

ornl

**OAK RIDGE
NATIONAL
LABORATORY**

MARTIN MARIETTA

Spark Source Mass Spectrometry Software Documentation and Verification

David O. Vick
Larry Landau
Warner H. Christie

OAK RIDGE NATIONAL LABORATORY
CENTRAL RESEARCH LIBRARY
CIRCULATION SECTION
4500 JENKINS LANE
LIBRARY LOAN COPY
DO NOT TRANSFER TO ANOTHER PERSON
If you wish someone else to see this
report, send in name with report and
the library will arrange a loan.

OPERATED BY
MARTIN MARIETTA ENERGY SYSTEMS, INC.
FOR THE UNITED STATES
DEPARTMENT OF ENERGY

This report has been reproduced directly from the best available copy.

Available to DOE and DOE contractors from the Office of Scientific and Technical Information, P.O. Box 62, Oak Ridge, TN 37831; prices available from (615) 576-8401, FTS 628-8401.

Available to the public from the National Technical Information Service, U.S. Department of Commerce, 5285 Port Royal Rd., Springfield, VA 22161.

NTIS price codes—Printed Copy: A03 Microfiche A01

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise, does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

ORNL/TM-11328

Analytical Chemistry Division

SPARK SOURCE MASS SPECTROMETRY SOFTWARE
DOCUMENTATION AND VERIFICATION

David O. Vick
Larry Landau
Warner H. Christie

Published Date - December 1989

Prepared by the
OAK RIDGE NATIONAL LABORATORY
Oak Ridge, Tennessee 37831
operated by
MARTIN MARIETTA ENERGY SYSTEMS, INC.
for the
U.S. DEPARTMENT OF ENERGY
under Contract DE-AC05-84OR21400



3 4456 0328596 9

TABLE OF CONTENTS

	<u>Page</u>
Abstract	1
1. Introduction	2
2. Software Description	3
2.1 Overview	3
2.2 Function of the Individual Routines	3
2.2.1 EMLCAL	3
2.2.2 PLATE	5
2.2.3 PEAK	7
3. Verification of the Individual Routines	8
3.1 EMLCAL	8
3.2 PLATE	9
3.3 PEAK	11
4. Validation of the Complete Software Package	12
5. Appendix	13
5.1 Comparative Computer Printouts from EMUL and EMLCAL Programs for the Calibration of Emulsion #16	13
5.2 Sample Computer Printout from EMLCAL Program .	15
5.3 Sample Computer Printout from PEAK Program . .	16
5.4 Definition of Labels and Variables	17
5.4.1 Program EMLCAL	17
5.4.2 Program PLATE	18
5.4.3 Program PEAK	21

5.5	User Instructions	24
5.5.1	EMLCAL Instructions	24
5.5.2	PLATE Instructions	24
5.5.3	PEAK Instructions	26
5.6	Example of the Data Files	27
5.6.1	<u>AB</u> Abundance Table	27
5.6.2	<u>SENS</u> Relative Sensitivity Table	29

ACKNOWLEDGEMENT

The authors acknowledge the assistance of R. J. Warmack, who wrote much of the original FORTRAN code (for the Digital Equipment Corporation PDP-11 computer) discussed in this report.

SPARK SOURCE MASS SPECTROMETRY SOFTWARE
DOCUMENTATION AND VERIFICATION

David O. Vick, Larry Landau, and Warner H. Christie

ABSTRACT

The Analytical Spectroscopy Section of the Analytical Chemistry Division has had software to process spark source mass spectrometric (SSMS) data in operation for over two decades. Although the system has been verified in analysis of standards numerous times throughout its operation, documentation has never been of primary concern. In recent years the quality assurance (QA) requirements by both Martin Marietta Energy Systems (MMES) and various sponsoring agencies have increased. This report provides the documentation, verification, and validation of the software used to process SSMS data that will satisfy the QA requirements of most analytical programs.

The operation of each of the three major computer routines--EMLCAL, PLATE, PEAK--is described in enough detail to give a clear understanding of its function. Verification was accomplished by comparing code results to hand calculations, to physical data, and to an alternative code designed to perform the same type of analysis. Validation was accomplished by an isotopic analysis of a natural erbium standard and comparison of the results with the accepted isotopic abundances. Appendices contain user instructions, samples of outputs, examples of the data files, and definitions of all the labels and variables used within the program code.

1. INTRODUCTION

The Analytical Spectroscopy Section of the Analytical Chemistry Division has four spark source mass spectrometers (SSMS). The instruments are Associated Electrical Industries (AEI) models of the same basic design involving rf spark ion sources and Mattauch-Herzog double focusing geometry. The operation of these instruments involves atomization and ionization of the sample, followed by extraction of a small fraction of the ions into the electrostatic and magnetic sectors. The mass resolved ions are collected on special photographic plates which are then removed for development and processing.

The high inherent sensitivity and resolution of the spark source double-focusing mass spectrometer lends itself effectively to the analysis of a wide variety of materials. SSMS is used to simultaneously detect impurity elements in the mass range 7 to 245 amu at the atom parts per million level. There are few matrix complications and only infrequent interferences. In general the technique will obtain useful results with as little as 10^{-10} to 10^{-11} g of an isotope. Successful analyses have been performed on concentrations ranging from 10 ppb to 10%.

A photographic emulsion is a non-linear integrating detector and therefore each new emulsion requires calibration of its response to the number of collected ions. A data system is used to calibrate the emulsion, collect data from the photoplate, determine ion intensities and calculate elemental concentrations. This system consists of a photodensitometer, an interface, and a Digital Equipment Corporation PDP-11 computer. The photodensitometer is scanned across the desired lines of the mass spectrum, and its output is digitized and stored in the core of the PDP-11 as percent transmittance. When the desired lines have been scanned, the computer is used to convert percent transmittance into ion intensity by comparison with a previously determined calibration curve. Ion intensity data is then converted into compositional information (by comparison with the ion intensity of an internal standard), and a report is printed.

The Analytical Spectroscopy Section has had software to process mass spectrometric data in operation for over two decades. The software programs have undergone frequent modifications to accommodate the requirements of changing equipment. The system has been verified in analysis of standards numerous times throughout its operation, but documentation has never been of primary concern.

Hundreds of samples are analyzed every year with the four spark source mass spectrometers. Many Martin Marietta Energy Systems (MMES) programs as well as agencies outside of MMES are supported by these instruments. In recent years the quality assurance (QA) requirements by both MMES and other sponsoring agencies have increased. We perceived the need to undertake the documentation, verification, and validation of the software used to process SSMS data.

2. SOFTWARE DESCRIPTION

2.1 OVERVIEW

This software is used to acquire SSMS line intensity data from a photodensitometer (Jarrell Ash Microphotometer) and convert it to compositional information. The complete software package is composed of three major computer routines. A conceptualization of the flow of data and the computer routines utilized is depicted in Figure 2.1.

The isotope mass lines on a photoplate are scanned individually and an electrical signal proportional to the photomultiplier current (an indirect measure of the isotopic concentration) is sent to the analog-to-digital converter (ADC), where the signal is digitized. The program PLATE controls the acquisition of this digitized raw data. PLATE uses photoplate emulsion calibration factor (previously determined by the program EMLCAL) to correct for the photoplate characteristics; it calculates ion intensity values for each isotope and stores the results. PLATE calls upon the subroutines EMUL, Z100, RDPKA, ADATA, FINIPL, TTOFF, and VDON. The program PEAK converts the ion intensity values to compositional information; it uses the subroutines FILE, SUB1, SUB2, and MSENS.

2.2 FUNCTION OF THE INDIVIDUAL ROUTINES

2.2.1 Program EMLCAL

The EMLCAL program determines the SSMS photoplate emulsion calibration constants A1 and A2 (coefficients of the quadratic equation describing the preliminary emulsion calibration curve) that are used in the PLATE program. (A series of graduated exposures is made on a photoplate using an erbium oxide standard to produce spectral lines with optical densities ranging from barely detectable to saturated.) EMLCAL prompts the operator to scan (measure optical densities of) pairs of Er-166 and Er-167 lines. For each scan, the program finds the point of highest ion intensity and calculates transmittance and optical density. After the operator signals that the scans are complete, the program calculates A1 and A2.

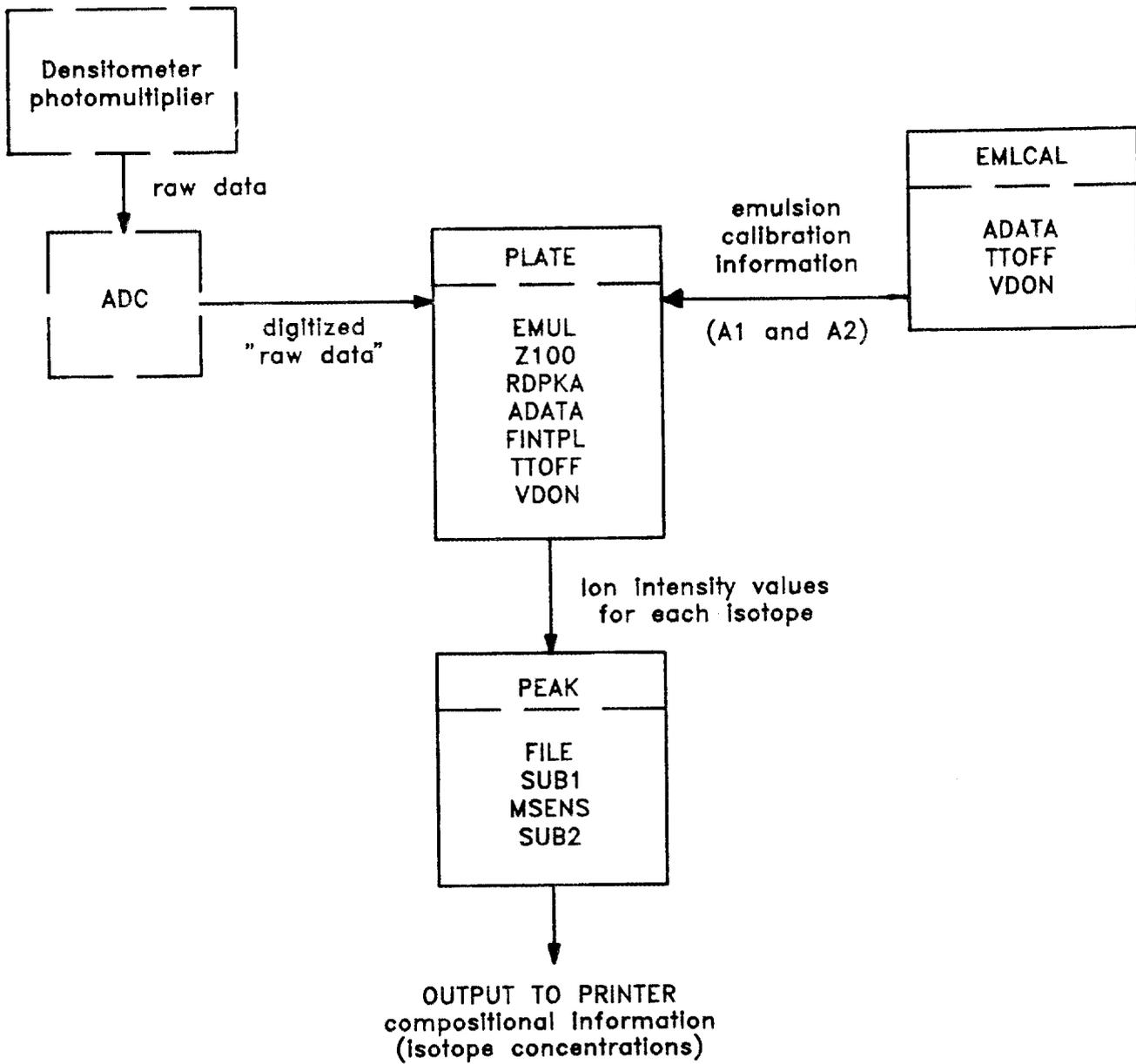


Fig. 2.1 Schematic representation of computer routines employed during data processing.

Subroutine ADATA

This machine language subroutine takes data values on a clock basis (128 data values per mass line) from the analog-to-digital converter (ADC) and stores the data as array of points. The ADC data values are proportional to the densitometer photomultiplier current.

Subroutine TTOFF / TTON

This machine language subroutine turns off/on the character echo at the terminal. It is used to redirect keyboard strokes and to associate characters that are input via the keyboard with a variable (allowing a FORTRAN program access to the keyboard receiver buffer).

Subroutine VDON

This machine language subroutine plots out and displays on the oscilloscope the peak intensity tracing of each mass line--allowing the operator to observe the peak (and then to decide whether to accept the data or to repeat the scan).

2.2.2 Program PLATE

This program controls the acquisition of the raw photodensitometer data, corrects for the photoplate characteristics, and stores these results (as ADC [analog-to-digital converter] values which are proportional to the photomultiplier current from the densitometer) for later calculation.

The program PLATE prompts the operator to identify the element, charge, and mass associated with a particular line just before the scan of the line commences. PLATE sets up a file containing the sample identification, the photoplate emulsion number, and the ion intensity, length of exposure, element name, charge, and mass of each mass line that was scanned.

Subroutine EMUL

This subroutine is called to set up an ADC-to-ion intensity table. (Note that these ADC values are proportional to the densitometer photomultiplier current which is determined by the optical density of each mass line.)

Initially a transmittance-to-ion intensity table is set up using the following method. An optical density (D) of 0.30103 (transmittance of 0.5) is arbitrarily assigned an ion intensity of 100. The equation $A_2x^2 + A_1x - D = 0$ is solved for x which becomes the new D in the calculation of the next ion intensity value. (The incremental steps in ion intensity depend on the Er isotopic ratio that was used to establish the original A_1/A_2 quadrati equation in EMLCAL.) D is used to calculate transmittance (T) values for each increment in ion intensity.

Next, each T is assigned a corresponding ADC value by using the calibration scale obtained by subroutine Z100.

Subroutine Z100

This subroutine calibrates the photodensitometer by setting the percent transmittance scale. It prompts the operator to perform a scan with the slit covered and then with nothing blocking the light path; the subroutine receives the ADC values for zero and 100% transmittance.

Subroutine RDPKA

This subroutine acquires raw photodensitometer data (ADC values for 128 points) for each mass line scanned (using ADATA); utilizes the function routine FINTPL to convert the data to ion intensities; determines the background intensity of each mass line (using the first 10 points and the last 10 points that were scanned for the base line); corrects the ion intensities for background; finds the point of highest value (the peak); and integrates the remaining 108 points to get the peak area.

Subroutine ADATA

Refer to section 2.2.1.

Function FINTPL

This function interpolates between the incremental values in the ADCTBL ("ADC table" set up by the EMUL subroutine) to derive exact ion intensity values.

Subroutine TTOFF / TTON

Refer to section 2.2.1.

Subroutine VDON

Refer to section 2.2.1.

2.2.3 Program PEAK

This program uses the data files created by PLATE to calculate elemental concentrations relative to the concentration of the internal standard.

In order to ratio values of a particular element of interest to those of the internal standard (spike), a "spike factor" is calculated for each exposure and used within the program calculations. The program lists the isotopes scanned in order of increasing mass and uses subroutine SUB2 to calculate and output the concentration of each isotope. The operator has the choice of calculating the concentration based on peak height (point of highest intensity), or on the area (the sum of the intensities of all 108 data points per mass line), or both.

Subroutine FILE

This subroutine prompts input for the plate identification number and for the spike concentration used. It reads the data file from PLATE that contains the sample information and the isotopic charge, mass, peak ion intensity, and the area for each mass line scanned. (ELE, MASS, CHG, PEAK, & AREA are tables containing information about the mass lines scanned in PLATE; particular "I,J" positions in the different tables correspond to the same mass line.)

Subroutine SUB1

This subroutine outputs (writes): sample information; spike concentration; abundance and relative sensitivity filenames used if different from the default files that are normally used (AB and SENS); any modifications to the parameters of individual isotopes; and emulsion number used.

Subroutine MSENS

This subroutine is used to modify the sensitivity of an element if multiple charged ions have been scanned.

Subroutine SUB2(SENS)

This subroutine calculates the apparent concentration value (based on the ion intensity, relative sensitivity factor, isotopic mass, isotopic abundance, and the spike factor) for each mass line that was scanned. It provides most of the printed output of this program, including the averaged concentration values.

3. VERIFICATION OF THE INDIVIDUAL ROUTINES

3.1 EMLCAL PROGRAM VERIFICATION

The coefficients (A1 and A2) of the quadratic equation that describes the preliminary emulsion calibration curve for photoplate #6753R (emulsion #16) were obtained using two different programs on two different computers (see 5.1 in Appendix):

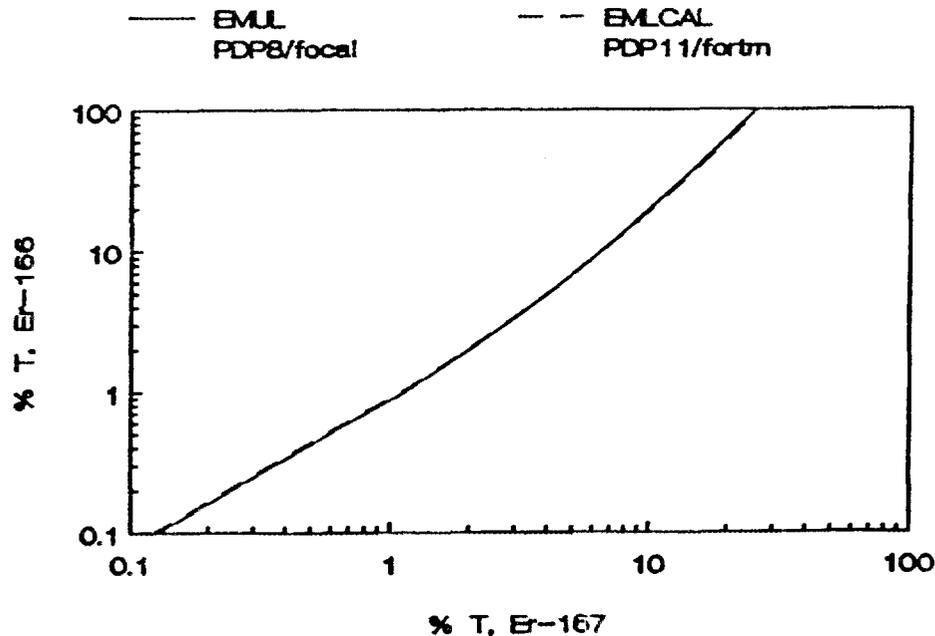
EMUL program (written in focal language) on a PDP8 computer

A1- 0.74 A2- 0.12

EMLCAL program (written in fortran language) on a PDP11 computer

A1- 0.77 A2- 0.11

Plots (the preliminary emulsion calibration curves) of the quadratic equations defined by the two sets of coefficients were made for visual comparison:



3.2 PLATE PROGRAM VERIFICATION

The following is actually a verification of the entire data acquisition system.

Various neutral density filters were used to partly occlude the light beam entering the slit on the microdensitometer. The program PLATE was then used to acquire data from the densitometer via the analog-to-digital converter (ADC). In addition, the percent transmittance (%T) was manually (visually) read from the analog meter on the densitometer. The ADC-transmittance (ADC-T) values obtained from using each filter (in addition to the ADC values for 0%T and 100%T) were recorded manually from a digital readout.

For each filter, the "peak" (maximum occlusion) ADC-T readings are averaged over the number of "scans" made. The 0%T ADC value is subtracted from the peak ADC-T average to give the transmittance (T). %T is calculated by dividing the transmittance by the full ADC-T range. (The range is the difference between the average 100%T baseline or background and the 0%T ADC value.) The results follow:

Jarrell Ash Step Filter

0%T (ADC value; all scans = 54
 100%T (avg ADC value) = 4095
 full ADC-T Range = 4041

meter readings (0%T):	<u>8</u>	<u>10</u>	<u>14</u>	<u>24</u>	<u>39</u>	<u>60.5</u>
peak ADC-T values:	367	466	651	1019	1632	2484
	359	463	650	1023	1649	2574
	364	460	655	1012	1628	2516
	364	466	659	1021	1638	2514
average ADC - T	364	464	654	1019	1637	2522
transmittance	310	410	600	965	1583	2468
% T (from ADC)	7.7	10.1	14.8	23.9	39.2	61.1

Spex Industries 50% T filter # 9022

0%T (ADC value) = 54

100%T (avg) = 4089

ADC - T range = 4035

meter reading = 48% T

peak ADC-T values:	2055
	2061
	2067
	2056

average ADC-T = 2060

transmittance = 2006

% T (from ADC) = 49.7

Neutral Density Filters from Ealing Optics Corp. (South Natick, MA)

0%T (ADC value) = 54

100%T (avg) = 4092

ADC - T range = 4038

Filter number:	<u>ND 0.5</u>	<u>ND 0.3</u>	<u>ND 0.1</u>
Nominal Transmittance:	.316	.500	.794
Densitometer			
meter readings (%T)	31.5	57.5	86.0
peak ADC-T values:	1263	2473	3528
	1246	2404	3597
	1253	2396	3592
average ADC-T:	1254	2424	3572
transmittance:	1200	2370	3518
% T (from ADC)	29.7	58.7	87.1

3.3 PEAK PROGRAM VERIFICATION

Tables 3-1 and 3-2 present the concentration calculation of two isotopes, Sr-88 and Sm-151, using the respective peak heights read on the photodensitometer (photoplate #H1069). The tables also compare the results of using the PEAK program to perform the calculation (on the PDP11 computer) with the results of hand calculation using the following equation:

Equation for concentration of isotope

$$\text{Isotope concentration (ppm)} = \frac{\text{isotope PH}}{\text{standard}} \times \frac{\mu\text{g standard}}{\text{g sample}} \times \frac{\text{atomic wt isotope}}{\text{atomic wt standard}} \times \frac{\text{RSF isotope}}{\text{RSF standard}}$$

where PH = peak height on photodensitometer
RSF = relative sensitivity factor

The concentration calculations yield the same results irrespective of the mode of calculation.

Table 3-1 Verification of PEAK Program using Sr-88

10 nC exposure; plate #H1069

	Sr-88	peak height = 876.813
(standard)	Nd-143	peak height = 1117.216
	Nd-143	concentration = 926.6 $\mu\text{g/g}$
		RSF Sr = 0.3 (from sensitivity tables)
		RSF Nd = 0.9 (from sensitivity tables)
		Concentration Sr-88 = 149.172 (hand calculation)
		= 149.172 (from PEAK program calculation)
		difference = 0

Table 3-2 Verification of PEAK Program using Sm-151

10 nC exposure; plate #H1068

Sm-151	peak height = 6.924
standard Nd-143	peak height = 1179.919
Nd-143	concentration = 926.6 $\mu\text{g/g}$
	RSF Sm = 1.2
	RSF Nd = 0.9
	Concentration Sm-151 = 7.656 (hand calculation)
	= 7.655 (from PEAK program calculation)
	difference = .001

4. VALIDATION OF THE COMPLETE SOFTWARE PACKAGE

A natural erbium standard was analyzed by SSMS. Using a photodensitometer, all of the isotopic lines of erbium were scanned for the four exposures that were made on the photoplate #17005. EMLCAL was used to obtain emulsion calibration constants A1 and A2 FOR EMULSION #254 (see Appendix 5.2 for the computer print-out). These constants were then used in the PLATE program for calculating ion intensities of the isotopes. Appendix 5.3 displays a copy of the computer print-out from the PEAK program showing the calculated and averaged concentrations. An average concentration of each isotope was calculated (from both the peak and the area average results) and normalized to 100%:

Mass/charge	Peak height	Area	Average	Normalized to 100%	Literature	% Deviation
162	0.824	1.085	0.954	.139	.136	2.2
164	9.770	10.426	10.098	1.469	1.56	5.8
166	235.247	213.595	224.421	32.638	33.41	2.3
167	161.390	157.422	160.406	23.328	22.94	1.7
168	197.249	186.199	191.724	27.883	27.07	3.0
170(reference)	100.000	100.000	100.000	14.543	14.88	2.3

A comparison of the results to the accepted isotopic percent abundances shows a difference ranging from 1.7% (for Er-167) to 5.8% (for Er-164).

5. APPENDIX

5.1 COMPARATIVE COMPUTER PRINT-OUTS FROM EMUL AND EMLCAL PROGRAMS FOR THE CALIBRATION OF EMULSION #16 (PLATE #6753R)Using EMUL (PDP8):

PLATE PARAMETERS

A1 = 0.73720
 A2 = 0.11817
 RA = 0.68660

	ER166	ER167	*T(CALC)
	8.54	12.94	11.95
	10.64	14.44	14.82
	18.74	25.84	25.20
	67.01	65.14	65.06
	40.54	59.94	69.04
	70.24	77.04	76.58
	85.94	89.24	89.32
	89.74	91.54	92.27
	86.84	89.34	89.25
	18.74	23.04	25.20
	17.94	23.14	24.22
	<6.14	57.44	54.83
	85.74	88.94	89.17
	83.44	87.34	87.36
	86.24	89.34	89.56

GOODNESS OF FIT = 1.864130

Using EMLCAL (PDP11):

*T(ER-166)	*T(ER-167)
16.71	20.90
18.22	22.77
27.60	34.49
58.00	64.29
52.66	59.87
67.62	72.40
80.23	81.72
29.68	38.97
28.73	37.37
56.54	62.84
78.06	80.59
76.19	78.24
79.73	80.41
75.96	78.15
73.43	76.91

EMULSION NUMBER: 16

A1 = 0.772607

A2 = 0.109454

5.2 SAMPLE COMPUTER PRINT-OUT FROM EMLCAL PROGRAM

(plate #17005)

%T(ER-166)	%T(ER-167)
9.66	10.31
12.44	13.33
19.68	23.14
36.76	43.53
56.89	63.50
73.37	76.36
14.36	16.25
23.40	27.90
42.85	50.74
62.35	67.05
74.50	76.92
25.44	30.88
44.41	50.24
63.12	66.84
10.43	10.87
13.59	15.60
22.37	26.86
37.44	44.86
58.27	64.01
75.89	78.96
82.59	83.33
13.48	16.08
26.80	32.51
45.69	53.31
64.95	70.01
77.93	80.59
26.39	31.26
47.75	54.26
67.61	71.51

EMULSION NUMBER: 254

A1 = 0.747133

A2 = 0.220059

16-JAN-88

SSMS ANALYSIS

PLATE: 17005

ER

SPIKE CONCENTRATION =
ABUNDANCE FILE: ABISO

100.0

Emulsion: 254

UNITS: PPM (MICROGRAMS/___)

PEAK

		Standard:		ER 170	ER 170	ER 170	ER170
AVERAGE		Exposure:		10.000	3.000	1.000	0.300
		RSF					
0.824	ER	162	1.0	0.824	-0.581	-	-
9.770	ER	164	1.0	12.321	9.482	7.505	-
235.247	ER	166	1.0	-183.843	-217.342	217.814	252.680
161.390	ER	167	1.0	-152.628	-151.584	158.307	164.474
187.248	ER	168	1.0	-147.782	-176.399	187.521	206.877
100.000	ER	170	1.0	-100.000	-100.000	100.000	100.000

AREA

		Standard:		ER 170	ER 170	ER 170	ER170
AVERAGE		Exposure:		10.000	3.000	1.000	0.300
		RSF					
1.085	ER	162	1.0	1.085	-0.821	-	-
10.426	ER	164	1.0	13.160	10.415	7.705	-
213.595	ER	166	1.0	-186.046	-206.689	206.955	220.236
157.422	ER	167	1.0	-154.577	-149.352	155.029	159.815
186.199	ER	168	1.0	-154.427	-175.298	182.390	190.008
100.000	ER	170	1.0	-100.000	-100.000	100.000	100.000

NOTE: Minus "flags" indicate values <5% or >95% transmission. These values are not averaged.

5.3 SAMPLE COMPUTER PRINT-OUT FROM PEAK PROGRAM

5.4 DEFINITION OF LABELS, SYMBOLS, AND VARIABLES

5.4.1 Program EMLCAL

- BK# where # is 166 or 167; ADC value ("raw transmittance") of the background at this ER line
- IC the particular point (of the 128 points) where the cursor lies
- IER# where # is 166 or 167; an array containing raw data from ADC (128 points taken and stored per mass line; each point has been averaged over 256 samplings)
- ITT variable that temporarily stores the value of any character struck on the keyboard during a call to subroutine TTOFF.
- IZ ADC value for 0% transmittance (integer form)
- M ADC value for 100% transmittance (integer form)
- MN# where # is 166 or 167; ADC value of the peak (ie. the most intense point)--uncorrected for background
- N the number of Er166-Er167 line pairs scanned
- NEMUL Emulsion number
- OD# where # is 166 or 167; optical density of the peak calculated from the corresponding relative transmittance (TR) value
- PK# where # is 166 or 167; raw transmittance of the peak, calculated by subtracting the ADC value for 0%T (dark current) from the ADC value of the peak (MN)
- PX a variable for input in a READ statement; may be S for stop (finished scanning lines), R for repeat the scan; also used to cause the computer to pause in program execution (until the RETURN key is struck for commencing the scan)
- PY a variable for input in a READ statement; actually used to cause the computer to pause in program execution (until the RETURN key is struck for commencing the scan)
- RIZ ADC value for 0% transmittance (real number form)
- RM ADC value for 100% transmittance (real number form)

SCALE factor that converts the transmittance of the peak to a relative 100 unit scale (ie. percent transmittance)

TR# Relative Transmittance; percent transmittance (%T) of the peak, calculated by multiplying the corresponding ADC value (PK) by SCALE

V# where # is 167 or 168; background correction for Er-166 and Er-167 lines; the slope of the line that passes through the point representing the averages of the first 10 points of the line scan and the average intensity of the last ten points

5.4.2 Program PLATE

Al&A2 coefficients of the quadratic equation which plots the emulsion calibration curve relating to the optical density with the ion exposure

ADCTBL analog-to-digital converter table; an array of 30 ADC (raw transmittance) values that correspond to particular percent transmittance (%T) values; $\%T = (ADC - IZ)/M - IZ$ where (M - IZ) is the full range of ADC values; therefore, ADC (of, for instance, a peak) = (%T)(M - IZ) + IZ

ALPHA a function that checks a character to be A through Z or blank (and returns 'True' if either of these conditions is true)

AREA an array containing the areas under the peaks of all the lines scanned; "area under the peak" is the sum of all the background-corrected intensities of the 108 points of a complete scan of a particular mass line; found in the file FILSPC and used in program PEAK

BELL a variable associated by a data statement to device #7 which is an audible tone; used as a warning signal

BI an array of background intensities of the points of a mass line

BK background intensity at the point of highest peak intensity

CHG an array containing the charges of the ions whose isotopic lines were scanned; stored in the file FILSPC and used in program PEAK

- D optical density; the log of the ratio of the intensity of a beam of light passing through air or a clear portion of the plate (the incident light, I_i) to the intensity of the same beam after passing through an exposed portion of the plate (the transmitted light, I_t); $D = \log (I_i/I_t)$
- E ion density
- ELE an array containing the element symbols of the isotopic lines scanned; stored in the file FILSPC and used in program PEAK
- EXP exposure; the ionic exposure (in nanocoulombs) of a particular series of lines on the photographic plate; this is for cataloging purposes only and is not used in calculation.
- FILSPC name of data file containing the plate number and all the data acquired for a particular sample
- IBKGND background intensity (ADC value); appropriates the value at IC if "B" is chosen
- IC the cursor index; the particular point (out of 128 pts.) where the cursor lies
- ICSI a system subroutine that calls the RT-11 system Command String Interpreter in special mode to parse a command string, decode file specifications and options, and return file descriptors and options to the program
- IDEN an array that stores the 128 points (ADC values that are proportional to the densitometer photocell current) that are read per mass line
- IFREEC a system subroutine that frees and returns the specified channel to the available pool of channels for the FORTRAN I/O system
- IGETC a system subroutine that obtains a channel for use; it allocates a channel to be used by a system routine and marks it in use so that the FORTRAN I/O system will not access it
- ILED an array that stores the 128 points read per mass line (and found in IDEN) in binary format to be used by an LED display
- INIT a variable which enables operator to avoid calling EMUL if the program is re-entered

IPEAK peak intensity (ADC value); the uncorrected transmittance of the particular line on the photoplate; the actual corrected transmittance can be found by subtracting the 0%T value from IPEAK; IPEAK assumes the value at IC if "P" is chosen

ITT variable that holds a character from keyboard input during a call to TTOFF subroutine

ITYPE type of data file reserved to indicate data format; may be used in future changes of the program

IZ ADC value for 0% transmission

L a particular line that was scanned in an exposure of lines; the final L is the total number of lines scanned (for a particular exposure)

LOOKUP a system subroutine that associates a specified channel with a device and/or file for the purpose of performing I/O operations

M ADC value for 100% transmission

M1 low mass identifier in MIDENT

MASS an array containing the mass numbers of the particular isotopes scanned; found in the file FILSPC

MN ADC value ("raw transmittance") of the peak (peak height) uncorrected for background

MO high mass identifier in MIDENT

NEMUL emulsion number

NEXPL number of exposures left to scan

NX21 the (next) record number to be read in a read statement; (the "associated variable" of a file)

PEAK an array containing the maximum ion intensity values of each of the scanned lines (PK) and used in program PEAK

PI an array containing the ion intensities of each point in a particular mass scan (before background correction)

PK ion intensity of peak (peak height) after background correction

- PURGE a system subroutine that deactivates (clears out) a channel for reuse and prevents entered files from becoming permanent directory entries
- R ratio of natural abundance of Er-167 : Er-166 (0.68662)
- RCTRL0 a system subroutine that makes sure that the console terminal is able to print by overriding any previously switched CTRL/O (which, when typed, inhibits the output from printing until reset)
- SAMP sample identification (input from keyboard)
- SPEED speed at which the plate is moved (ie. the mass line is scanned) in mm/min
- STRING a variable for optional input (such as changing the plate speed) in a READ statement
- T transmittance of transparency; the ratio of the intensity of a beam of light after passing through an exposed portion of the photoplate (the transmitted light) to that of the incident light (ie. the intensity of the same beam after passing through air or a clear portion of the photoplate); I_t/I_i
- V the slope of the line that passes through the point representing the average intensity of the first 10 points of the mass line and the average intensity of the last 10 points; used in background correction

5.4.3 Program PEAK

- AB a library data file containing isotopic relative abundances (as integer values) of the naturally occurring elements
- AB8 a data file containing isotopic relative abundances (as real numbers) of the naturally occurring elements
- ABUND relative abundance of a particular isotope, read from data file AB
- ANS answer to a question posed by the program; eg. "Do you want peak height data, area under the curve, or both?"
- AREA area under the peak that traces the ion intensity scan for each mass line (from PLATE)

BK a (bookkeep) data file containing element symbols, record numbers, and number of isotopes for each element (all as integer values)

BK8 the Bookkeep file as real number values

CHG an array containing the ionic charges of the isotopic lines scanned in PLATE (stored in FILE)

CSPK concentration of the internal standard (spike) in ppm

ELE an array containing element symbols of the isotopic lines scanned in PLATE (stored in FILE)

EXMAS exact mass of particular isotope, read from data file AB; (a real number)

EXP exposure; the ionic exposure (in nanocoulombs) of a particular series of lines on the photographic plate scanned in PLATE

FILE a data file, named (same name as the plate number) and set up in the PLATE program; contains such data as EXP, NL, ELE, CHG, MASS, PEAK, AREA

FOUND an array that records all the isotopes (scanned in PLATE) that were not found in the BK data file

IREC elemental record number, read from data file BK

ISYM array of element symbols, read from data file BK

ITYPE type of data file, indicating data format

MASS an array containing mass numbers of the isotopes whose lines were scanned in PLATE (stored in FILE)

MCF a modification in the multiple charge factor of an isotope whose line was scanned

MCFAC multiple charge factor for modifying the isotope relative sensitivity factors in the case of multiply charged ions

MCHG a modification in the ionic charge of an isotope whose line was scanned

MELE a table for the element name(s) (maximum of six) whose parameter(s) have been modified

MIN a variable used to determine the minimum MTEST value for ordering the lines of a particular element according to isotopic mass and charge

MSENS a modification in the relative sensitivity factor (RSF) of an element whose line was scanned

MTEST a variable (mass added to the product of the ionic charge and 1000) used in sorting the lines scanned (of a particular element) and in ordering them according to isotopic mass and charge

NE the number of exposures that were scanned (and data stored) in PLATE

NEMUL the number of the emulsion of the plate scanned in PLATE

NIST the number of isotopes for a particular element, read from data file BK

NL the number of lines scanned in each exposure in PLATE

NXAB the (next) record number to be read; (made equivalent to the current IREC)

NXBK the (next) record number to be read in a read statement

PEAK an array containing the maximum ion intensity values (on a relative scale, where a T of 0.5 = intensity of 100) of each of the lines that were scanned in PLATE

SAMP sample information (input from keyboard in PLATE)

SENS relative sensitivity factor for a particular element, read from data file SN

SFLAG a flag on the program output to indicate a modified sensitivity ("s") or a modified ionic charge ("c") was used

SN a data file containing relative sensitivity factors as integer values

SN8 the RSF data file containing real number values

SPKFAC spike factor; used in ratioing values of a particular element of interest to those of the internal standard (spike)

TFLAG a flag ("?") on the program output to indicate that a mass was not found in a search of AB data file; (ABUND assigned = 1)

5.5 USER INSTRUCTIONS

5.5.1 EMLCAL Instructions

- 1) Type R EMLCAL. The computer will ask for "EMULSION number:"; type in the emulsion identification number (up to 6 digits).
- 2) The computer will ask for "0%:" (transmittance). Cover the slit and press return.
- 3) The computer will ask for "100%:" (transmittance). Remove the plate from the light path or allow the light to pass through a clear part of the plate and adjust the amplifier (span) to give 100 microamps on the output meter. Press return.
- 4) The computer will cue ("ER-166") for a scan over the erbium-166 isotopic line. Press the return key just before the mass line crosses the slit; a trace of the line intensity will appear on the oscilloscope. Pressing the space bar will accept the data. (If the scan was unsuitable, then press the R key and the computer will prompt you to repeat the scan, ":")
- 5) The computer will cue "ER-167" (for a scan over the erbium-167 isotopic line).
- 6) Continue scanning pairs of erbium 166 and 167 lines, trying to get data from very lightly exposed pairs and very heavily exposed pairs as well as exposures between the extremes. You may also scan lines due to doubly and triply charged ions.
- 7) When finished, type an S at the prompt for the erbium-166 scan and the computer will calculate and store the values for A1 and A2, the constants of the quadratic calibration equation.

5.5.2 PLATE Instructions

- 1) Type R PLATE. The computer will ask for "EMULSION number:"; type in the emulsion identification number (up to 6 digits). The computer will display the A1 and A2 values if it has them; if not, it will prompt you to enter the appropriate values for the emulsion calibration constants.
- 2) The computer will ask for "0%:" (transmittance). Cover the slit and press return.
- 3) The computer will ask for "100%:" (transmittance). Remove the plate from the light path or allow the light to pass through a clear part of the plate and adjust the amplifier (span) to give 100 microamps on the output meter. Press return.

- 4) The computer will prompt "PLATE (5 char's)"; enter the plate identification number and press return. If the computer already has data stored for this plate number, it will ask if you want to add to it; a Y (yes) response will result in the computer displaying how many exposures remain that can be scanned. (Note: a maximum of six exposures may be scanned for a given plate number.)
- 5) The computer will ask for "Sample ID:"; type a brief (up to 32 characters) description of the sample.
- 6) The computer will ask for "EXP:", the exposure in nanocoulombs. Enter the proper exposure number. (This number is only for labeling purposes for the print-out and is not used for calculations.)
- 7) You are now ready to start scanning the mass lines of interest. The first line read must be the line you want to use as your standard. The computer will prompt "ELE, CHG, MASS"; you can only use six spaces for your response. The element symbol must be typed in the first two spaces (right justified if it is a single letter); the third space is left blank for singly charged ions. Type a 2 for doubly charged ions and a 3 for triply charged ions. The next three spaces are for the isotopic mass (right justified).
- examples: NA 23
 U 238
 B 11
 CL2 35
 Be 9
- (If you wish to use a plate speed different from 15 mm/min, then enter the new speed at this prompt, instead of the element symbol.)
- 8) Start scanning across the line to be measured; press the return key just before the mass line crosses the slit. A trace of the line intensity will appear on the oscilloscope. Pressing the space bar will accept the data. (If the scan was unsuitable, repeat the scan, pressing the R key instead of the return key just before the mass line crosses the slit. Again, pressing the space bar will accept the data.) If you wish only the peak height (maximum intensity) to be used in the concentration calculations, then, after moving the oscilloscope cursor to the top of the peak, press the P key instead of the space bar. Also, if a doublet (two unresolved lines) were scanned, indicate with the oscilloscope cursor the appropriate peak and press the P key rather than the space bar.
- 9) The computer will again prompt "ELE, CHG, MASS". You may scan up to 100 lines for this exposure. (The order of the consecutive scans is not important.) Typing a -R at the "ELE, CHG, MASS" prompt will erase the line previously scanned. Typing a -1 at the prompt indicates that you are finished scanning lines for the given exposure. (Typing "XM" will call the MIDENT subroutine to provide an accurate mass calibration.)

10) Repeat steps #6 through 9. When the computer asks for a new exposure and you are finished, type -1 and the program will end. All the data will be stored and labeled with the plate number.

5.5.3 PEAK Instructions

1) Type R PEAK. The computer will ask for "PLATE="; enter the plate identification number.

2) The computer will prompt "Spike (mmg/g)="; enter the concentration of the spike relative to the total solution that was analyzed.

3) The computer will display the sample description, the spike concentration, the emulsion number, and any previous requests for alternative abundance and sensitivity tables. It will then ask if you want any changes made. If you answer "Y", then the computer will give you five options for possible changes: Sample information, spike concentration, abundance table used, sensitivity table used, or a modification to the sensitivity of particular elements. For example, if you want an isotopic, rather than an elemental analysis, choose option "3" (abundance tables) and change the abundance table used to "ABISO".

4) The computer then asks whether you want isotopic concentrations calculated from peak height data, area under the curve, or both. Enter P, or A, or B and the program results will be printed.

5.6 EXAMPLE OF THE DATA FILES

5.6.1 AB Abundance Table

1	REC#	AB EXMAS	AB						
	1	1.00780	0.99985	50	46.95100	0.07290	100	88.90500	1.00000
	2	2.01410	0.00015	51	47.94700	0.73980	101	89.90400	0.51460
	3	3.01600	0.00000	52	48.94700	0.05510	102	90.90500	0.11220
	4	4.00260	0.99999	53	49.94400	0.05340	103	91.90400	0.17110
	5	6.01510	0.07420	54	49.94700	0.00240	104	93.90600	0.17400
	6	7.01600	0.92580	55	50.94400	0.99760	105	95.90800	0.02800
	7	9.01220	1.00000	56	49.94600	0.04310	106	92.90600	1.00000
	8	10.01200	0.19610	57	51.94000	0.83760	107	91.90600	0.15840
	9	11.00900	0.80390	58	52.94000	0.09550	108	93.90400	0.09040
	10	12.00000	0.98890	59	53.93800	0.02380	109	94.90500	0.15720
	11	13.00300	0.01110	60	54.93800	1.00000	110	95.90400	0.16530
	12	14.00300	0.99630	61	53.93900	0.05820	111	96.90500	0.09460
	13	15.00000	0.00370	62	55.93400	0.91660	112	97.90500	0.23780
	14	15.99400	0.99759	63	56.93500	0.02190	113	99.90700	0.09630
	15	16.99900	0.00037	64	57.93300	0.00330	114	98.90600	1.00000
	16	17.99900	0.00204	65	58.93300	0.99999	115	95.90700	0.05510
	17	18.99800	1.00000	66	57.93500	0.67760	116	97.90500	0.01870
	18	19.99200	0.90920	67	59.93000	0.26230	117	98.90600	0.12720
	19	20.99300	0.00257	68	60.93100	0.01190	118	99.90300	0.12620
	20	21.99100	0.08820	69	61.92800	0.03660	119	100.90000	0.17070
	21	22.98900	1.00000	70	63.92800	0.01080	120	101.90000	0.31610
	22	23.98500	0.78700	71	62.92900	0.69090	121	103.90000	0.18580
	23	24.98500	0.10130	72	64.92700	0.30910	122	102.90000	1.00000
	24	25.98200	0.11170	73	63.92900	0.48890	123	101.90000	0.00960
	25	26.98100	1.00000	74	65.92600	0.27810	124	103.90000	0.10970
	26	27.97600	0.92210	75	66.92700	0.04110	125	104.90000	0.22230
	27	28.97600	0.04700	76	67.92400	0.18570	126	105.90000	0.27330
	28	29.97300	0.03090	77	69.92500	0.00620	127	107.90000	0.26710
	29	30.97300	1.00000	78	68.92500	0.60400	128	109.90000	0.11810
	30	31.97200	0.95000	79	70.92400	0.39600	129	106.90000	0.51350
	31	32.97100	0.00760	80	69.92400	0.20520	130	108.90000	0.48650
	32	33.96700	0.04220	81	71.92100	0.27430	131	105.90000	0.01215
	33	35.96700	0.00014	82	72.92300	0.07760	132	107.90000	0.00875
	34	34.96800	0.75529	83	73.92100	0.36540	133	109.90000	0.12390
	35	36.96500	0.24471	84	75.92100	0.07760	134	110.90000	0.12750
	36	35.96700	0.00337	85	74.92100	1.00000	135	111.90000	0.24070
	37	37.96200	0.00063	86	73.92200	0.00870	136	112.90000	0.12260
	38	39.96200	0.99600	87	75.91900	0.09020	137	113.90000	0.28860
	39	38.96300	0.93100	88	76.91900	0.07580	138	115.90000	0.07580
	40	39.96400	0.00012	89	77.91700	0.23520	139	112.90000	0.04280
	41	40.96100	0.06880	90	79.91600	0.49820	140	114.90000	0.95720
	42	39.96200	0.96970	91	81.91600	0.09190	141	111.90000	0.00960
	43	41.95800	0.00640	92	78.91800	0.50537	142	113.90000	0.00660
	44	42.95800	0.00146	93	80.91600	0.49463	143	114.90000	0.00350
	45	43.95500	0.02060	94	84.91100	0.72150	144	115.90000	0.14300
	46	45.95300	0.00003	95	86.90900	0.27850	145	116.90000	0.07610
	47	47.95200	0.00185	96	83.91300	0.00560	146	117.90000	0.24030
	48	44.95500	1.00000	97	85.90900	0.09860	147	118.90000	0.08580
	49	45.95200	0.08000	98	86.90800	0.07020	148	119.90000	0.32850
				99	87.90500	0.82560	149	121.90000	0.04720

150	123.90000	0.05940	215	161.92000	0.25530	270	200.97000	0.13220
151	120.90000	0.57250	216	162.92000	0.24970	271	201.97000	0.29800
152	122.90000	0.42750	217	163.92000	0.28180	272	203.97000	0.06850
153	119.90000	0.00089	218	164.92999	1.00000	273	202.97000	0.29500
154	121.90000	0.02460	219	161.92000	0.00136	274	204.97000	0.70500
155	122.90000	0.00870	220	163.92000	0.01560	275	203.97000	0.01480
156	123.90000	0.04610	221	165.92999	0.33410	276	205.97000	0.23600
157	124.90000	0.06990	222	166.92999	0.22940	277	206.97000	0.22600
158	125.90000	0.18710	223	167.92999	0.27070	278	207.97000	0.52300
159	127.90000	0.31790	224	169.92999	0.14880	279	208.98000	1.00000
160	129.89999	0.34480	225	168.92999	1.00000	280	232.03000	1.00000
161	126.90000	1.00000	226	167.92999	0.00135	281	233.03000	1.00000
162	123.90000	0.00096	227	169.92999	0.03030	282	234.03999	0.00005
163	125.90000	0.00090	228	170.92999	0.14310	283	235.03999	0.00720
164	127.90000	0.01919	229	171.92999	0.21820	284	236.03999	1.00000
165	128.89999	0.26440	230	172.92999	0.16130	285	238.05000	0.99274
166	129.89999	0.04080	231	173.92999	0.31840	286	237.03999	1.00000
167	130.89999	0.21180	232	175.94000	0.12730	287	238.03999	1.00000
168	131.89999	0.26890	233	174.94000	0.97410	288	239.05000	1.00000
169	133.89999	0.10440	234	175.94000	0.02590	289	240.05000	1.00000
170	135.89999	0.08870	235	173.94000	0.00180	290	241.05000	1.00000
171	132.89999	1.00000	236	175.94000	0.05200	291	242.05000	1.00000
172	129.89999	0.00101	237	176.94000	0.18500	292	244.06000	1.00000
173	131.89999	0.00097	238	177.94000	0.27140	293	241.05000	1.00000
174	133.89999	0.02420	239	178.94000	0.13750	294	243.06000	1.00000
175	134.89999	0.06590	240	179.94000	0.35240	295	242.05000	1.00000
176	135.89999	0.07810	241	179.94000	0.00012	296	243.06000	1.00000
177	136.89999	0.11320	242	180.94000	0.99988	297	244.06000	1.00000
178	137.89999	0.71660	243	179.94000	0.00135	298	245.06000	1.00000
179	137.89999	0.00089	244	181.94000	0.26410	299	246.06000	1.00000
180	138.89999	0.99911	245	182.95000	0.14400	300	247.07001	1.00000
181	135.89999	0.00193	246	183.95000	0.30640	301	248.07001	1.00000
182	137.89999	0.00250	247	185.95000	0.28410	302	250.07001	1.00000
183	139.89999	0.88480	248	184.95000	0.37070	303	249.07001	1.00000
184	141.89999	0.11070	249	186.95000	0.62930	304	248.07001	1.00000
185	140.89999	1.00000	250	183.95000	0.00018	305	249.07001	1.00000
186	141.89999	0.27110	251	185.95000	0.01590	306	250.07001	1.00000
187	142.89999	0.12170	252	186.95000	0.01640	307	251.08000	1.00000
188	143.89999	0.23850	253	187.95000	0.13300	308	252.07001	1.00000
189	144.91000	0.08300	254	188.95000	0.16100	309	253.08000	1.00000
190	145.91000	0.17220	255	189.95000	0.26400	310	254.08000	1.00000
191	147.91000	0.05730	256	191.96001	0.41000	311	233.03000	1.00000
192	149.92000	0.05620	257	190.96001	0.37300	312	234.03999	1.00000
193	146.90999	1.00000	258	192.96001	0.62700	313	235.03999	1.00000
194	143.91000	0.03090	259	189.96001	0.00013	314	236.03999	1.00000
195	146.91000	0.14970	260	191.96001	0.00780	315	238.05000	1.00000
196	147.91000	0.11240	261	193.96001	0.32900			
197	148.91000	0.13830	262	194.96001	0.33800			
198	149.91000	0.07440	263	195.96001	0.25300			
199	151.91000	0.26720	264	197.96001	0.07210			
200	153.92000	0.22710	265	196.96001	1.00000			
201	150.91000	0.47820	266	195.96001	0.00146			
202	152.92000	0.52180	267	197.96001	0.10020			
203	151.91000	0.00200	268	198.96001	0.16840			
204	153.92000	0.02150	269	199.96001	0.23130			
205	154.92000	0.14730						
206	155.92000	0.20470						
207	156.92000	0.15680						
208	157.92000	0.24870						
209	159.92000	0.21900						
210	158.92000	1.00000						
211	155.92000	0.00052						
212	157.92000	0.00090						
213	159.92000	0.02294						
214	160.92000	0.18880						

5.6.2 SENS Relative Sensitivity Table

1 REC#	SENS SENS				
1	1.00000	40	1.00000	80	1.00000
2	1.00000	41	0.60000	81	0.50000
3	0.10000	42	0.60000	82	0.50000
4	0.30000	43	1.00000	83	2.70000
5	0.70000	44	0.50000	84	2.30000
6	1.00000	45	1.00000	85	2.30000
7	1.00000	46	0.50000	86	2.30000
8	1.00000	47	1.10000	87	1.60000
9	1.00000	48	0.50000	88	2.30000
10	1.00000	49	0.70000	89	1.90000
11	0.10000	50	0.50000	90	2.10000
12	0.20000	51	1.90000	91	2.30000
13	0.30000	52	1.00000	92	1.00000
14	0.30000	53	1.00000	93	1.00000
15	0.30000	54	0.10000	94	1.00000
16	0.50000	55	0.60000	95	1.00000
17	0.50000	56	0.50000	96	1.00000
18	1.00000	57	0.50000	97	1.00000
19	0.10000	58	0.50000	98	1.00000
20	0.20000	59	0.90000	99	1.00000
21	1.00000	60	1.00000	100	1.00000
22	0.30000	61	1.20000		
23	0.40000	62	1.50000		
24	0.50000	63	0.50000		
25	0.40000	64	1.00000		
26	0.50000	65	1.00000		
27	0.50000	66	1.00000		
28	0.50000	67	1.00000		
29	0.50000	68	1.00000		
30	0.30000	69	1.00000		
31	0.50000	70	1.00000		
32	0.50000	71	3.00000		
33	0.50000	72	3.00000		
34	0.90000	73	3.00000		
35	1.00000	74	3.00000		
36	0.10000	75	3.00000		
37	0.30000	76	3.00000		
38	0.50000	77	3.00000		
39	0.30000	78	3.00000		
		79	1.00000		

INTERNAL DISTRIBUTION

1. J. A. Carter
2. R. N. Ceo
3. W. H. Christie
4. R. Hydzik
5. L. Landau
6. W. D. Shults
7. D. H. Smith
- 8-10. D. O. Vick
11. R. J. Warmack
12. E. H. Waters
13. Central Research Library
14. Document Reference Section
15. ORNL Patent Office
- 16-17. Lab Records Department
18. Lab Records Department-RC
19. Technical Library Y-12 DRS

EXTERNAL DISTRIBUTION

20. Office of Asst. Mgr., Energy Research and Development, DOE
Oak Ridge Operations, Oak Ridge, TN 37831
- 21-30. Office of Scientific and Technical Information, P.O. Box 62,
Oak Ridge, TN 37831