2557.0	2557.0	+-	0.51E+02	0.00E+00	0.00E+00	0.00E+00	----	
166	3656.0	3656.0	+-	0.10E+03	0.00E+00	0.00E+00	0.00E+00	----	
167	2238.0	2494.3	+-	0.86E+02	0.26E+03	0.26E+01	0.10E+00	NNN-	F
168	2601.0	2934.6	+-	0.93E+02	0.33E+03	0.31E+01	0.11E+00	NNN-	F
169	1895.0	1895.0	+-	0.44E+02	0.00E+00	0.00E+00	0.00E+00	----	
170	2097.0	2114.0	+-	0.79E+02	0.17E+02	0.19E+00	0.81E-02	----	
171	2280.0	2301.6	+-	0.81E+02	0.22E+02	0.23E+00	0.94E-02	----	
172	3434.0	3518.5	+-	0.10E+03	0.84E+02	0.73E+00	0.24E-01	--N-	
173	2580.0	2599.8	+-	0.86E+02	0.20E+02	0.20E+00	0.76E-02	----	
174	5138.0	5138.0	+-	0.12E+03	0.00E+00	0.00E+00	0.00E+00	----	
175	3157.0	3157.0	+-	0.57E+02	0.00E+00	0.00E+00	0.00E+00	----	
176	2476.0	2389.8	+-	0.82E+02	-0.86E+02	-0.90E+00	-0.36E-01	--N-	
177	898.0	891.6	+-	0.49E+02	-0.64E+01	-0.11E+00	-0.72E-02	----	
178	1288.0	1308.1	+-	0.59E+02	0.20E+02	0.29E+00	0.15E-01	----	
179	748.0	653.1	+-	0.42E+02	-0.95E+02	-0.19E+01	-0.15E+00	--N-	
180	1691.0	1691.0	+-	0.67E+02	0.28E-13	0.36E-15	0.17E-16	----	
181	4125.0	4125.0	+-	0.64E+02	0.00E+00	0.00E+00	0.00E+00	----	
182	1681.0	1767.2	+-	0.76E+02	0.86E+02	0.10E+01	0.49E-01	--N-	
183	950.0	959.1	+-	0.56E+02	0.91E+01	0.14E+00	0.95E-02	----	
184	2058.0	2058.0	+-	0.82E+02	0.00E+00	0.00E+00	0.00E+00	----	
185	181.0	181.0	+-	0.22E+02	0.00E+00	0.00E+00	0.00E+00	----	
186	1981.0	1923.7	+-	0.79E+02	-0.57E+02	-0.63E+00	-0.30E-01	--N-	
187	0.0	303.0	+-	0.28E+02	0.30E+03	0.11E+02	0.10E+01	NNN-	F

END

DATE FILMED

12 / 28 / 90

