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**ESCADT: A FORTRAN Code for Computing the
Positions and Areas of X-Ray Photoelectron
Spectral Peaks**

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ESCADT: A FORTRAN CODE FOR COMPUTING THE POSITIONS AND AREAS OF X-RAY PHOTOELECTRON SPECTRAL PEAKS

by

Lawrence E. Cox

ABSTRACT

Program ESCADT uses least-squares-derived convoluting numbers to smooth and differentiate x-ray photoelectron spectra. Peak maxima are located by finding zero crossings of the first derivative and refined using a cubic polynomial fitting procedure. Background points are located using the product of the absolute value of the first derivative and the smoothed ordinate value. Peak areas, using both linear and scattered electron backgrounds, are computed. Spectra are corrected for changes in instrument sensitivity and energy calibration with gold-standard data retrieved from a disk file. Five determinations of the gold 4f peak positions yielded standard deviations of 0.011 and 0.031 eV for the $4f_{7/2}$ and $4f_{5/2}$ peaks, respectively. The relative standard deviation for the computed areas was 0.85%.

I. INTRODUCTION

Since its inception more than a decade ago, electron spectroscopy for chemical analysis (ESCA) has provided numerous insights into the nature of chemical bonding. Its ability to measure small shifts in core-level binding energies coupled with its extreme surface sensitivity make ESCA a uniquely powerful tool for the qualitative and quantitative characterization of the outermost, 5-20 atomic layers of almost any solid (or gaseous) material.

Although the great promise of ESCA for the elucidation of molecular charge distribution and for quantitative analyses was recognized by Siegbahn et al.¹ early in the development of the technique, subsequent investigators have encountered a variety of difficulties that seem to leave open to question the technique's reliability as a routine analytical tool. Among the earliest studies of the analytical applicability of ESCA was the measurement of peak intensities (height and area) of a variety of elements

in compounds containing sodium, potassium, or fluorine.² By comparing the intensities of other element lines to those of the reference element, a set of sensitivity factors of standard intensities was obtained. It was found, however, that such intensity ratios (for example, Na:F) varied considerably from compound to compound, presumably because of extrinsic or intrinsic electron energy-loss processes that are characteristic of a particular chemical environment. Although some progress for understanding these processes is being made, the theory is not yet sufficiently well developed as to have much predictive value. The accuracy attainable in quantitative analyses by ESCA may well be limited ultimately by intensity variations of this nature.

A more immediate problem in the development of ESCA as an analytical technique arises from the present lack of generally accepted procedures for sample preparation, instrument calibration, and data handling. That binding energy measurements from different laboratories often show disconcerting

discrepancies has been recognized for some time. Perhaps more disturbing is the fact that interlaboratory measurements on the same material often disagree by considerably more than the error quoted by either laboratory. The severity of the calibration problem was graphically illustrated by a recent round-robin experiment in which the participants' measurements of the binding energy difference between the Au $4f_{7/2}$ and Cu $2p_{3/2}$ lines differed by up to 2 eV.³ Several techniques for referencing such measurements have been proposed (adventitious carbon layer, gold decoration, and graphite admixture), but none of them is without shortcomings.

Quantitative analysis using peak areas is plagued by equally insidious problems, primarily because of uncertainties about the nature of the background resulting from inelastically scattered electrons. The spectra of metallic samples are often particularly intractable because small energy losses resulting from valence and conduction band electrons give rise to a base-line shift beneath the peak of interest, and larger energy-loss processes, such as plasmon peaks, produce rather ill-defined structures at lower kinetic energy. Owing to an insufficiently detailed understanding of these processes, the analyst has usually resorted to rather subjective criteria when selecting representative background points. Also, techniques of widely varying sophistication—from planimetry to computer curve fitting—are used for the measurement of peak areas. That alarming variability among reported quantitative measurements exists is not, therefore, unexpected.

Full realization of ESCA's analytical potential must await the formulation of more comprehensive theoretical treatments of photoionization and electron-loss processes in solids. At present, however, the most pressing need is for precisely defined criteria that will allow ESCA users to obtain peak positions and areas in a logical and reproducible manner. Program ESCADT represents some progress toward this end.

II. DESCRIPTION OF THE CODE

A. General Information

Program ESCADT was written to be used in conjunction with the Physical Electronics Industries (PHI) Multiple-Technique Analytical Computer

System (MACS). In its present form, the code processes ESCA data for a single spectral region. In the multiplex mode, MACS allows the acquisition of data for several regions, and if sufficient computer memory is available, ESCADT could be modified easily to process such data. We are currently using a Digital Equipment Corporation (DEC) 11/04 computer with 28k words of memory and a Plessey PM-DD/11B 5-megabyte disk. The computer operating system is DEC's RT-11, version 3. A complete program listing can be found in Appendix A. To facilitate modifying the code for use on other computers, a description of the input parameters is given in Appendix B.

B. Initial Dialogue

Data files created by MACS software are binary and therefore have an RT-11 extension of "OBJ." The response to the initial query "DEVICE AND FILE NAME?" will be "DEV:FILENM.OBJ" where DEV is an RT-11 device name, FILENM is the name previously assigned to the data file, and OBJ indicates a binary file. The computer then reads the specified file consisting of an Acquisition Control Block (ACB) and a digitized spectrum.

The following acquisition parameters are printed: creation date of the file, the number of scans of the designated region (NO. SCANS), the data acquisition time at each point for each scan (T/S, in ms), x-ray source emission current and operating voltage (X-RAY MA and X-RAY KV), analyzer pass energy (PASS ENERGY, in eV), upper binding energy limit of the scan (BINDING ENERGY U.L.), scan range (RANGE EV), scan step size (EV/STEP), number of disk blocks occupied by the file (# DISC BLOCKS), number of data points in the spectrum (# DATA POINTS), and sample identification (SAMPLE ID). See Appendix C for a typical run.

ESCADT provides for both binding energy and intensity calibration of spectra. Calibration information is written into a disk file when a gold-calibration spectrum is processed. If the binding energy of the Au $4f_{7/2}$ peak differs from the accepted value of 83.8 eV, subsequently processed spectra are corrected accordingly. The magnitude of the correction, as well as the date of the calibration run, are printed. Also, at the operators option, the normalized area of the Au 4f peaks may be recorded for later reference. This is usually done immediately

after sputtering the gold-calibration standard and allows correction for any long-term changes in instrument sensitivity. The operator enters "AU CAL2" in the ACB comment field if both binding energy and intensity information is to be recorded on the disk and "AU CAL1" if only binding energy calibration is desired.

The program next requests input of the neutralizer emission current. The value entered is for reference purposes only; it is not used computationally. The spectrometer work function is required for calculating photoelectron kinetic energy; "WORK FUNCTION (EV)" is printed as a prompt, preceding operator input.

C. Location of Peaks

For the location of peak maxima and suitable background points, ESCADT uses polynomial smoothing and differentiation with least-squares-derived convoluting numbers. The theory and application of this method was described by Sterrett⁴ and later by Savitzky and Golay⁵. Briefly, the method obtains smoothed values for the ordinate and the first derivative for any set of x and y values that can be represented reasonably well by a polynomial (2nd degree in this case) over short intervals and in which the x values are equally spaced. We have found that an 11-point quadratic gives good results for spectra digitized at 0.1-eV intervals; however, point spreads of 9 to 21 points can be selected. Particularly noisy spectra may warrant the use of a smoothing interval larger than 11 points; whereas a 9-point spread might be appropriate for digitization intervals larger than 0.1 eV. The smoothing coefficients are stored as an ASCII file on the disk (RK1:SMCOEF.DAT). The values are given in Appendix D.

After generating the smoothed values and first derivatives [SMOTH(1,N) and SMOTH(2,N), respectively], peak maxima are located by examining the latter for zero crossings. That a zero crossing is not a result of noise is established by requiring that the average value of the first derivative exceed a specified threshold for a designated distance on either side of the suspected peak maximum. At the completion of the search, the number of peaks found is compared to the number requested, and the threshold is adjusted iteratively until the specified number of peaks is found. The peaks located will

generally be the most prominent ones in the spectrum. Therefore, to identify smaller spectral features, the number of peaks specified must include all peaks more prominent than those of interest.

D. Peak Widths and Background Points

The most convenient measure of peak width is the full width at half maximum height (FWHM). Accurate estimation of this quantity requires base-line subtraction; however, the separation of the points of maximum and minimum slope on the peak sides provides a reasonably accurate first approximation. These points are located starting at the peak maximum and proceeding down either side. The average of three points is used to further reduce the effects of noise.

The search for background points is begun at a distance equal to twice the peak width on each side of the maximum. Although the criteria for suitable background points are somewhat arbitrary, we have chosen them to correspond as closely as possible to what more traditional methods have used, that is, relatively flat areas and/or minima near the peak. We have found that spectral points at which the product of the smoothed y value and the absolute value of the first derivative is a minimum are generally suitable for delimiting peak areas. The factor 0.5 is added to the derivative so that it will not dominate the product at slopes near zero.

E. Refining Peak Positions

Steinhaus et al.⁶ have shown that accurate peak positions can be obtained by computing the maximum in a least-squares polynomial that is fitted through an appropriate number of points near the estimated peak maximum. This approach has proved reliable for ESCA spectra and is used in ESCADT. A cubic polynomial is fitted through a number of points (NPOLY) equal to half the peak width plus one. NPOLY is restricted, however, such that $7 \leq \text{NPOLY} \leq 15$. The refined peak position is found by differentiating the cubic polynomial, setting the result equal to zero, and solving the resulting quadratic equation. For a cubic polynomial of the form ax^3+bx^2+cx+d , the desired solution is

$$x_{\max} = \frac{-2b - \sqrt{4b^2 - 12ac}}{6a} \quad (1)$$

In rare cases, the cubic coefficient is zero within computer accuracy and Eq. (1) cannot be solved. If this occurs, the program substitutes a quadratic equation for the cubic polynomial. Also, if the average error in the polynomial fit exceeds 5%, a warning diagnostic is printed.

F. Peak Overlap

ESCA spectral peaks frequently consist of two or more partially resolved peaks. Often, it is the area of the composite peak that is of interest because areas computed using a background point between the peaks would give misleading results. The criterion used for peak overlap is that the separation between adjacent peaks is less than 1.5 times the sum of the individual peak widths. If the operator chooses to omit the background point between the peaks, the partially resolved multiplet is then considered as a single peak for integration. However, the positions of both maxima are still printed. The check for overlap starts with the peak at highest binding energy and is continued until all peaks have been considered. Also, a diagnostic is printed if a peak is less than four times the peak width from either end of the spectrum. If, after inspecting a peak, the operator decides that the area cannot be accurately determined, that peak may be omitted from consideration.

G. Base-Line Slope Correction

Spectra obtained with spectrometers possessing a transmission function that is inversely proportional to kinetic energy often show pronounced base-line slopes at low kinetic energies. Because the first derivative is used for establishing background points, such slopes can adversely affect the reliability of peak-area calculations. ESCADT can subtract a linear base line and recalculate the pertinent spectral parameters. The slope of the base line to be subtracted is obtained by averaging the value of the first derivative at all points except those bounded by the background points for each peak. The linear function defined by this slope and the lowest y value in the spectrum are then subtracted from the spectrum. The corrected spectrum is subjected to the entire smoothing and peak-locating routine.

H. Peak Areas

Two methods are used for computing peak areas. The first involves adding all ordinate values above the line connecting the previously determined background points and multiplying the sum by the binding energy step width. The second method⁷ is based on the fact that inelastically scattered photoelectrons are detected at lower kinetic energies than those that are elastically scattered. Therefore, the background amplitude at any point beneath the peak is proportional to the total peak area at higher kinetic energy. ESCADT designates areas computed in this way. "SB" is for an electron scattered background, and "LB" indicates a linear background. The ratio of each peak area to that of the Au 4f peak area (see above) is also printed; these values are designated "PEAK AREA/AU."

I. Analyzer Transmission Function and Escape Depth Correction

As discussed above, the cylindrical mirror analyzer with preretarding electron optics exhibits a transmission function that is inversely proportional to kinetic energy. To compare measured peak-area ratios with theoretical photoionization cross sections, a correction must be applied to the raw data. In addition, the variation in electron inelastic mean free path (IMFP) with kinetic energy (escape depth correction) must be taken into account. Both theory and experiment indicate that the IMFP's are proportional to $KE^{0.7}$. The net effect is that observed peak intensities differ from cross sections by a factor proportional to $KE^{-0.3}$. ESCADT output therefore includes peak heights and areas that have been multiplied by $KE^{0.3}$. These values are designated "AREAS*KINETIC ENERGY**0.3."

III. PERFORMANCE OF THE CODE

Meaningful tests of ESCADT are complicated somewhat by the fact that changing instrument sensitivity and energy calibration may contribute to variations in repetitively determined peak areas or positions. One test of the code's ability to obtain peak positions and areas reproducibly involved processing five 4-min scans of the Au 4f doublet. The

TABLE I

SUCCESSIVE DETERMINATIONS OF THE
Au 4f PEAK POSITIONS AND AREAS

Run	4f _{5/2} Position	4f _{7/2} Position	Area
1	87.46	83.79	33.12
2	87.43	83.77	33.07
3	87.45	83.78	32.90
4	87.44	83.78	33.20
5	87.38	83.76	32.50
<hr/>			
Average	87.43	83.78	32.96

data were acquired after the instrument had been on for about 6 h and was thermally equilibrated. The peak areas and positions computed by ESCADT are shown in Table I.

The standard deviations in the positions of the 5/2 and 7/2 peaks are 0.031 and 0.011, respectively. Moreover, the 5/2 and 7/2 peak positions are highly correlated ($r_{xy} = 0.943$) indicating that the peaks tend to shift in the same direction, presumably because of instrumental drift. The relative standard deviation for five determinations of the peak area was 0.85%.

Although values for elemental photoionization cross sections are available in the literature⁸, they are not as well known as the intensity ratios of the spin-orbit doublets of individual elements. We have therefore chosen the latter to test the code. The ratio of the Cu 2p_{1/2} to 2p_{3/2} peak areas was found to be 0.5022 with a 95% confidence interval (CI) of 0.031. The theoretical ratio is 0.5155. A value of 0.849 ± 0.037 (95% CI) was obtained for the Pb 4f_{5/2} to 4f_{7/2} area ratio; this compares with a theoretical ratio of 0.783. These results and others obtained with ESCADT indicate that precision and accuracy of 2-5% (RSD) should be routinely attainable. At present, the major limitation on accuracy is the unavailability of reliable standard intensities for many elements.

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APPENDIX A

PROGRAM LISTING

LASL Identification No. LP1069

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FORTRAN IV      V02.04      Thu 21-Jun-79 15:21:08      PAGE 001

0001      PROGRAM ESCADT
0002      INTEGER SPECID
0003      INTEGER*4 ITIME
0004      INTEGER*4 IASPEC
0005      REAL*8 CALTST
0006      REAL*8 AUCAL1
0007      REAL*8 AUCAL2
0008      EQUIVALENCE(CALTST,SPECID(1))
0009      EQUIVALENCE(IASPEC,ITEM(1))
0010      DIMENSION ISPEC(1002),IPARM(512),MAX(16),MAXSV(16),NLO(16),NHI(16)
0011      DIMENSION IWIDE(16),NRKG(24),JWIDE(16),IDENT(16),PFOS(16),PMAX(16)
0012      DIMENSION BAKPT(16),RSPEC(510),SMOTH(501,2),B(30,4),SPECID(24)
0013      DIMENSION SDUMP(2),FMAX(14),PCOF(6),RX(15),AREASB(10),AREALB(10)
0014      DIMENSION PKINT(500),FWHM(16,2),PEAKH(16,2),PKBK(16,2)
0015      DIMENSION PKHKE(6),PKBKE(6),ITEM(2)
0016      DATA AUCAL1/'AU CAL1'/
0017      DATA AUCAL2/'AU CAL2'/
0018      DATAY/'Y'/
0019      WRITE(7,1000)
0020      1000  FORMAT('*****')
0021      C      GET DATE AND TIME
0022      CALL IDATE(JMON,JDAY,JYR)
0023      1      WRITE(7,1)JMON,JDAY,JYR
0024      FORMAT('/ DATE ',I2,'-',I2,'-',I2,*)
0025      CALL GTIM(ITIME)
0026      CALL CVTTIM(ITIME,IHRS,IMIN,ISEC,ITCK)
0027      60      WRITE(7,60)IHRS,IMIN,ISEC
0028      FORMAT(1H+, ' TIME ',I2,':',I2,':',I2)
0029      DEFINE FILE 4(10,256,U,NREC)
0030      2      WRITE(7,2)
0031      FORMAT(' DEVICE AND FILE NAME?',3X,*)
0032      CALL ASSIGN(4,TTIN,-1,'OLD')
0033      CALL ASSIGN(3,'RK1:SMCOEF',10)
0034      CALL ASSIGN(2,'RK1:BECL',9)
0035      IF(CALTST.NE.AUCAL1)CALL ASSIGN(1,'RK1:AREACL',10)
0036      C      READ SPECTRUM PARAMETERS FROM DISC FILE
0037      READ(4,1)(IPARM(I),I=1,256)
0038      RATE=IPARM(115)
0039      XBU=FLOAT(IPARM(12))/10.
0040      XBI=FLOAT(IPARM(13))/10.
0041      EPASS=FLOAT(IPARM(98))
0042      NSWEEP=IPARM(8)
0043      NBLK=IPARM(110)
0044      NSTEP=IPARM(112)
0045      BRE=FLOAT(IPARM(113))
0046      VSTEP=FLOAT(IPARM(116))/100.
0047      RANGE=FLOAT(IPARM(114))
0048      NYR=(*37.AND,IPARM(97))+72
0049      NDAY=(*1740.AND,IPARM(97))/32
0050      NMON=(*76000.AND,IPARM(97))/1024
0051      2000  WRITE(7,2000)NMON,NDAY,NYR
0052      FORMAT(' FILE CREATION DATE ',I2,'-',I2,'-',I2)
0053      DAT=IPARM(8)*IPARM(115)
0054      3      WRITE(7,3)
0055      FORMAT(' NO. SCANS      T/S      X-RAY KV      X-RAY MA      PASS ENERGY')
0056      4      WRITE(7,4)NSWEEP,RATE,XBU,XBI,EPASS
0057      FORMAT(3X,I3,9X,F4.0,4X,F6.1,5X,F5.0,6X,F5.0)
0058      5      WRITE(7,5)
0059      FORMAT('/ BINDING ENERGY U. L. RANGE(EV) EV/STEP # DISC BLOCKS
0060      1 #DATA POINTS')
0061      6      WRITE(7,6)BRE,RANGE,VSTEP,NBLK,NSTEP
0062      FORMAT(8X,F5.0,14X,F4.0,7X,F4.2,9X,I2,9X,I5)
0063      C      READ SAMPLE IDENTIFICATION AND CONVERT TO ASCII
0064      KONT=99

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APPENDIX A (cont)

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0062      DO 7 K=1,8
0063      KCNT=KCNT+1
0064 7      IDENT(K)=IPARM(KCNT)
0065      CALL R50ASC(24,IDENT,SPECID)
0066      WRITE(7,9)
0067 9      FORMAT(' SAMPLE ID: ')
0068      WRITE(5,10)(SPECID(I),I=1,12)
0069 10     FORMAT(1H+,12A2)
0070      AUAREA=1.0
0071  C      READ GOLD CALIBRATION DATA FROM DISC FILE
0072      IF(CALTST.EQ.AUCAL1.OR.CALTST.EQ.AUCAL2)GO TO 16
0073      READ(2,11)IMON,IDAY,IYR,AUBE
0074 11     FORMAT(3I2,F9.3)
0075      READ(1,12)KMON,KDAY,KYR,AUAREA
0076 12     FORMAT(3I2,F9.3)
0077      WRITE(7,13)IMON,IDAY,IYR,AUBE
0078 13     FORMAT(' AU 4F 7/2 B. E. OBTAINED ',I2,'-',I2,'-',I2,2X,F6.2,' EV')
0079      AUCORR=AUBE-83.80
0080      WRITE(7,14)-AUCORR
0081 14     FORMAT(' ALL BINDING ENERGIES CORRECTED BY ',F6.2,' EV')
0082  C      CORRECT BINDING ENERGIES FOR INSTRUMENT CALIBRATION ERROR
0083      BBE=BBE-AUCORR
0084      WRITE(7,15)KMON,KDAY,KYR,AUAREA
0085 15     FORMAT(' AU 4F 5/2,7/2 AREA OBTAINED ',I2,'-',I2,'-',I2,'-',F9.3)
0086 16     WRITE(7,17)
0087 17     FORMAT(' NEUTRALIZER EMISSION CURRENT? (I3) ')
0088      READ(5,18)INEUT
0089 18     FORMAT(I3)
0090      WRITE(7,180)
0091 180     FORMAT(' WORK FUNCTION (EV)? (F6.2) ')
0092      READ(5,181)WKF
0093 181     FORMAT(F6.2)
0094      NBLK=NBLK-2
0095      RFAC=2.**16
0096      IREC=2
0097      LK=0
0098      DO 19 I=1,NBLK
0099      IREC=IREC+1
0100  C      READ SPECTRUM AND CONVERT 2-WORD INTEGER FORMAT TO REAL
0101      READ(4,IREC)(ISPEC(L),L=1,256)
0102      DO 19 L=1,256,2
0103      LK=LK+1
0104      ITEM(2)=ISPEC(L)
0105      ITEM(1)=ISPEC(L+1)
0106      IDGN=IAJFLT(IASPEC,RSPEC(LK))
0107 19     CONTINUE
0108 30     FORMAT(A1)
0109      WRITE(7,35)
0110 35     FORMAT(' NUMBER OF POINTS IN SMOOTHING INTERVAL? (I2)',3X,*)
0111      READ(5,36)NPT
0112 36     FORMAT(I2)
0113      IF(NPT.EQ.9)KSTRT=1
0114      IF(NPT.EQ.11)KSTRT=10
0115      IF(NPT.EQ.13)KSTRT=21
0116      IF(NPT.EQ.15)KSTRT=34
0117      IF(NPT.EQ.17)KSTST=49
0118      IF(NPT.EQ.19)KSTRT=66
0119      IF(NPT.EQ.21)KSTRT=85
0120      KEND=KSTRT+NPT-1
0121      KK=0
0122  C      READ SMOOTHING COEFFICIENTS FROM DISC FILE
0123      DO 37 K=1,105
0124      READ(3,300)BA,BB
0125 300     FORMAT(2E13.6)

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APPENDIX A (cont)

FORTRAN IV

V02.04

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0130      IF(K,GE,KSTRT,AND,K,LE,KEND)GO TO 38
0132      GO TO 37
0133  38      KK=KK+1
0134      B(KK,1)=BA
0135      B(KK,2)=BB
0136  37      CONTINUE
          C      GENERATE SMOOTHED DATA (SMOTH(I,1)) AND FIRST DERIVATIVE(SMOTH(I,2))
0137      NNPT=NSTEP-NPT+1
0138      NBG=NPT/2+1
0139      NEND=NSTEP-NPT/2
0140  39      J=1
0141      DO 40 I=NBG,NEND
0142      J=J+1
0143      K=I-NBG+1
0144      KK=I+NBG-1
0145      SSUM=0.
0146      DRSUM=0.
0147      JK=0
0148      DO 50 L=K,KN
0149      JK=JK+1
0150      DRSUM=DRSUM+B(JK,2)*RSPEC(L)
0151      SSUM=SSUM+B(JK,1)*RSPEC(L)
0152  50      CONTINUE
0153      SMOTH(J,1)=SSUM
0154      SMOTH(J,2)=DRSUM
0155  40      CONTINUE
0156      IND=NPT/2+1
0157      IRNG=IFARM(114)
0158      NAVG=100/IFARM(116)
0159      NINT=NNPT/IRNG
0160      INT=0
0161  105     ISTEP=IFARM(116)
0162      IEND=NNPT-160/ISTEP
0163      REDFAC=50.
0164      THRESH=150.
0165      NGSET=0
0166      NLSET=0
0167      NITS=0
0168      WRITE(7,110)
0169  110     FORMAT(' NUMBER OF PEAKS? (I1)' *)
0170      READ(5,115)INPKS
0171  115     FORMAT(I1)
0172  190     IF(NITS,GT,15)GO TO 241
0174      I=14
0175      J=1
0176      N=1
0177  200     I=I+1
0178      IF(I,GE,IEND)GO TO 240
0180      MINST=0
0181      MAXST=0
0182      TSUM1=0.0
0183      TSUM2=0.0
          C      LOOK FOR ZERO CROSSING OF FIRST DERIVATIVE
0184      IF(SMOTH(I,2).GT,0.0,AND,SMOTH(I+1,2).LT,0.0)GO TO 210
0186      GO TO 200
          C      LOOK FOR 15 PREVIOUS POINTS WITH SUM GT 150, 15 SUCCEEDING
          C      POINTS WITH SUM LT -150
0187  210     KEND=I-140/ISTEP
0188      DO 215 K=I,KEND,-1
0189      IF(SMOTH(K,2).LT,0.0)GO TO 215
0191      TSUM1=TSUM1+SMOTH(K,2)
0192  215     CONTINUE
0193      IF(TSUM1,GT,THRESH)MAXST=1
0195      IF(MAXST,NE,1)GO TO 200

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APPENDIX A (cont)

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0197      LSTP=I+160/ISTEP
0198      DO 225 L=I+1,LSTP
0199      IF(SMOTH(L,2).GT.0.)GO TO 225
0201      TSUM2=TSUM2+SMOTH(L,2)
0202 225    CONTINUE
          C      SAVE MAXIMA
0203      IF(TSUM2.LT.-THRESH.OR.MAXST.EQ.1)MAX(N)=I
0205      IF(MAX(N).NE.I)GO TO 200
0207      MAXSV(N)=I
0208      I=I+9
0209      IF(I.GE.IEND)GO TO 240
0211      N=N+1
0212      GO TO 200
0213 240    NPEAK=N-1
0214      IF(INFKS-NPEAK)230,241,235
0215 235    IF(NLSET.NE.1)GO TO 236
0217      REDFAC=REDFAC/2.
0218      NLSET=0
0219 236    THRESH=THRESH-REDFAC
0220      NGSET=1
0221      NITS=NITS+1
0222      GO TO 190
0223 230    IF(NGSET.NE.1)GO TO 231
0225      REDFAC=REDFAC/2.
0226      NGSET=0
0227 231    THRESH=THRESH+REDFAC
0228      NLSET=1
0229      NITS=NITS+1
0230      GO TO 190
0231 241    CONTINUE
          C      LOCATE PEAK SIDES AT MAXIMUM AND MINIMUM IN FIRST DERIVATIVE
0232      K=0
0233 401    K=K+1
0234      IF(K.GT.NPEAK)GO TO 450
0236      NLOX=0
0237      L=MAX(K)-1
0238 405    L=L-1
0239      M=0
0240      DO 410 N=L,L-1,-1
0241      H=M+1
0242      SDUMP(M)=0.
0243      DO 410 JJ=N-1,N+1
0244      SDUMP(M)=SDUMP(M)+SMOTH(JJ,2)
0245 410    CONTINUE
0246      IF(SDUMP(2).GT.SDUMP(1))GO TO 405
0248      NLOX=L
0249      I=MAX(K)+1
0250 415    I=I+1
0251      M=0
0252      DO 420 N=I,I+1
0253      M=M+1
0254      SDUMP(M)=0.
0255      DO 420 JJ=N-1,N+1
0256      SDUMP(M)=SDUMP(M)+SMOTH(JJ,2)
0257 420    CONTINUE
0258      IF(SDUMP(2).LT.SDUMP(1))GO TO 415
0260      NHIX=I
0261 440    CONTINUE
0262      NHW1=MAX(K)-NLOX
0263      NHW2=NHIX-MAX(K)
0264      IF(MAX0(NHW1,NHW2).GE.5)GO TO 441
0266      DO 444 NK=K,NPEAK-1
0267      MAXSV(NK)=MAXSV(NK+1)
0268 444    MAX(NK)=MAX(NK+1)

```

APPENDIX A (cont)

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0269      NPEAK=NPEAK-1
0270      K=K-1
0271      GO TO 401
C      COMPUTE APPROXIMATE PEAK WIDTH (IWIDE)
0272 441      IWIDE(K)=MAX0(NHW1,NHW2)*2
0273      JWIDE(K)=IWIDE(K)
0274      NLO(K)=MAX(K)-2*NHW2
0275      IF(K.EQ.1)GO TO 442
0277      IF(NLO(K).LT.NHI(K-1))NLO(K)=NLOX
0279 442      IF(NLO(K).LT.1)NLO(K)=1
0281      NHI(K)=MAX(K)+2*NHW1
0282      IF(K.EQ.NPEAK)GO TO 443
0284      NHIF=NHI(K)
0285      IF(NHI(K).GT.MAX(K+1).OR.SMOOTH(NHIF,1).GT.SMOOTH(NHIX,1))
      INHI(K)=NHIX
0287 443      IF(NHI(K).GT.NNPT)NHI(K)=NNPT
0289      GO TO 401
0290 450      CONTINUE
C      REFINE PEAK POSITION (PPOS)BY COMPUTING MAXIMUM OF
C      CUBIC POLYNOMIAL THROUGH NPOLY POINTS
C      CENTERED AT PEAK MAXIMUM
0291      DO 470 L=1,NPEAK
0292      I=MAX(L)
0293      NPOL=IWIDE(L)/4
0294      IF(NPOL.GT.7)NPOL=7
0296      IF(NPOL.LT.3)NPOL=3
0298      NPOLY=2*NPOL+1
0299      KK=0
0300      DO 460 JK=I-NPOL,I+NPOL
0301      KK=KK+1
0302      RX(KK)=JK+NPOL/2
0303 470      FMAX(KK)=RSPEC(JK+NPOL/2)
0304      CALL LSQE(NPOLY,3,RX,FMAX,PCOF,IFIT)
C      IF AVERAGE RELATIVE ERROR IN POLYNOMIAL FIT EXCEEDS 5% FLAG BAD FIT
0305      IF(IFIT.EQ.1)WRITE(7,465) L
0307 465      FORMAT(' BAD POLYNOMIAL FIT PEAK ',I3)
C      IF CURIC COEFFICIENT/QUADRATIC COEFFICIENT LESS THAN 1E-6 USE
C      QUADRATIC FIT
0308      IF(ABS(PCOF(4)/PCOF(3)).LT.1E-6)GO TO 466
0310      PPS=(-2.*PCOF(3)-SQRT(4.*PCOF(3)**2-12.*PCOF(4)*PCOF(2)))
      1/(6.*PCOF(4))
0311      GO TO 467
0312 466      PPS=-PCOF(2)/(2*PCOF(3))
0313 467      PPOS(L)=BBE-PPS*VSTEP
0314 470      CONTINUE
0315      NPSAV=NPEAK
0316      NHIFLG=0
0317      LFLG=0
0318      LSET=0
0319      NHISSET=0
0320      IST=1
0321      IFN=NPSAV
C      CHECK FOR PEAKS NEAR ENDS OF SPECTRUM
0322      IF(NLO(1)-2*IWIDE(1).GT.1)GO TO 520
0324 500      LSET=1
0325      WRITE(7,505)
0326 505      FORMAT(' INSUFFICIENT BACKGROUND POINTS AT LOW END OF SPECTRUM')
0327      WRITE(7,510)
0328 510      FORMAT(' USE PRESENT DATA FOR AREA CALCULATION? Y OR N',3X,*)
0329      READ(5,515)BKDL
0330 515      FORMAT(A1)
0331      IF(BKDL.EQ.Y)LFLG=1
0333 520      IF(NHI(NPEAK)+2*IWIDE(NPEAK).LT.NNPT)GO TO 540
0335 530      NHISSET=1

```

APPENDIX A (cont)

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0336      WRITE(7,535)
0337 535    FORMAT(' INSUFFICIENT BACKGROUND POINTS AT HIGH END OF SPECTRUM')
0338      WRITE(7,510)
0339      READ(5,515)BKDH
0340      IF(BKDH.EQ.Y)NHIFLG=1
0342 540    CONTINUE
0343      IF(LSET.EQ.0.AND.NHISSET.EQ.0)GO TO 580
0345      IF(LSET.EQ.1.AND.LFLG.EQ.0)NPEAK=NPEAK-1
0347      IF(NHISSET.EQ.1.AND.NHIFLG.EQ.0)NPEAK=NPEAK-1
0349      IF(NPEAK.EQ.0)GO TO 550
0351      GO TO 560
0352 550    WRITE(7,555)
0353 555    FORMAT(' NO PEAKS')
0354      STOP
0355 560    CONTINUE
0356      M=0
C      OMIT END PEAKS AT OPERATOR'S OPTION
0357      IF(LSET.EQ.1.AND.LFLG.EQ.0)IST=2
0359      IF(NHISSET.EQ.1.AND.NHIFLG.EQ.0)IFN=NPSAV-1
0361      DO 570 I=IST,IFN
0362      M=M+1
0363      NLO(M)=NLO(I)
0364      MAX(M)=MAX(I)
0365      NHI(M)=NHI(I)
0366      MAXSV(M)=MAXSV(I)
0367      JWIDE(M)=IWIDE(I)
0368      PPOS(M)=PPOS(I)
0369 570      IWIDE(M)=IWIDE(I)
0370      NPSAV=M
0371 580    CONTINUE
0372      NNPK=NPEAK
0373      L=0
0374      K=0
0375 640      K=K+1
0376      L=L+1
0377      IF(L.GT.NNPK-1)GO TO 695
C      CHECK FOR PEAK OVERLAP AND ADJUST INTEGRATION LIMITS AT OPERATOR'S
C      OPTION
0379      ISEP=MAX(K+1)-MAX(K)
0380      NWIDE=1.5*(IWIDE(K)+IWIDE(K+1))
0381      IF(ISEP.GT.NWIDE)GO TO 640
0383 660      WRITE(7,665)L,L+1
0384 665      FORMAT(' OVERLAP BETWEEN PEAKS' 2I3)
0385      WRITE(7,670)
0386 670      FORMAT(' INTEGRATE AS DOUBLET? Y OR N',3X,*)
0387      READ(5,515)DBLT
0388      IF(DBLT.NE.Y)GO TO 640
0390 680      NPEAK=NPEAK-1
0391      MAX(K)=MAX(K+1)
0392      IWIDE(K)=IWIDE(K+1)
0393      NEND=NPEAK
0394      NHI(K)=NHI(K+1)
0395      IF(NPEAK.LT.K+1)NEND=K+1
0397      DO 682 JJ=K+1,NEND
0398      NLO(JJ)=NLO(JJ+1)
0399      IWIDE(JJ)=IWIDE(JJ+1)
0400      MAX(JJ)=MAX(JJ+1)
0401 682      NHI(JJ)=NHI(JJ+1)
0402      K=K-1
0403      GO TO 640
0404 695      CONTINUE
0405      ICNT=2*NPEAK
C      LOOK FOR BACKGROUND POINTS WITH MINIMUM IN ABSOLUTE VALUE OF
C      FIRST DERIVATIVE*SMOOTHED Y VALUE

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APPENDIX A (cont)

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```

0406      DO 800 I=1,ICNT
0407      IF(I.GT.NPEAK)GO TO 700
0409      JRNG=2*IWIDE(I)
0410      INC=-1
0411      JSTRT=NLO(I)
0412      JSTP=NLO(I)-JRNG
0413      IF(JSTP.LT.3)JSTP=3
0415      GO TO 710
0416 700   JRNG=2*IWIDE(I-NPEAK)
0417      INC=1
0418      JSTRT=NHI(I-NPEAK)
0419      JSTP=NHI(I-NPEAK)+JRNG
0420      IF(JSTP.GT.NNPT)JSTP=NNPT-2
0422 710   DMIN=0.
0423      DO 705 KL=JSTRT-2,JSTRT+2
0424 705   DMIN=DMIN+(ABS(SMOTH(KL,2))+0.5)*SMOTH(KL,1)
0425      JBK=JSTRT
0426      DO 720 J=JSTRT,JSTP,INC
0427      TDUMP=0.0
0428      DO 711 KK=J-2,J+2
0429 711   TDUMP=TDUMP+(ABS(SMOTH(KK,2))+0.5)*SMOTH(KK,1)
0430      IF(I.EQ.1.OR.I.EQ.ICNT)GO TO 730
0432      IF(I.GT.NPEAK)GO TO 740
0434      IF(J.LT.MAX(I-1)+IWIDE(I-1)/3)GO TO 720
0436      GO TO 730
0437 740   IF(J.GT.MAX(I-NPEAK+1)-IWIDE(I-NPEAK+1)/3)GO TO 720
0439 730   IF(DMIN.LT.TDUMP)GO TO 720
0441      JBK=J
0442      DMIN=TDUMP
0443 720   CONTINUE
0444      NBKG(I)=JBK
0445 800   CONTINUE
0446      J=0
0447      DO 760 I=1,ICNT-1,2
0448      J=J+1
0449      BAKFT(I)=BBE-(FLOAT(NBKG(J))+FLOAT(NPT/2))*VSTEP
0450 760   BAKFT(I+1)=BBE-(FLOAT(NBKG(J+NPEAK))+FLOAT(NPT/2))*VSTEP
0451      NBKFT=2*NPEAK
0452      IF(BKSLP.EQ.Y)GO TO 795
0454      WRITE(7,765)
0455 765   FORMAT(' CORRECT BACKGROUND SLOPE? Y OR N (%)
0456      READ(5,515)BKSLP
0457      IF(BKSLP.NE.Y)GO TO 795
0459      SLSUM=0.
0460      JM=0
0461      J=1
0462      M=0
0463 770   M=M+1
0464      IF(M.GT.NNPT)GO TO 780
0466      IF(M.LE.NBKG(J).OR.J.GT.NPEAK)GO TO 775
0468      M=NBKG(J+NPEAK)
0469      J=J+1
0470 775   JM=JM+1
0471      SLSUM=SLSUM+SMOTH(M,2)
0472      GO TO 770
0473 780   CONTINUE
0474      AVSLP=SLSUM/(VSTEP*FLOAT(JM))
0475      WRITE(7,781)AVSLP
0476 781   FORMAT(' AVERAGE BACKGROUND SLOPE=' ,E12.4)
0477      YLOW=RSPEC(1)
0478      DO 785 K=1,NSTEP
0479      IF(RSPEC(K).GT.YLOW)GO TO 785
0481      YLOW=RSPEC(K)
0482      XLOW=K

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APPENDIX A (cont)

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0483 785  CONTINUE
0484      AVSLP=AVSLP*VSTEP
0485      BKINT=YLOW-AVSLP*XLOW
0486      DO 787 L=1,NSTEP
0487      YBK=AVSLP*FLOAT(L)+BKINT
0488 787  RSPEC(L)=RSPEC(L)-YBK
0489      GO TO 39
0490 795  CONTINUE
      C      SUBTRACT LINEAR BACKGROUND AND COMPUTE PEAK AREA
0491      JM=0
0492      DO 910 K=1,NPEAK
0493      IX1=NBKG(K)
0494      IX2=NBKG(K+NPEAK)
0495      Y1=SMOTH(IX1,1)
0496      Y2=SMOTH(IX2,1)
      C      COMPUTE BACKGROUND SLOPE
0497      SLOPE=(Y2-Y1)/(IX2-IX1)
0498      RINT=Y1-IX1*SLOPE
0499      TSUM=0.
      C      COMPUTE BACKGROUND PROPORTIONAL TO PEAK AREA (PKINT) TO HIGHER
      C      KINETIC ENERGY
0500      DO 810 J=IX2,IX1,-1
0501      YNET=RSPEC(J+NBG-1)-SMOTH(IX2,1)
0502      TSUM=TSUM+YNET
0503      PKINT(J)=TSUM
0504 810  CONTINUE
0505      SCALE=(SMOTH(IX1,1)-SMOTH(IX2,1))/TSUM
0506      DO 820 N=IX1,IX2
0507 820  PKINT(N)=PKINT(N)*SCALE+SMOTH(IX2,1)
0508      AREALB(K)=0.
0509      AREASE(K)=0.
0510      DO 910 L=IX1,IX2
0511      BGFNT=L*SLOPE+RINT
0512      YDIFF=RSPEC(L+NBG-1)-BGFNT
0513      IF(YDIFF.LT.0.)YDIFF=0.
      C      SAVE PEAK HEIGHTS AND BACKGROUND AT PEAK MAXIMUM POSITIONS
0515      DO 825 M=1,NPSAV
0516      IF(L-MAXSV(M))825,823,825
0517 823  JM=JM+1
0518      PEAKH(JM,1)=YDIFF
0519      PKBK(JM,1)=BGFNT
0520      HFHT=YDIFF/2.
0521      KPTS=0.6/VSTEP
      C      COMPUTE PEAK WIDTH AT HALF MAXIMUM HEIGHT (FWHM)
0522      PKAMP=HFHT+BGFNT
0523      NST=MAXSV(JM)-JWIDE(JM)/2
0524      JST=MAXSV(JM)+JWIDE(JM)/2
0525      SVPT=ABS(SMOTH(NST,1)-PKAMP)
0526      KLO=NST
0527      DO 906 IL=NST-KPTS,NST+KPTS
0528      ADIF=ABS(SMOTH(IL,1)-PKAMP)
0529      IF(ADIF.GT.SVPT)GO TO 906
0531      SVPT=ADIF
0532      KLO=IL
0533 906  CONTINUE
0534      SVPT=ABS(SMOTH(JST,1)-PKAMP)
0535      KHI=JST
0536      DO 907 JL=JST-KPTS,JST+KPTS
0537      ADIF=ABS(SMOTH(JL,1)-PKAMP)
0538      IF(ADIF.GT.SVPT)GO TO 907
0540      SVPT=ADIF
0541      KHI=JL
0542 907  CONTINUE
0543      FWHM(JM,1)=(KHI-KLO)*VSTEP

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APPENDIX A (cont)

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      C      CORRECT PEAK HEIGHTS AND BACKGROUND FOR DATA ACQUISITION TIME (DAT)
0544      PEAKH(JM,1)=PEAKH(JM,1)/DAT
0545      PKBK(JM,1)=PKBK(JM,1)/DAT
0546      825      CONTINUE
0547      AREALB(K)=AREALB(K)+YDIFF
0548      YDIFF=RSPEC(L+NBG-1)-PINT(L)
0549      IF(YDIFF1.LT.0.)YDIFF1=0.
0551      AREASB(K)=AREASB(K)+YDIFF1
0552      910      CONTINUE
0553      DO 912 L=1,NPEAK
      C      CORRECT AREA FOR STEP WIDTH AND DATA ACQUISITION TIME
0554      AREALB(L)=AREALB(L)*VSTEP/DAT
0555      912      AREASB(L)=AREASB(L)*VSTEP/DAT
0556      IF(CALTST.NE.AUCAL1.AND.CALTST.NE.AUCAL2)GO TO 917
0558      WRITE(2,913)JMON,JDAY,JYR,FPDS(2)
0559      FORMAT(3I2,F9.3)
0560      915      IF(CALTST.NE.AUCAL2)GO TO 917
0562      WRITE(1,913)JMON,JDAY,JYR,AREASB(1)
0563      917      LS=0
0564      IF(CALTST.NE.AUCAL1)CALL CLOSE (1)
0566      CALL CLOSE (2)
0567      WRITE(7,918)
0568      918      FORMAT(' ARE ANY PEAKS TO BE DECONVOLUTED? Y OR N ')
0569      READ(5,30)DCON
0570      IF(DCON.NE.Y)GO TO 919
0572      WRITE(7,9180)
0573      9180     FORMAT(' WHICH PEAK? (1)')
0574      READ(5,115)NDECON
0575      WRITE(7,9185)
0576      9185     FORMAT(' DECONVOLUTION DATA FILE NAME?')
0577      CALL ASSIGN(2,TTIN,-1,'NEW')
0578      JLO=NBKG(NDECON)
0579      JHI=NBKG(NPEAK+NDECON)
0580      NDATA=JHI-JLO+1
0581      BKLO=SMOTH(JLO,1)/DAT
0582      BKHI=SMOTH(JHI,1)/DAT
0583      WRITE(2,9190)NDATA,BKLO,BKHI
0584      9190     FORMAT(I4,2F8.3)
0585      XVALB=BAKPT(2*NDECON-1)+VSTEP
0586      KK=0
0587      DO 9195 K=JLO,JHI
0588      KK=KK+1
0589      XVAL=XVALB-VSTEP*FLOAT(KK)
0590      YVAL=RSPEC(K+NBG-1)/DAT
0591      WRITE(2,9196)XVAL,YVAL
0592      9196     FORMAT(2F8.3)
0593      9195     CONTINUE
0594      919      DO 990 M=1,NPEAK
0595      RKE=0.
0596      K=0
0597      DO 920 N=1,NPSAV
0598      IF(MAXSV(N).GT.NLO(M).AND.MAXSV(N).LT.NHI(M))GO TO 930
0600      GO TO 920
0601      930      K=K+1
0602      LS=LS+1
0603      PMAX(K)=PPDS(LS)
0604      RKE=RKE+1254.6-WKF-PMAX(K)
0605      PEAKH(K,2)=PEAKH(LS,1)
0606      FWHM(K,2)=FWHM(LS,1)
0607      PKBK(K,2)=PKBK(LS,1)
0608      920      CONTINUE
      C      CORRECT PEAK AREAS AND HEIGHTS FOR ANALYZER TRANSMISSION FUNCTION
0609      IF(K.GT.1)RKE=RKE/K
0611      DO 925 LC=1,K

```


APPENDIX A (cont)

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0612      PKHKE(LC)=PEAKH(LC,2)*RKE**(0.3)/10.
0613      PKBKE(LC)=PKBK(LC,2)*RKE/1000.
0614  925      CONTINUE
0615      ANLB=(AREALB(M)/AUAREA)
0616      ANSB=(AREASB(M)/AUAREA)
0617      ANLBKE=ANLB*RKE**(0.3)/10.
0618      ANSBKE=ANSB*RKE**(0.3)/10.
0619      ARLBKE=AREALB(M)*RKE**(0.3)/10.
0620      ARSBKE=AREASB(M)*RKE**(0.3)/10.
0621      WRITE(7,935)M,(PMA(I),I=1,K)
0622  935      FORMAT(/' PEAK(S)',I3,3X,' MAXIMA',5F7.2)
0623      WRITE(7,940)(PEAKH(I,2),I=1,K)
0624  940      FORMAT(' PEAK HEIGHTS ',5F7.3)
0625      WRITE(7,945)(PKHKE(I),I=1,K)
0626  945      FORMAT(' PEAK HEIGHTS*K.E.**0.3 ',5F7.3)
0627      WRITE(7,950)(PKBK(LR,2),LR=1,K)
0628  950      FORMAT(' BACKGND AT PEAK MAX ',5F7.3)
0629      WRITE(7,955)(PKBKE(LR),LR=1,K)
0630  955      FORMAT(' PK BACKGROUND*K.E. ',5F7.3)
0631      WRITE(7,960)(FWHM(J,2),J=1,K)
0632  960      FORMAT(' PEAK WIDTHS HALF HT.',5F7.2)
0633      WRITE(7,965)
0634  965      FORMAT(' BCKGND POINTS (EV) PK AREA (LB) PK AREA (LB)/AU PK ARE
1A (SB) PK AREA (SB)/AU')
0635      WRITE(7,970)BAKPT(2*M-1),BAKPT(2*M),AREALB(M),ANLB,AREASB(M),ANSB
0636  970      FORMAT(FB,2,3X,FB,2,4X,FB,3,7X,FB,6,7X,FB,3,7X,FB,6)
0637      WRITE(7,975)
0638  975      FORMAT(' AREAS * KINETIC ENERGY**0.3 ')
0639      WRITE(7,980)ARLBKE,ANLBKE,ARSBKE,ANSBKE
0640  980      FORMAT(23X,FB,3,7X,FB,6,7X,FB,3,7X,FB,6)
0641  990      CONTINUE
0642      WRITE(7,1000)
0643      END

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APPENDIX A (cont)

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0001      SUBROUTINE LSQE(M,KM,X,F,B,IFIT)
0002      DIMENSION X(100),F(100),P(100),B(6),A(6,6),FM(100)
0003      EQUIVALENCE(FM,PM,FM)
0004      DATA A(1,1),A(2,2),A(3,3),A(4,4),A(5,5),A(6,6)/6*1.0/
0005      FM=M
0006      FBAR=F(1)
0007      XBAR=X(1)
0008      DO 10 I=2,M
0009      FBAR=FBAR+F(I)
0010 10      XBAR=XBAR+X(I)
0011      XBAR=XBAR/FM
0012      A(2,1)=-XBAR
0013      PXF=0.0
0014      PXP=0.0
0015      DO 20 I=1,M
0016      PM(I)=1.0
0017      P(I)=X(I)-XBAR
0018      PXF=PXFP(I)*F(I)
0019 20      PXP=PXFP(I)*F(I)
0020      KMM=KM+1
0021      IF(KMM.GT.6)KMM=6
0022      B(2)=PXF/PXP
0023      B(1)=FBAR/FM+B(2)*A(2,1)
0024 60      DO 190 K=3,KMM
0025 65      XPXP=0.0
0026      XPXPM=0.0
0027      B(K)=0.0
0028      DO 70 J=1,M
0029      XP=X(J)*P(J)
0030      XPXP=XPXP+XP*P(J)
0031 70      XPXPM=XPXPM+XP*PM(J)
0032      ALPHA=XPXP/PXP
0033      BETA=XPXPM/FMXPM
0034      PFXF=0.0
0035      PMXPM=XPX
0036      PXP=0.0
0037      DO 90 I=1,M
0038 80      PT=F(I)
0039      P(I)=(X(I)-ALPHA)*PT-BETA*FM(I)
0040      PPXF=PFXF+P(I)*F(I)
0041 82      PXP=PXP+P(I)*F(I)
0042      PXP=PXP+P(I)*F(I)
0043 90      PM(I)=PT
0044      T=PPXF/PXP
0045      A(K,1)=-ALPHA*A(K-1,1)-BETA*A(K-2,1)
0046      A(K,K-1)=A(K-1,K-2)-A(K-1,K-1)*ALPHA
0047      IF(K-3)150,150,110
0048 110      K1=K-2
0049      DO 120 I=2,K1
0050 120      A(K,I)=A(K-1,I-1)-ALPHA*A(K-1,I)-BETA*A(K-2,I)
0051 150      DO 160 I=1,K
0052 160      B(I)=B(I)+T*A(K,I)
0053 190      CONTINUE
0054      IFIT=0
0055      DFSUM=0.
0056      DO 175 I=1,M
0057      FX=0.0
0058      DO 180 K=1,KM+1
0059      L=K-1
0060      IF(L)182,185,182
0061 185      FX=FX+B(K)
0062      GO TO 180
0063 182      FX=FX+B(K)*X(I)**(L)
0064 180      CONTINUE
0065      DF=((FX-F(I))/F(I))*100.
0066      DFSUM=DFSUM+DF
0067 175      CONTINUE
0068      DFSUM=DFSUM/M
0069      IF(DFSUM.GE.5.)IFIT=1
0071 220      RETURN
0072      END

```

APPENDIX B

DESCRIPTION OF ESCADT INPUT PARAMETERS

<u>Variable Name</u>	<u>Comments</u>
RATE	Data acquisition time at each point, in ms.
XBV	X-ray source voltage in kV, not used computationally.
XBI	X-ray source current in mA, not used computationally.
EPASS	Analyzer pass energy in eV, not used computationally.
NSWEEP	Number of scans.
NBLK	Number of disk blocks occupied by the data file.
NSTEP	Number of spectral data points.
BBE	High binding energy limit of scan.
VSTEP	Digitization interval in eV.
RANGE	Scan range in eV.
INEUT	Flood gun emission current, not used computationally.
INPKS	Number of peaks to be located (see text).
RSPEC	Array containing spectral ordinate values.
B	Array containing convoluting numbers for smoothing and differentiation (see text).
WKF	Spectrometer work function in eV.

APPENDIX C

TYPICAL PROGRAM RUN (Operator responses are underlined.)

```

R ESCADT
*****

DATE 6-21-79 TIME 16: 6: 4
DEVICE AND FILE NAME? *BK1:C1S4.DBJ
FILE CREATION DATE 2- 1-79
NO. SCANS      T/S      X-RAY KV      X-RAY MA      PASS ENERGY
   36          100.      10.0         40.          50.

BINDING ENERGY U. L.  RANGE(EV)  EV/STEP  # DISC BLOCKS  #DATA POINTS
   300.          20.         0.10         4           201

SAMPLE ID: KAP BLAKE
AU 4F 7/2 B. E. OBTAINED 6-21-79 83.80EV
ALL BINDING ENERGIES CORRECTED BY 0.00 EV
AU 4F 5/2,7/2 AREA OBTAINED 2- 2-79- 48.765
NEUTRALIZER EMISSION CURRENT? (I3) 0
WORK FUNCTION (EV)? (F6.2) 5.0
NUMBER OF POINTS IN SMOOTHING INTERVAL? (I2) 11
NUMBER OF PEAKS? (I1) 4
INSUFFICIENT BACKGROUND POINTS AT HIGH END OF SPECTRUM
USE PRESENT DATA FOR AREA CALCULATION? Y OR N Y
OVERLAP BETWEEN PEAKS 1 2
INTEGRATE AS DOUBLET? Y OR N Y
OVERLAP BETWEEN PEAKS 2 3
INTEGRATE AS DOUBLET? Y OR N N
OVERLAP BETWEEN PEAKS 3 4
INTEGRATE AS DOUBLET? Y OR N Y
CORRECT BACKGROUND SLOPE? Y OR N N
ARE ANY PEAKS TO BE DECONVOLUTED? Y OR N N

PEAK(S) 1      MAXIMA 293.97 291.17
          PEAK HEIGHTS 0.496 1.066
PEAK HEIGHTS*K.E.**0.3 0.389 0.835
          BACKGND AT PEAK MAX 0.513 0.522
          PK BACKGROUND*K.E. 0.491 0.500
          PEAK WIDTHS HALF HT. 2.00 1.80
BCKGND POINTS (EV)  PK AREA (LB)  PK AREA (LB)/AU  PK AREA (SB)  PK AREA (SB)/AU
298.60 288.70 2.961 0.060724 3.018 0.061880
AREAS * KINETIC ENERGY**0.3
          2.321 0.047603 2.366 0.048510

PEAK(S) 2      MAXIMA 287.08 283.26
          PEAK HEIGHTS 0.401 1.812
PEAK HEIGHTS*K.E.**0.3 0.315 1.424
          BACKGND AT PEAK MAX 0.493 0.401
          PK BACKGROUND*K.E. 0.475 0.387
          PEAK WIDTHS HALF HT. 1.70 1.70
BCKGND POINTS (EV)  PK AREA (LB)  PK AREA (LB)/AU  PK AREA (SB)  PK AREA (SB)/AU
288.80 280.60 4.108 0.084233 4.009 0.082206
AREAS * KINETIC ENERGY**0.3
          3.228 0.066186 3.150 0.064593
*****
STOP --

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APPENDIX D

QUADRATIC COEFFICIENTS FOR OBTAINING THE SMOOTHED VALUE AND SMOOTHED FIRST DERIVATIVE FOR POINT SPREADS OF NINE THROUGH TWENTY ONE

SMOOTHED VALUE	FIRST DERIVATIVE	SMOOTHED VALUE	FIRST DERIVATIVE
N=9		N=17	
-0.909091E-01	-0.666667E-01	-0.650155E-01	-0.196078E-01
0.606061E-01	-0.500000E-01	-0.185758E-01	-0.171569E-01
0.168831E+00	-0.333333E-01	0.216718E-01	-0.147059E-01
0.233766E+00	-0.166667E-01	0.557275E-01	-0.122549E-01
0.255411E+00	0.000000E+00	0.835913E-01	-0.980392E-02
0.233766E+00	0.166667E-01	0.105263E+00	-0.735294E-02
0.168831E+00	0.333333E-01	0.120743E+00	-0.490196E-02
0.606061E-01	0.500000E-01	0.130031E+00	-0.245098E-02
-0.909091E-01	0.666667E-01	0.133127E+00	0.000000E+00
N=11		0.130031E+00	0.245098E-02
-0.839161E-01	-0.454545E-01	0.120743E+00	0.490196E-02
0.209790E-01	-0.363636E-01	0.105263E+00	0.735294E-02
0.102564E+00	-0.272727E-01	0.835913E-01	0.980392E-02
0.160839E+00	-0.181818E-01	0.557275E-01	0.122549E-01
0.195804E+00	-0.909091E-02	0.216718E-01	0.147059E-01
0.207459E+00	0.000000E+00	-0.185758E-01	0.171569E-01
0.195804E+00	0.909091E-02	-0.650155E-01	0.196078E-01
0.160839E+00	0.181818E-01	N=19	
0.102564E+00	0.272727E-01	-0.601504E-01	-0.157895E-01
0.209790E-01	0.363636E-01	-0.225564E-01	-0.140351E-01
-0.839161E-01	0.454545E-01	0.106148E-01	-0.122807E-01
N=13		0.393631E-01	-0.105263E-01
-0.769231E-01	-0.329670E-01	0.636886E-01	-0.877193E-02
0.000000E+00	-0.274725E-01	0.835913E-01	-0.701754E-02
0.629371E-01	-0.219780E-01	0.990712E-01	-0.526316E-02
0.111888E+00	-0.164835E-01	0.110128E+00	-0.350877E-02
0.146853E+00	-0.109890E-01	0.116762E+00	-0.175439E-02
0.167832E+00	-0.549451E-02	0.118974E+00	0.000000E+00
0.174825E+00	0.000000E+00	0.116762E+00	0.175439E-02
0.167832E+00	0.549451E-02	0.110128E+00	0.350877E-02
0.146853E+00	0.109890E-01	0.990712E-01	0.526316E-02
0.111888E+00	0.164835E-01	0.835913E-01	0.701754E-02
0.629371E-01	0.219780E-01	0.636886E-01	0.877193E-02
0.000000E+00	0.274725E-01	0.393631E-01	0.105263E-01
-0.769231E-01	0.329670E-01	0.106148E-01	0.122807E-01
N=15		-0.225564E-01	0.140351E-01
-0.705882E-01	-0.250000E-01	-0.601504E-01	0.157895E-01
-0.117647E-01	-0.214286E-01	N=21	
0.380090E-01	-0.178571E-01	-0.559006E-01	-0.129870E-01
0.787330E-01	-0.142857E-01	-0.248447E-01	-0.116883E-01
0.110407E+00	-0.107143E-01	0.294214E-02	-0.103896E-01
0.133032E+00	-0.714286E-02	0.274600E-01	-0.909091E-02
0.146606E+00	-0.357143E-02	0.487087E-01	-0.779221E-02
0.151131E+00	0.000000E+00	0.666885E-01	-0.649351E-02
0.146606E+00	0.357143E-02	0.813992E-01	-0.519481E-02
0.133032E+00	0.714286E-02	0.928408E-01	-0.389610E-02
0.110407E+00	0.107143E-01	0.101013E+00	-0.259740E-02
0.787330E-01	0.142857E-01	0.105917E+00	-0.129870E-02
0.380090E-01	0.178571E-01	0.107551E+00	0.000000E+00
-0.117647E-01	0.214286E-01	0.105917E+00	0.129870E-02
-0.705882E-01	0.250000E-01	0.101013E+00	0.259740E-02
		0.928408E-01	0.389610E-02
		0.813992E-01	0.519481E-02
		0.666885E-01	0.649351E-02
		0.487087E-01	0.779221E-02
		0.274600E-01	0.909091E-02
		0.294214E-02	0.103896E-01
		-0.248447E-01	0.116883E-01
		-0.559006E-01	0.129870E-01