

The Computer Analysis of High Resolution
Gamma-Ray Spectra from
Instrumental Activation Analysis Experiments

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ABSTRACT

The large volume of data generated by activation analysis experiments involving high resolution gamma-ray spectroscopy can only be handled conveniently by the use of computer oriented data reduction methods. Procedures for the analysis of gamma-ray spectra including data smoothing, peak location, centroid and energy determination, and peak integration are described. Iterative fitting and non-fitting methods for the analysis of partially resolved complex peaks are presented. Elemental concentrations are calculated when the spectra are derived from instrumental activation analysis experiments. Corrections for gain and zero drift, pulse pile up, and spectral interferences are incorporated in the program. A graphics subroutine is described for interactively processing complex spectral features during INAA processing. Additional programs for creating input data files, and for report form generation of analytical data are described. Graphics algorithms are available to compare the data from alternate photopeaks, to evaluate detector performance during a given counting cycle, to compare the data from reference samples with accepted values, to prepare quality control charts to evaluate long term precision and to search for systematic variations in data on reference samples as a function of time.

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Acknowledgments

The programs described in this document have evolved over a period of approximately 20 years. The initial development of the SPECTRA program was carried out while the first author was associated with the Nuclear Chemistry Center at the Massachusetts Institute of Technology, and the Institute of Geophysics and Planetary Physics at U.C.L.A. The authors have benefited from numerous discussions and suggestions made by colleagues during the development of these programs, particularly: W.V. Boynton, G. W. Kallemeyn, J. Kimberlin, F. T. Kyte, J.P. Op de Beeck, C.A. Palmer, K.L. Robinson, J.J. Rowe, L.J. Schwarz, G.A. Wandless and J.T. Wasson.

1. INTRODUCTION

Instrumental neutron activation analysis (INAA) involving high resolution gamma-ray spectrometry with solid state detectors has been shown to be a particularly powerful method for the rapid determination of a number of major, minor, and trace elements in material of geochemical interest (Gordon et al., 1968; Hertogen and Gijbels, 1971; Filby et al., 1970; Baedecker et al., 1977). The high resolution of solid state detectors used for gamma-ray spectrometry demands that they be coupled to multichannel pulse height analyzers capable of breaking the spectrum down into thousands of increments or energy "channels". Typical multichannel scaler information from a single Ge detector count in an INAA experiment contains 4096 channels of data [the data from an Low Energy Photon Detector (LEPD) count is typically stored in 2048 channels]. The analysis of one spectrum of an irradiated rock sample may involve the location and measurement of between 50 and 70 photopeaks within this 4096 channel spectrum. Since the analysis of a single sample by INAA can involve several countings during a two month decay period (typically three Ge detector counts and two LEPD counts -- Baedecker and McKown, 1987) the data reduction process can involve the analysis of 16,384 channels of information (not including standard samples). For several years, the combined requests for INAA analysis to the Reston and Denver laboratories have been between three and four thousand samples per year. The flood of data generated in the application of INAA can only be processed within a reasonable period of time by utilizing the speed and efficiency of a computer. Sections 2 and 3 and the appendices of this report present a description of a computer program, SPECTRA, written in FORTRAN-77, that has been developed for processing gamma-ray spectra from INAA experiments. Section 4 describes supplementary interactive programs for defining input data files, and processing output data files from the SPECTRA program to produce a report of analysis.

Myriad methods have been devised for extracting quantitative information from gamma-ray spectra by means of a computer, and a critical evaluation of the relative merits of the various programs that have been written would represent a Herculean, if not an impossible, task. No attempt will be made here to review the various techniques that have been applied. Several papers have reviewed alternative methods of spectral analysis (e.g. Op de Beeck, 1975; McNelles and Campbell, 1975; Baedecker, 1977). The results from the International Atomic Energy Agency (IAEA) intercomparison, that may represent the most straightforward approach to making such an evaluation, showed a wide range in the quality of the results - even among laboratories where similar methods (or the same program!) were used (Parr et al., 1979). The most clear-

cut way of differentiating between programs is by the method used to evaluate peak areas: by the iterative fitting of the spectral features to an often complex model, or by a simple summation procedure. Previous comparisons (Baedeker, 1971; Baedeker, 1977) have shown that relatively simple algorithms can compete favorably with fitting procedures, although fitting holds the greatest promise for the detection and measurement of complex peaks. However, fitting algorithms, which are generally complex and time consuming, are often ruled out by practical limitations based on the type of computing equipment available, cost limitations, the number of spectra to be processed in a given time period, and the ultimate goal of the analysis.

The program described in this paper has evolved over a period of 20 years and has been designed for both batch and interactive processing of gamma-ray spectra. The program has been designed for great flexibility in terms of the variety of experimental conditions that can be met. For example, alternative algorithms are available to the user for rapid, non-iterative analysis of overlapping photopeaks, however more complex and time-consuming fitting routines have been included so that they are available for special problems.

2. ANALYSIS OF SPECTRA

This section provides a general overview of gamma-ray spectra analysis, with particular emphasis on the methods and options available in the SPECTRA program. The topics discussed include: the optional smoothing of the spectral data; methods for the detection of peaks, including special procedures for the detection of overlapping peaks; the determination of peak boundaries and baseline definition of single or multiple peaks; alternate methods of determining peak areas including tests of precision and accuracy; and the determination of gamma-ray energies.

2.1. Smoothing

One of the challenges of computerized spectra analysis is to differentiate small peaks from random fluctuations in the multichannel data. Many programs adopt smoothing algorithms in order to attempt to eliminate random noise in the data that might be recognized as peaks by the peak search algorithm. Op de Beeck (1979) has argued against smoothing on the basis that it decreases the information content of the spectral data. Baedeker (1980) has observed improved precision by digital methods of photopeak integration after spectral smoothing. A smoothing procedure is available as an option in the program "SPECTRA" that uses the least squares data convolution technique of Savitzky and Golay (1964). This method has been evaluated by Yule (1967), and involves fitting $(2n+1)$ data points to a polynomial, calculating a new "smoothed" value for the center data point, moving the $(2n+1)$ channel "window" one channel and repeating this procedure for the entire spectrum. The smoothed value of the central data point in the set is given by

$$D_i = N_n^{-1} \sum_{j=-n}^{j=+n} a_{nj} C_{i+j} \quad (1)$$

where a_{nj} is the value of a constant of the convolute function depending on the order of the polynomial, N_n is a normalization factor, and C_{i+j} is the number of counts in channel $i+j$. In the program presented here, five data points are used as the convolution interval, and the data points are fitted to a quadratic. For this case, the constants and normalizing factor as given by Savitzky and Golay are:

$$D_i = \frac{1}{35} (-3C_{i-2} + 12C_{i-1} + 17C_i + 12C_{i+1} - 3C_{i+2}) \quad (2)$$

The smoothing algorithm is included in the program as a subroutine, and a different convolution function can easily be substituted. Some caution should be exercised in using the smoothing algorithm presented, because for very narrow peaks [full width at half maximum (FWHM) < approx. 3.0 channels] the

smoothing operation may cause the spectrum to undershoot the baseline on either side of the peak. For this reason the smoothing operation may be bypassed as an option in the program. In general for detectors having FWHM < 2.3 keV for the 1332 ⁶⁰Co photopeak, the smoothing operation is used only when the analyzer gain is set at <0.75 keV per channel.

2.2. Peak-search procedures

This section presents a general evaluation of alternate methods of peak detection. The recognition of complex peaks is described in sections 2.3 and 2.5. Most peak search procedures, although differing in approach, are similar in practice and involve the convolution of the spectral data into a new spectrum, that facilitates the location of peaks, by using a transform function that has zero area in the absence of a peak. One class of procedures computes derivative spectra (Mariscotti, 1967; Yule, 1968), generally by least squares fitting using the now classical procedures of Savitzky and Golay (1964). Various cross correlation procedures have been proposed that generally use a square wave or rectangular wave correlator (Robertson et al., 1972; Op de Beeck, 1975) or a normal distribution (Black, 1969). The application of five different convolutes to a weak gamma-ray line is illustrated in figure 1. The signal is computed as:

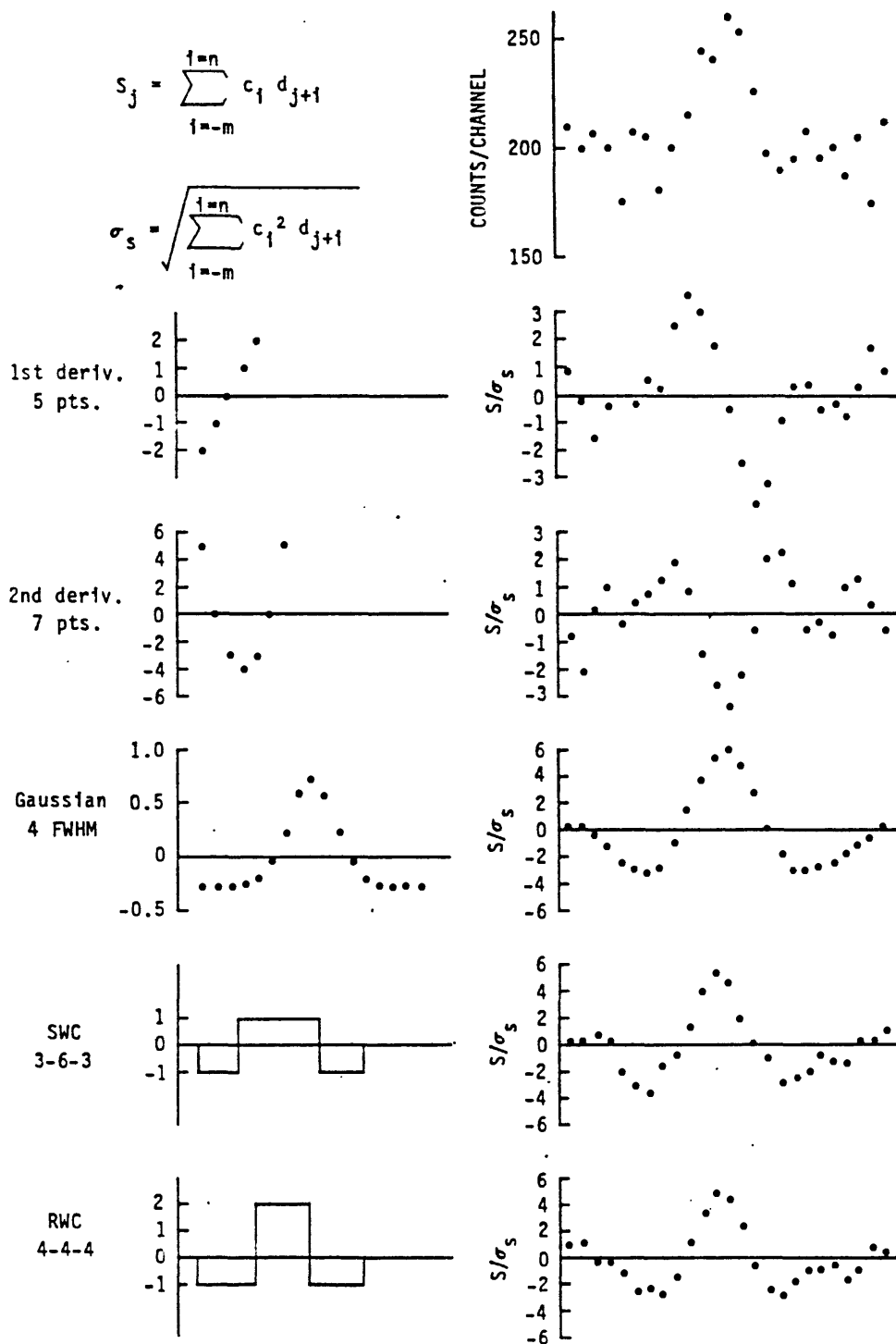
$$S_j = \sum_{i=-m}^{i=n} c_i d_{j+i} \quad (3)$$

where j is the channel number, c_i is the coefficient and d_j is the number of counts in channel j , and i is the i th channel relative to channel j within the convolute. The convolution procedure involves moving an $m+n+1$ channel "window" across the spectrum or region of interest. j is the centermost channel in the window, and for a convolute having an odd number of channels, $n=m$, whereas for an even number of channels, $n=m-1$. When derivative spectra are computed, the channels within the "window" are fit to a polynomial by least squares (c_i being the least squares coefficient for data point i), and the derivative at $i=0$ is computed as the derivative of the spectrum at channel j . In the correlation procedure, c_i is a coefficient that gives the correlator function the approximate shape of the signal sought. The standard deviation of the signal, based on the Poisson counting error, is:

$$\sigma_s = \sqrt{\sum_{i=-m}^{i=n} c_i^2 d_{j+i}} \quad (4)$$

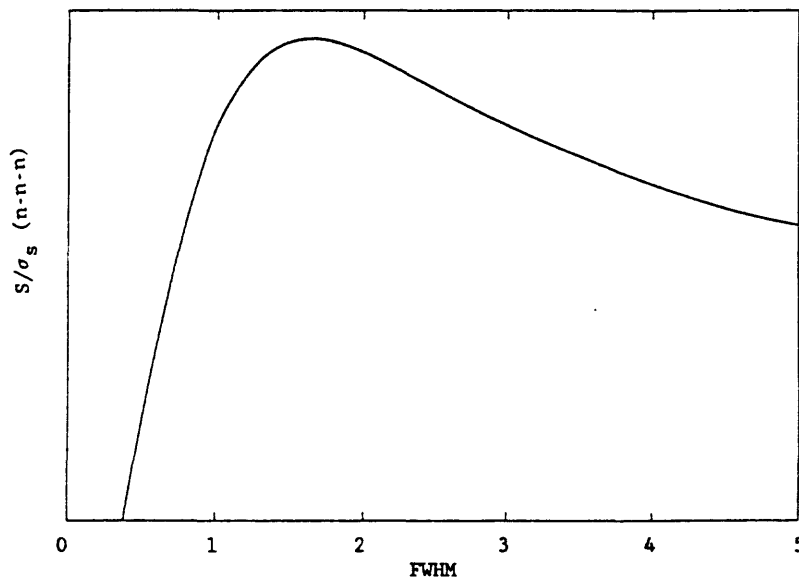
Plotted on the left hand side of figure 1 are the coefficients used, and on the right is the ratio of the signal to its standard deviation. The first two

Figure 1. Convolution procedures used for the location of photopeaks in gamma-ray spectra.



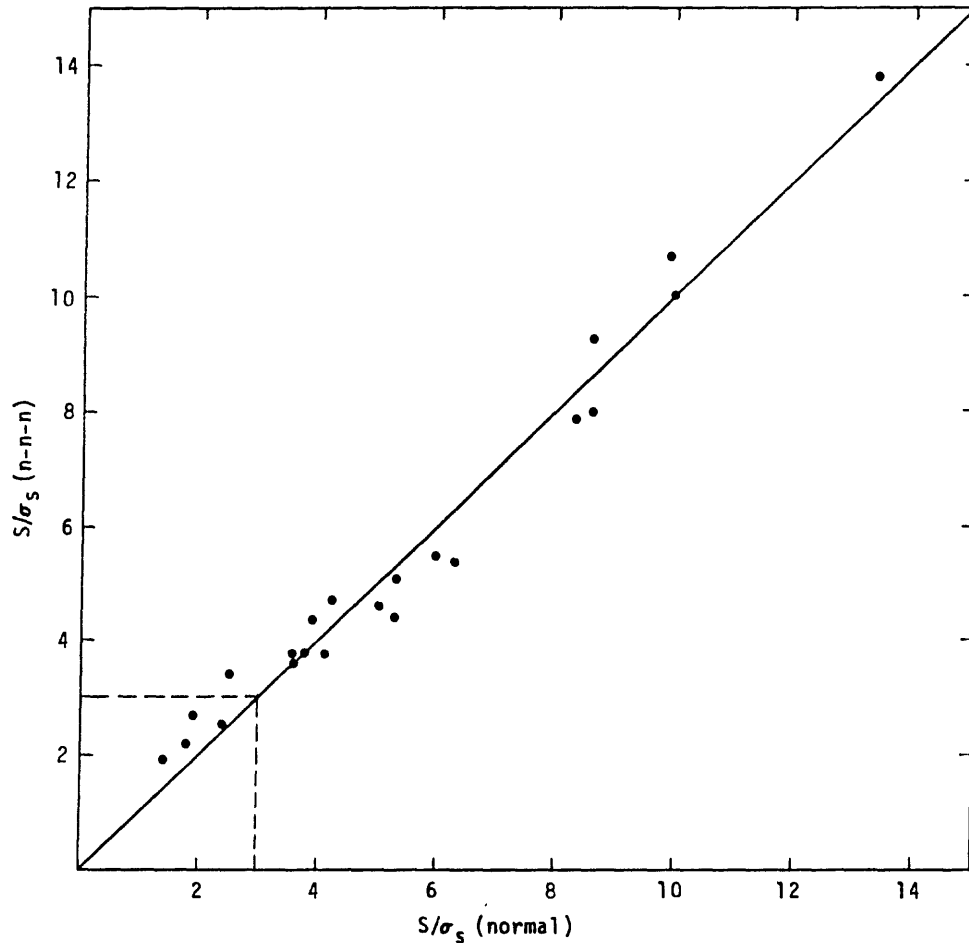
examples are first and second derivative spectra using the Savitzky-Golay coefficients for fitting 5 and 7 channels, respectively, to a quadratic, and determining the derivative of the centermost channel. The last three examples represent cross correlation procedures. One would expect, a priori, that the best correlator would be a signal that is virtually identical with the signal sought (Anstey, 1964): a symmetrical normal distribution, normalized to zero area within the width of the convolute, with a FWHM that is the same as that of the gamma-ray line sought. The last two examples represent the simplest type of cross correlation function in that the coefficients have values of -1, 1 or 2, and therefore are the easiest to program with a computer. The fifth method, the rectangular wave (or "n-n-n") convolute (RWC), has some advantages over the fourth, square wave (or "n-2n-n") convolute (SWC), in that the central positive component can be any integer number of channels, and, for a given width of the central component, produces a stronger signal to noise ratio. The cross-correlation procedures can be seen to produce a signal that is an inverted second derivative spectrum. The signal to noise ratio produced by a correlator of fixed width is dependent on the width of the photopeak sought. This is shown in figure 2 that is a plot of signal-to-noise ratio as a function of the ratio of correlator width to peak width for an RWC correlator applied to a normal distribution on a linear baseline. The RWC signal is a maximum when n is approximately 1.5 FWHM. The signal falls off slowly above 2 FWHM, and sharply below 1 FWHM, this illustrates that the optimum results for a peak-search procedure using the RWC signal would utilize relatively broad convolutes.

Figure 2. Signal to noise ratio for a rectangular wave correlator as a function of the ratio of correlator width to peak width.



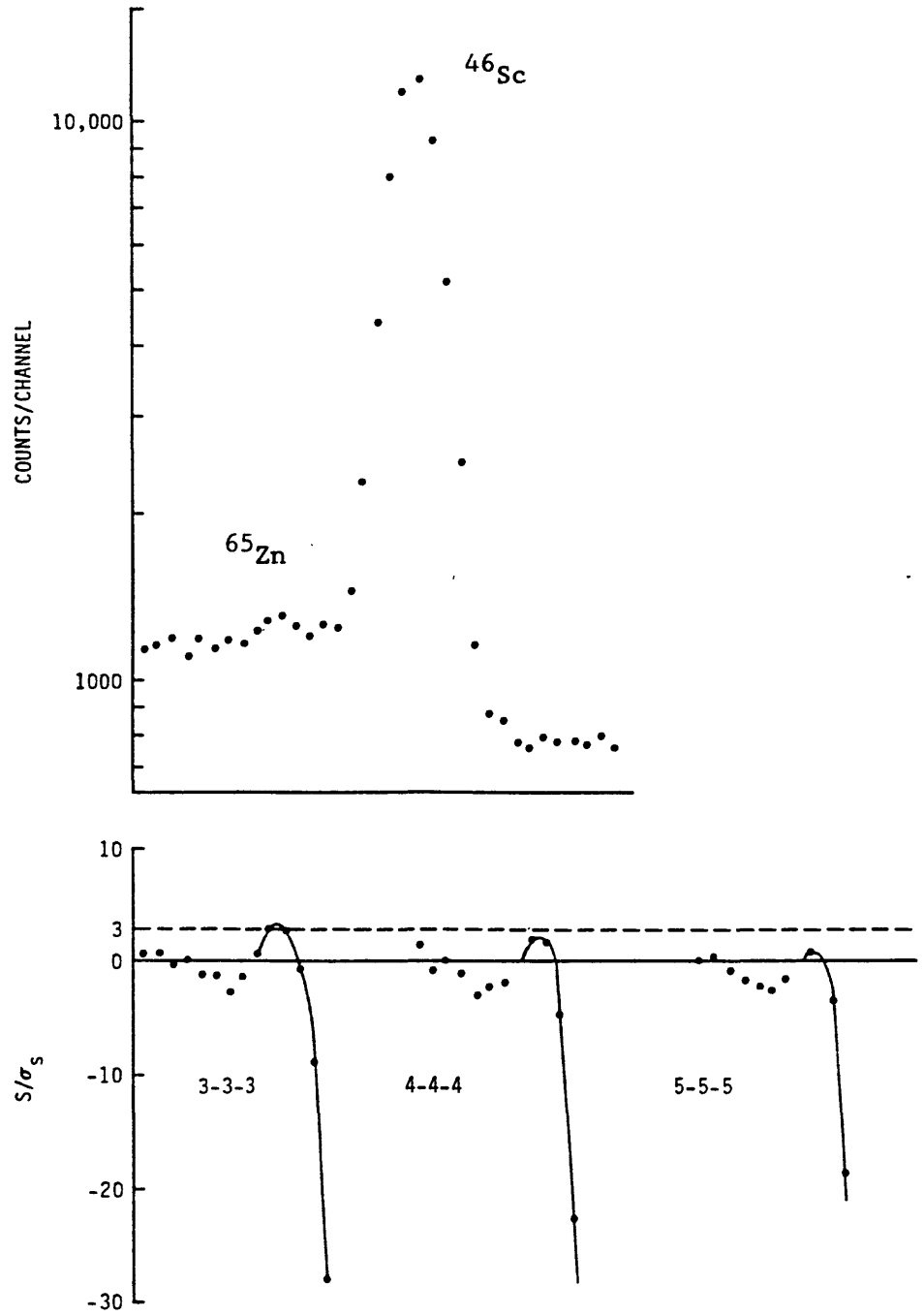
The Savitzky-Golay, SWC, and RWC convolutes were tested using the IAEA intercomparison spectrum 200, that is a 2048 channel spectrum containing 22 peaks of varying intensity, that are near the limit of detection. The spectrum was synthesized from a Ge(Li) detector spectrum, and a computer was used to multiply the channel contents by a constant factor, shift the photopeak locations, and superimpose the photopeaks on a synthetic Compton continuum. The continuum was constructed in the form of a step function providing about 10,000 counts/channel in the lower half of the spectrum, and about 200 counts in the upper half. The resulting spectrum was then subjected to a random-number generation process to simulate the effect of counting statistics (i.e. the channel contents all conform to Poisson statistics) (Parr et al., 1979). The resolution (FWHM) of the peaks in the spectrum ranged from 2.7 to 5.0 channels, and is comparable with the range in values found in a typical 4096 channel Ge(Li) spectrum, where a detector was used that had a FWHM of 2.0 keV for the 1332 photopeak of ^{60}Co , calibrated at 0.5 keV/channel. The response of each convolute was tested against the response from the normal distribution convolute (NDC), where the coefficients were recomputed at each channel based on a FWHM vs. channel-number correlation obtained from the IAEA calibration spectrum number 100. This latter approach represents an overly cumbersome approach to peak location, but is an interesting basis for comparison with the other simpler convolutes. The result of this comparison showed that the RWC correlator had a sensitivity comparable with the NDC correlator (that has a width of 4 FWHM) when the width of the positive central component had an integer value closest to 1.5 FWHM, based on the FWHM calibration. The relative signal strengths of the two approaches for the 22 peaks in the IAEA inter-comparison spectrum are shown in figure 3. Most peak-search procedures test the strength of the signal at each channel location against its associated standard deviation to accept or reject a provisional photopeak. As suggested by the work of Hnatowicz (1976), a s/σ_s cutoff of 3.0 was found to be the most effective limit for all the procedures tested. Where this limit was used the RWC and NDC procedures reported no spurious peaks, except near the Compton edge (that can be rejected using other criteria). Figure 3 shows that the RWC had 18 peaks above the 3σ cutoff, whereas the NDC procedure had 17. If a limit lower than 3σ was used in order to include the difficult peaks at channels 119, 353, 870, and 1517, then spurious peaks were introduced. The Savitzky-Golay procedures were found to be less sensitive, because fewer channels were used for the convolute, and those convolutes having a larger number of channels involve large values for the coefficients.

Figure 3. Response of a variable width rectangular wave correlator relative to a variable width normal distribution correlator applied to the IAEA test spectrum 300.



The RWC filter used to determine the relative signal strengths shown in figure 3 had a total width of all three loops ranging from 12 to 21 channels. Although the use of relatively broad convolutes enhances the sensitivity for the detection of well-resolved photopeaks, they can be less successful for the detection of weak components near strong spectral lines. This is demonstrated in figure 4 that shows a weak 1115 keV ^{65}Zn line next to a strong 1120 keV peak of ^{46}Sc in a spectrum from an irradiated chondritic meteorite. Also shown is the RWC signal for three different widths of the central loop. The ^{65}Zn photopeak would be detected only by the 3-3-3 channel convolute, as broader convolutes all provide signals below the 3σ limit. The signals from the broader convolutes are all lowered because of the strong negative component in the inverted second derivative signal from the 1120 keV peak.

Figure 4. Response of rectangular wave correlators of different widths to a peak gamma-ray line.



In the program "SPECTRA" provisional photopeaks are located by an examination of the first derivative spectrum using a 5-point Savitzky-Golay convolute. When the first derivative is observed to change sign once from negative to positive within a three channel region, both the narrow 3-3-3 and the broader 5-5-5 RWC signals are examined in a region from -2 to +2 channels. The broad 5-5-5 correlator is used to provide sufficient sensitivity for peak detection, while the narrower 3-3-3 correlator is more satisfactory for locating weak lines in the neighborhood of strong lines. Where either RWC signal is above the 3σ limit, the peak is accepted.

2.3. The detection of complex peaks

If spectra of gamma-ray energy standards are provided as the initial spectra of the input file, such spectra are utilized in determining the energy vs. channel number calibration for the spectrometer used to acquire the data. The same spectra are also used to obtain a calibration of resolution (FWHM) as a function of energy. Such a calibration is then used to detect and analyze partially resolved complex peaks. (If calibration spectra are not provided, the program treats all peaks as singlets.)

Following the location of a photopeak the separation between the centermost channel of the peak and the center channel of the previous peak is determined. If the degree of separation is less than 5.0 times the FWHM for that region of the spectrum, the peaks are taken to be complex. The program continues to search for peaks until it locates a peak that passes the separation test. If it has been determined that two or more of the preceding peaks comprise a multiplet, the program branches to a section designed to analyze partially resolved peaks, that is described below. After a peak, or a group of partially resolved peaks, has been identified, minima on each side of the region of interest are defined by an examination of the first derivative to establish a linear baseline.

2.4. Peak boundaries and baseline determination

The minimum on each side of the region of interest is located by observing where the first derivative (using a 5 point fit) changes sign. The maximum value of the first derivative on the low energy end and the minimum value on the high energy end are also determined and used to test single photopeaks for significance and to eliminate Compton edges. The regions around the provisional limits of the photopeak (or group of photopeaks) are then examined to find the channels on each side of the region of interest with the fewest counts. The program then calculates a linear baseline between the

boundary channels and checks the right hand side of the peak to see if any channel within the boundaries falls below the baseline. If this occurs, the boundary channel is decreased by one and the operation repeated until all channels of the right hand side are above the baseline. A similar process is then carried out on the left hand side of the peak. The peak boundaries thus determined are accepted for purposes of determining a baseline under the photopeak, and are included in the printed output from the program.

Average baseline values are then established as follows. Four channels to the left and four channels to the right of the low energy and high energy peak limits respectively are examined. All channels within those regions are averaged with the corresponding boundary channel unless there is an indication of structure within the region. Structure is indicated by three successive channels differing by more than one standard deviation from their adjacent channel in the same direction. The averages of those channels in the absence of structure are then taken as the new values for the counts accumulated in the boundary channels for purposes of defining a baseline under the photopeak.

2.5. Search for additional unresolved components

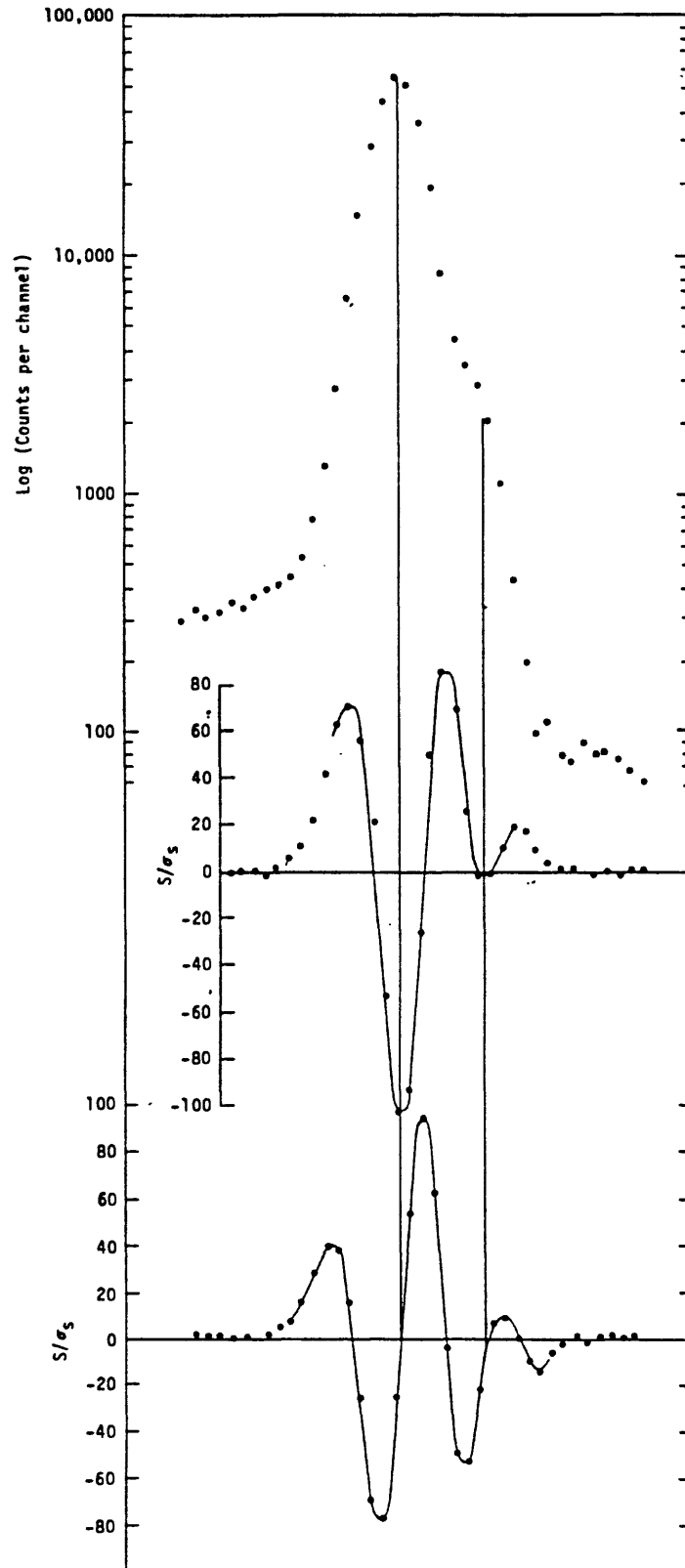
In SPECTRA, a separate algorithm is included for the detection of poorly resolved components adjacent to previously identified photopeaks. The improved resolution for the detection of overlapping peaks attainable by the use of the smoothed second derivative of spectral features has been described by Yule (1971). The detection of overlapping peaks can best be effected by a dual pass procedure, since relatively narrow convolutes, and weak statistical criteria for acceptance or rejection are required. Thus, a second pass of the region of interest is made to identify additional components by looking for minima in the second derivative spectrum. (Alternatively, the third derivative spectrum can be examined for changes in sign from negative to positive values as shown in figure 5.) The following criteria are applied in the search process:

- 1) $f''_i < f''_{i-1}$ and $f''_i < f''_{i+1}$
- 2) $f''_i < -S.D.(f''_i)$
- 3) $(D_i - B_i) > 3.0 \times B_i^{-2}$

where B_i is the calculated value for the baseline in channel i .

A provisional centroid for each peak is calculated from a parabola fit to f''_{i-1} , f''_i , and f''_{i+1} . This centroid is used for weak, unresolved components. The centroids for strong, completely or partially resolved peaks

Fig 5. The location of an unresolved peak using second (middle) or third derivative (bottom) spectra.



are calculated directly from the raw or smoothed data. The separation between a peak detected in the second pass and the adjacent peaks found in the initial pass is tested, and no additional peak is assumed if the separation is less than 2 channels or FWHM/2.0.

The separations test for multiplets is again applied between the lowest energy peak in the region of interest and the highest energy peak previously analyzed. If the test fails, the previous peak or multiplet is incorporated into the region of interest and the baseline redefined, before analysis of the multiplet. Similarly the separation test is also applied between the highest energy peak in the region of interest, and the last peak detected. If the test fails, the last peak is incorporated in the region of interest and the peak search procedure is continued.

The program attempts to reduce the number of components in a multiplet if possible, by checking the valley between adjacent peaks against the linear baseline. If the valley is within one standard deviation of the baseline, the provisional multiplet is divided, and the separate components treated as appropriate.

The program attempts to limit the number of components in a multiplet to four. If more than this number of peaks fail the separation test, the separation criterion is decreased to a minimum of 3.0 times FWHM. However, the program will process up to 20 components in a multiplet if the separation of each component is less than 3.0 FWHM from its neighboring peaks. If more than 20 peaks still fail the separation test, the multiplet is broken down into subgroups at the point in the multiplet where there is a maximum separation between two successive peaks.

2.6. Photopeak integration procedures

Procedures for peak-area estimation can generally be divided into two categories: non-iterative (or digital) methods of summing the channels within peak boundary limits, and iterative least squares fitting techniques. Algorithms that utilize both techniques are included as options in the SPECTRA program. The digital methods used in SPECTRA are described in sections 2.6.1 and 2.6.2; fitting algorithms are described in section 2.6.3. A third approach to processing gamma-ray spectra (not treated in this paper) does not involve the integration of gamma-ray photopeaks directly but rather uses the strength of the signal from the convolution procedure as a measure of peak intensity (Op de Beeck, 1975).

In previous studies of digital integration procedures (Baedecker, 1971; Hertogen et al., 1974) the relative precision attainable by alternate methods of photopeak integration was evaluated empirically, including the "total peak area" (TPA) method, and methods proposed by Covell (1959), Sterlinsky (1968, 1970), Quitner (1969) and Wasson (personal communication in Baedecker, 1971) (as well as some modifications of those methods). The last four methods involve fixed limits of integration and different procedures for baseline determination and for weighting the data during the summation process. The Wasson method yielded a precision comparable with or better than that at the other methods tested, but where comparable precision was obtained, the Wasson method was favored because of its relative simplicity. All digital methods that involve fixed limits of integration are susceptible to errors due to peak broadening at higher counting rates. The TPA method is less sensitive to this effect, whereas those suggested by Covell and Sterlinsky show the greatest variation. For experiments that require the comparison of peak areas between spectra obtained with substantial differences in counting rate, the TPA method may be used to advantage, or where fixed integration methods are preferred, a correction factor can be computed from the relative widths of strong, well resolved lines (Yellen, 1980).

2.6.1. The analysis of single photopeaks

When a well resolved photopeak has been identified, the program applies additional tests to the photopeak to reject spurious peaks. The base area of the provisional photopeak is calculated as

$$\text{Base Area} = 0.5(B_L + B_R)(R - L + 1) \quad (5)$$

where

B_L = baseline counts in left boundary channel(L)

B_R = baseline counts in right boundary channel(R)

$$\text{Peak Area} = \sum_{i=L}^{i=R} D_i - \text{Base Area} \quad (6)$$

The standard deviation of the peak area is then calculated

$$\text{S.D. (Area)} = \sqrt{\sum_{i=L}^{i=R} D_i + (B_L + B_R) [(R - L - 1)/2 - 1]} \quad (7)$$

The photopeak is then rejected if

$$\text{Peak Area} < 2.0 \text{ S.D. (area)}$$

The centroid of the photopeak is determined by fitting a quadratic equation to the three highest channels in the photopeak, after baseline subtraction [five channels are used for broad peaks (fwhm > 4 channels)]. The centroid is then taken to be the point where the parabola is a maximum (the first derivative is equal to zero).

The value of the parabola at the maximum is taken as the height of the peak for the purpose of determining the FWHM of the photopeak. A normal function is fitted to the two channels above and below half maximum on each side of the photopeak, and the FWHM is determined by interpolation. In the case of the calibration spectra the FWHM thus determined is employed in evaluating that quantity as a function of energy for the spectrometer. In subsequent spectra the FWHM is compared with the expected value in order to detect possible unresolved complex peaks. If the peak width determined exceeds the expected value by 10%, a warning is printed next to the tabulated area in the output.

Two methods for measuring the intensity of a photopeak are built into the program, to be selected as options by the user: the TPA and Wasson methods. The Wasson method is illustrated diagrammatically in figure 6. A number of channels specified by the user are taken as the limits of integration. The baseline under the photopeak is determined as a "step" baseline when $B_L > B_R$ and as a linear baseline when $B_L < B_R$. Thus the base area is calculated as

$$\text{Base Area} = \sum_{i=I-N}^{i=I+N} B_i \quad (B_L > B_R) \quad (8)$$

where

$$B_i = B_L - \frac{\sum_{j=L}^{j=i} D_j (B_L - B_R)}{\sum_{j=L}^{j=R} D_j} \quad (9)$$

or

$$\text{Base Area} = (B_L + B_R)(N + 0.5) \quad (B_L < B_R) \quad (10)$$

and

$$\text{Peak Area} = \sum_{i=I-N}^{i=I+N} D_i - \text{Base area} \quad (11)$$

where

I = the centermost channel in the photopeak

N = the number of channels on each side of the centermost channel to be included in the peak area determination

D_i = the number of counts in channel i

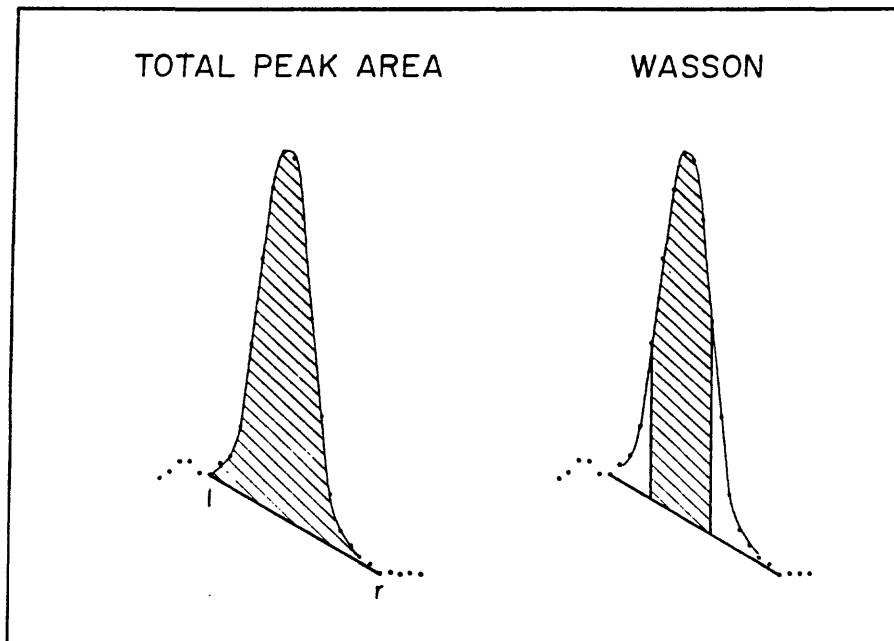
B_L and B_R = calculated values for the background channels I - N and I + N respectively, computed from the previously determined baseline

The standard deviation of the area is

$$\text{S.D. (Area)} = \sqrt{\sum_{i=I-N}^{i=I+N} D_i + (B_L + B_R)(N + 0.5)^2} \quad (12)$$

The performance of the Wasson method can be adversely affected by changes in resolution, that sometimes occur at high count rates. For this reason an alternative method of peak area estimation, the "total peak area method", is included as an option in the program. This method determines the area between the peak limits as in the statistical test described above (equations (5) - (7)), and illustrated in figure 6.

Figure 6. Two alternative digital methods of integration of single photopeaks employed in the program SPECTRA.



2.6.2 The analysis of partially resolved complex peaks

Having recognized two or more complex peaks that are not well resolved, centroids and peak heights are determined for each peak in the multiplet by a procedure identical to that used for singlets. The areas of the component peaks in the multiplet are then determined in the following manner. Let the height of a given peak above the baseline be represented by H_i . The baseline shape is as described above, linear when $B_L < B_R$ and a step (equation 9) when $B_L > B_R$.

Assuming a symmetrical Gaussian shape for all peaks in the multiplet,

$$H_i = h_i + \sum_{j=1} h_j e^{-(C_j - C_i)^2 / 2\sigma_j^2} \quad (13)$$

where the C 's are the centroids of the various peaks in the multiplet, σ_j is determined from the resolution calibration of the spectrometer from the centroid C_j , where

$$\sigma_j = \frac{(\text{FWHM})_j}{2 \sqrt{2 \ln(2)}} \quad (14)$$

The determination of the heights of the photopeaks (h_i), free from the contribution of other members of the multiplet, then simply involves the solution of n equations in n unknowns, where n is the number of peaks in the multiplet. A provisional area for each peak in the multiplet (A_i) is then calculated as:

$$A_i = \sqrt{2 \pi h_i \sigma_i} \quad (15)$$

The total area under the multiplet (A_m) is then evaluated in the same manner as the total peak area of a single photopeak (equations 5 and 6). If the total peak area method has been specified for the program, the peak area is determined as:

$$\text{Peak Area} = \frac{A_m A_i}{\sum A_i} \quad (16)$$

If the Wasson method has been specified, the Wasson area based on the Gaussian fit (A_i^w) is calculated as:

$$A_i = \sum_{j=I_i-N}^{j=I_i+N} h_i e^{-(C_i - C_j)^2 / 2\sigma_i^2} \quad (17)$$

where I_i is the centermost channel of the i th peak in the multiplet.

$$\text{Peak Area} = \frac{A_m A_i^w}{\sum A_i} \quad (18)$$

The standard deviation on the area is calculated from the standard deviation on A_m calculated as in equation (7).

2.6.3. Iterative least squares fitting procedures

Many procedures have been devised for the computer analysis of photo-peaks by non-linear least squares fitting of the spectral features to a variety of functional forms. Because of their complexity and the fact that chi-squared must be minimized by a time consuming iterative procedure, the fitting techniques require a much greater investment in computer time than simple digital techniques. Iterative fitting methods have been reviewed by Campbell and co-workers (McNelles and Campbell, 1975; Jorch and Campbell, 1977; Campbell and Jorch, 1979) who compared reduced chi-squared values obtained with various analytical forms for Si(Li) and Ge(Li) photopeaks. Yule (1973) and Baedeker (1977) have made earlier empirical evaluations of the relative precision attainable using digital and iterative fitting techniques. Both authors observed that for weak lines, the digital and iterative procedures yield comparable results. Yule and Baedeker, in their experiments used the analytical expressions for peak shape suggested by Routti and Prussin (1969) in their program "SAMPO", which was identified by the IAEA inter-comparison as outperforming three other programs of the four most commonly used (Parr et al., 1979).

Campbell and Jorch (1979) found that the optimum fits were obtained with four additive components: 1) a symmetrical normal distribution, 2) a linear or quadratic baseline, 3) a tailing term that consisted of an exponential tail on the left and a normal term on the right, and 4) a step function. In SAMPO, the analytical forms use a simpler expression to fit the low energy tail, and a quadratic to define the baseline. Although McNelles and Campbell (1975) reported less satisfactory fits using the SAMPO tailing equation, it has the advantage that both the equation and its first derivative are continuous with the normal distribution used to fit the upper and right hand side of the photopeak and it introduces only one additional adjustable parameter in the fitting process. The tailing term of Campbell and Jorch is additive and introduces four additional terms. In experiments carried out during the development of SPECTRA, we have continued to use the SAMPO analytical form to account for low energy tailing but have introduced a step function to describe the baseline. Thus the data were fitted to the sum of two functions, one representing the peak and the second representing the base area:

$$Y(x) = F(x) + B(x) \quad (19)$$

where x is the channel number. The peak is defined by a normal distribution:

$$F(x) = \sum_{i=1}^{i=N} H_i e^{-(x_i - C_i)^2 / 2\sigma^2} \quad (20)$$

that is joined to an exponential tail on the low energy side:

$$F(x) = \sum_{i=1}^{i=N} H_i e^{-t[t+2(x-C_i)]/2\sigma^2} \quad \text{for } x < (C_i - t) \quad (21)$$

where N is the number of peaks in the fitting region, H_i is the height and C_i is the centroid of the i th component. σ is the standard deviation of the normal distribution and t is the junction point (distance from the centroid) where the normal distribution changes to an exponential tail. The baseline is defined by the height of the background at the right-hand side of the fitting interval, plus a step function for each component:

$$B(x) = B_R + \sum_{i=1}^{i=N} 1/2 \frac{(B_L - B_R) H_i}{\sum_{j=i}^{j=N} H_j} \text{erfc} [(x - C_i) / \sigma] \quad (22)$$

where B_R and B_L are the baseline values defined for the right- and left-hand sides of the fitting interval respectively. The complementary error function is computed using an algorithm developed by Phillips (1979) (Alternatively the baseline may be represented by equation 9.) H_i , C_i , B_L , and B_R are adjustable parameters in the fitting process. The parameters σ and t are the same for all components in the fitting region. (In the program SPECTRA, an exception is the 511 keV annihilation peak -- when the 511 peak appears in a multiplet the peak is processed as a symmetrical gaussian whose width is variable in the fitting process.) Initial estimates of σ and t are obtained from gamma-ray calibration spectra and could be held fixed or allowed to vary in the fitting process. Chi-squared is minimized by either the Gauss-Seidal (Moore and Ziegler, 1960) or Marquardt (Bevington, 1969) procedures. The quantity X^2 is defined as follows:

$$X^2 = \sum_{i=1}^{i=N} w_i [y_i - Y(x)]^2 \quad (23)$$

where y is the measured number of counts in channel x , with n channels in the fitting interval and where w_i is the weight for datum y and is generally taken as $1/\sigma_i^2$ where σ_i is the standard deviation. In counting experiments w_i is therefore usually replaced by $1/y_i$ based on the Poisson counting error.

As discussed by Phillips (1978), this may lead to biased results when fitting peaks with very low statistics, because those channels that have the fewest counts are given the greatest weight in the fitting process. Phillips has observed that the problem can be alleviated by using a three-point average or a five-point smoothing of the data to calculate the weights. Kohman (1970) has shown that the use of the geometric mean of the input and calculated value as the weight has the advantage that both high and low data with the same error factors each make the same contribution to the sum of the squares. In SPECTRA we have followed Kohman's suggestion and set

$$w_i = 1 / \sqrt{Y(x_i)y_i} \quad (24)$$

Failure to converge to meaningful values can be a problem with any iterative method. The reliability of convergence is dependent on the functional forms employed, the number of adjustable parameters, and the statistical quality of the data. In general X^2 is very sensitive to the height, width, and positions of strong well resolved peaks and to low-order terms in the background function, and it is rather insensitive to the parameters of weak peaks and weak components of multiplets, small tailing corrections to the shape function and higher order background terms. Convergence to meaningful values is best obtained by minimizing the number of adjustable parameters to which X^2 is insensitive or by constraining their values. The fitting algorithm that has been developed as part of the SPECTRA program limits the number of baseline parameters to two, and uses only one additional parameter to correct for low energy tailing. As discussed by Lederer (1972), it is often desirable to constrain the fitting parameters by functional substitution. In the SPECTRA subroutine FITTIT these have the following forms:

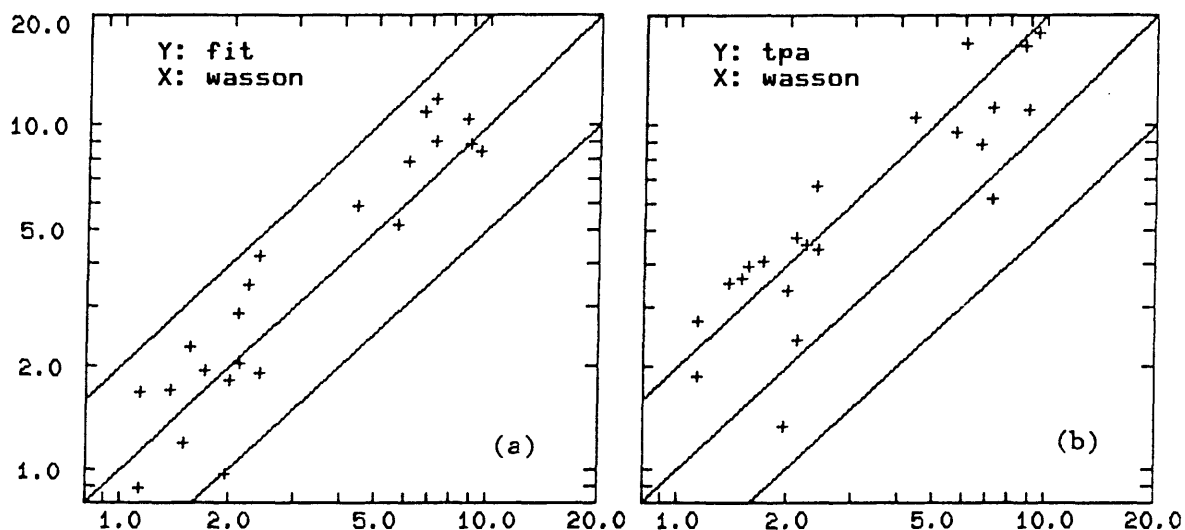
Parameter		Constraint	Function
baseline	b_1	$b_1 > 0$	$b_1 = (b_1')^2$
baseline	b_2	none	
width	w	$w_1 \leq w \leq w_u$	$w = w_1 + (w_u - w_1) \sin^2 (w')$
tailing	t	$t_1 \leq t \leq t_u$	$t = t_1 + (t_u - t_1) \sin^2 (t')$
height	h	$h > 0$	$h = (h')^2$
location	c	$c_1 \leq c \leq c_u$	$c = c_1 + (c_u - c_1) \sin^2 (c')$

where the indicated functions are substituted for the corresponding parameters (p), and the parameters (p') are adjusted to minimize X^2 , and p_1 and p_u represent lower and upper limits on the corresponding parameters.

2.6.4 Precision of peak area determination

The relative precision of the various photopeak integration procedures available within the SPECTRA program has been evaluated using six replicate spectra provided by the IAEA in their 1977 inter-comparison. The results of the analysis are presented in figure 7. Shown are log-log plots of the percent standard deviation for one procedure against that of a second. Lines drawn at 45° represent ratios of 2, 1 and 0.5. A comparison of the precision attainable by means of the fitting algorithm to that obtained by means of the Wasson method is shown in figure 7a. For most of the test peaks, the non-fitting algorithm showed improved precision. The mean precision ratio for the FIT to Wasson plot was $1.17 \pm .03$ where the error value is the 95% confidence limits on the mean. The relative performance of the Wasson and TPA procedures is indicated in figure 7b. The Wasson method yielded improved precision over the TPA method for most of the photopeaks in the test spectra with an average precision ratio of $1.91 \pm .06$.

Figure 7. Log-log plots of the percent standard deviation observed for one method of spectral analysis plotted against that of a second for 22 photopeaks in the six IAEA replicate test spectra.



The SPECTRA program reports an estimate of precision for each peak area determined. Heydorn (1979) has reported a methodology for testing the agreement between the calculated and the actual variability of results using replicate test spectra. The test is based on the Analysis of Precision and the use of the IAEA replicate test spectra. The test parameter T is calculated from the equation

$$T = \sum_j^m \sum_i^6 \frac{(y_{ij} - \mu_j)^2}{\sigma_{ij}^2} \quad (25)$$

where m is the number of peaks in each spectrum (=22), y_{ij} is the area of the jth peaks in the ith spectrum, l_j is the weighted mean of the peak areas of the jth peak in the 6 spectra,

$$\mu = \frac{\sum_1^n (y_i / \sigma_i^2)}{\sum_1^n (1 / \sigma_i^2)} = \frac{\sum_1^n w_i y_i}{\sum_1^n w_i} \quad (26)$$

σ_{ij} is the calculated standard deviation from the program for the peak of the jth peak in the ith spectrum. This parameter should be chi-squared distributed with 5 x m degrees of freedom. Since the underestimation of the precision for some photopeaks may be compensated by the overestimation of others, the Kolmogoroff-Smirnov test has been suggested by Heydorn to test the statistic T_j against the chi-squared distribution with five degrees of freedom.

$$T_j = \sum_i^6 \frac{(y_{ij} - \mu_j)^2}{\sigma_{ij}^2} \quad (27)$$

The test parameter d is defined by plotting the function

$$S_m(T) = \begin{cases} 0 & \text{for } T < T_1 \\ i/N & \text{for } T_i \leq T \leq T_{i+1}, \quad i=1, \dots, m-1 \\ 1 & \text{for } T > T_m \end{cases}$$

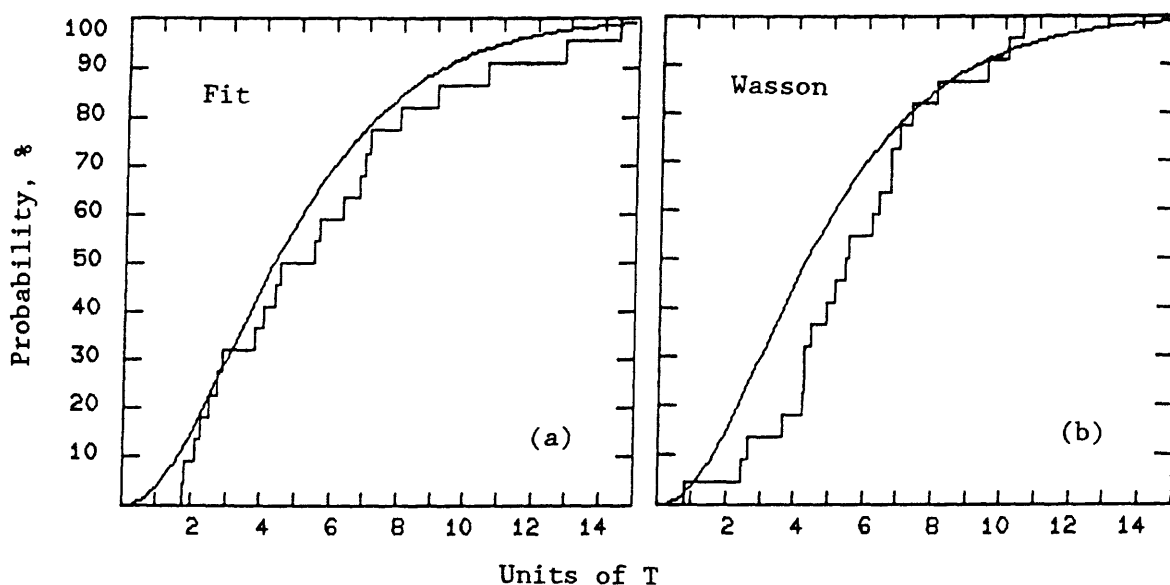
The maximum deviation of the function $S_m(T)$ from the X^2 (5) cumulative distribution is the test variable d that can then be tested.

A Kolmogorov-Smirnoff test plot for the peak areas determined using the iterative least squares fitting algorithm is shown in figure 8a, and a similar plot using fixed limits of integration (Wasson method) are shown in figure 8b. The results of the overall precision test and the Kolmogorov-Smirnoff Test for peak area calculation are shown in the following table:

Peak Area Calculation	T	Deg. of freedom	$P(X^2 > T)$	d	prob.
Fixed limits (Wasson)	126.5	110	0.13	0.30	>0.02
Total Peak Area	132.8	110	0.07	0.18	>0.2
Iterative Fit	126.1	110	0.14	0.12	>0.2

where P is the cumulative probability of exceeding the value of T . The last two columns present the result of the Kolmogorov-Smirnov test where d is the maximum deviation from the X^2 distribution and prob. is the probability of exceeding the observed deviation for each method of integration. The results from all three methods appear to be random samples of the X^2 distribution and the errors reported for all three methods of integration appear to be in statistical control.

Figure 8. The Komogoroff-Smirnov test curves for the peak areas obtained for the IAEA test spectra 300-305 with the Wasson integration procedure (a) and iterative least squares fitting procedure (b).



2.6.5 Accuracy of doublet analysis

In order to test the accuracy of procedures for doublet resolution, 11 spectra with synthetic open doublets (doublets with a discernable valley between the peaks) were produced by counting a ^{60}Co source for a preset time and changing the zero offset of the ADC by five to eight channels and continuing to count for an additional period of time. The ratio of the intensities of the left peak to the right peak in the doublets varied from 0.0101 to 99.0. The Ge(Li) detector used in this experiment had a resolution of 2.2 keV and a peak to Compton ratio of 40:1. In the same experiment 10 spectra with closed doublets (doublets with no valley between the peaks) were produced that had the same range in peak ratios. The degree of separation varied from five to seven channels, so that the two peaks were detectable using a second or third derivative convolute.

The test spectra were subjected to both iterative and non-iterative fitting procedures. The percent errors in the analysis of the synthesized open doublets with variations in the ratio of the lower to higher energy peaks are presented in figure 9. Figure 9a presents the data for the iterative least squares fitting procedure. The errors are less than or equal to 10 percent in most cases. The non-iterative fit was somewhat less successful, particularly for doublets with low ratios as demonstrated in figure 9d. The principal source of error in the non-iterative procedure is in the centroid determination.

The effects on the iterative fitting process of deleting either the tailing correction or the step function (replaced by a linear baseline) are shown in Figs. 9b and 9c. Failure to correct for tailing results in large positive errors for a small component on the low energy side of a photopeak. Figure 9c shows that the use of a linear baseline results in positive errors for a small component on either the high or low energy side of the peak; and indicates that the step function is a better representation for the baseline under a photopeak.

The results for the analysis of closed doublets are shown in figure 10. The data show many of the same features as shown in figure 9. Closed doublets with ratios of less than 0.1 were not detected by the peak search algorithm. The non-iterative fit was less successful owing to positive errors of up to one channel in the observed separation. This is the source of the positive error for ratios > 1 . For roughly two thirds of the doublets, the errors were $< 10\%$. The iterative fitting procedure was successful in treating closed doublets with an error of less than about 6% in all but four cases. Figures 10b and 10c show the same features as their counterparts in figure 9. The positive errors for ratios greater than 1 indicate that the use of a linear baseline has overestimated the baseline on the high energy side of the major component in the doublets tested. The negative errors at a ratio of 0.11 in figures 10a and 10b are caused by errors in the definition of the tailing parameter inspite of constraints imposed by functional substitution. Holding the tailing parameter constant to a value based on the calibration spectra improves the fitting results.

2.7 Calibration of the spectrometer for energy and resolution

In its simplest application, the computer program is designed to read spectral data from magnetic tape or from hard disk, provide a printout of the data, and perform analyses of the spectra for single photopeaks. The program will also determine the energies of the photopeaks based on their centroids

Figure 9. The percent error in the determination of the relative intensities of the components of synthesized open doublets plotted against the log of the true ratio of the intensities of the lower energy to the higher energy peaks. The two data points at each ratio represent the results from the 1173 keV and 1333 keV lines of the spectrum. (More than two data points represent the results from replicate spectra.)

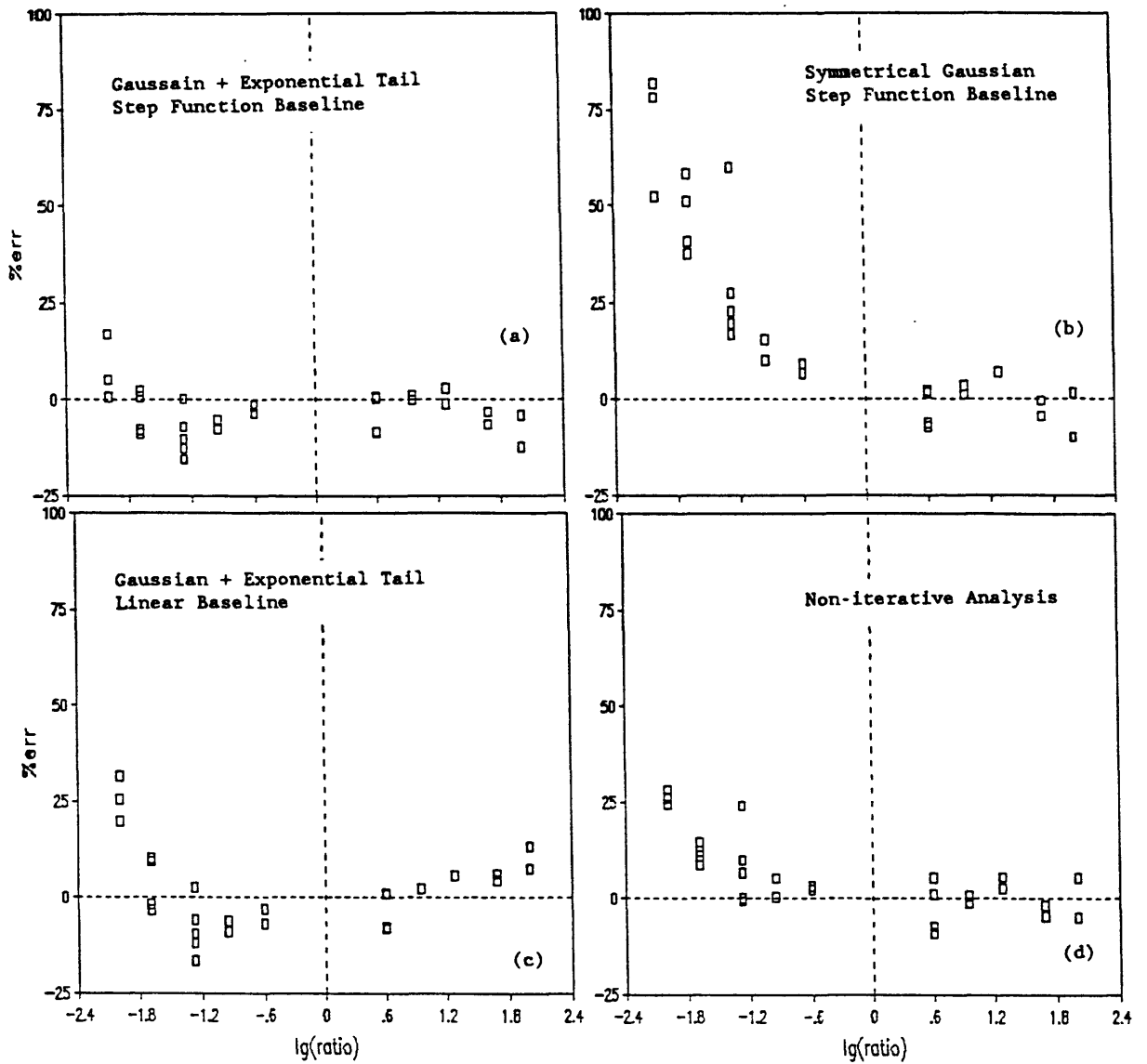
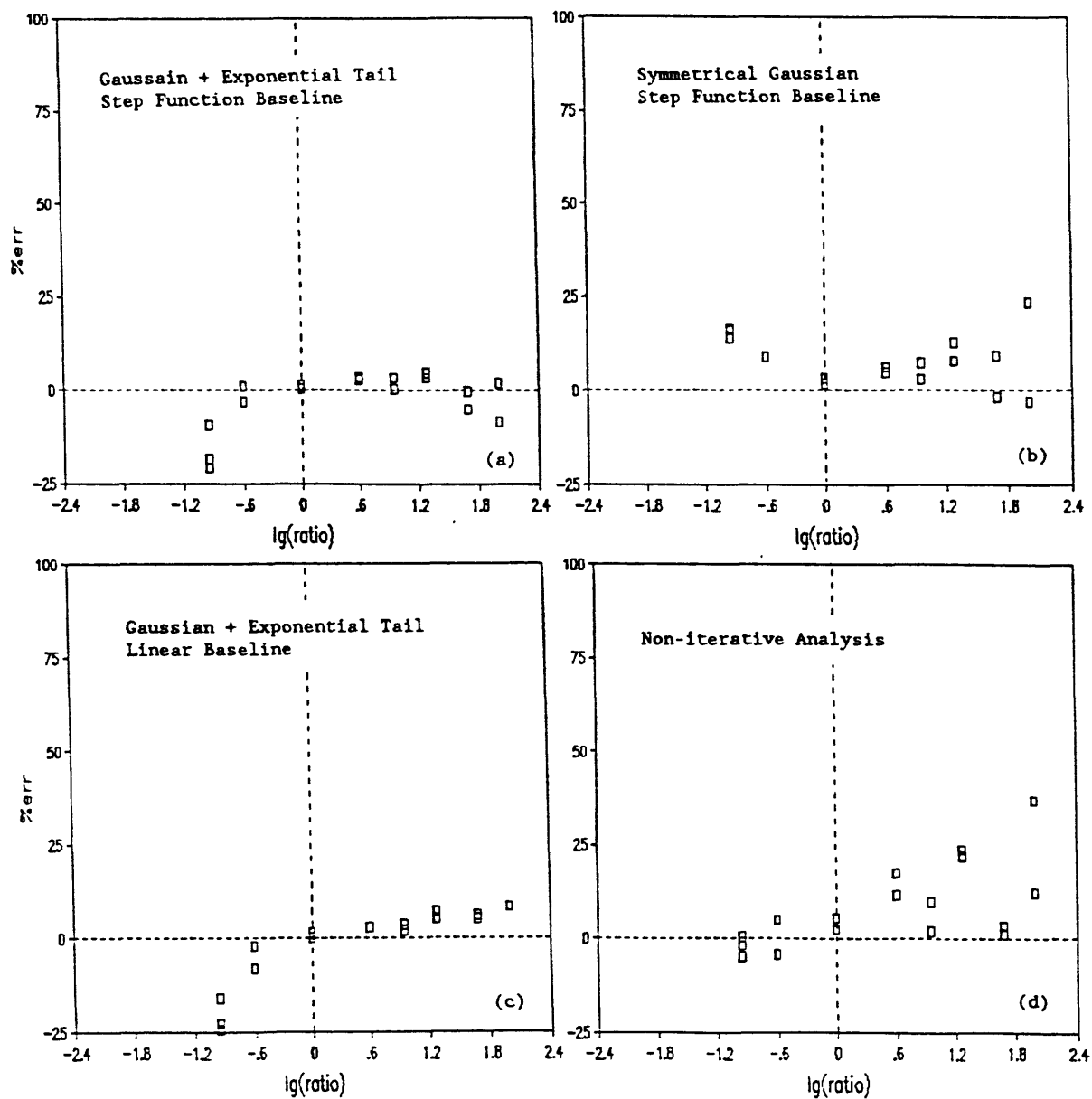


Figure 10. The percent error in the determination of the relative intensities of the components of synthesized closed doublets. The abscissa is the same as that in Figure 9.



and analyze partially resolved complex peaks, provided that spectra of gamma-ray calibration standards are included in the spectral data file. In order to obtain a rough calibration of the spectrometer, a ^{137}Cs spectrum (that has a single gamma-ray at 661.6 keV) must precede the spectra of gamma-ray standards on the input tape, or, alternatively, the approximate centroid of the ^{137}Cs photopeak must be included on the first line of the input data file. For experiments using a low energy photon detector, the 122 keV photopeak of ^{57}Co is used as a reference line. The purpose of the reference spectrum is to aid in locating peaks of known energy in the subsequent calibration spectra. The approximate energy calibration is based on the channel location of the 661 (or 122) keV photopeak, and the assumption that the digital offset of the analog to digital converter (A.D.C.) has been set so that channel 'zero' represents zero energy. Due to possible non-linearity in the spectrometer it may be advisable to include an ^{88}Y spectrum (that has a gamma-ray with an energy of 1836 keV) as a second reference spectrum to aid in locating peaks in the spectra used for calibration with energies greater than approximately 2 MeV. Alternatively, the centroid of the 1836 keV photopeak of ^{88}Y may be included in the first input record.

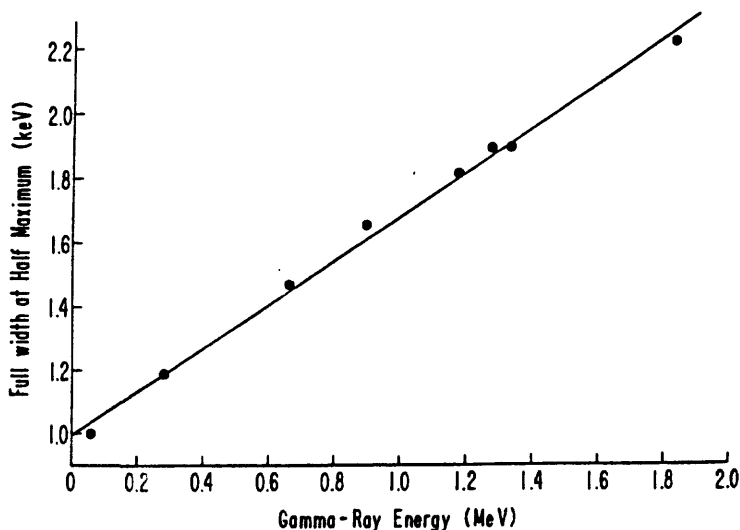
In order to avoid confusion resulting from the use of terms that could otherwise be considered ambiguous, in the remaining discussion the following terms will be used only in the manner indicated. "Reference spectra" will refer to the ^{137}Cs and ^{88}Y (or ^{57}Co) spectra that are used to provide an approximate energy calibration of the spectrometer. "Calibration spectra" will refer exclusively to those spectra on the input tape used to provide an exact energy and FWHM calibration of the spectrometer. "Flux monitor spectra" will apply to spectra of standard reference samples used to calculate elemental concentrations during an activation analysis experiment.

Following the reference spectra in the spectral data file, up to 20 spectra of gamma-ray standards may be used to calibrate the spectrometer. The energies of the lines in each spectrum are specified in the input data file, and based on the rough calibration of the spectrometer obtained from the reference spectra, the corresponding lines are located and their centroids and FWHM determined. If the zero offset of the spectrometer has not been carefully set so that zero energy corresponds to channel zero, the program may encounter some difficulty in locating the calibration lines based on the information regarding the location of the reference peaks. In this case the approximate location of the calibration lines in the spectrum may also be included in the input data file. Up to 50 lines may be used for the calibration. The program then determines the gamma-ray energies in all

subsequent spectra either by interpolation, assuming that the relationship between energy and channel number is linear between calibration lines, or by fitting an n^{th} degree polynomial to the energy calibration data, where n may have any value from 1 to 7. The program does not extrapolate beyond the highest energy of the gamma-ray standards when the linear interpolation method is specified.

The FWHM vs. channel number calibration is determined by fitting a least squares straight line to the data. A plot of FWHM vs. channel number is shown in Figure 11.

Fig. 11. Full width at half maximum plotted against gamma-ray energy.



A provision for correcting gamma-ray energies for gain and zero drift in all spectra encountered after calibration is also included in the program. Two peaks, one at the high energy end and one at the low energy end of each spectrum (within 20 channel windows) may be specified for gain and zero drift correction, respectively. (Alternatively, a single peak may be specified for gain drift corrections alone.) If more than one peak is found within ± 10 channels of the expected location, the program assumes that the most intense peak within that window is the peak sought for the purpose of making gain or zero drift corrections. If the energies of the peaks used are known and specified, the correction factors will be calculated so that the specified peaks will have the specified energies. Alternatively, the gain and/or zero drift correction can be made based on the shift of the specified peaks relative to their locations in the first unknown (or, alternatively, the first calibration spectrum).

3. INSTRUMENTAL NEUTRON ACTIVATION ANALYSIS PROCESSING

When processing gamma-ray spectra from an activation analysis experiment, the program utilizes the gamma-ray energy as determined above to search for the lines of interest in the spectrum used for the analysis. The energies of these lines are designated as part of the input data file. The program selects the line in the spectrum that has a gamma-ray energy closest to the energy expected for the photopeak of interest, within an energy interval of ± 1 keV (or as specified by the user).

The program first makes a pass through a set of spectra on the tape or disk file and analyzes the flux monitor spectra. It selects the peaks of interest in each flux monitor spectrum and calculates the decay corrected specific activity (henceforth referred to as the "monitor comparator factor" or MCF), for each peak. After all flux monitor spectra have been analyzed, the MCF's for each peak are averaged to yield "average monitor comparator factors", that are used to calculate concentrations when the sample spectra are analyzed.

The tape or disk file is then backspaced (or rewound) to the first spectrum of the sample set under consideration [there may be more than one sample set in a given spectral data file (or reel of tape); in this paper the term "sample set" refers to a group of samples, including one or more flux monitor samples]. Each sample spectrum is then analyzed, a "sample comparator factor" (SCF) calculated for each peak of interest, and, from the average MCF previously calculated, concentrations are determined for the elements of interest. The standard deviation of the concentration is calculated based on counting statistics alone. The computation of the MCF and SCF is described below in section 3.6. Algorithms for handling special problems prior to the computation of comparator factors are described in sections 3.1 through 3.5. The algorithms used for pulse pile-up corrections and spectral interference corrections are described in sections 3.1 and 3.5 respectively. The computation of upper limits when expected photopeaks are not detected is described in section 3.2. A subroutine for the interactive analysis of spectral components is described in section 3.3. Under some circumstances peak areas may be recomputed during INAA processing -- these situations are described in section 3.4.

3.1 Pulse pile-up correction

Two methods of correction for counting losses due to the pile-up of pulses in the detector-amplifier system have been incorporated in the program. The simplest approach is to generate a peak in the spectrum from a constant rate pulser fed into the detector preamplifier. When the location of the pulser peak is specified to the program, that peak is integrated in each spectrum, and the observed counting rate is used to compute a pulse pile-up correction factor as

$$f_n = \frac{(\text{pulser area})_n / (\text{duration})_n}{(\text{pulser area})_1 / (\text{duration})_1} \quad (28)$$

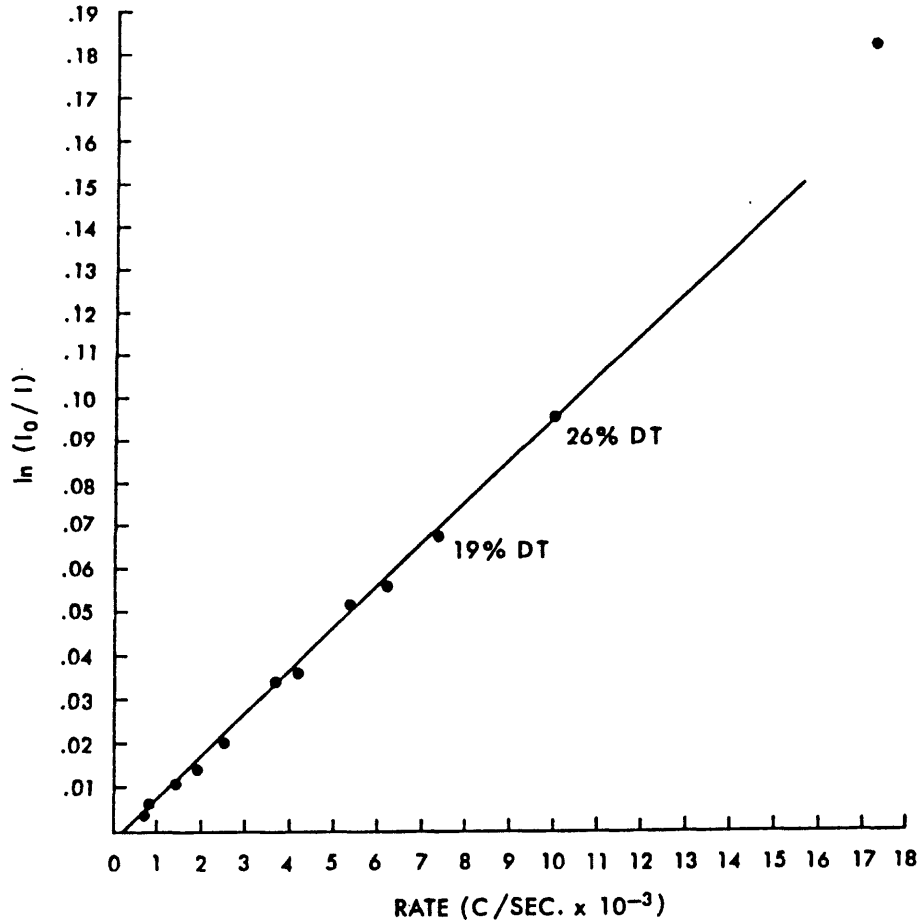
where n is the spectrum number, and the subscript 1 refers to the spectrum of the first sample in a set of activation analysis data. The primary difficulty with this approach is that the pole-zero setting on the amplifier for the pulser pulses is generally different than that for pulses from the detector, and detector pulses arriving on the undershoot from pulser pulses can lead to distorted or "shadow" photo-peaks in the spectrum.

A second approach is to incorporate a pulse pile-up correction factor using an experimentally determined pulse pile-up resolving time for the detector amplifier system used for an experiment. Following an approach used by Wyttenbach (1971), the pulse pile-up correction factor for a given detector-amplifier combination can be computed as

$$f_n = I_o / I = e^{2nt} \quad (29)$$

where I is the observed counting rate, I_o is the corrected counting rate, n is the mean pulse rate from the detector, and t is the measured pile-up resolving time. An estimate of n can be obtained by integrating the entire spectrum and dividing by the live time duration of the count. t can be estimated by measuring the losses in a peak with constant intensity at different total counting rates controlled by positioning a source at different distances from the detector. A plot of $\ln(I_o/I)$ vs. n should be linear, with the slope equal to $2t$. Such a plot is shown in figure 12 for a Ge(Li) detector coupled to an amplifier with a time constant set at 2 microseconds. The data were obtained using a ^{60}Co source to vary the counting rate, and a Nuclear Data 100 MHz ADC. The plot is nearly linear up to a dead time of 20%. The apparent resolving time becomes longer at higher counts, possibly due to errors in the dead time correction of the ADC. When a value of t is provided to the program, a pile-up correction is included in the activation analysis calculations using equation 29.

Figure 12. Log of the pulse pile-up correction factor plotted against counting rate.



The largest source of error using this approach is that the counting rate N may be underestimated if there is appreciable activity with an energy greater than the high energy cut-off of the spectrum being analyzed. If an observed counting rate of 8000/s underestimated the true counting rate by 20%, there would be a 1.3% error in the correction factor of 1.066 with a pulse pile-up resolving time of 4 microseconds.

3.2 Computation of upper limits

In the case where a gamma-ray line has been specified for use in the analysis and has been observed in a flux monitor but not in the unknown, an upper limit on the concentration of the element in question is calculated.

This is carried out by estimating an upper limit on the peak area by calculating the minimum detectable peak area above the observed background using the peak detection criterion used in SPECTRA: a rectangular 3-3-3 correlation function (equation 3) where the coefficients are -1, +2, and -1 (see figure 1). Adding a hypothetical gaussian peak above the observed baseline, the correlation function becomes:

$$S_j = \sum_{i=-n}^{i=n} c_i (d_{j+i} + h g_i) \quad (30)$$

where d_j is the number of observed counts in channel j , h is the height of the superimposed gaussian and

$$g_i = e^{-i^2/2\sigma_j^2} \quad (31)$$

where σ_j is determined by the width of the gaussian (equation 14). The standard deviation on the signal S is estimated as

$$S = \sqrt{\sum_{i=-n}^{i=n} c_i^2 (d_{j+i} + h g_i)} \quad (32)$$

since the minimum detectable peak determined by

$$S_j = 3.0 \sigma_S \quad (33)$$

the height of the gaussian h is calculated by combining equations 30 through 33 and solving for h . The upper limit is then taken to be

$$\text{area} = h \sigma \sqrt{2 \pi} \quad (34)$$

If the Wasson area has been specified the upper limit on the area is multiplied by the fractional area for the specified fixed limits of integration

$$\text{area} = \text{area} \cdot \text{erf}(w / 2 \sqrt{2 \sigma_j^2}) \quad (35)$$

where w is the $2n + 1$ channel integration width.

3.3 Interactive plotting of selected photopeaks

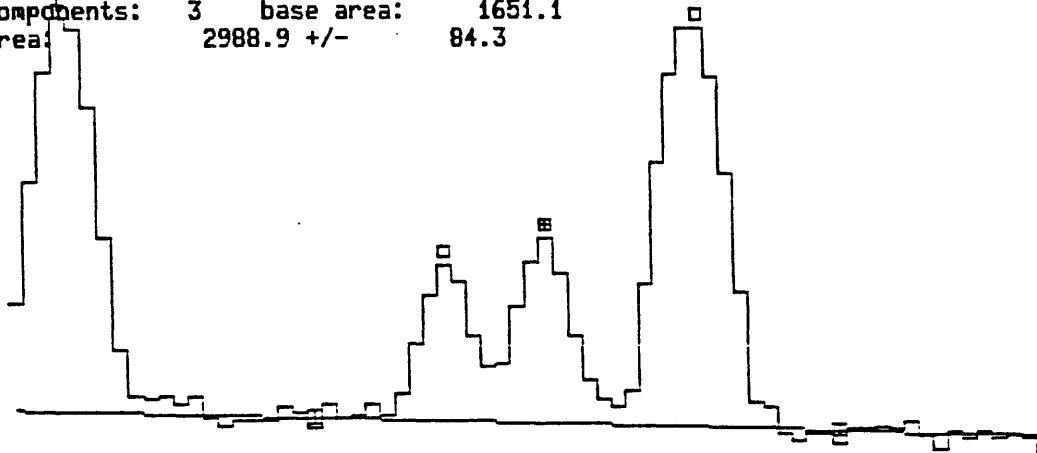
A graphics subroutine (PLOTPK), callable from the main SPECTRA program, is available to assist in processing potentially difficult peaks during the activation analysis calculations. Individual spectra and individual lines can be designated in the input files for plotting within the activation analysis section. The user may elect to set the program to automatically plot peaks with poor counting statistics and peaks with possible interferences. The spectral region containing a designated peak of interest can be displayed on the terminal screen (figure 13a), and the analyst is provided with numerous options that give him greater control over the computer peak area determination. These options include a) redefining the baseline on each side of the region of interest; b) adding or deleting components within a multiplet; c) shifting the location of a previously defined centroid; d) splitting a multiplet into two (or more) sub-groups of peaks; e) redefining a multiplet region to include an adjacent peak/multiplet; f) calling an iterative least squares fitting algorithm for a given peak or multiplet; g) converting the analytical result for a poorly resolved peak to an upper limit, or integrating a peak previously treated by SPECTRA as an upper limit to produce a real value.

In addition to the above options, numerous commands are available to control the display of the spectral data, and display information regarding the lines within the region of interest. These options include: a) listing the energy, channel number and net counts at the cross hair location; b) displaying the location and expected intensities (scaled to the observed intensity of a specified line in the sample spectrum) of known spectral lines of a designated isotope within the plotted region; c) listing to the terminal screen the peak search data (centroids, baseline limits, peak areas and isotope identification) for peaks in the display region; d) plotting the results of the fitting procedure and the residuals (figure 13b); e) changing the plotting scaling factor to expand or contract the peak intensity scale; f) shifting the plotting region to the left or right; g) expanding or contracting the number of channels displayed within a region of interest; h) changing from a logarithmic to linear scale; i) choosing between continuous and histogram display of the raw data; j) deleting the header information from the terminal screen and k) plotting the entire spectrum, or a selected region of the spectrum on the terminal screen.

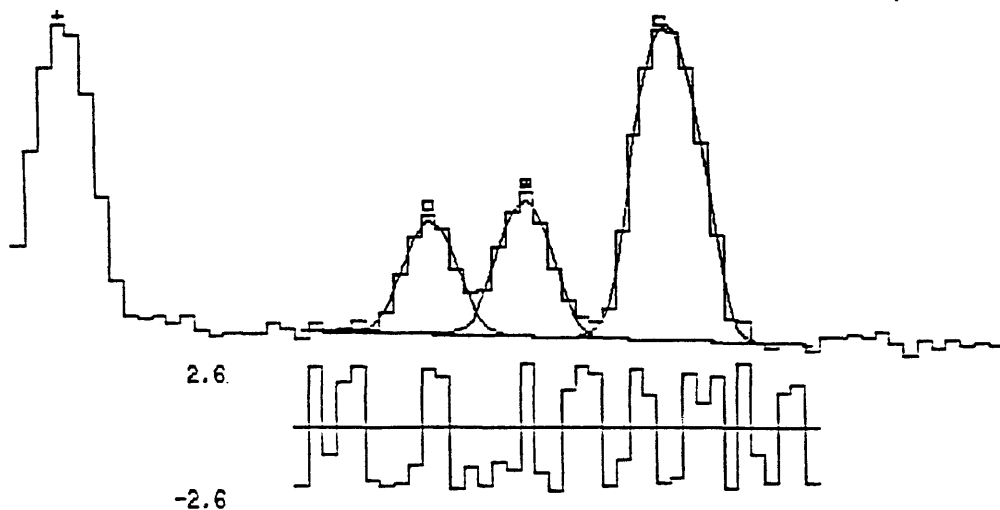
Figure 13. Output from PLOTPK:

- a) multiplet
- b) fitted multiplet and residuals

tagword: 5 sample: FLUX HMS-3 LOG SCALE
element: ZN energy: 1115.4 centroid: 2230.9
limits: 2215 to 2252 region: 2195 to 2272 peaks: 140 to 142
components: 3 base area: 1651.1
area: 2988.9 +/- 84.3



X-HAIR 1: Space-bar=Set baseline, Q=Accept plotted area, ?=Help



X-HAIR 1: Space-bar=Set baseline, Q=Accept plotted area, ?=Help

An important capability that has been incorporated in the PLOTPK subroutine is the definition of "regions-of-interest" (ROI) to control the analysis of a particular peak or multiplet in all subsequent spectra. An ROI defines the peak analysis limits, number of components in a multiplet, and mode of integration in any spectrum of an activation analysis data set, and constrain the program to analyze all subsequent spectra in the same manner, as described in section 3.4.3. An additional option with the PLOTPK subroutine permits the analyst to redefine the plotting control parameter for any line of any isotope designated for analysis. A menu of PLOTPK commands is available to the user, and is presented in figure 14.

Figure 14. Menu of PLOTPK commands

```

***** PLOTPK : MENU OF CROSS-HAIR OPTIONS *****

          GRAPHICS DISPLAY
A B C: Increase scaling factor
l 2 3: Decrease scaling factor
H      : Histogram toggle
L      : Log/Linear toggle
R      : Residuals toggle (fitting)
X x    : Expand/contract region
[{}])  : Shift plotting region l/r
=      : Refresh screen
|      : Redraw (original scale/width)
*      : Header information toggle
^ V    : Change plotting control list
!      : Store ROI parameters

          DATA DISPLAY
E      : Energy, Channel, Counts
O      : Peak Search Data to Screen
P      : Spectral lines for isotope
z Z    : Plot first/second derivatives

          PEAK INTEGRATION
F      : Fit ROI (< 7 peaks)
M      : Move analytical line centroid
N      : Move X-hair line centroid
U      : Upper limit (convert to)
+ -    : Add/Subtract 2**20 (overflow)
SpBar: Change baseline (left & right)

          MODIFY NO. COMPONENTS IN ROI
D I    : Delete/Insert Peak at X-hair
S      : Split multiplet ( 2 groups)
T      : Split multiplet (> 2 groups)
< >   : Include next peak/multiplet

          MISCELLANEOUS
G      : Plot region of spectrum
W      : Baseline Parameters to Screen
K &    : K:Quit SPECTRA, or &:Spawn out
Q      : Accept all peak area values

```

The entire graphics package used throughout the data reduction process was developed for the increased speed and efficiency required for the interactive analysis of spectral data. All commercial software packages that were tested during the development of PLOTPK were found to be too slow. The graphics package developed for this work is switch selectable to use either the REGIS (specifically for a DEC VT200 series terminal) or TEKTRONIX graphics protocol (specifically for TEKTRONIX 4014 series and GRAPH-ON 200 series terminals). The PLOTPK subroutine has proven to be particularly valuable, both

in assuring that interferences are properly treated in complex spectral features, and that baselines are properly defined when counting statistics are poor, in regions of the spectrum with unusual baseline shape, as well as in diagnosing problems in the detection and measurement of complex multiplets during the peak search and analysis procedure.

3.4 Recomputation of peak areas

There are three situations within SPECTRA, whereby the peak areas for a particular line of interest may be re-calculated during INAA processing: a) if the centroid of an analytical line appears to be outside of expected limits, b) if an unexpected overlapping peak is detected and deleted, or c) if a region-of-interest has been defined using the interactive plotting capability.

3.4.1 Centroid location

Analytical lines are located based on their gamma-ray energy within limits that may be set by the analyst. As indicated above, the program selects the line that is closest to the expected location, within a region whose default is ± 1 keV. However, for relatively broad peaks in regions of poor counting statistics, the peak centroid may not be well defined. A capability has therefore been introduced into the section for INAA processing to automatically redefine the peak centroid, and recompute the peak area, if the analytical line is within the search criteria, but is two or more channels removed from its expected location based on the energy calibration. However, the centroid is not changed if the peak has been identified as being part of a complex region, if there is an indication of significant positive or negative slope at the expected peak location, or if gain shift corrections have not been applied for the current spectrum. If interactive plotting has been enabled then the peak in question will be plotted if it is more than two channels removed from its expected location, whether or not the above criteria are met.

3.4.2 Detection and deletion of unexpected overlapping peaks

The SPECTRA program contains a sensitive test for changes in peak shape in order to test for closely spaced overlapping lines. However, there is some danger that in regions with poor counting statistics the algorithm used to detect complex structure may introduce spurious peaks into the peak analysis process. The SPECTRA program therefore contains an algorithm to test for and to optionally delete weak overlapping lines adjacent to analytical lines during INAA processing. If an overlapping peak is detected and if no potential interference has been specified at that energy in the input data file, it is

listed in a report of interferences (see section 3.5). If interactive plotting is enabled, the peak will be plotted on the terminal screen even if the peak has not been designated for plotting. The user may also enable a switch to automatically delete all unexpected weak overlapping lines; deleted peaks are similarly reported in the interference correction summary report.

3.4.3 Definition of regions of interest

As described above, regions-of-interest (ROI) may be defined for any analytical line using the interactive plotting capability in order to control the processing of that line in all subsequent spectra within an activation analysis set. If a region of interest has been defined for an analytical line, the program first defines provisional analysis limits for the region by searching for minima within ± 2 channels of the previously established peak analysis limits (these limits may subsequently be revised during the peak analysis procedure). The number of peaks that were located within the established limits is then compared with the number expected based on the number of peaks within the region when the ROI was defined. If a peak appears to have been missed during the peak search procedure (the number of peaks in the current region is less than the number in the original ROI) an attempt is made to match all the peaks in the current spectrum with their expected locations in order to define the location(s) of the missing peak(s). Additional peak(s) are inserted in the appropriate location(s) providing the channel contents are three standard deviations above the provisional baseline. However, if a greater number of peaks were located during the peak search process for the current spectrum than were found in the initial spectrum, no peaks are deleted. The peak analysis procedure is then called using the same analysis mode as was used when the ROI was defined. Note that in this manner it is possible to designate certain peaks for automatic analysis using iterative least squares fitting techniques, even though the default analysis mode may have been for a non-fitting procedure.

3.5 Interference corrections

The program is able to correct for those spectral interferences that are too poorly resolved to be recognized as multiplets when a second interference free line of the interfering radionuclide can be observed in the spectrum. For example, data for Se based on the 264.7 keV line of ^{75}Se can be corrected for the 264.1 keV interference from ^{182}Ta using any one of several interference free Ta lines in the spectrum. Similarly, the area of the 1115.5 keV line of ^{65}Zn can be corrected for the interference from the 1115.1 line of ^{160}Tb , using the 879.4 or 1178.1 keV lines of ^{160}Tb . The line that the interference correction is to be based on (the "reference line") is specified

by the user, along with the ratio of the intensities of the interfering line to that of the line specified. Either the measured ratio for the detector used in the experiment or the ratio of the true intensities along with the slope of a log-log plot of relative photopeak efficiency vs. gamma-ray energy for the detector can be specified. The interference correction is calculated as

$$A_i = A_r \frac{I_i}{I_r} \left\{ 10.0^f + \log(E_i/E_r) \right\} \quad (36)$$

Where

- A_i = Calculated interference correction
- A_r = Measured area of the reference line
- E_i = Energy of the interfering line
- I_i = Intensity of interfering line
- E_r = Energy of the reference line
- I_r = Intensity of reference line
- f = slope of the detector efficiency curve

For example, for the 264.7 keV line of ^{75}Se :

$$\text{AREA}(\text{corrected}) = \text{AREA}(\text{measured})(264.7) -$$

$$\text{AREA}(\text{measured})(1221.4) \times \frac{8.40}{62.1} \times (10.0^f \times \log(264.1/1221.4))$$

where 8.40 and 62.1 are the relative intensities of the of the ^{182}Ta 264.1 and 1221.4 lines respectively. Two corrections may be made for each line used for analysis.

When fixed limits of integration (Wasson method) have been specified for peak integration, it is important to correct the estimated interference intensity for the difference in peak width between the interference and the reference line:

$$g = \frac{\text{erf}(v/\sigma_i\sqrt{2})}{\text{erf}(v/\sigma_r\sqrt{2})} \quad (37)$$

Where the error function has been used to calculate the expected fraction of the peak area define by the fixed limits of integration, and

v = the half width of the fixed integration region ($N+0.5$ channels)

σ_i = is defined by equation 14 for the interfering peak

σ_r = is defined by equation 14 for the reference peak

It is also necessary to calculate the fraction of the interfering line that would be within the integration limits of the peak of interest:

$$h = \frac{0.5 \left| \operatorname{erf}\left(\frac{u - v}{\sigma_i \sqrt{2}}\right) - \operatorname{erf}\left(\frac{u + v}{\sigma_i \sqrt{2}}\right) \right|}{\operatorname{erf}\left(\frac{v}{\sigma_i \sqrt{2}}\right)} \quad (38)$$

Where

u = the separation (in channels) between the interfering peak and the analytical line.

and therefore for fixed limits of integration:

$$A_i = A_i \cdot g \cdot h \quad (39)$$

For some interferences, the interfering line may be detected in the peak search procedure for some spectra, and remain undetected in others. This has been observed in rock analysis for the interference of the 299.9 keV line of ^{233}Pa on the 298.5 keV line of ^{160}Tb . Therefore, the separation between an analytical line and its expected interference is provided as an input parameter to the program. If the peak search routine locates a line within 0.25 keV of the expected location based on the separation parameter, the interference correction is not made, and the region is treated as a normal multiplet.

The SPECTRA program produces a data file that contains the magnitude (in percent) of the interference corrections made. The data file may then be processed by the program ICREPORT to produce a printable file that consists of two reports: a) a report of interference corrections made during INAA processing, and b) a tabulation of overlapping peaks detected near analytical lines that were designated as interference free. The first report presents a matrix that lists the magnitude of the interference correction for each line designated for correction, for every sample in the data set. The second report lists the magnitude and degree of separation for overlapping peaks observed in the spectra, where the separation is less than one full width at half maximum from analytical lines that were expected to be interference free. The latter report is intended to point up unexpected spectral interferences, or problems with peak shape (e.g. caused by gain/zero drift or poor counting statistics) that could cause the computer to erroneously treat an interference free peak as complex.

3.6 Computation of element concentrations

In calculating comparator factors the program corrects the counting data for decay during the count and corrects each count for decay back to the time of the start of the first count in a sample set, or a time specified by the user.

$$\text{MCF} = \frac{(\text{peak area}) \cdot \lambda \cdot t_c \cdot e^{\lambda t_d}}{(\text{flux monitor weight}) \cdot t_1 \cdot (1 - e^{-\lambda t_c})} \quad (40)$$

$$\text{SCF} = \frac{(\text{peak area}) \cdot \lambda \cdot t_c \cdot e^{\lambda t_d}}{(\text{sample weight}) \cdot t_1 \cdot (1 - e^{-\lambda t_c})} \quad (41)$$

$$\text{Concentration} = \frac{\text{SCF}}{\text{average MCF}} \quad (42)$$

where

- λ = the decay constant for the indicator radionuclide
- t_d = the elapsed time between the start of the first count in the sample set and the start of the count being processed.
- t_1 = live time duration of the count
- t_c = clock time duration of the count
(If t_c is unknown, the program assumes that $t_c = t_1$.)

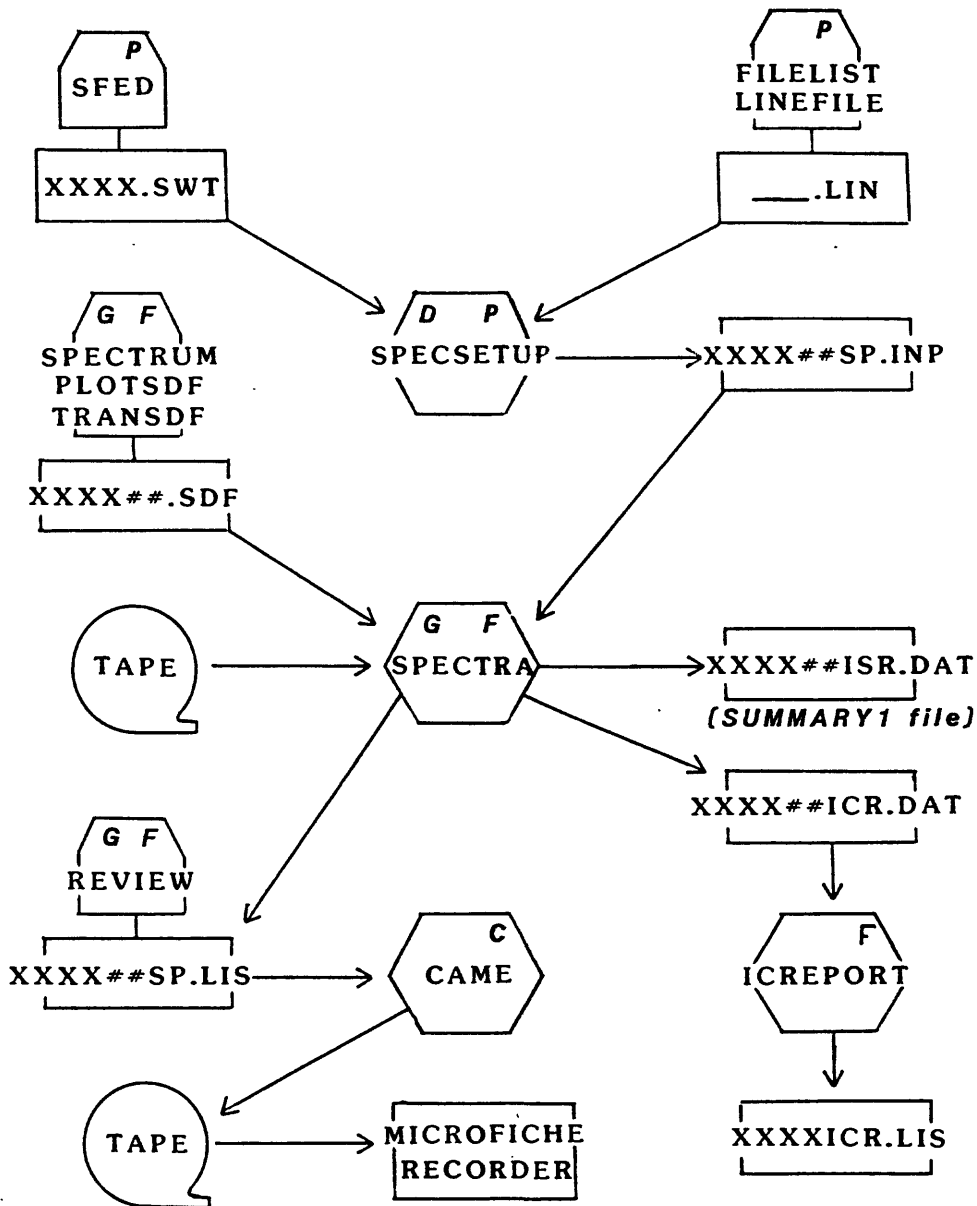
4. SUPPLEMENTARY PROGRAMS

4.1 Spectral data analysis

The SPECTRA program described above is the primary program in the first stage of a complete data analysis procedure that consists of the following four stages: 1) spectral data analysis; 2) averaging of the data from multiple lines; 3) averaging of the data from multiple counts to produce a report of analysis; 4) transmission of both the analytical data and quality control data to data base management systems. A large number of supplementary programs have been developed to interactively define the input data files for the SPECTRA program, and to process the output data files that lead ultimately to a final report of analysis. A flow chart of the spectral analysis stage of the data processing procedure is shown in figure 15. The input control file (XXXX##SP.INP; where XXXX identifies the irradiation sample set, and ## identifies the count number of irradiation XXXX) for the SPECTRA program is defined by an interactive program SPECSETUP, that merges information from the sample i.d. and weight file (XXXX.SWT) and the appropriate library file that defines the spectral lines used for the determination of each element of interest for the particular counting of the samples (e.g. GE.LIN), depending on type of detector, sample matrix, and length of decay since the end of irradiation. Both the (XXXX.SWT) and (.LIN) files have their own editor programs (SFED and LINEFILE respectively). (In the flow chart the letters in the hexagons representing programs have the following meanings: G -- produces screen graphics; D -- deposits or retrieves information from the radio-chemistry laboratory sample control data base). The SPECTRA program is able to read spectral data files either from disk storage (.SDF files) or directly from computer compatible magnetic tape. Two graphics display programs (SPECTRUM and PLOTSDF) and one editor (TRANSDF) are available to treat spectral data files. SPECTRUM plots individual spectra, and regions of interest, while PLOTSDF can be used to overlay regions of interest from multiple spectra so that the analyst can visually check for gain and/or zero shift and line broadening. TRANSDF is used to transfer spectra to a second file for the purpose of reordering spectra, deleting spectra or merging spectra from multiple files.

The SPECTRA program creates three output data files: a) a printable listing of all results from the peak search and peak integration procedures, along with the results of activation analysis calculations for each analytical line; b) the concentration data based on each analytical line of each element of interest stored in a direct access data file (XXXX##ISR.DAT) for subsequent processing in the next stage of the analytical procedure; and

Figure 15. Flow chart of spectral data analysis

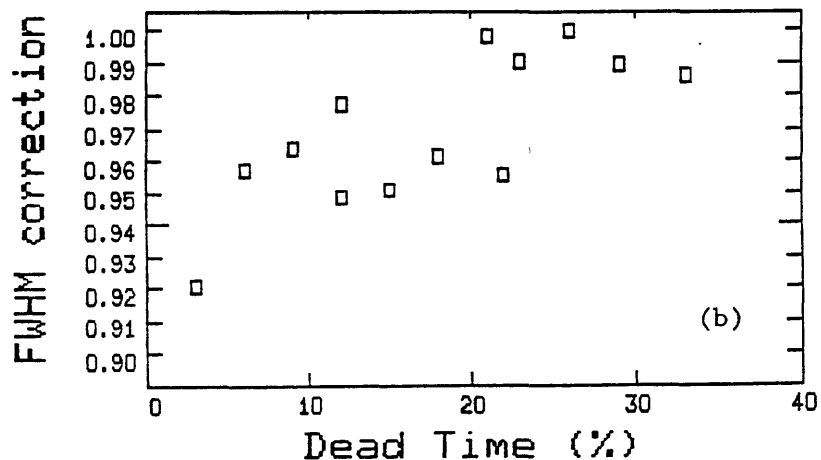
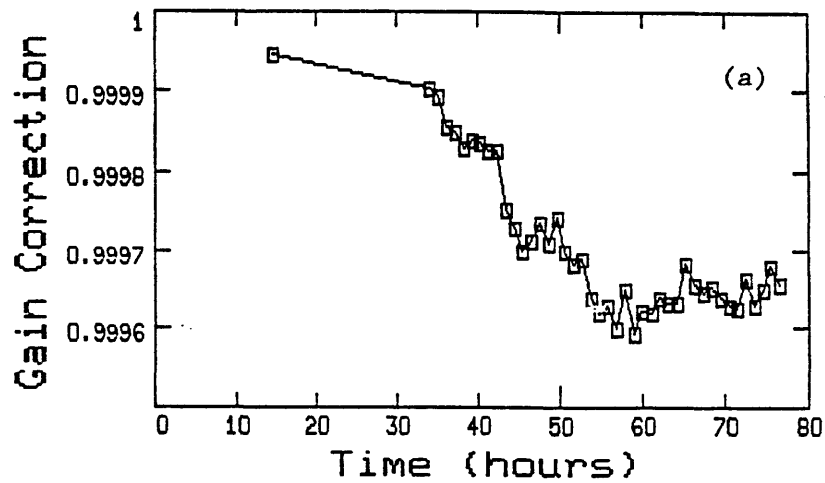


c) a file (XXXX##ICR.DAT) that contains information on interference corrections made and line overlap detected during INAA processing. The lineprinter data file (XXXX##SP.LIS), which may be 1 Mbyte in size for a 40 sample irradiation, can be scanned by a text editor or by using a special editor program (REVIEW) to search for any problems that may have been encountered during the running of SPECTRA. A matrix of relative decay corrected specific activities (analytical line vs. flux monitor number) can be quickly reviewed for internal consistency among the multielement standards.

Plots of detector performance vs. time can be displayed on the terminal screen (figures 16a and 16b), to examine gain drift, and detector resolution during the counting cycle. The results from the peak search and peak integration procedure can also be reviewed, particularly to search for any problems that may have been encountered in corrections to the data for gain and zero drift or for spectral interferences. If no problems are detected, the data file (XXXX##SP.LIS) is processed by the program CAME to produce an output tape that will drive a microfiche recorder; all peak search data from SPECTRA, as well as intermediate report files are transferred to microfiche for long term storage. (note: the program CAME is written in COBOL, all other programs described in this document are written in FORTRAN.)

Figure 16. Output from the REVIEW program for data sets in which detector performance drifted during analysis.

- a) Gain shift vs. time
- b) FWHM vs. dead time

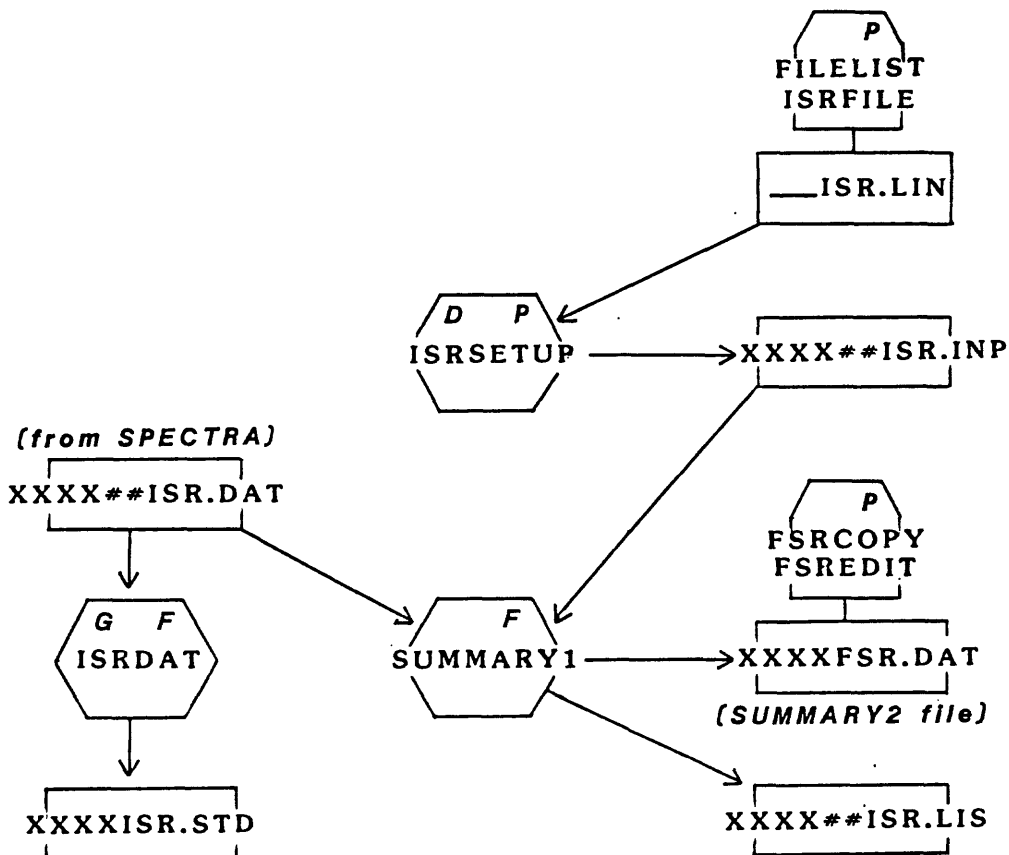


The data file (XXXX##ICR.DAT) is processed by the program ICREPORT and produces a printable file (XXXX##ICR.LIS) that consists of a report of interference corrections made during INAA processing, and a tabulation of overlapping peaks detected near analytical lines that were designated as interference free as described in section 3.5.

4.2 Intermediate report of analysis

Following spectral analysis, the direct access data file produced by the SPECTRA program (XXXX##ISR.DAT), that contains the elemental concentration data for each sample based on each analytical line, is processed using the SUMMARY1 program to produce an "Intermediate Summary Report" (ISR). A flow chart for this stage of the data reduction procedure is displayed in figure 17. The input data file for the SUMMARY1 program is created by the program ISRSETUP. Input data files to ISRSETUP (GEISR.LIN or IGISR.LIN) contain a list of elements and the energies and priorities attached to each line for each element. These data files may be created and edited by the program ISRFILE and listed to a lineprinter using the FILELIST utility. SUMMARY1 processes the data in the XXXX##ISR.DAT file by averaging the results from multiple lines, and producing an intermediate report of analysis that contains a single concentration value for each element of interest in each sample.

Figure 17. Flow chart of Intermediate Summary Report generation.

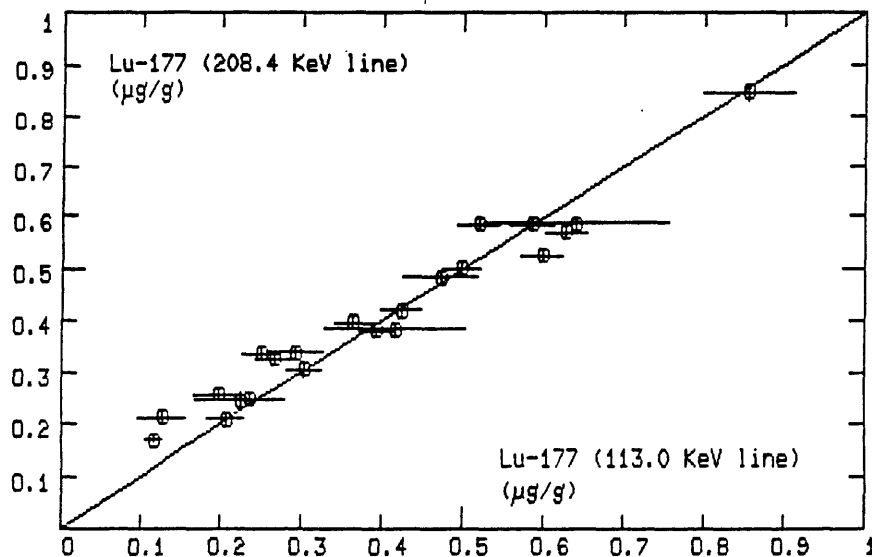


The lineprinter report is contained in the output file (XXXX##ISR.LIS), while the concentration data are also stored in a direct access data file (XXXXFSR.DAT) for processing in the next stage of the procedure.

The averaging of results in the SUMMARY1 program is based on assigned priorities for each analytical line for a given element. Thus all priority-one lines are automatically included in the average value reported and are weighted by their estimated variances based on counting statistics. The results from lower priority peaks are included in the mean only if they fall within two standard deviations of the mean of the higher priority lines. Once a lower priority line is excluded the averaging procedure is terminated without examining any remaining lines.

The data in the direct access data file (XXXX##ISR.DAT) can be treated with the program ISRDAT, that permits the creation of plots on a graphics terminal of the analytical results based on a given line of interest against that of a second (either from the same counting sequence or from another counting). This program has proven useful in making decisions regarding line selection and in the assignment of priorities. An example of a plot of LEPD data from the 113 KeV peak of ^{177}Lu against Ge(Li) data using the 208 KeV peak of the same nuclide is shown in figure 18. This example was useful in directing our attention to the fact that the LEPD detector was producing anomalously low results for Lu at low counting rates due to poor separation of the analytical line from an interference by ^{175}Yb .

Figure 18. Scatter plot of data from the 208 keV line of ^{177}Lu against data from the 113 keV line for a suite of samples in a single irradiation set.

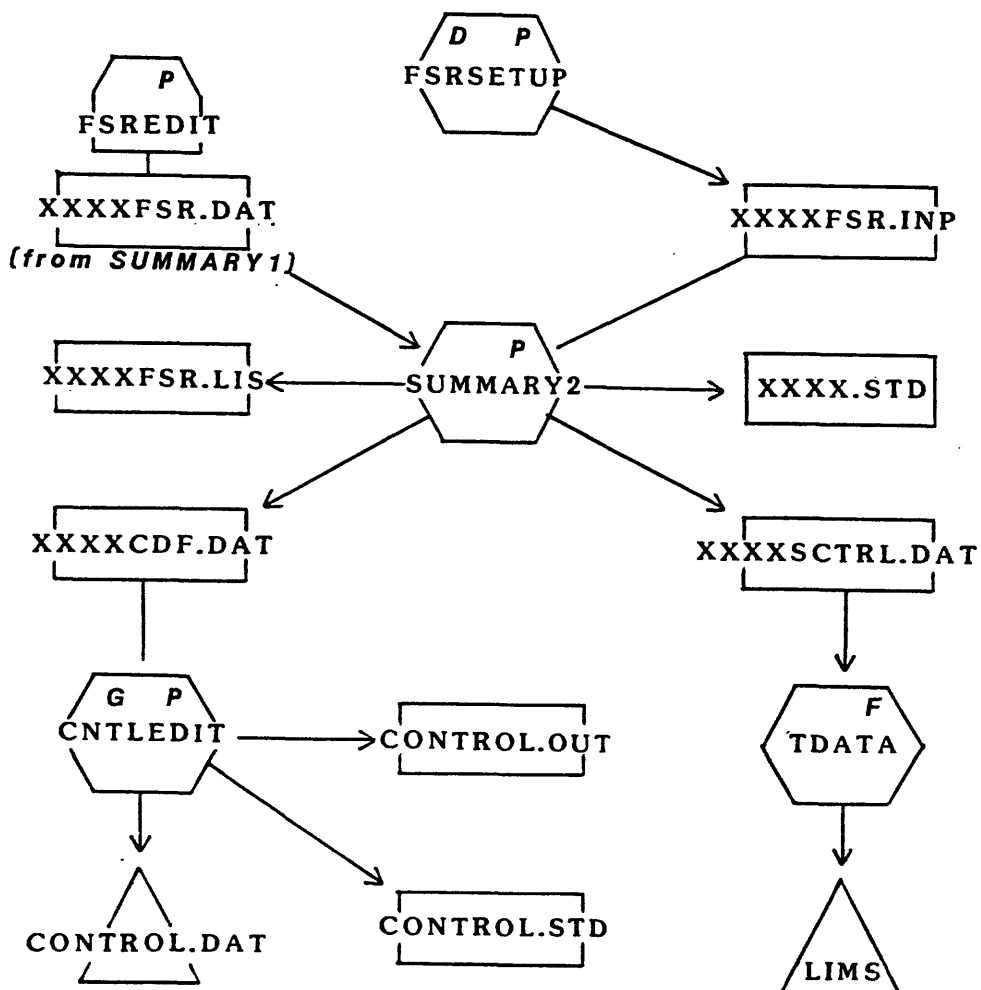


The data in the direct access data file (XXXX##ISR.DAT) can also be reformatted for analysis using ISRDAT to produce the ASCII file XXXX##ISR.STD for analysis using our more sophisticated graphics software package for data display and analysis. Finally, ISRDAT can be used to produce a summary of the counting errors for all lines in all samples in one or more XXXX##ISR.DAT files that allows a rapid assessment of which elements are above detection limits in the irradiation set.

4.3 Final report of analysis

Two to five counts (Coaxial Ge and LEPD) of each irradiation set of samples are made over a two to three month period. After all countings have been completed, the elemental concentration results from each counting, that are stored together in the XXXXFSR.DAT direct access data file, are processed by the SUMMARY2 program to produce a "Final Summary Report" (FSR) of analysis. A flow chart for this stage of the analytical procedure is shown in figure 19.

Figure 19. Flow chart of Final Summary Report generation.



The input data file (XXXXFSR.INP) for controlling the execution of the SUMMARY2 program is created interactively by the FSRSETUP program. The SUMMARY2 program produces three sections of lineprinter output (XXXXFSR.LIS): 1) a listing of all data in the XXXXFSR.DAT data file, with the concentration values from multiple counts for a given sample in adjacent columns; 2) average results from multiple countings for each sample, with the data for replicate samples in adjacent columns to facilitate comparisons; and 3) average results from the analysis of replicate samples. The SUMMARY2 program tests for and rejects outliers when the averages of multiple counts (for report number 2) are calculated, based on the following criteria:

- 1) all data with counting errors greater than 30% (relative standard deviation) are treated as upper limits.
- 2) when only upper limits are available, the lowest value is reported.
- 3) all data listed as upper limits are ignored in the computation of a mean value.
- 4) all values are weighted by their variance in the computation of the mean.
- 5) the standard deviation values are all arbitrarily increased by 2% in order to avoid over-weighting results with very small (<1%) Poisson counting error.
- 6) any datum for which the 2-sigma error does not overlap the 2 sigma error on the mean is flagged (with a "!"). (If any datum has an error greater than 15%, then the criterion for flagging is 1.5 sigma. This is to prevent low precision data from being retained in the mean when higher precision data may be omitted.)
- 7) If less than 50% of the data are flagged, then the flagged data are omitted (and the "!" flags converted to "D") in a recalculation of the mean. After recalculation of the mean, the criteria of step 6 are reapplied. If more than 50% of the remaining data are now flagged, the "!" flags (second pass) are converted to "?", and the mean calculated in step six is retained.

All flags are reported along with the individual analytical results in the first section of the SUMMARY2 output. The analyst then has the option of reviewing the flagged data, and editing (either inserting or deleting) the "D" flags (that specify data deletion in computing sample means) using the FSREDIT program. The FSREDIT program can also be used to correct incorrect sample names and sample weights (with appropriate renormalization of the data), or to renormalize sample data to correct for apparent systematic errors (e.g. due to variations in counting geometry between samples and standards), or to renormalize data for a given element (based on an alternate standard).

The FSRCOPY program can be used to merge XXXXFSR.DAT files, or to break them apart into LLNNFSR.DAT files, where LLNN again signifies the job names [as designated by the laboratory information management system (LIMS)].

A special utility program called ANALYZE_SUM2 can be used to assist in the detection of systematic errors during a series of multiple counts. This program searches a final summary direct access data file to find the names of all counting sequences present (these correspond to the XXXX## designations of the original input files used to run SPECTRA). The analyst chooses one of these counts to use for normalization. The program then finds all records belonging to a given sample and divides all elemental concentrations by those in the normalizing record (if present in that record). Next, in each record all data with relative precisions below 10% are averaged. An average of 1.0 indicates complete agreement between that count and the normalizing count. Deviations from 1.0 indicate systematic errors (such as improper counting geometry, poor dead-time corrections, etc.); such errors can be corrected using the FSREDIT program. ANALYZE_SUM2 next calculates the agreement between counts for specific elements. First, a correction is made internally for the systematic errors between records calculated above. Then the average ratio of each element between all possible pairs of counts is calculated and presented in a report. Here, deviations from a value of 1.0 may indicate poor flux monitor calibration in a specific count, improper interference corrections in a specific count, etc. These errors may be corrected by re-running SPECTRA or by using FSREDIT.

After an analyst has reviewed the initial run of the SUMMARY2 program, the program is re-executed to produce a final report of analysis if any of the editing options provided by the FSREDIT program have been exercised. In generating the final summary report, the program makes corrections for fission product interferences in the determination of zirconium, molybdenum, lanthanum, cerium, and neodymium if uranium has been determined (via the 2.35-day ^{239}Np). Where the magnitude of the correction exceeds 20% of the uncorrected value, the value is flagged (with a "*") in the report of analysis.

Another uranium fission product, ^{103}Ru , has a gamma-ray line at 497.1 keV that interferes with the best line from ^{131}Ba at 496.2 keV. Because ^{103}Ru does not have a second line that is strong enough to use to make a correction, this interference is treated like a direct fission product correction using a special program called BARIUM. This program, normally run prior to running SUMMARY2, reads the direct access final summary data files

and calculates a mean uranium content for each sample in the file based on all counts (usually one Ge(Li) and one LEPS). It next locates those records that contain barium data derived solely from the 496.2 keV line and makes the correction as follows:

$$[\text{Ba}]_{\text{corr}} = [\text{Ba}]_{\text{meas @496.2}} - [\text{U}] * k * e^{0.0402 * t}$$

where t is the time in days from the end of the irradiation to the start of the count, and k is an experimentally determined constant with a value of 2.8.

Four different output data files can be produced by the SUMMARY2 program: 1) lineprinter output (XXXXFSR.LIS) that presents the data in tabular form (samples vs. elements -- 10 samples per page). Since 10 rare-earth elements are typically determined in our INAA procedure and variations in rare-earth distribution patterns are a powerful geochemical tool, the SUMMARY2 program also provides line-printer and/or high resolution laser printer plots of the chondrite normalized rare-earth distribution for each sample, along with a tabulation of the ratios plotted. 2) An ASCII data file (XXXXSCTRL.DAT), in a format that is compatible with the centralized analytical laboratory information management system. 3) An ASCII file (XXXX.STD) that is compatible with all of our software for graphic presentation and statistical analysis (e.g. regression, factor, and cluster analysis). These data files can also be used to produce high quality chondrite normalized rare earth plots. 4) A direct access data file (XXXXCDF.DAT) that contains all of the data for the reference samples included in a given irradiation set.

4.4 Data base management system for Quality Control

U.S. Geological Survey standard rocks are used as reference samples in all silicate rock or manganese nodule/crust irradiations. The CNTLEDIT program is used to process the control data files (XXXXCDF.DAT) from each irradiation to build and edit a data base (CONTROL.DAT) for laboratory quality control. The CNTLEDIT program is used interactively to 1) enter data into the data base, 2) prepare a tabulation of control data for a given irradiation, with comparison to mean values on the same reference samples, 3) produce tabulations of data on reference samples (either individual determinations or tabulations of mean values), and 4) produce data files (CONTROL.STD) compatible with our graphics display programs in order to visually check for consistency in the reference sample data base. Two forms of data presentation are used routinely to evaluate the results on control samples.

Figure 20 shows a plot of element data for a given analysis of reference sample G-2 relative to the mean values for the same sample as contained in the database. Figure 21 presents a plot of data for Fe (relative to the mean) in reference samples G-2 and AGV-1 as a function of time, in order to check for temporal variations in the database.

Figure 20. Plot of element data for an analysis of reference sample G-2 relative to the mean values for the same sample as contained in the database.

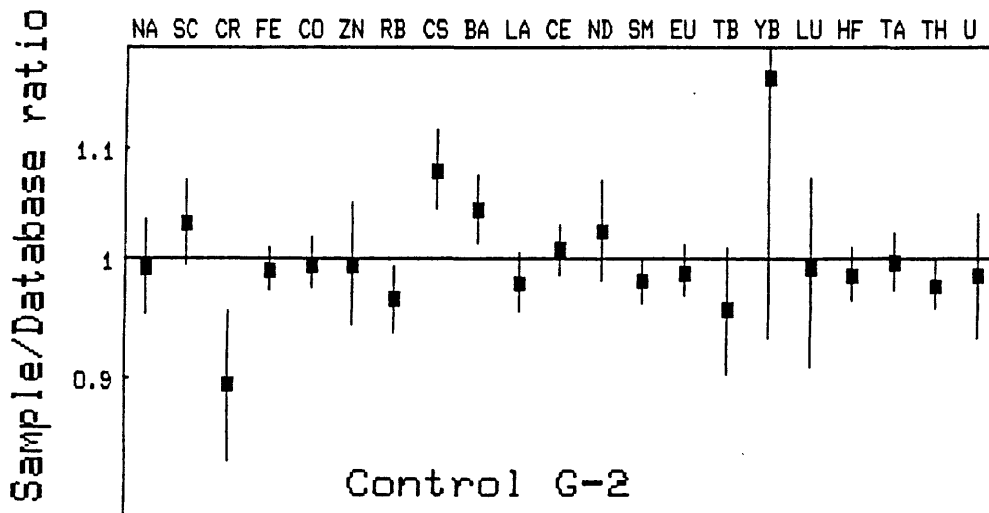
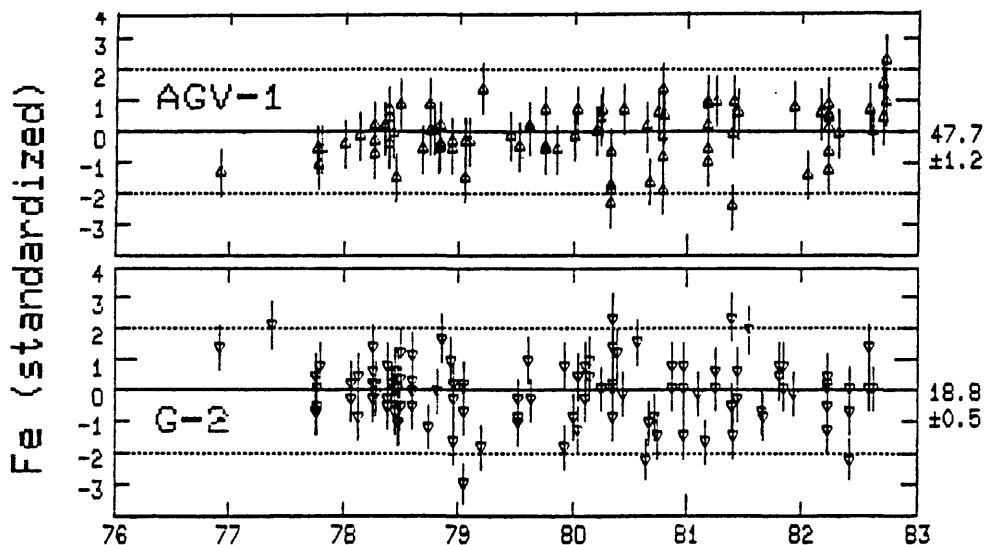


Figure 21. Plot of data for Fe relative to the mean in reference samples AGV-1, and G-2 as a function of time.



5. PROGRAM IMPLEMENTATION

The software described above is written in structured FORTRAN-77 and is currently implemented on both VAX and micro-VAX computer systems. The SPECTRA program (available by request from the authors) processes spectral data as it is formatted by spectrometers (Nuclear Data 2200, 6720 and Tracor Northern 1710) in the authors' laboratory, either as disc files transmitted directly to a VAX computer system, or on computer compatible magnetic tape. Since the format of the data as stored on magnetic tape or disk may vary depending on the spectrometer used, some modification of the subroutine that calls the spectral data may be required by anyone attempting to utilize the code. A few of the subroutines (particularly those called by the PLOTPK subroutine for terminal graphics) are VAX dependant. Extensive documentation has been included in the source code to aid in the implementation of SPECTRA on non-VAX systems. For example, the calls to graphics subroutines are clearly documented so that they can be replaced by subroutine calls to other graphics software packages.

Three appendices are included in this report to assist those who may wish to implement the SPECTRA program. Appendix 1 is a description of the input data required to run spectra, and lists all of the control parameters and their use. The input data file can be created interactively with the SPECSETUP program. The SPECTRA program is modular in design, and appendix 2 is a listing of all of the SPECTRA subroutines and their function. Appendix 3 lists all of the parameters passed in common blocks within SPECTRA and their use. The latter appendix should be particularly useful to anyone interested in modifying SPECTRA, or implementing only selected subroutines. Appendix four describes the method used within SPECTRA to correct for changing dead time during the analysis of short lived nuclides as currently implemented in the CLOCKT subroutine.

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APPENDIX 1

Input Data for "SPECTRA"

The following is a list of the input data records required to run the program. Listed are the variable names used for the input parameters for each record, as well as the record format. (All records are <|= to 80 characters in length in order to maintain punched card compatibility).

Record 1 FORMAT(A1,I1,2I2,2I6,2A1,15A4)

Variable	Type	Field	Description
INTRCT	alph	1	A '*' in column 1 indicates spectra are being processed interactively, and inaa peak plotting is enabled. A '+' in column 1 indicates spectra are being processed interactively, and inaa peak plotting is disabled.
NRFSPC	int	2	Number of "reference spectra" on input tape (Cs-137, Y-88, or Co-57 used to provide a rough energy calibration for location of standard lines in the "calibration spectra". Must have a value of 1 or 2, but must be 0 if CSSPOT is defined.)
NSTSPC	int	3-4	Number of "calibration spectra" on input tape used to provide energy and FWHM calibration (<20).
NPFIT	int	6	0 : energy calibration by linear interpolation between standard lines 1 to 7 : fit energy calibration data to (NPFIT) degree polynomial by least squares
CSSPOT	int	7-12	Approximate centroid of Cs-137 photopeak (122 keV Co-57 centroid for LEPD data) (required if NRFSPC=0 and NSTSPC ^-0, and the location of the calibration lines are not specified on record 5)
YSPOT	int	13-18	Approximate centroid of the 1836 keV photopeak of Y-88 (optional)
OUT	alph	19	A "*" in column 19 sends microfiche output to logical unit 1 (sets OUT = 1)
CCH	alph	20	'*': correct for gain, zero drift, and pulse pile-up as specified on record 2

LABEL(I) alph 21-80 Labeling information. Experiments utilizing a low energy photon detector are indicated by entering "LEPD" in columns 77-80. "4420" entered in columns 73 - 76 indicates that the tape was written on the Nuclear Data 4420 or 6620 analysers with acquisition time in channels 2 and 3. "1710" entered in columns 73 - 76 indicates that the tape was written on the Tracor Northern 1710 analyser.

Note: If NSTSPC equals zero, records 2, 3, 4, and 5 are to be omitted.

Record 2 FORMAT(2(I6,F9.3),I1,3X,I6,F10.3)

Variable	Type	Field	Description
IGAIN	int	1-6	Correct for gain drift using the peak in channel IGAIN +/- 10. If more than one peak is found in this window, the most intense peak is used. If GAIN is not specified, all spectra are adjusted relative to the first spectrum processed. If CLSHFT is 0, this would be the first spectrum following the calibration spectrum.
GAIN	real	7-15	Energy of peak used for gain drift correction.
IZERO	int	16-21	Correct for zero drift using peak in channel IZERO +/- 10. If IZERO is not specified, no zero drift correction is made. If ZERO is not specified, all spectra are adjusted relative to the first spectrum processed. If CLSHFT is 0, this would be the first spectrum following the calibration spectra.
ZERO	real	22-30	Energy of peak used for zero drift correction.
CLSHFT	int	31	If >0, gain and zero drift correction will be based on variations in the positions of the peaks specified by IGAIN and IZERO, relative to their positions in the first calibration spectrum. (e.g., used if pulser peaks rather than gamma-ray lines are used for gain and zero drift correction in all spectra.) GAIN and ZERO should not be specified in this case.
PULSER	int	35-40	Location of pulser peak for pulse pile-up and dead time correction.
TPU	real	41-50	Pulse pile-up resolving time (in microseconds) of detector-amplifier system. Correction factor is computed as: $f = \exp(2.0 * \text{RATE} * \text{TPU})$ where $\text{RATE} = (\text{total counts in spectrum}) / \text{duration}(\text{min.})$

MINT	int	39	0: peak area measured by fixed limits of integration using 2*NDEL+1 channels 1: peak area measured by TPA method 2: fit peaks with symmetrical Gaussian (shape parameters fixed to calibration values) 3: fit peaks with symmetrical Gaussian 4: fit peaks with Gaussian + exponential tail (shape parameters fixed to calibration values) 5: fit peaks with Gaussian + exponential tail 6: Data analysis bypassed. Data printed as controlled by NPRINT and MPRINT
JANAL	int	40	0: activation analysis routine is bypassed 1: program will calculate elemental concentrations from activation analysis data 2: activation analysis results written onto direct access storage device
NDEL	int	41-42	Integer number of channels on each side of center channel to be included in peak area determination by fixed limits of integration
ICHST	int	43-47	Channel No. at which peak search is to begin (Default = 10)
ICHSP	int	48-52	Channel No. at which peak search is to terminate (Default = SIZE)
NRGTST	int	53-56	Filter for location of standard lines -- lines must be within +/- NRGSTST channels of expected location based on reference line (s). (Default = SIZE*0.005)
NRGFIT	int	57-60	Filter for location of standard lines -- lines must be within +/- NRGFIT channels of expected location based on least squares fit of all standard lines. (Default = 2)
LMTERR	int	61-64	Limit on number of tape read errors (Default = 10)
DSKVAR	int	65-68	Next record to be written to output disk data file.
NSENS	int	69-70	Sensitivity for peak detection (number of standard deviations; Default = 3)
CMPCHK	alph	73	A "-" in column 73 deletes the second derivative search within a region of interest
OUT	alph	74	A '*' in column 74 sends microfiche output to logical unit 1 (sets OUT = 1)
PSOUT	alph	75	A '*' in column 75 sends peak search data to logical unit 11 if JANAL = 0 (sets PSOUT to 11)

C	alph	76	If C = "*", enter revised label parameters on next record. FORMAT(15A4)
VIW	alph	77	A "*" in column 77 indicates than NDEL is to be incremented at the channel locations indicated on record 7 (after new label, if any)
IFPLOT	int	78	1: Prepare lineprinter plots of fitted region (MINT = 2,3,4 or 5 only) 0: Bypass plotting
MRESID	int	79	1: check residulas for additional components (MINT = 2,3,4 or 5 only) 0: Bypass checking
MCFOUT	alph	80	A "*" in column 80 indicates that the mean monitor comparator factors are to be output to a file on logical unit number 12.

In general only one parameter (TAGSKP, BLKSKP, or SKP) need be specified to skip spectral data. If more than one skipping parameter is non-zero, then the tagword TAGSKP is located before BLKSKP records are skipped, before SKP spectra are skipped.

Record 6 may be repeated any number of times in order to alternately skip and process spectra, or to vary any of the options controlled by the record. Within an activation analysis set, skipping spectra is controlled by parameters on record 10.

In order to reinitialize the program to process a new set of reference and calibration spectra, place a record with a negative number (FORMAT(I6)) following a set of records. The next record expected will be record 1.

If JANAL was set to 0, omit records 8, 9, 10 and 11 which control the handling of activation analysis data.

Record 7 FORMAT(12I6)

Variable	Type	Description
JIW(I)	int	If VIW = "*" then JIW contains the channel locations in the spectrum where NDEL is to be incremented by 1.

Record 8 FORMAT(2I6,A4,5I2,2F10.5,A1,3F9.4,2A1,A4)

Variable	Type	Field	Description
NFM	int	1-6	Number of flux monitors in an activation analysis set (<21). If NFM=0 then specific activities will be computed for all spectra for all lines specified on records: 9.
NPKAN	int	7-12	Number of peaks to be used for activation analysis (<71)
FLUX	alph	13-16	Keyword used to identify flux monitor spectra via the first four characters on records: 10.
J,K,L, HRST, MINST	int	17-26	Month, day, year, and time of day to which all activities are to be corrected. Default is NDAY, HRCT, MINCT of first (flux monitor) spectrum processed as specified by records: 10.
FILT	real	27-36	Filter for photopeak identification (+/- FILT keV) (Default = 1.0)
SLOPE	real	37-46	Slope of a Log-Log plot of relative photopeak efficiency vs. gamma-ray energy for the detector employed. This parameter is used for making corrections for interferences as described below.
ICOUT	alph	47	a "*" in column 47 sends data for an interference correction summary report program (ICREPORT) to logical unit 7 (sets ICOUT = 7)
DTHFLF	real	48-56	Half-life (in minutes) of dead time variation in experiment involving short-lived activities.
ADCTIM(1), ADCTIM(2)	real real	57-65 66-74	ADC resolving time = ADCTIM(1) + ADCTIM(2) * N, where N is channel number. Can be used to compute dead time of a count.
CSHIFT	alph	75	a "*" in column 75 indicates that the peak centroid may be shifted based on the energy calibration and the peak area redetermined during INAA processing for MINT=0. This option can only be used if a gain correction is specified on card 2 (IGAIN, GAIN > 0).
DFLG	alph	76	A "*" in column 76 causes overlapping peaks (< 1 fwhm from analytical line) encountered in INAA processing to be deleted when no interference has been indicated on record 9.
SPCDO	real	77-80	After processing the designated flux monitor spectra, the program will process both flux monitor and sample spectra for elemental concentrations when the keyword "BOTH" is entered in columns 77-80.

Record 9 FORMAT(A2,F8.1,F9.3,A1,F10.5,A4,5X,A1,2(F6.3,F7.1,F7.4))

Set of records, one record for each photopeak to be used in the analysis.

Variable	Type	Field	Description
ELEMNT(I)	alph	1-2	Symbol of element being determined via the listed photopeak
GAMKEV(I)	real	3-10	Energy of photopeak in keV used for determination of ELEMNT(I)
HFLF(I)	real	11-19	Half-life of the indicator radionuclide
HFLFTU(I)	alph	20	Units of HFLF(I) (S, M, H, D, or Y)
FMWT(I)	real	21-30	Weight (or concentration) of ELEMNT(I) in the flux monitor
FMDIM(I)	alph	31-34	Units of FMWT(I) (e.g., UG, MG)
PLOT(I)	alph	40	controls interactive plotting of peaks during INAA data reduction: ' ': plot if upper limit or weak line (sigma >5%) '+' : plot peak in samples only '*' : plot for all spectra '-' : never plot
CISEP(J,I)	real	41-46 61-66	Separation between energy of interference and GAMKEV(I) (Energy of Interference - GAMKEV(I))
CILINE(J,I)	real	47-53 67-73	Line used for making interference correction on line GAMKEV(I)
CIFACT(J,I)	real	54-60 74-80	Interference correction factor.

The interference correction factor (CIFACT(J,I)) is the ratio of the intensity of the interfering line to an interference free line (CILINE(J,I)) of the interfering radionuclide. In the output of the program, two areas will be reported for the GAMKEV(I) line, the observed area, and the area corrected for the interference (as indicated by the letter "C").

$$\text{AREA(Corrected)} = \text{AREA(observed)} - \text{AREA(CILINE(J,I))*CIFACT(J,I)}$$

In this case, CIFACT(J,I) must be the ratio observed for the detector employed in the measurement. The ratio of the "true" intensities may be used if SLOPE is specified on record 8.

$$\text{AREA(c)} = \text{AREA (o)} - \text{AREA(CILINE(J,I))*CIFACT(J,I)*F}$$

where $F = 10.0^{**}(\text{SLOPE} * \text{ALOG10}(\text{GAMKEV(I)}/\text{CILINE(J,I)}))$

If the value of SLOPE is negative and CIFACT is positive, CIFACT is assumed to be the "true" intensity ratio, and a detector efficiency correction is applied. If CIFACT is negative, the absolute value of CIFACT is accepted as the "detector" intensity ratio and no efficiency correction is applied.

Two lines and correction factors may be specified for each line used for analysis.

Interference corrections are performed in the order determined by the order of the analytical lines listed as records 9. The order of the analytical lines may be critical to correct interference correction in a hierarchical situation. For example, there is a Se-75 interference on the 279 keV Hg-203 peak. However, the Se-75 reference line at 264 keV, used for the interference correction, often suffers interference from Ta-182. Therefore, the Se-75 264 keV peak should be processed before the Hg-203 279 keV peak.

If the weights of the elements in the flux monitors are constant from flux monitor to flux monitor, they may be entered in the FMWT(I) field of the record, and no sample weights would be entered for the flux monitors on record 10. If the flux monitors used are standard powders or solutions, the weights of which will vary, the concentrations of the elements in the standard material may be placed in the FMWT(I) field, and the weights of the standards entered in the sample weight field on the records for the flux monitor spectra.

The flux monitor weights may also be defined or redefined by using data record 11, described below, following the corresponding spectrum record (:10). This option is used where the concentrations of the elements in the flux monitors are variable.

If more than one set of activation analysis data is included on the input tape, and the same photopeaks are to be used in one set as in the immediately preceding set, record set 9 may be replaced by a record with the keyword "SA" entered in columns 1-2. This instructs the program to seek the same photopeaks in the next activation analysis set to be processed.

Record 10 FORMAT(4A4,A2,I2,F10.5,A4,A1,I3,I2,I2,A1,I6,A1,
 A1,1X,F8.5,I4,2I3,2(1X,2I2))

Set of records, one record for each spectrum to be analyzed for activation analysis on the input tape, placed in the order that the spectra appear on the tape.

Variable	Type	Field	Description
SAMPNM(I)	alph	1-18	Sample name (for flux monitor spectra, the first four columns must contain the keyword specified in the FLUX field on record 7)
NELEM(I)	int	19-20	Specifies the number of elements whose flux monitor weights are to be defined by data record(s) :11, which follow immediately -- five elements/record.
SAMPWT(I)	real	21-30	Sample weight (Default = 1.0)
SMPDIM(I)	alph	31-34	SAMPWT(I) units (Default = "GRAM")
ATU	alph	35	a '*' in column 35 changes NDAY, HRCT & MINCT units to hours, minutes & seconds
NDAY	int	36-38	Day that the count was started.
HRCT(I)	int	39-40	Time of day that the count was started (8:30 pm would be 2030. This parameter need not be specified if CLKSEC, CLKMIN, ETMIN, and ETSEC are specified, or if "4420" is entered in columns 73-76 of record 1.
MINCT(I)	int	41-42	
PCODE(I)	int	43	A minus '-' in column 43 deletes processing for this sample, and subsequent samples until a '+' or '^' is encountered. Interactive plotting of peaks is controlled by the PLOT(I) parameter on data records 9, and can be turned off and on as follows: A plus '+' in col. 43 specifies processing and begins interactive plotting for this and subsequent samples. A '^' in col. 43 specifies processing but stops interactive plotting for this and subsequent samples.
NURLIV(I)	int	44-49	Live time duration of the count. This parameter need not be specified if the live time duration is provided by the input tape.
DLIVTU(I)	alph	50	units of NURLIV(I) (S, M, H, or D)

CHDRFT(I)	alph	51	A minus (-) in column 51 deletes the gain and zero shift correction. A plus (+) or star (*) in column 51 specifies that new gain and zero shift parameters are to be read in as formatted on record 2. The revised parameters are set by the next record (or following record(s) 10, if NELEM(I) > 0). A (+) indicates that the new parameters apply only to the current spectrum, a (*) makes the change permanent (or until redefined).
FF(I)	real	53-60	Correction factor for flux variation during irradiation. Corrected activity = activity/FF(I). Correction factor need not be specified on each record, but is assumed to be constant until redefined. (Default = 1.0)
LSKIP(I)	int	61-64	Tagword of spectrum to be processed following the spectrum described by the record.
MSKIP(I)	int	65-67	Number of records to be skipped following the spectrum described by the record.
NSKIP(I)	int	68-70	Number of spectra to be skipped following the spectrum described by the record.
CLKMIN(I), CLKSEC(I)	int int	72-73 74-75	Clock time duration of the count (in minutes and seconds)
ETMIN(I), ETSEC(I)	int int	77-78 79-80	Elapsed time between subsequent counts (in minutes and seconds)

Note that within an activation analysis set of spectra, skipping cannot be accomplished using record 6, and that the LSKIP, MSKIP, and NSKIP parameters of record 9 are available for this purpose.

The last four parameters on record 10 are required only in the case of counts involving short-lived radio-nuclides, where a correction is to be made for changing analyzer dead time. CLKMIN and CLKSEC are required when the clock time duration is not stored in channel 6, and ETMIN and ETSEC are required when HRCT(I) and MINCT(I) have not been specified, or the acquisition time is not stored in channels 2 and 3 in the spectrum being processed. ETMIN and ETSEC provide the elapsed time between the start of the current count and the start of the next count.

If NELEM(I) equals zero, record 11 must be omitted.

Record 11 FORMAT(5(A2,F10.5,A4))

set of records used to define the composition of a flux monitor, 5 elements per record.

Variable	Type	Description
ELMBUF(I)	alph	Element whose flux monitor weight (concentration) is to be defined
WTBUF(I)	real	Weight (or concentration) of ELMBUF(I) in the flux monitor. Processing for an element, whose flux monitor weight has previously been defined, may be bypassed may setting WTBUF(I) = 0.0.
DIMBUF(I)	alph	Units of WTBUF(I) (e.g., UG, MG)

The program assumes that all flux monitors have the same composition, until the composition is redefined by a set of records (:11) placed immediately after the record (:10) for that flux monitor spectrum. Once an element concentration for a flux monitor is defined by rec. 9 or rec. 11, it is assumed that all subsequent flux monitors have that concentration, unless the concentration is changed or set to zero by rec. 11.

APPENDIX 2

Components of SPECTRA

SPECTRA (main) -- Main SPECTRA routine. Controls all input and output. Calls the following subroutines:
convuppr, ecalib, egamma, diskio, inaa,
ndtape, peaks, smooth, tntape
(dread, dskip, drwnd are entry points to diskio)
(ndread, ndskip, ndrwnd are entry points to ndtape)
(tnread, tnskip, tnrwnd are entry points of tntape)
(calib, cspeak, match, ypeak are entry points to ecalib)
(mcfavg and inaacalc are entry points to inaa)
lib\$date_time(*), batch(*)
(*) are VAX system dependant but are non-essential to the running of SPECTRA

BATCH Calls VAX system software to determine if SPECTRA is being run in batch or interactive mode (non-essential)

CLOCKT Calculates the deadtime from the spectral data based on the resolving time of the ADC. The entry point DTCORR corrects for dead time changes during counting of short lived nuclides, assuming that dead time changes exponentially with time. (See Appendix IV)

CONVRT Converts channel number to energy and energy to channel number for polynomial energy calibration. Polynomial solved by Newton-Raphson method.

CROUT Solves n simultaneous linear equations with n unknowns. maximum value of n=20. Used for non-iterative multiplet analysis, and polynomial energy calibration.

DISKIO reads spectral data from disk

DRAWSPEC Plots spectral data on terminal screen interactively sets markers on the screen based on gamma lines listed in an isotope library
Calls the following subroutines:
box, clear, convrt, convuppr, goto, line, line_id, regis
sfun, square, text, vector, xhair

DTFUNC is a function subroutine to retrieve the pulse pile-up resolving time for a specified detector from a data file

ECALIB Processes calibration spectra for energy and fwhm calibration. Calls the following subroutines:
convrt, crout, fittit
(gzdrft is an entry point of egamma)

EGAMMA Determines gamma-ray energies and corrects for gain and zero drift. Monitors detector resolution. Calls the subroutine convrt

ERFC A fast approximation to the complimentary error function used to define baselines in peaks and fittit

INAA Performs inaa calculations. Calls the following subroutines: clockt, convrt, dtcorr, dtfunk, erfc, insert, mcfstd, pkarea, plotpk (pkarea is an entry point of the peaks subroutine) (dtcorr is an entry point of the clockt subroutine)

INSERT Prepares peak search arrays to insert (or delete) entries

LINEID A function subroutine which provides the gamma energies and intensities for a specified radionuclide using an isotope library.

MCFSTD creates a data file containing the monitor comparator factors for a given counting of a sample set

NDTAPE reads spectral data from Nuclear Data BCD tapes

TNTAPE reads spectral data from Tracor Northern binary tapes

PEAKS locates gamma-ray photopeaks, determines peak areas by digital (non-fitting) methods. Calls fitting subroutines. Calls the following subroutines: crout, erfc, fittit, lpplot

PLOTPK Program to plot regions of interest on the terminal screen and to interactively adjust baselines, divide multiplets within a region of interest, insert or delete peaks within a multiplet, measure peak intensity using iterative fitting routine, define regions of interest to control subsequent inaa processing.

 Calls the following subroutines:
check, convrt, convuppr, erfc, pkarea, hold, insert, line_id, peaks, sfun, tfun, vplot
(pkarea is an entry point of peaks)
Calls the following graphics subroutines:
alpha_text, box, cc_text, chardef, clear, dump, goto, laser_dump, laser_dump_off, line, regis, square, text, vector, xhair

SMOOTH smooth spectral data using five point convolution technique of Savitzky and Golay

The following subroutines [] are used for iterative least squares fitting. It is recommended that they only be used in conjunction with interactive plotting of peaks and multiplets.

[FITFIT]	Iterative least squares fitting of gamma-ray photopeaks using Marquardt or Gauss - Newton minimization of chi-squared. Calls the following subroutines: check, (erfc), convrt, invert
INVERT	Inverts matrix, called by fittit.
[CHECK]	Checks residuals from least squares fitting for additional components
[LPPLOT]	Produces line printer plot of fitted regions of spectra and residuals

APPENDIX 3

COMMON Blocks included in SPECTRA subroutines

BLOCK	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19
batch -																			
check	*									*	*			*					
clockt -																			
convrt			*		*	*													
crout							*												
diskio	*								*										
drawspec	*			*				*											
ecalib	*		*	*	*	*	*	*		*	*		*	*					
egamma	*		*	*	*	*													
erfc -																			
fittitm	*						*			*	*		*	*	*				
inaa	*	*	*	*	*	*		*	*	*	*	*	*	*		*		*	*
insert		*		*				*											
invert							*												
lineid -																			
lpplot	*									*				*	*				
peaks	*			*			*	*		*	*		*	*	*				*
plotpk	*	*		*	*	*	*	*	*	*	*	*	*	*		*			*
smooth	*																		
spectra	*	*	*	*	*	*		*	*	*	*	*	*	*		*		*	*
BLOCK	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19

Parameters passed in common blocks

Block 1:

Variable	Type	Size	Description
SDATA	real	4100	spectral data
AP	real	10	work array (not used to pass data)

Block 2:

Variable	Type	Size	Description
EGAM	real	200	gamma-ray energy of photopeak in keV as specified by data card 8
SCF	real	200	comparator factor (decay corrected specific activity)
SIGSCF	real	200	error (% stnd. dev.) on SCF
DATA	real	200	element concentration
SIGDAT	real	200	error (% stnd. dev.) on DATA
UNITS	real	200	concentration units
ELNAM	real	200	element symbol
MONWT	real	200	flux monitor concentration as specified on card 10

Block 3:

ENCAL	real	10	coefficients for polynomial energy calibration
ENLIN	real	2	coefficients for linear energy calibration

Block 4:

Variable	Type	Size	Description
CENTRD	real	200	peak centroids
AAREA	real	200	peak areas
SIGMA	real	200	one standard deviation on peak area
UNERGY	real	200	gamma-ray energy
LCH	integer	200	low energy boundary channel
MCH	integer	200	center most channel in peak
NCH	integer	200	high energy boundary channel
MCOMP	integer	200	number of components if peak is part of a multiplet (NCOMP) & return code from least squares fitting: NCOMP + MINT * 100 + ITER * 1000 + ICODE * 100000 MINT : integration mode ITER : number of iterations ICODE: return code (see common block 13)
BAREA	real	200	base area of peak or multiplet
PKINFO	real	200	"<" : value of DATA is an upper limit; "c" : AAREA corrected for interference; "p" : plotted by PLOTPK, PEAKS not called "P" : multiplet Plotted, PEAKS not called "s" : singlet, PEAKS called by PLOTPK "M" : Multiplet, PEAKS called by PLOTPK "f" : singlet fitted by PLOTPK "F" : multiplet Fitted by PLOTPK "z" : centroid shifted to assigned energy
PKHT	real	200	peak height
W	real	200	FWHM of peak
BKGL	real	200	average baseline at channel LCH
BKGR	real	200	average baseline at channel NCH
VBKGL	real	200	variance of BKGL
VBKGR	real	200	variance of BKGR
WSLOPE	real	1	slope of linear FWHM vs. energy calibration
WYINT	real	1	intercept of linear FWHM vs. energy calibration
SLOPE	real	1	slope of log-log plot of relative photopeak efficiency vs. gamma-ray energy for the detector employed.
NRUN	integer	1	number of peaks in spectrum
LEPDET	logical	1	".TRUE." if LEPD spectra
EFLAG	logical	1	".TRUE." if calibration spectra have been processed

Block 5:

Variable	Type	Size	Description
SENTRD	real	50	Centroids of calibration lines
ENERGY	real	50	Energies of calibration lines
DIFF	real	50	Difference between observed and expected location of calibration lines
LINES	integer	50	Expected location of calibration lines
REJECT	real	50	"+" or "*" indicates that the calibration line was rejected
FTVAR	real	3,50	1: fwhm of calibration peaks (non-fitting) 2: fwhm of calibration peaks (fitting) 3: junction point for gaussian low energy tail of calibration peaks (fitting)
MCODE	integer	50	return code from least squares fitting
NSTAND	integer	20	Number of calibration lines in a spectrum
REFLIN	real*8	1	"Cs-137" if Ge(Li); "Co-57" if LEPD
NPEAKS	integer	1	Total number of calibration lines
NPFIT	integer	1	Degree of polynomial for fitting energy calibration data
CSSPOT	real	1	Expected location of 661.6 keV peak
YSPOT	real	1	Expected location of 1836.1 keV peak
NRGTST	integer	1	Filter for location of calibration lines
NRGFIT	integer	1	Filter for polynomial fit of calibration data
JFLAG	integer	1	>0 if energy calibration complete
LSTSPC	integer	1	Calibration spectrum counter
LSTPKS	integer	1	Calibration line counter
RAT	real	1	Approximate slope of energy calibration based on Cs-137 or Co-57 reference line
ARAT	real	1	Approximate slope of energy calibration based on Y-88 1836.1 keV line
LOCATE	logical	1	If ".TRUE." expected location of calibration lines will be specified
CLSHFT	logical	1	".TRUE." if energies of gain or zero shift peaks have not been specified
LNCNT	integer	1	Line counter for printed output

Block 6:

Variable	Type	Size	Description
SKPDRF	logical	1	".TRUE." if gain and zero shift correction is to be bypassed
IGAIN	integer	1	location of peak used for gain drift correction
IZERO	integer	1	location of peak used for zero drift correction
GAIN	real	1	energy of peak used for gain drift correction
ZERO	real	1	energy of peak used for zero drift correction
GAIN1	real	1	centroid of peak used for gain drift correction in first spectrum
ZERO1	real	1	centroid of peak used for zero drift correction in first spectrum
FWHM1	real	1	fwhm of peak used for gain drift correction in first spectrum
SHIFT	real	1	gain drift correction factor
DRIFT	real	1	zero drift correction factor
VFWHM	real	1	change in fwhm of peak used for gain drift correction relative to FWHM1
ZSHIFT	logical	1	".TRUE." if peak centroid may be redefined in INAA processing based on gamma-ray energy. ZSHIFT is set by EGAMMA.

Block 7:

Variable	Type	Size	Description
ARRAY	real*8	21,21	used for multiplet analysis and least squares fitting

Block 8:

Variable	Type	Size	Description
SIZE	integer	1	number of channels in spectrum
MSIZE	integer	1	last channel of smoothed spectrum
ICHST	integer	1	1st channel in search region
ICHSP	integer	1	last channel in search region
LIMPK	integer	1	limit on number of peaks
LIMCMP	integer	1	limit on number of components in a multiplet
IPASS	integer	1	spectrum counter
NSTSPC	integer	1	number of calibration spectra
SENS	real	1	peak search sensitivity parameter
MINT	integer	1	designates peak integration method
NDEL	integer	1	channels used by "Wasson" method
NIW	integer	1	number of locations in the spectrum where NDEL is to be incremented by 1
JIW	integer	12	channel locations in the spectrum where NDEL is to be incremented by 1
OUT	integer	1	logical unit for printed output or microfiche output
GFACT	real	1	$2.0 * \sqrt{2.0 * \log(2.0)}$
AFACT	real	1	$\sqrt{2.0 * \pi}$
CMPCHK	logical	1	".TRUE." to bypass 2nd derivative search in region of interest
INTRCT	logical	1	".TRUE." if program is being run interactively
HANDPL	logical	1	".TRUE." if inaa peak plotting is enabled
PLTMOD	integer	1	Defines terminal type for graphics output: 1=VT240/REGIS 2=TEKTRONIX 3=VT240/4010 Tektronix 4=VT640/Tektronix 5=GRAPH-ON 250

Block 9:

Variable	Type	Size	Description
TAGWRD	integer	1	tagword of current spectrum
TAGSKP	integer	1	tagword to be searched
BLKSKP	integer	1	records to be skipped
SKP	integer	1	spectra to be skipped
NBLOCK	integer	1	number of records per spectrum
NREC	integer	1	record counter
NPASS	integer	1	spectrum
ITGSKP	integer	1	record counter for skipping routine
IBLK	integer	1	record counter
SKPFLG	integer	1	tagword last searched
NRDERR	integer	1	tape read error counter
LMTERR	integer	1	limit on tape read errors
NEOF	integer	1	limit on number of eofs (end-of-files) less eofs found
INEOF	integer	1	limit on number of eofs
ECODE	integer	1	error code from NDTAPE subroutine

Block 10:

Variable	Type	Size	Description
NCOMP	integer	1	number of components in region of interest
JPK	integer	1	index of low energy peak in region
KPK	integer	1	index of high energy peak in region
KL	integer	1	low energy boundary channel of region
KR	integer	1	high energy boundary channel of region
DYDX	real	1	slope of linear baseline under region
YINT	real	1	intercept of linear baseline under region
AVBKGL	real	1	average baseline value at channel KL
AVBKGR	real	1	average baseline value at channel KR
VAV	real	1	variance/channel in baseline
VL	real	1	variance of AVBKGL
VR	real	1	variance of AVBKGR
PLTFLG	logical	1	".TRUE." if the subroutine(s) PEAKS (and FITTIT) are being called by PLOTPK or INAA

Block 11:

Variable	Type	Size	Description
AREAFT	real	20	peak areas of components in region
ERRAFT	real	20	estimate of 1 s.d. on areas
BKGFT	real	20	base area for each component
CENTFT	real	20	centroid of each component in region
FWHM	real	1	peak width (fwhm) for each component
EP	real	1	junction point for low energy tail
LIMIT	integer	1	limit on number of components in region: 7 for fitting algorithm 20 for non-fitting algorithm
NFT	integer	1	number of calls to subroutine FITTIT

Block 12:

Variable	Type	Size	Description
CISEP	real	2,71	Separation between energy of interference and energy of analytical line (EInt-EAnal)
CILINE	real	2,71	Line used for making interference correction
CIFACT	real	2,71	Interference correction factor
CORINT	real	70	Magnitude of interference correction as % (interf./((interf.+corrected area))*100. -or- magnitude of overlapping peak as % (overl./((overl.+peak area))*100.
CORLOC	real	70	separation in keV of overlapping peak from analytical line (energy of anal. line - energy of overlap.) = 0.0 for interference corrected peaks = 99.0 for two overlapping peaks
CORINF	real	70	"z" if peak centroid shifted during INAA processing to expected location based on calibration and gain and zero shift analysis.
IMID	integer	1	Peak center channel as determined by PEAKS (used in INAA and PLOTPK)
MID	integer	1	Peak center channel as expected from energy calibration (used in INAA and PLOTPK)

Block 13:

Variable	Type	Size	Description
FF	real	4,2	linear peak shape calibration based on calibration spectra: 1: fwhm calibration (slope and intercept) non-fitting procedure 2: fwhm calibration (least squares fit) 3: junction point calibration (l.s. fit) 4: non-used
JINT	integer	1	integration method for fitting: 2: Gaussian (fwhm fixed) 3: Gaussian (variable fwhm) 4: Gaussian + tail (shape fixed) 5: Gaussian + tail (variable shape)
MRESID	integer	1	1: Check residual 0: Bypass residual search (default)
IFPLOT	integer	1	1: Prepare lineprinter plot of region 0: Bypass plotting (default)
IDO	integer	1	0: Use value of fwhm passed to FITTIT Do not check residuals 1: Use value of fwhm passed to FITTIT residual check controlled by MRESID 2: Get initial guess on shape parameters from calibration spectra [ff()] 3: shape parameters from calibration spectra, do not check residuals
ITER	integer	1	number of iterations
CHISQR	real	1	value of chi-squared from least squares fit
ICODE	integer	1	return code from fitting algorithm 1: wont converge -- > 30 iterations 2: singular matrix -- inversion failed 3: negative fitting parameter 4: junction point out of range (exp. tail) 5: greater than 7 peaks in fitting region 6: greater than 200 channels in region
NEGP	integer	1	return code when fitting parameter goes negative: (peak#) * 100 + (parameter#)

Block 14:

Variable	Type	Size	Description
FT	real	2,300	Results of least squares fitting: 1: -- background 2: -- residuals 300 channels
AFT	real	20	fitting parameters: baseline parameters (1,2) peak width parameter: $\sqrt{4 \cdot \log(2) / (\text{fwhm}^2)}$ junction point for exponential tail peak parameters (1-ncomp): peak height peak position
KLF	integer	1	left boundary channel for region of fit
KRF	integer	1	right boundary channel for region of fit
NS	integer	1	index of last shape parameter in AFT
NA	integer	1	index of last fitting parameter in AFT
NB	integer	1	index of last baseline parameter in AFT
NAS	integer	1	index of sigma parameter in AFT
NAJ	integer	1	index of junction point parameter in AFT
N511	integer	1	location of 511 keV annihilation peak in an integration region

Block 15:

Variable	Type	Size	Description
FTP	real	7,300	1 to ncomp -- data for component i maximum of 7 components, 300 channels (required only if LPLOT is included)

Block 16:

Variable	Type	Size	Description
CFARAY	real	70,21	array of flux monitor comparator factors maximum of 70 peaks, 20 standards the 21st index is reserved for the average value
SCFARY	real	70,21	array of errors on the flux monitor comparator factors stored in CFARAY
GAMKEV	real	71	Energy of photopeak in keV used for the determination of ELEMNT
ELEMNT	alph	71	Symbol of the elemnt being determined via the photopeak GAMKEV
LAMBDA	real*8	70	Decay constant for the indicator radio- nuclide used for the determination of ELEMNT via the GAMKEV photopeak
PLOT	alph	71	Controls interactive plotting of peaks during INAA data reduction: ' ': plot if upper limit or weak line '+' : plot peak in samples only '*' : plot peak for all spectra '-' : never plot
NPKAN	integer	1	Number of peaks to be used for INAA processing

Block 17:

not used in current implementation of SPECTRA
reserved for program development

Block 18:

Variable	Type	Size	Description
ROIDAT	integer	20,25	data for peak integration region (region of interest) as defined by PLOTPK: 20 regions may be defined 1: index of peak of interest in GAMKEV 2: left hand boundary of region 3: right hand boundary of region 4: peak integration mode (as set by PLOTPK) 5: number of components in region 6 - 25: center channel of each component
RISHFT	real	20,2	gain drift and zero shift parameters for

spectrum used to define integration region

NROI	integer	1	Number of integration regions that have been defined by PLOTPK subroutine (maximum of 20)
ROIFLG	logical	1	Logical variable that indicates to the PEAKS and PLOTPK subroutines that a region of interest is being processed by the INAA subroutine

Block 19:

Variable	Type	Size	Description
ACQCH	Integer	3	Acquisition data, time, & clock time duration as stored in channels 3, 4, & 5
ADCTIM	real	2	ADC resolving time = ADCTIM(1)+ADCTIM(2)*N N is channel number. Can be used to compute dead time of a count.
CTIME	real	100	Clock time duration of a count (in minutes)
DLIVTU	alph	100	units of NURLIV(I) (S, M, H, or D)
ETIME	real	100	Elapsed time between counts (in minutes)
FMDIM	alph	71	units of FMWT (e.g. UG, MG)
FMNAME	char*8	20	Flux monitor names (1st 8 characters)
FMWT	real	71	Weight (or concentration) of ELEMNT in the flux monitor
HRCT	integer	100	Time of day that the count was started in
MINCT	integer	100	hours (HRCT) and minutes (MINCT). (8:30 pm would be 2030). If SHORT is .TRUE. then acquisition time is in minutes (HRCT) and seconds (MINCT).
NURLIV	integer	100	Live time duration of the count.
PCODE	integer	100	'-': delete inaa processing for this sample ' ': inaa processing is enabled '+': interactive plotting is enabled '^': interactive plotting is disabled
SAMPNM	alph	100,5	sample names
SAMPWT	real	100	sample weights

TEMPCF	real	70	working array of comparator factors used in the INAA subroutine
TIMECT	real	100	acquisition time as computed from HRCT and MINCT and NDAY
TMPCFS	real	70	working array of errors on TEMPCF
CSHIFT	logical	1	if .true. peak centroid may be redefined using energy calibration data during INAA processing.
DFIRST	integer	1	number of first day of first count
DLFLG	logical	1	if .true. then overlapping peaks (< 1 fwhm) from the analytical line) encountered during INAA processing will be deleted when no interference has been indicated.
DTHFLF	real	1	half-life (in minutes) of the dead time variation in an experiment involving short lived radio-nuclides
FILT	real	1	filter for photopeak identification in keV
FLXFCT	real	1	correction factor for flux variation during the irradiation. Corrected activity = measured activity / FLXFCT.
FLXMON	logical	1	.true. if sample currently being processed is a flux monitor
FPU	real	1	pulse pile-up correction factor
FPULSE	real	1	area of pulser peak used for dead time corrections in first spectrum processed
FTIME	real	1	duration of count of first spectrum
HPCFLG	logical	1	indicates that PLOTPK has been called during INAA processing
IDATE	integer	1	date [month,day, & year (MMDDYY)] to which all activities are corrected for decay (see START)
IDET	integer	1	identified the detector used in the expt. used to get pulse pile-up resolving time
IFM	integer	1	counter for number of flux monitors processed.
INDEL	integer	1	initial value of NDEL (used when NDEL is incremented during processing.

INTPLT	logical	1	.true. when interactive plotting is enabled
MCFOUT	logical	1	.true. when flux monitor comparator factors are to be read out to a data file.
NFM	integer	1	number of flux monitors to be processed in an activation analysis set (<21).
NPCALL	integer	1	number of calls to the PLOTPK subroutine
NUMSPC	integer	1	variable which defines the number of the spectrum currently being processed within an activation analysis set.
PULSER	integer	1	channel location of the pulser peak used for puls pile-up and dead time correction
RUNTIM	real	1	acquisition time as defined by CTIME & ETIME
SET	integer	1	number of the activation analysis set with a given SPECTRA run.
START	real	1	time of day to which all activities are to be corrected on the day IDATE
TAPACQ	logical	1	acquisition date and time is obtained from spectra data file (not defined by control file)
TIMECH	real	1	live time duration as stored in channel 1
TOTAL	real	1	total number of counts in entire spectrum
TOUT	logical	1	if .true. the program output is directed to a separate logical unit for conversion to microfiche.
TPU	real	1	pulse pile-up resolving time (in micro-seconds) of the detector amplifier system. The correction factor is computed as: $f = \exp(2.0 * \text{rate} * \text{TPU})$ where $\text{rate} = \text{TOTAL} / (\text{duration in minutes})$

APPENDIX 4

ACTIVATION ANALYSIS INVOLVING SHORT-LIVED NUCLIDES

In an activation analysis experiment involving the counting of short-lived nuclides, it is frequently necessary to correct for the effect of changing dead time during sample counting. A subroutine DTCORR is available to the SPECTRA program that corrects for changing dead time using two simplifying assumptions. The first assumption is that the spectrum is dominated by one short-lived nuclide such that the dead time changes with the half-life of the dominant radionuclide. This situation is generally observed in geological samples, where, for the first several minutes following irradiation, ^{28}Al is the dominant activity. The second assumption is that the shape of the spectrum is the same throughout the measurement period.

The treatment that follows is a variation of the approach use by Low (1964), who treated the special case where only one radionuclide is involved. The following notations are used in the derivation:

- T = live time duration of the count
- ΔT = total dead time of the measurement
- t = time counted from the beginning of the count
- $n_{i,t}$ = the counting rate in channel i at time t
- $n_{i,t}$ = the counting rate in channel i at time t corrected for the dead time
- N_i = the number of counts in channel i during the measurement
- $100D_t$ = the percent dead time at time t
- λ_1 = the decay constant of the dominant activity
- λ_2 = the decay constant of the radionuclide of interest

The equation for radioactive decay is

$$n'_{i,t} = n'_{i,0} e^{-\lambda_2 t} \tag{4.1}$$

whereas

$$n_{i,t} = n_{i,0} f(t), \quad f(0) = 1 \tag{4.2}$$

where $f(t)$ is a function of t but independent of i.

The fractional dead time is given by

$$D_t = k_i n_{i,t} = e^{-\lambda_1 t} k_i n_{i,0}$$

or

$$D_t = d_0 e^{-\lambda_1 t} \quad (4.3)$$

since

$$n'_{i,t} - n_{i,t} = n'_{i,t} D_t \quad (4.4)$$

$$\frac{n'_{i,t}}{n_{i,t}} = \frac{1}{1 - D_t} = \frac{1}{1 - D_0 e^{-\lambda_1 t}} \quad (4.5)$$

and

$$\frac{n'_{i,0}}{n_{i,0}} = \frac{1}{1 - D_0} \quad (4.6)$$

Dividing (4.5) by (4.6) and inserting (4.1) and (4.2)

$$f(t) = \frac{e^{-\lambda_2 t} (1 - D_0 e^{-\lambda_1 t})}{1 - D_0} \quad (4.7)$$

The total dead time ΔT for the measurement lasting from $t = 0$ to $t = T + \Delta T$ is

$$T = \int_0^{T+\Delta T} D_t dt = D_0 \int_0^{T+\Delta T} e^{-\lambda_1 t} dt \quad (4.8)$$

which yields the following expression for D_0 :

$$D_0 = \frac{\Delta T \lambda_1}{1 - e^{-\lambda_1 (T+\Delta T)}} \quad (4.9)$$

The total number of counts recorded in channel i during the measurement is given by

$$N_i = \int_0^{T+\Delta T} n_{i,t} dt = n_{i,0} \int_0^{T+\Delta T} f(t) dt \quad (4.10)$$

inserting equation (4.7) and integrating yields

$$N_i = \frac{n_{i,0}}{1 - D_0} \left\{ \frac{D_0 [e^{-(\lambda_1 + \lambda_2)(T + \Delta T)} - 1]}{(\lambda_1 + \lambda_2)} + \frac{1 - e^{-\lambda_2 (T + \Delta T)}}{\lambda_2} \right\} \quad (4.11)$$

Inserting equations (4.6) and (4.9) yields

$$n'_{i,0} = N_i \left\{ \frac{\lambda_1 T [e^{-(\lambda_1 + \lambda_2)(T + \Delta T)} - 1]}{(1 - e^{-\lambda_1 (T + \Delta T)}) (\lambda_1 + \lambda_2)} + \frac{1 - e^{-\lambda_2 (T + \Delta T)}}{\lambda_2} \right\}^{-1} \quad (4.12)$$

This provides an expression for the activity at the beginning of a count, where in an experiment involving changing dead time, N_i would represent the peak area, and $T + \Delta T$ the clock time duration of the count, that can be measured and included in the input data for the corresponding spectrum. The correction factor in brackets () in equation (4.12) is calculated by the entry point DTCORR of the CLOCKT subroutine.

The correction for changing dead time has been tested experimentally by irradiating two identically prepared flux monitor samples for the elements Al, V, and Mg. The samples were counted successively for 200 seconds live time, and the 9.46 minute ^{27}Mg , 3.75 minute ^{52}V , and 2.31 minute ^{28}Al activities were assayed by integration of the 1014 keV, 1434 keV and 1779 keV photopeaks, respectively. The more intense 844 keV ^{27}Mg peak was not employed because of interference from the 846 keV ^{56}Mn photopeak. After applying the correction factors for decay and varying dead time developed above, the ratios of the activities in the two samples were calculated. Since the samples were identical, the deviation of the ratios from unity provides an indication of the errors induced by making the assumptions used in developing the correction in analyzer dead time. Table 4.1 tabulates the results, both with and without dead time correction. In the latter case, equation 30 was used to correct for decay. The peak areas for the photopeaks used in the experiment are also tabulated. It can be seen that the ^{28}Al activity dominated the spectrum.

Since analyzer dead time is proportional to channel number, the Al activity would be the primary contributor to the dead time, not only because of its higher activity, but because the ^{28}Al photopeak has the highest energy of those peaks appearing in the spectrum.

Table 4.1 Ratios of decay-corrected specific activities between two identical samples counted successively for 200 live seconds.

<u>Radio-nuclide</u>	<u>Energy (keV)</u>	<u>Peak area in first spectrum</u>	<u>No Correction for dead time</u>	<u>Dead Time corrected</u>	<u>Standard deviation*</u>
^{27}Mg	1014	955	0.895	0.922	± 0.116
^{52}V	1434	4892	0.903	0.968	± 0.042
^{28}Al	1779	49397	0.854	0.950	± 0.009

* Based on counting statistics

The fact that the dead time correction brought the ratio closer to unity for the three activities supports the use of the expression developed above. The ratios for ^{27}Mg and ^{52}V lie within one standard deviation of unity based on counting statistics, although the ratio for Al lies well outside of one sigma. Using the approach described by Low (1964), that would be appropriate only in the case of Al, yields a ratio of 0.942 for that element, and represents no appreciable improvement over the more generalized treatment described above.

In an activation analysis experiment involving the counting of short-lived nuclides, one flux monitor may be irradiated and counted for each sample analyzed. The SPECTRA program handles this as a special case when (on input record 8) the number of flux monitors (NFM) is set to a negative number. This simplifies the input in that every pair of samples does not need to be defined as a separate INAA sample "set". The flux monitor spectrum does not need to precede its associated sample spectrum in the input data file.