Computer Analysis of Gamma-Ray Spectra

9.1 INTRODUCTION

I discussed the basic algorithms for spectrum analysis in Chapter 6 under ‘Calibration’ and in part in Chapter 5 under ‘Statistics’. Although most of the useful information within a spectrum can be extracted manually, it is almost certain nowadays that a computer will be used to perform the spectrum analysis. In this chapter, I will examine the ways in which this is accomplished and discuss some of the pitfalls. To a large degree, computer programs follow (or should follow!) the principles I have already discussed.

At one time, the computer programs available could only be implemented on mainframe computers, but the increases in memory size and speed of the personal computer (PC) have put spectrum analysis on one’s own desktop (as the advertising literature might have it) and nowadays there will be few people who do not use PC-based programs. Modern spectrum analysis programs are sophisticated packages that provide many facilities and I will refer to a number of commercial programs by way of example. These references are not intended to be endorsement of the programs, nor should any relative merit or demerit be implied. The programs will be referred to by name. Full details and attribution of these programs are given at the end of this chapter.

Before continuing, we perhaps ought to distinguish the different types of computer program available. The term ‘software’ will refer to the computer programs and ‘hardware’ to the computer on which they run. A hardwired MCA system is one in which the program is not loaded from an external source but is built into the wiring of the hardware. The distinction is somewhat blurred by the fact that some systems with a fixed program can be updated by installing a new version of the program, i.e. by loading new software:

- MCA emulators are concerned mainly with the acquisition of the spectrum data. They emulate the functions of the hardwired multichannel analyser. Examples are the Canberra System 100 (no longer available) and ORTEC Maestro-32. These programs will provide for energy calibration but not necessarily width or efficiency calibration. Peak area measurement and peak search may be provided but this is unlikely to be as complex as a dedicated off-line analysis package. In our context, I will define ‘online’ as being work done interactively with data held and displayed in the MCA emulator. ‘Off-line’ would then be work done with spectra stored on computer disk.
- There are several ‘off-line’ programs which are intended to perform full calibration and analysis of spectra which have been acquired either by an MCA Emulator program or by a hardwired analyser and stored on disk. Examples of such programs are Sampo 90, FitzPeaks and CompAct.
- Since the first edition of this book, it is more likely that laboratory-based spectrum analysis will be achieved using one of the programs that combine the two functions, such as GammaVision and Genie 2000, and spectra may be analysed immediately after acquisition within the same program. Full energy, width and efficiency calibrations are provided in an interactive manner.

The programs within modern portable gamma spectrometers can, in some cases, rival that of the more sophisticated PC-based systems, especially where acquisition is controlled by a laptop PC. However, improvements have also been made to the PC-based software. In particular, and most laudable, is the introduction of true coincidence summing corrections into GammaVision and Genie 2000, even though, as I explained in Chapter 7, there
is some room for improvement. It is disappointing that most of the changes to spectrum analysis programs have been cosmetic – more bells and whistles – rather than addressing known problems with the core algorithms that remain unchanged since the first edition of this book.

More often than not, spectrum analysis software is purchased with the hardware, if only to be certain of compatibility between them, and the market is dominated by software produced by the major gamma spectrometry equipment manufacturers. There are, however, a small number of software providers, independent of the manufacturers, providing reputable programs at a much lower cost; these are worthy of consideration. Such companies may be more amenable than the major players to rapid ‘bug-fixes’ when problems in their programs are identified and may be prepared to customize the program to suit a particular buyer.

It is evident that there is often an unwarranted faith in the power of computer programs which leads to a ‘black-box’ mentality. A spectrum is inserted into one end of the ‘black-box’ and out of the other end come results which are accepted uncritically as ‘the truth’. Anyone who understands computers and has experienced the joys of programming is likely to have a much more jaundiced view of computer output. There are sound philosophical and logical arguments to suggest that it is impossible to prove without doubt that a computer program will work in every possible situation. Bearing that in mind, we would do well to keep an open mind about computer-generated spectrum analysis results. At the least, an understanding of the processes of calculation – the algorithms – used by the computer program to perform the analysis will help to alert the gamma spectrometrist to potential problems. Modern spectrum analysis packages will provide many analysis options and setting up the program may not be a trivial task. The user owes it to himself or herself to ensure that whenever an option is chosen it is a considered and informed choice rather than a blind reliance on conventional wisdom or the default option predetermined by the computer programmer.

In this chapter, I will consider in a general way the principles behind spectrum analysis. I shall leave aside the detailed implementation of those principles because that will vary from program to program. In Chapter 15, I will discuss the testing and validation of spectrum-analysis software. There are a large number of tasks that an ideal gamma spectrum analysis program might be asked to perform. As a minimum, the program should:

- Determine the position of peaks in the spectrum.
- Estimate the areas of the peaks in the spectrum, together with uncertainties.
- Calculate the energy of the gamma-ray each peak represents.
- Correct for counting losses due to dead time and random summing.
- Make corrections for decay from a reference time and, when necessary, decay during the count interval.
- Convert peak areas to activity (or concentration depending upon usage), either by reference to an efficiency function or by direct comparison with a reference spectrum.

It would be an advantage if the program could also:

- Create efficiency, peak width and/or efficiency calibration curves.
- Resolve multiplet peaks, either by peak stripping or by deconvolution.
- Make corrections for irradiation or sample collection time where appropriate.
- Estimate an upper limit activity when appropriate peaks are not detected.
- Identify nuclides in the spectrum.
- Make corrections for gamma-ray absorption within the sample and/or between source and detector.
- Make corrections for true coincidence losses.
- Make a full account of all sources of uncertainty within the measurement process.

Not all programs will perform all tasks and not all tasks will be relevant for all analyses but one might expect a typical commercial analysis program to be able to cope with the majority. In this chapter, I will discuss all of these items individually with the exception of true coincidence summing, which was discussed separately in Chapter 7. In general, a full computer spectrum analysis will consist of three phases:

- Set up data libraries for energy, peak width and efficiency calibration and for sample analysis. Different libraries might be needed for each phase of the analysis.
- Use spectra of reference sources to generate energy, width and efficiency calibration data files.
- Analyse sample spectra by referring to those data libraries and calibration files.

The processes involved are shown in flow chart format in Figures 9.4, 9.9, 9.12 and 9.13 and I will consider the various parts of these in due course but first we must consider how the program locates peaks in the gamma-ray spectrum.
9.2 METHODS OF LOCATING PEAKS IN THE SPECTRUM

9.2.1 Using regions-of-interest

At the root of all spectrum analysis programs is the ability to locate gamma-ray peaks. However, it is well to bear in mind that our objective is to measure the number of gamma-rays detected within a particular energy range. That objective does not determine or demand any particular energy distribution of the gamma-rays. There is, therefore, nothing reprehensible or shameful in ignoring the sophisticated peak search facilities and simply telling the program where the peaks are by defining regions-of-interest (ROIs). This is more likely to be appropriate when using an MCA emulator than a full spectrum analysis program. Using ROIs, such programs can calculate, and subsequently print out, peak areas corrected for the background continuum and a peak area uncertainty. The use of ROIs is probably an under-utilized option in gamma-ray spectrometry. Many laboratories will measure the same few gamma-ray peaks day in and day out. If the spectrometer is free from gain drift, there is no harm and there are potential benefits in using such a simple approach. It is a pity that the MCA systems only allow ROIs to be set up in terms of channel number, rather than energy. If the latter were possible, a certain degree of gain shift would be tolerable.

In most spectrum analysis, an active peak search will be involved. Although the energy calibration procedure for an MCA emulator usually requires the operator to set up ROIs about the reference peaks, even then an active search will be performed within these regions to determine the exact peak position.

9.2.2 Locating peaks using channel differences

Peak search is not as straightforward as one might imagine. Figure 9.1 demonstrates the essential problem. Figure 9.1(a) shows a moderately well-defined peak. A simple, intuitive peak search method might scan through the spectrum seeking a number of channels each successively significantly greater, in the statistical sense, than its earlier neighbour. Having established a consistent rise, a corresponding series of channels with significantly falling contents might be sought. The pattern of rise and fall would then indicate the presence of a peak, and the onset of the rise and cessation of fall could be used to determine the peak limits. Such a naïve algorithm fails, however, when presented with the data in Figure 9.1(b) where few channels are statistically different from their neighbours and there is certainly no consistent sequence of statistically significant differences. Yet, the human eye and brain detect the peak with ease. In effect, the brain suppresses the statistical uncertainties (it smooths the data) and detects the underlying structure. That, in essence, is the modus operandi of practical peak search programs.

9.2.3 Derivative peak searches

The most commonly used method for peak search is that attributed to Mariscotti and, in general terms, might be called a derivative method. Many years ago, this was incorporated into a mainframe computer program called SAMPO which has since formed the basis for many other spectrum analysis programs, including those still in use today. Figure 9.2 demonstrates the principle. Figure 9.2(a) shows a basic Gaussian shape on a horizontal straight
line (the model for our spectrum peak) with the first and second differentials of that Gaussian, also known as the first and second derivatives. Both of these curves have features which can in principle be used to detect the presence of peaks. For example, the first derivative changes sign as it crosses the peak centroid, the second derivative reaches a minimum at the centroid and so on. Third and even fourth derivatives have been discussed as potential search functions. Of course, gamma-ray peaks are not mathematical Gaussian curves; they are histograms that approximate a Gaussian curve. Because this is so, we cannot calculate a differential as such but must use the differences between channels as an approximation to the gradient.

The commercial programs Genie-2000, GammaVision and Fitzpeaks are all based upon the Mariscotti algorithms using the second difference method, as in the original mainframe program SAMPO. The actual implementation of the algorithm means that several channels are taken into account at any one time, smoothing out the statistical uncertainty in the data. Figure 9.2(b) shows such an algorithm applied to actual spectrum data. The two larger negative excursions of the second difference function (cross-hatching) indicate the position of the two gamma-ray peaks. In this particular example, the peaks are two FWHM apart. Clearly, as the separation between the peaks gets smaller, it becomes more difficult to resolve them. In general, two peaks of similar size are likely to be detected individually as long as the separation between channels is more than about one FWHM. Small peaks will tend to be lost in the presence of larger peaks at separations smaller than this.

9.2.4 Peak searches using correlation methods

Another less used, but useful, method of peak location is based upon cross-correlation. This is demonstrated in Figure 9.3. A search function, here shown as a Gaussian, is scanned across the spectrum. Over the width of the search function, each spectrum count is multiplied by the corresponding value of the search function. The sum of these products is then a point on the correlation spectrum. After applying an appropriate bias to take into account the underlying continuum, any channels in the correlation spectrum which are greater than zero represent channels within a peak. This author’s experience is that correlation peak search works well and is easily set up to avoid spurious peak detection. A correlation search is used in the CompAct spectrum analysis program. As with the derivative search methods, because several channels are taken into account at one time, statistical scatter is effectively smoothed out without the need for a separate smoothing operation.

The correlation method is quite general and need not use a Gaussian search function, although that does have...
9.2.5 Checking the acceptability of peaks

Whichever method is used to locate the peaks, the magnitude of the peak search function will be compared with some parameter related to a user set sensitivity value. Unless the function exceeds this value, a peak will not be detected. The sensitivity parameter might be related to peak area uncertainty – peaks with an uncertainty greater than the threshold being rejected, or some sort of empirical threshold factor might be used.

Whichever search method your chosen software uses, it is important that the peak location sensitivity criteria are set up properly; too high a sensitivity (which is very likely to mean a smaller sensitivity factor within the program) would mean that many spurious peaks are reported, while too low a sensitivity would mean small, but real, peaks are ignored. Having located a peak, the program may make some attempt to check that the peak shape is acceptable. Tests may be included to discriminate between true peaks and features such as Compton edges, backscatter peaks and the like. Sometimes, such peak shape tests are self-defeating when applied to ill-defined peaks where the estimation of FWHM is barely valid, resulting in rejection of real peaks.

9.3 LIBRARY DIRECTED PEAK SEARCHES

There are two ways of approaching spectrum analysis. One might search the spectrum, take all of the peaks detected and measure their areas and then assign them to nuclides. Alternatively, one might specify which peaks of which nuclides to measure and then perform a limited peak search and measurement within the expected peak regions. This latter, library directed, method is reputed to be more sensitive than the former open search methods and there is some evidence to support that assertion. Certainly if a particular nuclide must be determined, even if only as an upper limit, then a library directed search must be used – otherwise nothing would be reported at all if the appropriate peak were not detected. Of course, unless a library directed search has associated with it a general search, the user will not be alerted if unexpected nuclides are detected. There is a need for both facilities within the same program and most software will provide them.
9.4 ENERGY CALIBRATION

Energy calibration will often be performed before acquisition of the spectrum as part of the setting up procedure. It is included here because, in some cases, the MCA calibration may only be rudimentary (especially if a hardwired MCA is used) and a more precise calibration might be required before analysis of the spectra. Energy calibration involves the following steps (see Figure 9.4):

- Measure the spectrum of a radioactive source which emits gamma-rays at precisely known energies.
- Tell the system, whether hardwired or software, which peaks to measure.
- Supply the precise energies of the selected peaks.

The system can then search for the required peaks, find their centroids and fit an appropriate function to the pairs of position/energy data. In most cases, the choice of 'appropriate' function will be determined by the system itself. A hardwired analyser is unlikely to allow more than a two point calibration. Even in an MCA emulator system such as Maestro-II, users are limited to a two point linear calibration. Using the companion full spectrum analysis program, GammaVision, this initial calibration can be replaced by a multi-point calibration fitted to a quadratic equation:

\[
\text{Energy} = \text{Intercept} + \text{Factor1} \times \text{Channel} + \text{Factor2} \times \text{Channel}^2
\]  
(9.1)

In some programs, a higher-order polynomial fit may be allowed and could provide a more precise fit. However, care should be taken. We have no theoretical reason to suppose that the energy/voltage relationship of any amplifier/ADC combination is quadratic. In fact, they are designed to be linear. The specification sheets for our amplifiers and ADCs tell us to expect serious non-linearity only at the extremities of the linear range. Without a theoretical basis, curve fitting is merely a mathematical game to achieve a more precise fit to the experimental data. It is not necessarily the case that a higher-order fit will provide a more satisfactory fit in a practical sense. The peak position data have uncertainties associated with them. Are they taken into account in the curve fitting? (Most likely not!) It may be the case that a higher-order fit is simply 'bending' its way around the uncertainties. A particular, and possibly non-typical, example is illustrated in the Figure 9.5(a). This shows the difference between actual and derived energies using a manual linear fit and a 13 point quadratic fit for the calibration spectrum associated with the Sanderson test spectra (see Chapter 15). It is quite clear that, although the errors are smaller at low energy, overall the quadratic fit gives larger errors than the linear. Evidently, a perfect fit to the data would require something more sophisticated than a quadratic.
A typical modern ADC might claim integral non-linearity of better than 0.05 % over the top 99 % of the channels. That implies a maximum error on an energy estimate of 1 keV, assuming an energy range of 0 to 2000 keV. Experience shows that the actual non-linearities are rather lower than this except, perhaps, at the extremities of the energy scale.

At the acquisition stage, there is probably little need to use anything more than a two point (and therefore) linear calibration. Whether subsequently there is need for a multi-point, and perhaps, non-linear calibration may depend to some extent on the use to which the information is to be put. At one extreme, if the MCA system is stable and always used to measure the same gamma-ray peaks using preset ROIs then a precise measurement of energy becomes irrelevant. At the other extreme, studies of the energy levels within nuclei would need very high-precision calibrations and it could be that a commercial program would not provide sufficient flexibility to do this directly.

Whichever particular mathematical function is chosen, the energy calibration data should span the intended measurement energy range. Extrapolation beyond the calibrated energy range should be done with caution. This is particularly important if polynomial fits are used. Higher order polynomials will certainly provide a better fit to all the nuances of the data but may deviate far from the ‘true’ curve beyond the first and last data points. Small changes in the data within the data can result in the ends of the curve ‘waggling’ in an unexpected way.

It is common practice for interactive spectrum analysis programs to provide a visual display of the energy-calibration data, together with the fitted line. This is always so nearly a straight line that it is impossible to distinguish between different fits visually. (If it were not so, one would probably have a serious instrumental problem.) It is usually necessary to examine carefully the printed-out results of the calibration. I look forward to the program that provides a graphical display of the differences between measured and fitted positions together with a goodness-of-fit factor to aid comparison between different types of it.

9.5 ESTIMATION OF THE PEAK CENTROID

It is unlikely that the true centroid of a peak will coincide with a channel number. If we are to estimate the gamma-ray energy represented by the peak, then we must have a means of determining the position of the peak centroid to within a fraction of a channel. An almost universal algorithm for this is to calculate the following:

\[
\text{Centroid} = \frac{\sum C_i / \sum C_i}{\sum C_i}
\]  

(9.2)

where \( C_i \) is the count in the \( i \)th channel, usually corrected for the underlying continuum background. After an active peak search, it is more likely that the value of the search function will be used for this calculation rather than the actual spectrum data. After a derivative peak search, the summation might be taken over the region where the derivative is negative and for a correlation method where the correlation function is positive. Alternatively, the summation width might be equivalent to a full peak width.

9.6 PEAK WIDTH CALIBRATION

Knowledge of peak width is fundamental for the measurement of peak area and for peak fitting. As we will see later, the computer program will, at some stage, need to know this. The gamma-ray peaks measured on a good modern detector free of neutron damage and other charge collection problems can usually be approximated by a Gaussian shape. In fact, as Figure 9.6 demonstrates, the actual shape is much more complicated. Even a cursory visual examination of a well-defined gamma-ray peak reveals that the continuum level on the low-energy side of the peak is higher than that on the high-energy side. In principle, this ‘step’, which is attributed to the loss of primary or secondary electrons from the sensitive volume of the detector, should be accounted for in some way. In
the particular case in Figure 9.6, subtraction of the Gaussian peak and a step function from the channel counts reveals that there are also ‘tails’ on both sides of the peak. Again, a rigorous definition of the peak shape ought to include a description of these.

In practice, assuming that the detector is set up correctly and there are no gross problems which might affect the peak shape adversely, these underlying features are only significant when large well-defined peaks are analysed. In Figure 9.6, the departure from Gaussian only becomes significant below 1/400th of the full peak height. For the majority of peaks in routine spectra there is little to be lost by neglecting deviations from Gaussian. Nevertheless, some spectrum analysis programs will allow tails and/or step functions to be included in the peak description. For example, the current version of Genie-2000 will allow low-energy tails to be included. Fitzpeaks, and possibly future versions of Genie-2000, will take into account low- and high-energy tails. GammaVision does not take into account tailing but will, under some circumstances, provide a stepped continuum.

The actual profile of the step beneath a peak does not appear to have been defined theoretically. Debertin and Helmer list eight functions which have been suggested in the literature. In practice, for peaks where the step is a noticeable feature, the measured peak area would be unlikely to alter significantly if the step function were changed as long as it remained symmetrical about the peak centroid. Sometimes, there are occasions where the peak background is obviously not linear. Typically, this would be the case for peaks on the low-energy side of a backscatter peaks. To cope with this, GammaVision will use a parabolic background function. FitzPeaks is able to use a number of different background functions based on polynomials, including the parabolic function.

In spite of all such qualifications, for many purposes the peak shape can be indicated to the program by supplying a single Gaussian width parameter – either the standard deviation or FWHM. The width of a peak increases with energy and it is necessary, therefore, to provide the parameters of a width equation similar to the energy calibration.

The arrangements for peak width calibration may not be as explicit as for energy calibration. For example, the ORTEC Maestro-II MCA emulator automatically performs a two point peak width calibration simultaneously with the energy calibration and stores both sets of information within the spectrum file. The equivalent program from Canberra, the System 100, makes no attempt at peak width calibration. GammaVision also does its multi-point peak width calibration at the same time as energy calibration.

Of the methods for FWHM estimation discussed in Chapter 7, the interpolation method (Section 7.5.2) is usually used. In some cases, (programs based on SAMPO for example) the peak width is deduced within the nonlinear least squares peak fitting process which derives width, position and peak area simultaneously. It is well to remember that unless the peak is well defined any estimate of the peak width is likely to be of dubious value.

The analysis program must construct a mathematical relationship between FWHM and energy (or channel number). Unlike energy and efficiency calibration, it is possible to suggest a theoretical form for the FWHM/energy relationship as expressed by Equations (6.10) in Section 6.5. None of the available spectrum analysis programs allows a fit to the square root quadratic. Most programs assume a simple quadratic or other polynomial relationship. Genie-2000 and SAMPO 90 programs use Equation (9.3), perhaps believing that it is equivalent to Equation (6.11). It is not.

\[
\text{FWHM} = F_1 + F_2 \times E^2
\]  
(9.3)

Figure 9.7 shows a typical FWHM calibration derived from a Genie 2000 calibration fitted to Equation (9.3). (Spectrum nbstd.cnf, distributed with the program.) Clearly, the fit is not satisfactory.

In fact, there is no theoretical justification for any of these alternative equations. The quadratic has a particular failing in that the statistical scatter of points can lead to an FWHM curve that curls upwards rather than downwards. This clearly flies in the face of physical reality. It would be useful if, whatever other FWHM fit options were
provided, analysis programs always allowed a linear fit, which experience shows is a reasonable practical approximation to the theoretical square root quadratic equation.

Figure 9.8 show the data of Figure 9.7, together with the curves derived from fits to five mathematical equations: linear, quadratic, Genie-2000 (Equation (9.3)), Debertin and Helmer and the square root quadratic equations. For this particular data, all the relationships but the Genie-2000 equation give similar root mean square differences between measured and fitted widths. Over most of the calibrated energy range, any of them would provide a reasonable estimate of FWHM. However, the figure does suggest that Equation (9.3) would seriously underestimate the FWHM at low energy and this is borne out by other similar calibrations. The reader should also remember the fact that X-ray peaks are unlikely to have the same width response to energy as gamma-rays (see Chapter 1, Section 1.7.4) and are likely to be wider than expected at low energy.

As with the energy calibration, a quadratic can produce a poorer fit than a linear relationship, as shown in Figure 9.5(b) above where the differences between measured and calculated FWHM using linear and quadratic fits are compared. It is up to the analyst, if there is a choice, to select the most realistic and sensible fit rather than the mathematical best fit.

In worrying about the ‘true’ mathematical width/energy relationship, perhaps we should consider the use to which the width calibration is put. Values interpolated from the curve are most likely to be used for defining the peak-integration limits, in which case there will be a rounding to the nearest channel, or, by comparing the value with its width, to establish whether a peak is a singlet or a multiplet. In either case, the errors caused by fitting the ‘wrong’ function (with the possible exception of the Genie 2000 function at the ends of the calibration range) are not likely to be serious enough to affect the outcome of the analysis.

9.7 DETERMINATION OF THE PEAK LIMITS

Let us assume that we have established the position of a peak in the spectrum (or at least its expected position if it has not been detected). Before the peak area can be measured, making use of the algorithms discussed in Chapter 5, a decision must be made as to the limits of

Figure 9.8 A peak width calibration (FWHM) for a p-type HPGe detector. The diamonds represent the measured points and the lines various computer fitted functions. The quadratic and square root quadratic fits are indistinguishable in this particular case.
the peak region. Limits too far from the centroid will tend to include channels which are really background and will tend to render the area measurement vulnerable to the influence of near neighbour peaks. A peak region which is too narrow will result in an underestimate of the true peak area. (However, as suggested in Chapter 5, that would not necessarily be an overwhelming problem.)

A sensible strategy is to define what proportion of the total peak area we wish to measure and set the limits accordingly. Let us say that we would be content to measure 99.7% of the peak area. If we assume that the peak is Gaussian, taking the data from Chapter 4, Table 4.3 we can see that that would imply a peak region of twice 3 standard deviations width (i.e. both tails of the distribution) equivalent to a total peak width of about 2.5 FWHM. We can then fix the peak integration limits at 1.25 FWHM below and 1.25 FWHM about the centroid.

Lars-Erik de Geer (De Geer 2005) argues that the minimum peak area uncertainty is achieved if the total integration width is restricted to 1.25 times the FWHM, which encompasses only 85.9% of the total area. He has used that principle within the peak search algorithms used in CTBTO monitoring stations, where a high degree of confidence in the detection of small peaks is demanded (see Chapter 17, Section 17.1).

### 9.7.1 Using the width calibration

Since the program does have access to a peak width calibration function, the FWHM can be calculated for each individual peak by using its measured energy. This approach has the advantage of consistency; every time the same peak is measured the same peak limits will be selected. Peak area estimates measured by using limits selected in this way must be unbiased since no account is taken of the detail of the spectrum scatter. However, there are limitations. Unless special arrangements are made, incorrect peak limits will be selected for peaks which have anomalous widths, such as the annihilation peak at 511 keV and single escape peaks (see Chapter 7, Section 7.5.4). Since these are all wider than normal gamma-ray peaks at the same energy, their peak areas will be underestimated. However, such anomalous peaks would not normally be selected for nuclide activity measurement and so the problem is academic.

### 9.7.2 Individual peak width estimation

An alternative is to measure the FWHM of each peak as it is located and use that value to define the peak limits. That steps around the problem of anomalous peak widths but there are disadvantages when the peak statistics are poor. Estimates of the FWHM of poorly defined peaks are inevitably uncertain and this means that the peak limits for the same peak in different spectra may appear to be different. Whatever the size of a peak or the particular statistical scatter of the points, the physical reality is that peaks at a particular energy measured on a particular detector system should have a constant width and position (leaving aside problems such as gain drift and count rate associated peak shape changes). It is possible that choosing peak limits in this manner could be biased. For example, if the FWHM algorithm were to consistently underestimate the width of peaks with large uncertainty then small peak areas would also tend to be underestimated.

### 9.7.3 Limits determined by a moving average minimum

Both Genie 2000 and GammaVision use a method of peak-limit detection which uses a moving five point average to search for a minimum on each side of the peak. This is again subject to the same qualification noted above that the position of the peak limits might alter from spectrum to spectrum. More importantly, such a method must, in principle, be biased to some extent. If the position of the peak limits is always chosen to be at minimum points, then the estimate of the peak background underlying the peak must also be minimized, and the net peak area must therefore tend to be biased high. Although myself, and others, have confirmed that there is a positive bias in GammaVision results, it is only barely significant for very small peak areas, and not at all significant otherwise. Presumably the five point averaging almost removes the bias.

### 9.8 MEASUREMENTS OF PEAK AREA

Having detected the peak, determined its centroid (and therefore energy) and set peak limits, the peak-area measurement can proceed by peak integration (as described in Chapter 5, Section 5.4) as long as the peak is a singlet. Indeed, many programs do use the algorithms defined there. Exceptions are SAMPO-based programs (e.g. Genie 2000 and Fitzpeaks) which perform a non-linear least squares fit on all of the peaks, including singlets. In such a fit, the peak area, width and position are determined simultaneously. It has been shown that, for a singlet peak, there is no advantage to be gained, in terms of measurement uncertainty, by fitting a peak instead of using peak integration. Peak-Fitting will be discussed later in Section 9.10.
Section 5.5.1 (Chapter 5) discussed in some detail the optimum number of channels to use for peak background estimation. In view of the significant influence of this, it is important that users of automatic spectrum analysis software be aware of how the program assigns the background channels. Many programs will simply use a fixed number of channels, say three, regardless of the peak situation. This is particularly so for MCA emulator programs where analysis facilities are more rudimentary. For example, in Maestro-32 three channels are chosen and in the Canberra System 100 four. This must be taken into account when setting up ROIs; the appropriate number of channels must be provided, within the ROI, to represent background. More sophisticated programs may make a more intelligent selection of background channels. Genie-2000 will make sure that at least five channels are available beyond the peak limits to allow a valid background estimate. If there is a peak too close to the current peak, the pair will be treated as a doublet and deconvoluted together. GammaVision will look for five consistent background channels on each side of the peak. If necessary, the number will be reduced to three or even one channel if the neighbouring peak is too close. This could mean different background widths on each side of a peak. This is a sensible approach which mirrors that which one might take if calculating the peak area of a particularly awkward peak manually. There is after all no fundamental objection to using different background region widths below and above a peak, as long as the calculations take that into account.

9.9 FULL ENERGY PEAK EFFICIENCY CALIBRATION

The construction of a full energy peak efficiency curve was discussed in Chapter 7, Section 7.6 and is shown as a flowchart in Figure 9.9. I shall discuss here only the facilities available in spectrum analysis programs. The advice given earlier in that section about the quality of data is worth re-iterating. Only singlet peaks with good precision in conjunction with good quality nuclear data should be used to construct an efficiency calibration.

The option of efficiency calibration is usually not available on simple emulator programs and until recently was restricted to off-line analysis packages. More recent software, such as Genie 2000, GammaVision and Fitzpeaks, provide online efficiency calibration facilities within the overall acquisition/analysis package. Regardless of which of the many mathematical functions the analyst might choose to fit to the data, the spectrum analyst is constrained by the choice of functions provided within.

Figure 9.9 Flow chart for the measurement of an efficiency calibration point

his/her system. These might be one or more of the following:

- Polynomials in log (ε) against log (E_p):

\[
\log (\varepsilon) = a_0 + a_1 \log (E_p) + a_2 [\log (E_p)]^2 + \cdots + a_n [\log (E_p)]^n \tag{9.4}
\]

where \(E_p\) is the gamma-ray energy, \(\varepsilon\) the full energy peak efficiency and \(a_0, a_1, \ldots\) are coefficients determined by the fitting algorithm. The order, \(n\), may be as high as 8. It is sometimes possible to take only the first two terms to provide a linear relationship, which satisfies the initial impression of efficiency calibration data that, above the knee, the data are approximately linear when plotted on log-log scales. Taking the first three terms of Equation (9.4) provides a quadratic – again a common option. Because of the two distinct regions of the efficiency curve, programs may allow the data above and below the knee to be fitted separately, maybe using different functions, in a way that ensures that the two curves meet reasonably convincingly.

Gunnink (1990) described polynomial equations of this type for calculating intrinsic efficiency, from which absolute efficiency can be calculated. By examining the efficiency calibrations of a large number of detectors, he was able to relate some of the parameters of these equations to the dimensions of the detector and other details of the detector system. Different equations were used from 50–90 keV, 90–200 keV (second order polynomial) and above 200 keV (sixth order polynomial). At first sight,
An interpolative efficiency curve is an option within GammaVision. A number of other functions are suggested in Debertin et al. (1988) and examined in a paper by Kis et al. (1998). An interpolative efficiency curve is an option within GammaVision which is intended for situations where the actual efficiency curve is known to be complicated and unlikely to conform to the other options available. In effect, the pairs of energy/efficiency data are simply stored as provided. Efficiencies at points between the calibration energies are then estimated by interpolation between an appropriate pair of data points. In general, this is of dubious value – if the data is too scattered to provide a proper efficiency curve, do interpolated values have any meaning? However, I will discuss in Section 9.12.4 how such an option might be used in situations where true coincidence summing is a problem.

It is important to recognize that none of these equations has any theoretical basis. They are all simply empirical relationships – mathematical games – which may fit the experimental data to a greater or lesser degree. The actual choice of function from the limited options provided within a particular program can only be made on the basis of experience. A function that performs well on a p-type detector may not be satisfactory for an n-type where the low-energy behaviour of the efficiency curve differs. Where a choice in the order of the fitting polynomial may be exercised, care should be taken. A higher-order polynomial will certainly be able to fit all of the slight variations in the data better than a lower one and will give a better ‘goodness-of-fit’ factor (assuming this is displayed by the program). However, if these extra ‘wiggles’ in the data are simply due to statistical uncertainty, then the higher-order fit may be further from the ‘true’ curve (whatever that may be) than a lower-order fit. Beware of removing points from the data set on the basis that they ‘don’t fit’ without finding out why. Certainly, if true coincidence summing is a problem, it is conceivable that a single odd point could be the only correct point.

It is desirable that the fitting process should take into account the uncertainty of each point so that less reliable points have less influence on the fit. This would be described as a weighted fit. Ideally, the weighting factors would include not only the counting uncertainty but the calibration source strength uncertainty (which should, in turn, include the uncertainty on the decay correction) and the uncertainty on gamma emission probability. At the present time, not every program available weights the fit and no program takes into account all sources of uncertainty.

Figure 9.10 shows an efficiency calibration using a source of $^{152}$Eu (under conditions where summing was not significant) to which three particular functions have been fitted; double log–linear, double log–quadratic and a single linear polynomial with six terms. Within the data points above the knee of the curve, there is little to choose between the three relationships. The goodness-of-fit improves as the complexity increases but as we have already discussed above unless the fit is weighted to take into account the statistical uncertainty of the data points such improvement may be more apparent than real. The data below the knee point is clearly unsatisfactory and is shown here merely as an example of how a
complex fit can be led astray by inconsistencies within the data. The two low-energy points appear to be 'the wrong way round', which probably indicates a problem somewhere in the peak-area measurement, and this causes the polynomial curve to behave in an unreal manner at low energy. Had this particular data been intended to be used below the knee point, more low-energy data points would have been needed to define the curve below the knee. In this case, since the curve was intended only to be used above the knee, perhaps it would have been better to omit the low-energy points altogether to avoid any distortion of the high-energy part of the curve.

The problems of efficiency curve fitting are greater the longer the energy range. The energy range necessary for prompt gamma-ray measurements must extend to 10–12 MeV. Beyond 3 MeV, the log–log HPGe efficiency plot curves downwards after being approximately linear below that energy down to around 200 keV. Kis et al. (1998) compared a number of functions with a straightforward polynomial of log (\(E_r\)) against log (\(E_g\)) as implemented in the Hypermet-PC program. They found all functions, other than the Hypermet-PC’s 9th-order polynomial, to be wanting. In many cases, the alternative functions became unstable as the number of terms increased. This polynomial provided an acceptable fit up to 10 MeV.

9.10 MULTIPLET PEAK RESOLUTION

**BY DECONVOLUTION**

Deconvolution is the term given to the process of extracting peak area information from a composite (multiplet) peak. The results of deconvolution should be treated with caution. Most other spectrum analysis calculations can be checked manually. That is not the case with deconvolution and the analyst is in the hands of the computer programmer.

In principle, each peak within a multiplet is described by three terms:

- its area, which, of course, we wish to determine;
- its position;
- its shape.

If we know any two of these factors the third can be easily estimated – give or take a little matrix arithmetic. (Some programs work with the height of a peak rather than its area. The two are linked, of course, but since height depends upon both area and width, using the area alone would seem to be more appropriate.) The shape of the peak we know (Section 9.6). The program may simplify matters by using a Gaussian approximation utilizing the peak width calibration to estimate the standard deviation.

The position can be determined either from information derived from the peak location or by taking account of library data which indicate which peaks to expect within the particular multiplet. Both have their advantages and disadvantages. Obviously, unless a gamma-ray is in a library then it will not be taken account of and so a simple library directed approach cannot cope with the unexpected. On the other hand, small peaks within a multiplet and very close multiples may not be resolved by the peak search and incorrect peak areas may again result.

Having reasonable estimates of the shape and position, we can say that for each channel over the region of the spectrum covered by the multiplet that the count, \(C_i\), in each channel \(i\) can be represented by:

\[
C_i = \sum a_j A_j g(i, s_j) + R_i \quad (9.8)
\]

where the summation is taken over the \(j\) components of the multiplet, \(a_j\) is the fitting factor (i.e. the proportion of the nuclide in the multiplet. This, in due course, would give us our nuclide activity), \(A_j\) is the peak area of the \(j\)th component and \(g(i, s_j)\) the mathematical function describing the peak, with \(s_j\) being the peak standard deviation. \(R_i\) represents an unknown adjustment to the channel count due to statistical factors. Equation (9.8) represents a set of simultaneous equations which can be solved by simple matrix operations in such a way that the sum of the squares of the differences between each actual channel count and an estimate of the channel count from the fit is a minimum. (Which is why it is referred to as a least-squares fit. For a simple implementation, see Gilmore, 1979.)
As it stands, the fit would take equal account of every channel within the composite peak. Clearly, from what we know of counting statistics, channels with fewer counts have a greater uncertainty and should not be allowed an equal say in the fitting process. To take this into account, the equations generated by Equation (9.8) are weighted by the inverse of the variance of the corresponding channel count, \( C_i \). Each weighting factor, \( w_i \), is:

\[
w_i = \frac{1}{\text{var}(C_i)} = \frac{1}{C_i} \tag{9.9}
\]

Non-linear fits treat the data in the same sort of way but do not assume that the position and peak width are constant but deduce them together with the peak area (or height) in an iterative process.

If a library directed fit is chosen, it is essential that the library is tailored specifically to the job in hand. Libraries for this purpose should not contain ‘just-in-case’ entries. While the least squares fitting program would normally be written so as to reject any non-significant or negative components, there is often sufficient slack within the statistical scatter to fit another component. If your library tells the software to expect four components when there are really only three, you should not be surprised to find results for four components as the rule rather than the exception. This tendency to self-fulfilling prophecy is exacerbated when statistical scatter is large or when small uncorrected peak shifts are encountered.

While there is good reason to use the library directed approach, unless it is known in advance which interfering gamma-rays will be present, the open peak fitting approach must be used. Whichever approach is used, the results of deconvolution should be treated with caution. Published reports by the software vendors (see Reading List) on the analysis of artificially generated doublet peaks demonstrate that, unless the peak separation is greater than 1 FWHM, substantial errors in the deconvoluted peak areas are likely. This is especially so when the peak area ratio is high. Small peaks may be consistently under-represented in the peak fit. (Although it may be claimed that the error is within the statistical uncertainty of the individual peak area estimations, there would still be a bias on the final results. Whether this is significant or not depends upon the context of the analysis.) The moral is clear – view with some suspicion the results reported for the minor components of multiplets especially if the separation from their neighbours is less than 1 FWHM or so.

Blaauw et al. (1999), using the 1994 IAEA reference spectra, compared the performance of three programs that used different methods of peak area determination. The program Apollo measures peak areas by a simple peak-integration method, Hypermet-PC uses iterative fitting to derive peak areas and GammaVision uses a library-directed approach. The authors commented on the sensitivity of GammaVision with respect to the quality of the data in the nuclide library. The Apollo program was reported to provide the best results for doublets, but at the expense of manual intervention. Hypermet-PC came into its own when good library data was not available and when the highest deconvolution power was needed.

### 9.11 PEAK STRIPPING AS A MEANS OF AVOIDING DECONVOLUTION

Bearing in mind the uncertainties in deconvolution and the difficulty of checking the performance, it is worth considering whether it can be avoided altogether. In fact, for many routine measurements gamma-ray peaks can be selected that will never be interfered with by other gamma-rays under normal conditions. It is worth looking carefully at one’s analysis libraries with a view to removing peaks which would need deconvolution. It may be better to use a gamma-ray with a lower emission probability which is unhindered than one of higher emission probability which is. What you lose in terms of counts, you may gain in precision and accuracy of measurement by not having to deconvolute.

If one component of a doublet must be measured it is worth considering whether a simple peak strip could be used. The procedure is demonstrated in Figure 9.11. The peak to be measured is labelled A and the interfering peak B. Nuclide B is known to have one or more

---

**Figure 9.11** Doublet peak resolution by peak stripping
other gamma-rays which can be measured (e.g. B₂ in the figure). If a source of pure nuclide B is measured, then analysis of its spectrum will allow a peak area ratio, B₁/B₂, to be calculated. (Note that this measurement must be under identical conditions of geometry to the sample measurement or otherwise differences in true coincidence summing might alter the peak ratio.) It is, of course, possible to calculate the peak ratio by using gamma-emission probabilities and the detector efficiencies for the two gamma-rays. (Which is how the peak stripping operation within *GammaVision* works?) However, that ratio will be in error if true coincidence summing is involved.

In subsequent sample analyses, the area of peak B₂ can be multiplied by this empirical correction factor and subtracted from the total peak area of the doublet A + B₁. While this all seems very straightforward, it is not always as useful as expected. An oft-quoted example of the use of peak stripping is the resolution of the 186 keV peak in the spectra of naturally occurring radionuclides. This is a composite of the 185.72 keV peak from ²³⁵U and the 186.21 keV from ²²⁶Ra. ²³⁵U also emits a 143.76 keV gamma-ray and, in principle, this can be used to calculate the proportion of the 186 keV peak due to ²³⁵U. However, the 143.76 keV gamma-ray has a much smaller emission probability than the 185.72 (see Chapter 16, Table 16.1) and there will be a much greater uncertainty on its measurement, which will have a large effect on the uncertainty of the estimation of ²²⁶Ra. The method is of limited use unless the correction peak (143.76 keV, in this case) can be measured with good statistics.

Although the procedure is simple and direct it will not necessarily be available within a commercial spectrum-analysis program. Programs which do are *GammaVision* and the comparative analysis program *CompAct*. In the absence of facilities within the spectrum analysis program, a simple spreadsheet could be used to perform an off-line peak strip on the output from the analysis program.

We should perhaps make clear that peak strip is not the same as the spectrum strip option often provided on old MCA systems. That would subtract one spectrum, or a proportion of it, from another on a channel-by-channel basis. Spectrum stripping permanently alters the spectrum data and is not recommended. One particular problem with it is that the statistical scatter of the stripped spectrum is not representative of the actual data.

### 9.12 THE ANALYSIS OF THE SAMPLE SPECTRUM

Having constructed energy, peak width and efficiency calibration curves, the way is clear to performing a full spectrum analysis to detect and determine the nuclides represented in the spectrum. The overall procedure for a full spectrum analysis might follow the flow chart shown in Figure 9.12, with a continuation of this figure presented in Figure 9.13. Not every part of this will be followed by any one program and not every part of it would be necessary for all situations. During calibration, peak detection and measurement is straightforward because (ideally) only singlet well-defined peaks are involved. In handling sample spectra, the algorithms are tested to their limits. They must be able to cope with poorly defined peaks which may be subject to interference from other peaks.

There are two general ways in which we may approach sample spectrum analysis:

- Select a limited number of gamma-rays for each nuclide of interest and search the spectrum only for these peaks. This would be done via a nuclide library that might also contain information to allow deconvolution...
if necessary. This approach has the advantage of speed and simplicity but would not alert one to the presence of unexpected nuclides. It would be more usual to combine this with a general spectrum search which would provide additional information from which the presence of other nuclides could be inferred.

- Perform a general spectrum search and then assign every peak (as far as possible) to nuclides using data held in a general library. As we will see, nuclide identification can be a complicated matter and in many cases an overall search and identification such as this would seem to be ‘over the top’.

9.12.2 Corrections to the peak area for peaked background
If a peak overlies a peak in natural background (for example, the measurement of $^{137}\text{Cs}$ or $^{60}\text{Co}$ at low levels) a peaked background correction (see Chapter 5, Section 5.4.2) would be necessary and may as well be done at this stage. The uncertainty on the peak area should also be adjusted to take into account uncertainty of the background correction. At the present time, not all spectrum analysis programs incorporate peaked background correction, and even those that do may not make proper allowance for the uncertainty on the correction. For many analysts that would seldom be a problem. For near background counting and measurements on naturally occurring nuclides, it is essential if false positive peak identifications are to be avoided.

9.12.3 Upper limits and minimum detectable activity
In principle, the net peak area should be assessed for significance using a critical limit, as discussed in Chapter 5, Section 5.6.1. If the peak area exceeds the critical limit, the peak area can be legitimately passed on to the activity calculation. If not, the peak should be declared ‘NOT DETECTED' and an upper limit to the peak area calculated (Chapter 5, Section 5.6.2). That upper limit should then be passed through the calculation as any other peak area and reported as an activity upper limit – that activity which we are 95 % certain exceeds the actual activity.

In practice, all of the analysis programs carry through the net peak area without any significance test, together with a possibly outrageously large uncertainty. This is then tested later and may then be used to calculate the MDA. (Genie 2000 does allow a critical limit test to be applied. Unfortunately, if a peak fails the test it is then completely ignored! This seems somewhat drastic. It is possible for the peak search to detect a genuine peak whose area turns out to be insignificant. In that case, what is needed is an upper limit.) In Chapter 5, Section 5.6.7, I explained that MDA is not the Minimum Activity Detectable and should not be quoted in place of the activity upper limit.

One aspect of computer calculation of MDA is worthy of comment. Let us assume that a peak area is measured by the normal peak integration method (Chapter 5, Section 5.4), the peak background being estimated using a few channels beyond the peak limits on either side of the peak. It is a feature of some programs that if the net peak area fails the critical limit (or similar) test, the upper limit (or MDA) is then estimated from the channel counts within the peak region, using them as an estimate of the...
background. This is clearly perverse. Figure 5.11 demonstrated that if there were counts in the peak region equivalent to the MDA, a peak would be visible and detectable (95% of the time). In that case, we would have to use channel contents on either side of the peak to estimate the peak area. If we cannot use the channels within the peak region when we measure the peak background, how do we justify using them to estimate the MDA? MDA should be estimated from the uncertainty on the background as measured.

As I indicated in Chapter 5 and suggest above, there is a great deal of confusion over statistical decision levels and users of commercial programs should be aware of this. Bowing to this confusion, GammaVision provides twelve choices for MDA calculation so as to satisfy as many users as possible. Unfortunately, the equations I advocate in Chapter 5, Section 5.6 are not included in these choices. (The GammaVision MDA option ‘Nureg 4.16 Method’ may be acceptable. The manual quotes a valid equation for this option, but it unclear how the uncertainty on the background is calculated.)

9.12.4 Comparative activity estimations

It is unfortunate that spectrum analysis programs do not recognize that not every spectrometrists will want to analyze his or her spectra in the same way. All of the more sophisticated spectrum analysis programs assume that the analysis will be made by reference to an efficiency curve. Only one of the programs I have referred to, CompAct, makes specific provision for direct comparative analysis (as opposed to an analysis where both standards and samples are measured relative to an efficiency curve and the results compared afterwards to deduce the correct activity or concentration).

In particular, the neutron activation analyst, to whom efficiency curves may be an irrelevance, is not well served by most spectrum analysis packages. As far as activation analysis is concerned, there is much evidence to show that absolute analysis, calculating concentrations from first principles, is much less accurate than comparative analysis. Apart from all of the problems which derive from having to use efficiency calibration curves, there are specific problems associated with defining and measuring neutron fluxes and cross-sections which make absolute analysis not worthwhile, in my opinion (although there are those who have devoted a considerable amount of effort into developing absolute neutron activation analysis procedures who would dispute that). For that reason, almost every activation analysis involves irradiation of samples and standards. A direct comparison between them is the simplest solution.

In Chapter 7, where the problems caused by true coincidence summing in close geometry measurements were discussed, we saw how TCS can make nonsense of an efficiency curve and strongly recommended comparative analysis, particularly for environmental measurements.

In a comparative analysis, the sample peak count rates would simply be compared with those of a standard:

$$C_{\text{sample}} = R_{\text{sample}} \times C_{\text{standard}} / R_{\text{standard}}$$

where the $C$s may represent activity or concentration and the $R$s the appropriate peak count rates, ignoring for the time being decay and other corrections to be discussed below. The uncertainty of the final result would need to take into account the uncertainties of the individual items in Equation (9.10).

GammaVision provides a limited means for performing a comparative analysis in that there is an option to provide an ‘interpolative’ efficiency curve. If the efficiency calibration data is provided for each gamma-ray of each nuclide to be measured, then each request for an efficiency value would return the actual calibration data derived from the standard spectrum. If true coincidence summing were a problem, then as long as the standard spectra were of the same nuclides measured under the same conditions as the sample spectra, the summing errors would cancel out. The procedure is not elegant, but as far as I can see, should work satisfactorily.

9.12.5 Activity estimations using efficiency curves

Apart from CompAct, all of the programs referred to use the inverse of Equation (6.13) to convert peak count rate, $R$, to source strength, $S$, i.e. sample activity, calculating the efficiency, $e$, from the calibrated efficiency function. Ideally, the program would also fold into the uncertainty of the peak area measurement the additional uncertainties due to interpolation of the calibration curve.

$$S = R / (e \times P_a)$$

9.12.6 Corrections independent of the spectrometer

The activity estimate at this point may need correction for a number of counting losses which were covered in Chapter 6. Only the following are routinely catered for in spectrum analysis programs (numbers in parenthesis refer to the equation used to make the correction):

- decay from (or to) a reference time (6.29);
- decay during counting (6.30);
9.13 NUCLIDE IDENTIFICATION

Nuclide identification is included in several of the common analysis programs in one way or another. There are various approaches ranging from the naive look-up approach to very sophisticated programs which fit gamma-rays to the pattern expected from the known gamma-ray emission probabilities. Whichever is used, identifications should be treated with caution, especially when an unexpected nuclide is reported. My advice would be that in such a situation the spectra and results should be examined critically by an experienced spectrometrist.

9.13.1 Simple use of look-up tables

The simplest possible approach is, having found a peak, to compare the energy with a simple look-up table of energies with corresponding nuclide names. For example, both the MCA emulator Maestro-32 and GammaVision indicate on the computer screen a suggested nuclide by reporting the nearest library entry to the measured position. This is a very crude procedure and will often draw attention to library entries which are nowhere near the current peak. If there are two close entries, only the nearest will be given. For example, a peak at 122 keV might be reported as $^{152}$Eu (121.78 keV) or $^{57}$Co (122 keV) depending upon the energy calibration. A more useful approach would be to report all table entries within a specified energy tolerance of, say, 0.5 keV, with nothing at all reported if library entries are further away than that.

9.13.2 Taking into account other peaks

The simple look-up procedure cannot necessarily provide a definite identification and for that, some account must be taken of the presence or absence of other peaks in the spectrum and at least some account of their emission probabilities. For example, Genie 2000 subjects all preliminary nuclide identifications to three tests, each of which reduces a factor which indicates the degree of confidence in the nuclide assignment. These are based upon closeness of the energies of the peaks to the library energies, the proportion of the expected gamma-rays actually detected and a half-life criterion (nuclides with large decay factors are given less weight). Nuclides which still have a confidence factor greater than a user selected threshold are then declared as detected.

9.14 THE FINAL REPORT

The final report, a list of nuclide activities, optionally with individual peak areas, is the object of all of the preceding
analysis. It is very unlikely that the output format provided by the software vendor will satisfy exactly every user’s needs. The output might be too verbose, or not verbose enough, or not provide what the user regards as vital information. Fortunately, most general spectrum analysis packages provide the means to customize the output format to solve that particular problem.

For each nuclide, there may be several gamma-ray peaks measured, each with a different uncertainty depending upon its size and whether or not it has had to be deconvoluted or stripped. These must be combined in some way to produce a single result for each nuclide. It is worth consulting the software manual to establish how the final nuclide activity is calculated and just what is included in the quoted uncertainties.

All programs purport to provide a weighted mean of all of the peaks associated with a particular nuclide. However, not all do this in the same manner. The obvious way is to weight each individual result by the inverse of its variance. This is statistically sound and is often used. An exception to this is GammaVision where the individual calculated activities are completely ignored and a final result calculated as the sum of the individual peak counts for each gamma-ray of the nuclide divided by the sum of the emission probabilities. This does not provide a weighted mean. In fact, it gives equal weight to all of the counts whether they are derived from a poorly defined peak or a well-defined peak.

In situations where one or more peaks of a nuclide have an unresolved interference, there is a problem. If included in a normal weighted mean, they will affect the overall result for that nuclide adversely. It is common practice to quote a final uncertainty based only on the internal (or pooled) variance of the values (see Chapter 5, Section 5.3.2). It would be useful if programs also calculated the weighted (or external) variance and indicated when it exceeded the internal variance to alert the analyst to the fact that some other source of uncertainty was present.

More complicated is the situation where several nuclides have mutually interfering peaks. Genie 2000 and Sampo 90 use what the manual refers to as a ‘Common Algorithm Nuclide Identification’. That identifies unresolved mutual interferences by a process of least squares minimization of a set of simultaneous equations, one for each nuclide, involving all of the peaks measured. The process is a more general treatment of the peak stripping explained in Section 9.11.

There are programs which use the concept of a ‘key peak’. This might be the first entry for each nuclide in the nuclide library or be indicated by a flag within the library. A judgement may be made by the program on whether to include individual results in the calculation of the mean on the basis of their agreement with the key peak. A result not statistically consistent with the key peak value is rejected. Obviously, the selection of the key peak is critical. It must be able to be measured accurately and, hopefully, precisely, under all circumstances. (I have personal experience of a situation where inappropriate selection of the key peak could lead to mis-identification. The summing of the 554.3 keV and 618.7 keV gamma-rays of $^{82}$Br produces a peak certain to be confused with the 1173.2 keV peak of $^{60}$Co. In this case, the 1332.5 keV would be the better key peak.) When nuclides subject to coincidence summing are measured using GammaVision, it is quite common for all but the key peak to be rejected because they give significantly different activities – another factor to consider when choosing the key peak. In such circumstances, it is possible that it is the key peak that is most in error, rather than the less-intense peaks.

9.15 SETTING UP NUCLIDE AND GAMMA-RAY LIBRARIES

Throughout this chapter, nuclide and gamma-ray libraries have been mentioned in various contexts and it is evident that for a complete spectrum analysis several libraries may be needed – perhaps calibration libraries, nuclide-identification libraries, peak interference libraries and the like. It is worth reiterating the point made above that libraries should be tailored to their purpose. Putting in peaks ‘just-in-case’ is likely to cause trouble.

Libraries that include gamma-ray abundances and half-lives should contain the best available data. Again, Appendix B contains a highly recommended set of evaluated data for many common nuclides. Do not use the data in libraries provided by the software vendors without checking. They may be old and inaccurate. One could be more relaxed about the accuracy of gamma-ray energy data because of the tolerance within the peak-identification procedures but there seems little point when accurate information, at least for all common nuclides, is available. However, as reported by Blaaauw et al. (1999), accurate deconvolution does demand accurate gamma-ray energies.

All of the data within a nuclide library – energies, emission probabilities and half-lives – have an uncertainty and, ideally, it should be possible to incorporate all of those uncertainties into the library. This is not always the case and it may then be necessary to account for nuclear-data uncertainties by increasing the uncertainty on the final result by an appropriate amount.
9.16 BUYING SPECTRUM ANALYSIS SOFTWARE

It is not my intention here to suggest a ‘best buy’. Most programs readily available at the present time provide much the same sort of facilities and performance. Software is complex and not only must the algorithms and facilities within the software be considered but also the user interface. There is little point in having perfect algorithms within a program which is grossly inconvenient to use and cannot be tailored to one’s needs. A few general points are worth bearing in mind when shopping around:

- Try to arrange a ‘hands-on’ demonstration of the software, preferably with your own spectra and a real analysis to perform. That will immediately show how easy or otherwise a program is to use.
- Try to persuade the vendor to analyse standard spectra (see Chapter 15) using the program, preferably while you observe. The vendors will not thank you for this, but their response to your request will be instructive.
- If you need to run automatic count/analyse sequences, find out how easy it is to set these up. (These are often referred to as batch jobs because they run under the computer batch file system.) Some MCA emulator sequences are particularly inconvenient to set up. **Maestro 32** must have a text list of instructions specially compiled to a Maestro 32 readable form. **GammaVision** will allow you to control a number of detectors at the same time, but will only allow you one automatic sequence.
- Find out how easy it is to set up the necessary nuclide libraries. Libraries which are stored in text, rather than coded, form provide much more flexibility from the point of view of editing. On the other hand, plain text files are much more easily tampered with and, from a security point of view, a system with coded libraries might be deemed more appropriate.
- Don’t get carried away by the multiplicity of fringe benefits. As with word processors and spreadsheets, most users use only a small proportion of the facilities available. Just make sure that the program does its core business well.
- Try to borrow a copy of the software manual so that you can study the algorithms. If you can’t understand the manual, will you be able to understand the program?
- If you are buying a program to run on your existing computer, is it compatible in terms of both hardware and operating system?
- If you are not buying software from the manufacturer of your hardware, can the software handle your spectrum files easily?

9.17 THE SPECTRUM ANALYSIS PROGRAMS REFERRED TO IN THE TEXT

The MCA emulator and spectrum analysis programs referred to in this chapter were as follows:

- From **ORTEC** ([http://www.ortec-online.com/software/software-available.htm](http://www.ortec-online.com/software/software-available.htm))
  **Maestro-32**
  MCA emulator used in conjunction with ORTEC multichannel buffer modules.
  **GammaVision**
  Combined MCA emulator and full spectrum analysis used in conjunction with ORTEC multichannel buffer modules. Runs under Microsoft Windows. Comments in this book refer to version 6.01.
  **ScintiVision**
  Spectrum analysis system tailored to scintillation spectrometry (not referred to in the text).
- From **Canberra** ([http://www.canberra.com/products/831.asp](http://www.canberra.com/products/831.asp))
  **System 100**
  MCA emulator system interfaced to Canberra ADCs. Runs under Microsoft Windows (no longer available).
  **Genie 2000** (and other variants)
  MCA emulator and full spectrum analysis interfaces to the Canberra ADCs. Full multi-tasking facilities. Comments in this book refer to version 2.0.
  **SAMPO 90**
  Full off-line spectrum analysis facilities. Runs under Microsoft Windows.
- **Hypermet-PC**
- From **JF Computing**
  **FitzPeaks**
  Off-line spectrum analysis package ([http://www.jimfitz.co.uk/](http://www.jimfitz.co.uk/)).
- From **Nuclear Training Services Ltd**
  **CompAct**
  Off-line program for activity estimation. Intended for neutron activation analysis and general comparative analysis. Efficiency curves are not used ([http://www.gammaspectrometry.co.uk/compact](http://www.gammaspectrometry.co.uk/compact)).

PRACTICAL POINTS

- It is advisable to understand the way in which the spectrum analysis program handles the data.
• Whenever you must select options within the software, you should make an informed choice. Don’t accept the default uncritically.

• When buying software, find out as much about it beforehand as possible. Ask for test spectra to be analysed. Ask for a hands-on demonstration – yours, not theirs!

• Whenever a new analysis situation is encountered, the analysis options should be re-appraised. Don’t accept unexpected computer results uncritically.

• When, in a routine analysis, unexpected nuclides are identified or odd results obtained, the analysis should be assessed by someone who understands the spectrum-analysis program in depth.

FURTHER READING
• General:
The manufacturers’ software manuals (essential).
The above should be read in conjunction with the following letter: Seymour, R. (1991). Radioact. Radiochem., 2, 4–5.

• Deconvolution performance:

• Efficiency curves:

• Peak search algorithms:

• For program intercomparisons and other performance reports: Further Reading for Chapter 15.