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The analysis of environmental materials using gamma spectrometry

G. A. Sutton

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The author: G. A. Sutton MSc MSRP is a Senior Scientific Officer based in Aquatic Environmental Protection Division, Section 1 at Lowestoft.

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FOREWORD

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Technical report FRL 4 entitled *Gamma Spectrometric Analysis of Environmental Materials* (Dutton, 1969), described the analytical method used within the Directorate of Fisheries Research (DFR) to measure gamma radioactivity in aquatic environmental materials. The report gave explicit details of sample preparation, calibration and the methods used in the calculation of results. The technique described was used successfully for many years but was later superseded following the introduction of lithium-drifted germanium detectors (GeLi). These new 'solid state' detectors had the advantage of superior photon peak resolution and enhanced peak to Compton ratios but unfortunately suffered from poor efficiency, relative to the NaI(T1) counterparts, which rather overshadowed their other properties. In the late 1980s, Ge(Li) detectors were superseded by hyperpure germanium detectors (HPGe), these had vastly superior efficiencies very close to those of NaI(T1) detectors and were considerably better instruments.

The Directorate has almost completed the programme of replacing the older GeLi detectors with HPGes and a recognised system of analysis is in place. This report is intended as an up-to-date replacement for FRL 4 and describes the analytical system in use today. Detailed instructions of the whole process is described in such a way that the report may be used as a definitive guide to gamma spectrometry. It is intended that this report will be submitted to the National Measurement Accreditation Service (NAMAS) accreditation body as the Standard Operating Procedure for gamma spectrometry within the Directorate.

P. W. Greig-Smith
Deputy Director
(Aquatic Environment Protection)
Ministry of Agriculture, Fisheries and Food
Directorate of Fisheries Research

1. INTRODUCTION

An earlier technical note entitled *Gamma Spectrometric Analysis of Environmental Materials* (Dutton, 1969) discussed the method of gamma analysis employed within the Directorate in the late 1960s. It described in detail how Sodium Iodide NaI(Tl) detectors were used to monitor the marine environment. It can be seen from that note that NaI detectors, although high in efficiency, have very poor photon peak resolution resulting in limitations in peak identification and the subsequent activity measurements. Over the past ten years these problems have been eliminated by the production of lithium-drifted germanium detectors and, later, hyperpure germanium detectors. During this period the Directorate has maintained a policy of modernising and upgrading old equipment in order to improve analytical quality. We are now equipped with a suite of modern instruments capable of achieving limits of detection of less than 1 Bq kg^{-1} wet material.

The objectives of this paper are :

(1)   to provide a reference method describing in detail the current method of gamma spectrometric analysis within the Directorate;

(2)   to provide the necessary documentation to satisfy part of the requirements for NAMAS accreditation.

Throughout this technical note reference is made to certain manufacturers' equipment, software packages and trade names. It should not be construed that this constitutes a recommendation. The equipment currently in use within the Directorate was manufactured by Canberra, Nuclear Data. All software was originally designed by Canberra, Nuclear Data but has been substantially modified by Directorate staff to suit local requirements.
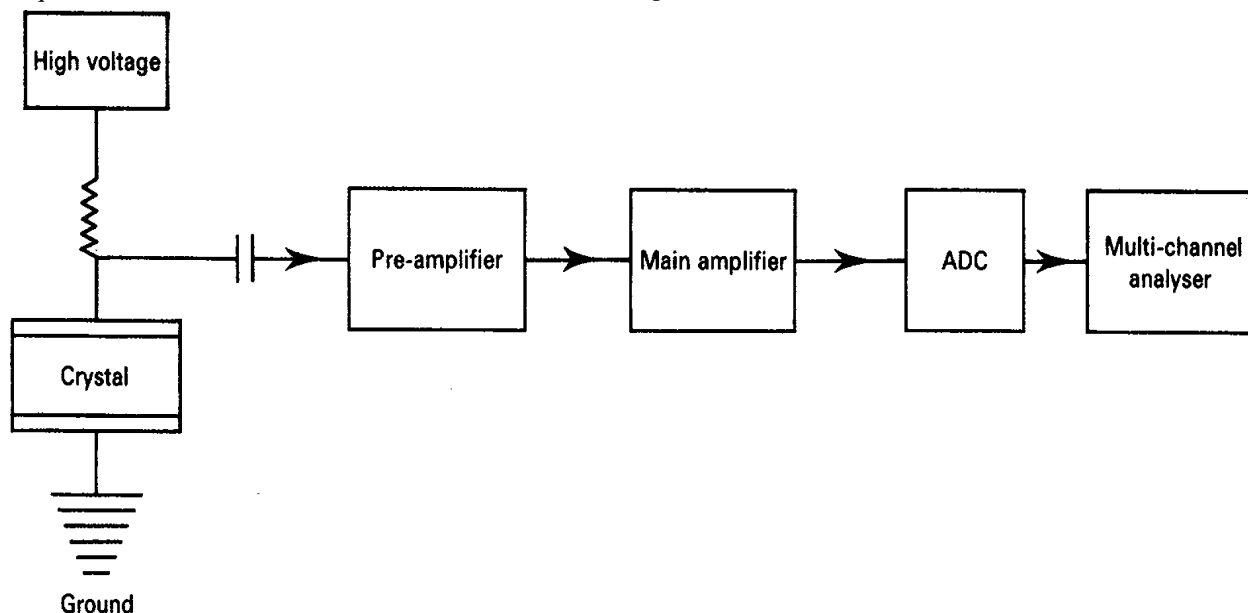
2. EQUIPMENT

2.1 Gamma spectrometry systems

Major developments have been made in the design of spectrometric systems over the past ten years. Computers now play an essential role in the collection, storage and reduction of data. Once a program has been initiated, a modern automated system will load a sample, allocate a counting time, perform the analysis and calculate the results. Despite this high degree of automation the personal skills of the analyst are still crucial to the interpretation of the final result. Many software packages have been written to improve the quality of the analysis and reduce the possibilities of operator error, these programs are under constant review and have proved invaluable.

Figure 1 shows a schematic diagram of a typical gamma spectrometer system. The detector is encased in a thin cylindrical metal container and is connected to a high voltage and a bias supply unit. Signals from the detector are fed via a linear amplifier and pulse shaping electronics to a multi-channel analyser, or more often nowadays, a micro-processor with display screen, printer and data storage facilities.

2.2 Detectors

Detectors have undergone similar radical changes. For many years sodium iodide detectors which operate at room temperature were in common use; although they have the advantage of high efficiency they suffer from very poor resolution and temperature control, problems which adversely affected spectral quality. Many of these problems have been overcome with the advent of semiconductor detectors, initially lithium-drifted germanium detectors (GeLi), and today, hyperpure intrinsic germanium detectors (HPGe), with very little loss in relative efficiency over their NaI(Tl) counterparts.

Figure 1. Schematic diagram of a typical gamma spectrometer

HPGe detectors operate at liquid nitrogen temperature (-196°C). This reduction in operating temperature reduces the thermal motion of the electrons in the detector such that the width of the resultant photo peak is reduced from over 100 keV to about 2 keV. This high resolution has simplified the analysis of complex gamma spectra and made the technique of gamma spectrometry a more powerful tool in the environmentalist's armoury.

The method discussed in this note describes only the use of intrinsic germanium detectors covering the approximate energy range 30 keV to 2 MeV.

2.3   Detector configurations

Germanium semiconductor detectors are produced in many different shapes and sizes. Detector sizes, and indirectly their shapes, are determined, first by the maximum size of the available blocks or ingots of pure germanium material, and second by the depth to which an intrinsic region can be formed in the manufacturing process. Therefore different shapes became available as different semiconductor material and manufacturing techniques were developed.

Figure 2 shows some of the different configurations available. One of the most commonly preferred configurations is the closed-end coaxial (Figure 2(a)). This provides a large sensitive surface area and spans a wide range of energies from about 30 keV to 2 MeV or even wider if required, furthermore, the relative efficiency of the closed-end coaxial ranges from a few percent to over 100, thus making this configuration a very popular choice. The ultimate choice of configuration depends on the analytical requirement. Planar detectors (Figure 2(f)) are used for very low gamma photon energy measurements (less than 100 keV) whereas a well configuration (Figure 2(e)) is used for small sample volumes, up to about 20 ml. It can almost be said that there is a semiconductor detector available for any analytical problem.

2.4   Typical detector specification

A typical detector specification currently used within the Directorate would be as follows:

a)   Energy range   30 keV to 2 MeV
b)   Energy resolution   Approximately 1.0 keV at 122 keV and 2.0 keV at 1.33 MeV
c)   Relative efficiency*   30 to 95%
d)   Peak to Compton ratio >60:1 for the Co-60 peak at 1.33 MeV.

Relative to a NaI (Tl) crystal under standard conditions described in ANSI/IEEE, 1986.

(a)   **(b)**   **(c)**

Intrinsic Coax   Ge(Li) Coax   Ge(Li)
                                     True Coax

(d)   **(e)**   **(f)**

Intrinsic-N   Intrinsic or Ge(Li)   Intrinsic or Si(Li)
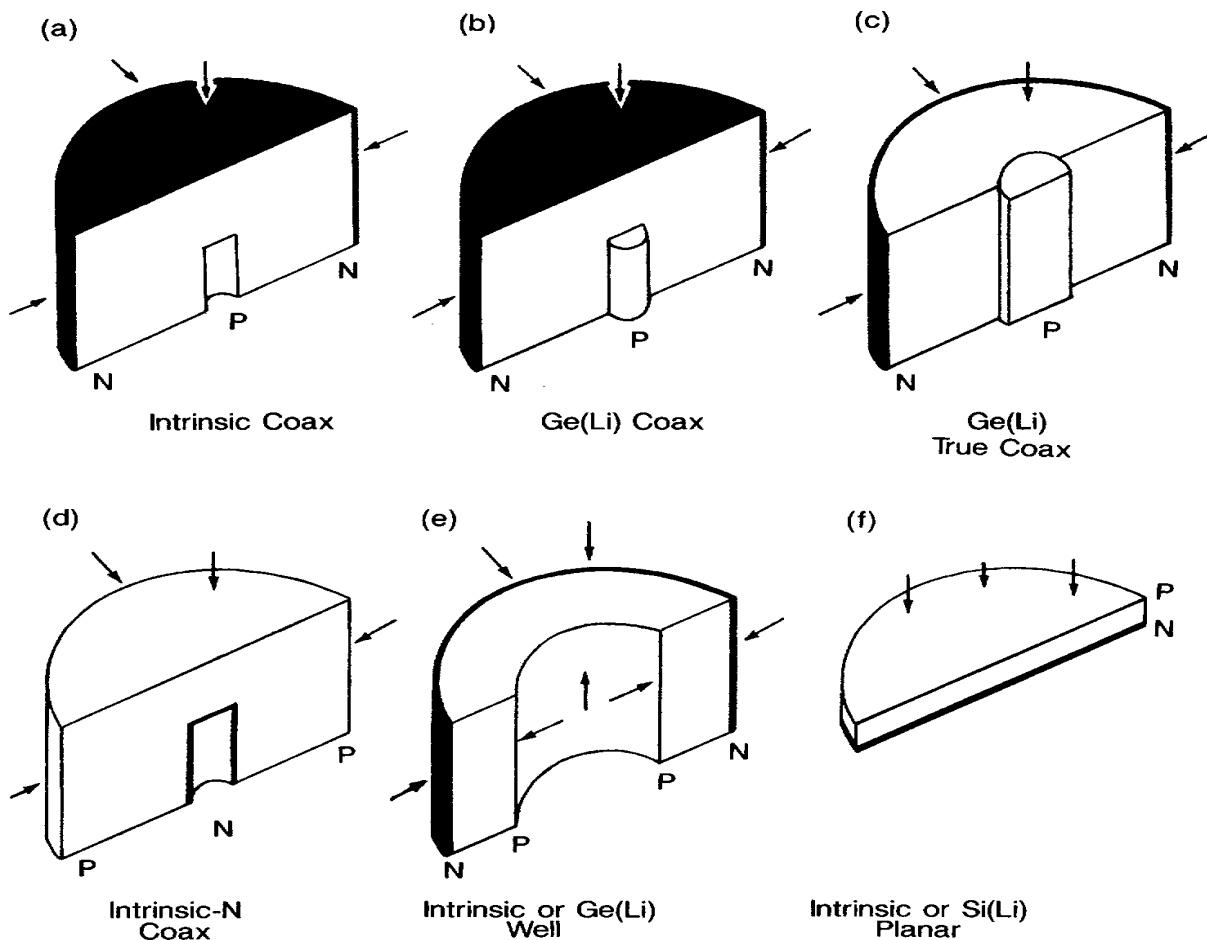Coax   Well   Planar

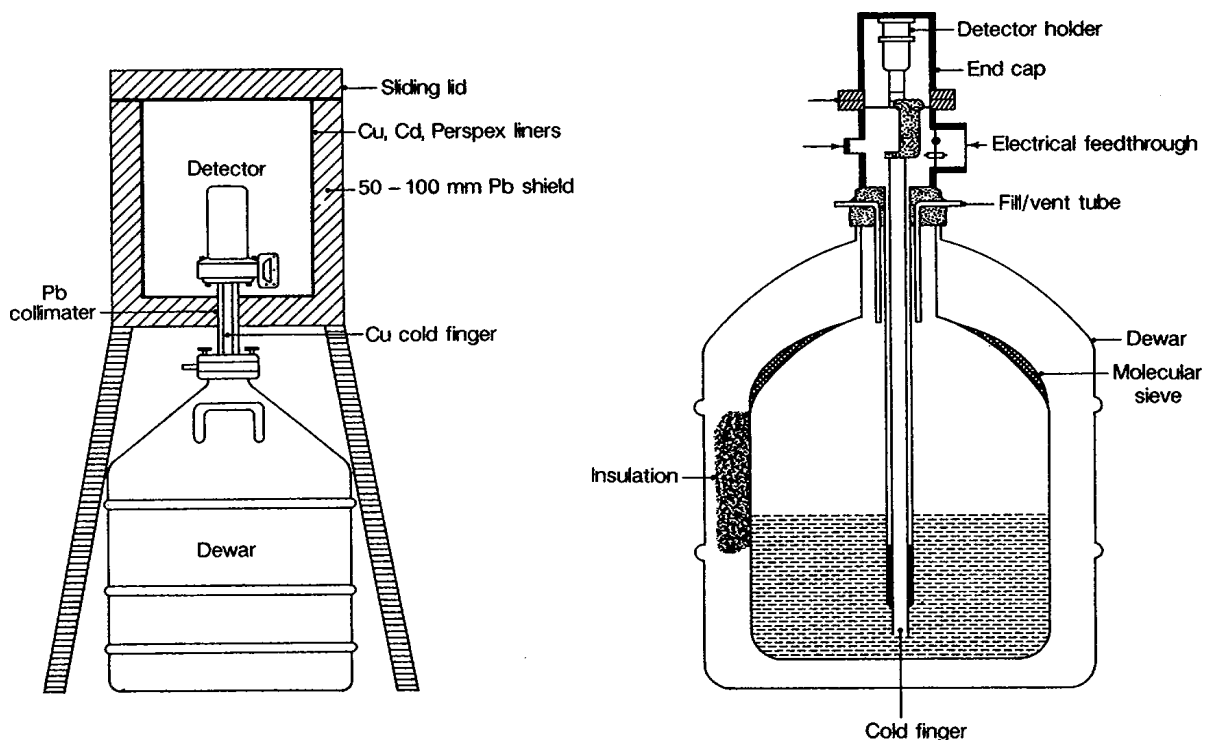*Figure 2. Configurations of germanium detectors*

Figure 3. Ge detector assembly showing cryostat and shielding

The high purity Ge detector is encased in a sealed metal cylinder held under vacuum which is maintained by a molecular sieve. The whole unit is held at liquid nitrogen temperature $(-196°C)$ whilst the high voltage is applied in order to allow a satisfactory signal to noise ratio to be achieved. The high vacuum conditions around the crystal are designed to exclude contaminants, and maintain the intrinsic purity of the detector. Figure 3 shows a typical detector cryostat assembly.

2.5 Shield assembly

Both the detector and the sample being counted need to be adequately shielded from background radiation. This is achieved by enclosing both in a 'castle' of heavy material (normally lead and not less than 5 cm thickness, but for low background systems often 10 cm). The shield is designed to reduce background contributions from both cosmic and terrestrial radiation. For such work old (pre-nuclear age) lead is preferable. If analysis below 100 keV is contemplated, steps must be taken to prevent fluorescence X-rays and Bremsstrahlung radiation produced by photon reaction with the lead, from reaching the detector. A graded shield built inside the castle is used for this purpose and comprises layers of cadmium, copper and perspex of optimised thickness with the cadmium layer next to the lead and the perspex nearest the detector.

2.6 Pre-amplifier

The detector can be thought of as a capacitor into which a charge is deposited. The primary purpose of the pre-amplifier is to collect and integrate this charge and, with the aid of an applied bias voltage, the pre-amplifier produces an output voltage pulse that is proportional to the input charge (and hence the energy of the photon).

The pre-amplifier is located as close to the detector as possible to minimise the effect of stray capacitance. This is one of the most critical components of the whole assembly, as both noise levels and energy resolution are affected by the characteristics of the pre-amplifier. This unit therefore determines to a large extent the quality of the entire measuring system.

Pre-amplifiers are usually factory-set and encapulsated; they cannot be adjusted by the user.

2.7 Main amplifier

For practical reasons the main amplifier and other associated electronics may need to be located some distance away from the pre-amplifier and detector, however, it is advisable to keep this distance as short as possible.

The function of the main amplifier is to shape and amplify the pulses arising from the pre-amplifier for optimum analogue to digital conversion. Whilst it is not recommended once set up, there are controls which will enable the operator to adjust the gain (amplification), pulse shaping (time constant), pulse tailing (pole zero) and pulse DC level (usually termed a DC restorer). To obtain optimum energy resolving performance from the system these latter two pulse shaping

controls must be adjusted correctly; these can readily be set with the aid of an oscilloscope. The pulse should be set as shown in Figure 4: the pole zero will affect the under- and overshoot of the pulse, and the DC level will affect the pulse baseline level.

The gain controls are set with the aid of a suitable calibration source so that the full energy range of interest is accommodated within the horizontal energy scale of the MCA. The gain controls should be set so that a suitable interval, compatible with the energy per channel chosen (frequently 0.5 MeV Ch^{-1}), exists between two well defined photo peaks. The absolute position of the peaks along the MCA axis can be adjusted by the zero control on the analogue to digital converter (ADC).

The amplifier should provide a 'dead time' signal for timing purposes. Dead time occurs in an amplifier when it cannot accept further pulses whilst it is analysing a previous one. The time taken to do this depends upon the height or amplitude of the pulse. An electronically imposed dead time is applied to enable correction to be made. Any pulse which arrives during this processing period will be lost because the analyser is effectively 'dead'.

The period of time during which an amplifier is capable of responding to pulses is known as the 'live time'. it should be clearly noted that live time differs from 'real' or clock time according to the following relationship:

Live time + Dead time = Real time.

2.8   Analogue to digital converter

An analogue to digital converter (ADC) is required to convert the analogue output signal from the main amplifier into a digitised form suitable for routing into a spectral analyser. There are several controls on this unit which may be adjusted by the analyst in order to set spectral peaks in the required position, (covered under section 4).

2.9   Multi-channel analyser

The MCA performs the essential functions of collecting the spectral data and timing signals, providing a visual monitor and producing an output either of raw data for subsequent analysis, or a calculated result.

As mentioned previously an alternative to the hard-wired MCA, is the MCB or multi-channel buffer. This type of unit, when used in conjunction with a relatively cheap personal computer (PC), can emulate quite sophisticated MCAs.
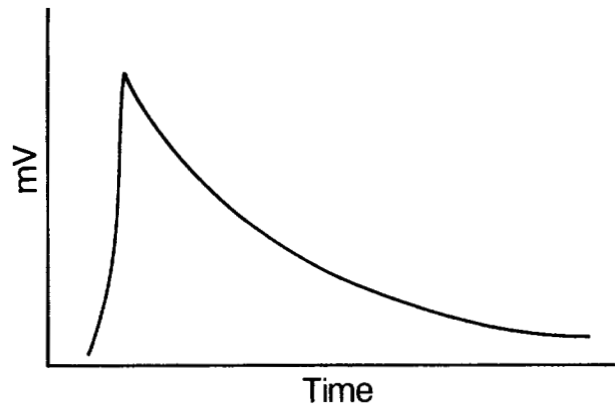
Figure 4. Pulse characteristics in a gamma spectrometer (oscilloscope displays)

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2.10   Data processing

The computer and software should ideally be capable of carrying out the following tasks:
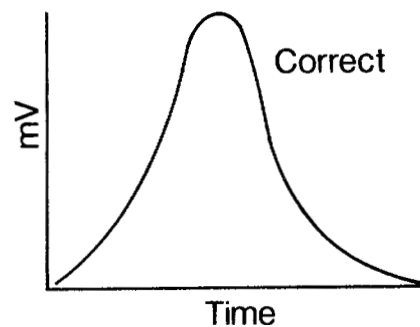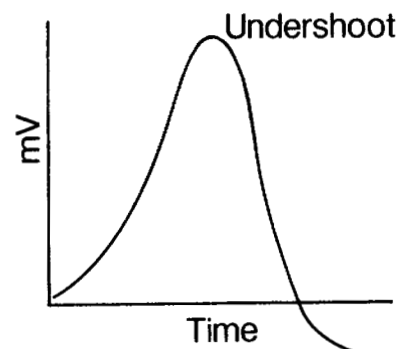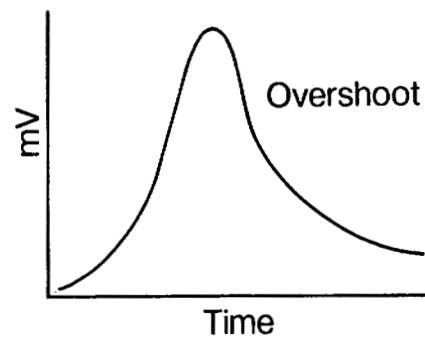
(i)   read data from the MCA or MCB;

(ii)   reproduce data on a screen, plotter or printer and store them;

(iii)   determine the relationship between channel number and energy over the entire energy range by using data obtained from appropriate reference sources;

(iv)   determine the energy-dependent counting efficiency over the entire energy range to be studied by making use of an appropriate reference source;

(v)   store 'background' data to enable correction procedures to be applied;

(vi)   detect peaks, determine the characteristics of the detected peaks such as the centroid, the FWHM, the number of net counts under the peak and determine the uncertainty associated with this number;

(vii)   recognise interfering peaks and apply appropriate separation procedures, de-convolute if applicable;

(viii)   identify the radionuclides responsible for the observed photo peaks by making use of radionuclide libraries;

(ix)   allow the user to form a library of radionuclides;

(x)   inform the user about the presence of unidentified radionuclides;

(xi)   calculate the activity and the activity concentrations of the respective radionuclides based on the number of counts, the count live-time, the counting efficiency, the data in the radionuclide libraries and the sample weight, mass or volume in the chosen units; and

(xii)   calculate the standard deviation of the activity of the identified radionuclides or a minimum detectable activity (MDA) or limit of detection (LOD) of radionuclides sought but not found in the sample and report in the units chosen.

3.   STANDARDS

The calibration of an analytical system is one of the most important tasks required of any analyst. If the calibration is incorrect then all the results produced will be inaccurate. It is essential that all calibration sources used in radiometric analysis are traceable to a national or international measurement standard. Certificates issued by the supplier must provide supporting information and data relating to the authenticity of the standard. NAMAS accreditation requires that one uses nationally traceable standards. Credibility in any court of law will demand some form of assurance that the system is properly calibrated as will the participants in any form of intercomparative exercise.

3.1   Mixed gamma calibration standard (liquid)

The National Physical Laboratory (NPL) is the UK's national standards laboratory for all physical quantities. The NPL provides standard materials suitable for the calibration of gamma spectrometer systems on a regular basis. Other suppliers of radioactive standards include Amersham International plc who manufacture at regular intervals a mixed nuclide source under their catalogue number QCY 48. This multi-nuclide source contains Am-241, Hg-203, Ce-139, Cs-137, Sn-113, Cd-109, Y-88, Sr-85, Co-60 and Co-57. Thus allowing the user to cover the energy range 0.060 - 1.836 MeV. For most users the Amersham QCY 48 standard may prove too active and a dilution will be necessary, lower specific activity is available from the NPL.

It is often necessary to use a diluent of suitable analytical composition to make up to the required geometry and density for calibration. If the correct diluent is not used, some radionuclides contained in the standard will almost certainly not be held in solution. For diluting QCY 48 a suitable inactive solution N441 is available from Amersham International. This contains 225 mg ml^{-1} each of Cd, Cs, Ce, Co, Hg, Sn, Sr, and Y in 4M HCl. For diluting the NPL standard the user is advised to contact NPL for information. As with the setting-up and single peak sources, the total activity in the calibration standard solution should be such that it does not lead to a dead-time in the detector system of more than about 5%: any dead-time should be corrected for.

3.2   Single peak sources (caesium-137)

This can be any source solid or liquid, with a dead-time of no greater than about 5%. Amersham International produce a range of sources which are suitable for this purpose.

3.3   Cobalt-60 'setting-up' source

This may also be any source, solid or liquid, with a dead-time of no greater than 5%.

4.   SETTING-UP PROCEDURE

The following procedures are designed for optimising equipment performance and are presented as a guide to understanding. Reference to manufacturers' manuals is essential when carrying out work of this type. Technical improvements may obviate many of these steps.

4.1   Optimising the equipment

(i)   The detector should be mounted in a shield in such a way that it is electrically and mechanically isolated from that shield (sub-section 4.7, note (a)).

(ii) Ensure the detector is mounted on supports designed to dampen vibrations.

(iii) Ensure that the liquid nitrogen filling tube is accessible at all times and so fixed as to prevent disturbance of the detector when filling.

(iv) Connect cables to pre-amplifier, amplifier, etc. in accordance with manufacturers' instructions. Ensure that all BNC cables are matched in the same impedance.

(v) Fill the cryostat with liquid nitrogen, taking note of safety instructions. Leave for 6 hours to stabilise.

(vi) Check the bias supply is set to the correct positive or negative bias polarity. With the detector bias **OFF** and set at zero (0) volts, switch on the high voltage. Set the amplifier coarse gain to 50 and the shaping time to that recommended for the detector.

(vii) Using a 'Tee' connector, couple the amplifier unipolar output to the input of the MCA/MCB and to an oscilloscope using BNC co-axial cables (sub-section 4.7, note (b)).

(viii) Increase the bias supply voltage slowly and continue to increase the voltage over a period of a few minutes until the recommended operating voltage is reached (sub-section 4.7 note (c)).

(ix) Leave the system to stabilise for approximately 1 hour before continuing with the set-up procedures.

(x) Place a sealed cobalt-60 source close to the detector and, using the gain adjustment on the amplifier, adjust the energy response to give a channel reading of about 2665 for the 1332 keV peak (sub-section 4.7, note (d)).

(xi) Remove the radioactive source from the vicinity of the detector before proceeding with the baseline checks.

If the amplifier has a factory-set DC baseline proceed to sub-section 4.3.

4.2 DC baseline adjustment

(i) Disconnect the cable between the amplifier and the pre-amplifier and adjust the DC potentiometer on the amplifier until the DC level is equal to or slightly more negative than the ground level (sub-section 4.7, note (e)).

(ii) Reconnect the amplifier to pre-amplifier cable.

4.3 Baseline noise check

(i) Adjust the oscilloscope controls such that the baseline signal can be observed in detail (sub-section 4.7, note (f)).

(ii) Check the detector for phonic response by clapping hands nearby with shield open and closed.

(iii) Minimise noise effects by adjusting the base line. If the amplifier has an automatic Pole Zero adjustment, follow the manufacturers' instructions. Then proceed to sub-section 4.6.

4.4 Pole zero adjustment

(i) Place the cobalt-60 source close to the detector.

(ii) Observe the unipolar output from the amplifier with the oscilloscope.

(iii) Adjust the pole-zero potentiometer control so that the trailing edge of the pulses returns to the baseline and thereby minimise over- and undershoot (sub-section 4.7, note (g)).

4.5 Baseline restorer threshold adjustment

After the amplifier gain and shaping time have been selected and the pole-zero adjustment made, the baseline restorer threshold adjustment can be used to establish the correct discriminator threshold for the baseline restorer circuit. For most applications the toggle switch can be set in the Auto position where the threshold level is set automatically just above the noise level. However, if desired the threshold can be set manually as follows:

(i) Remove the radioactive source from the vicinity of the detector.

(ii) Set the Baseline Restorer (BLR) switch on the amplifier to the Threshold position and adjust the potentiometer fully clock-wise.

(iii) Observe the unipolar output on the oscilloscope using a 100 mV/cm vertical scale and a 5 micro-second horizontal deflection.

(iv) Connect the 'busy' output on the amplifier to the external trigger input on the oscilloscope.

(v) Adjust the BLR potentiometer until the base line discriminator begins to trigger on noise (sub-section 4.7, note (h)).

(vi) Adjust the BLR potentiometer until the trigger level gives a horizontal response on the oscilloscope (sub-section 4.7, note (i)).

(vii) Switch the BLR toggle to the automatic mode and observe whether the automatic mode can cope to the same degree as the manual settings.

(viii) Disconnect the cable from the 'busy' output and the 'Tee' from the unipolar output of the amplifier.

(ix) Reconnect the signal cable from the MCA/MCB to the unipolar output of the amplifier.

The system is now ready for the initial MCA/MCB tests (sub-section 4.6)

4.6 Initial MCA/MCB tests

(i) Acquire a spectrum using a single peak source, e.g. caesium-137 (sub-section 4.7, note (j)).

(ii) If the peak is skewed, and manual adjustment of pole-zero is available then repeat the set-up procedure steps of sub-sections 4.4 to 4.5 (vii). In the case of automatic pole-zero adjustment consult the supplier.

(iii) Acquire a spectrum using a mixed gamma calibration standard (sub-section 4.7, note (k)).

The system is now ready for calibration.

4.7 Notes

(a) This will avoid earth loops.

(b) The oscilloscope must be DC coupled and contribute no distortion to the wave forms.

(c) Signals should be received on the MCA/MCB and the oscilloscope, if there is still no signal, consult the manufacturer.

(d) Channel 2665 is appropriate for a 4096 channel system. For systems of smaller or greater memory capacity the appropriate channel should be selected.

(e) There should be an horizontal trace on the oscilloscope showing the ground level for the system.

(f) There should be no obvious signals on the baseline display and the peak width should not exceed 5 mV.

(g) For examples of overshoot and undershoot see Figure 5.

(h) This corresponds to about 200 counts per second from the 'busy' output.

(i) for the correct oscilloscope output refer to Figure 4(d).
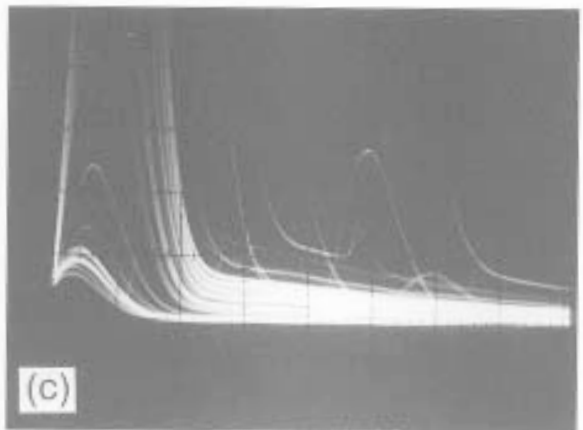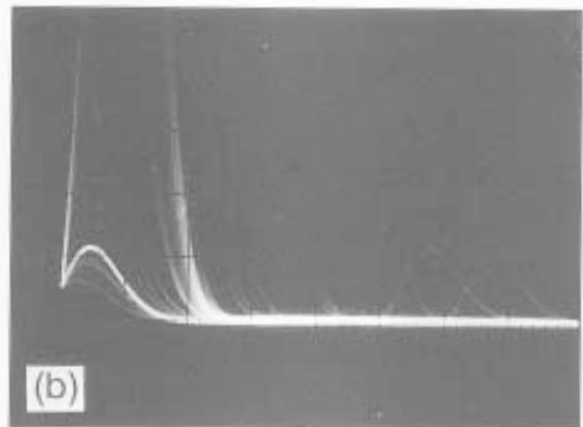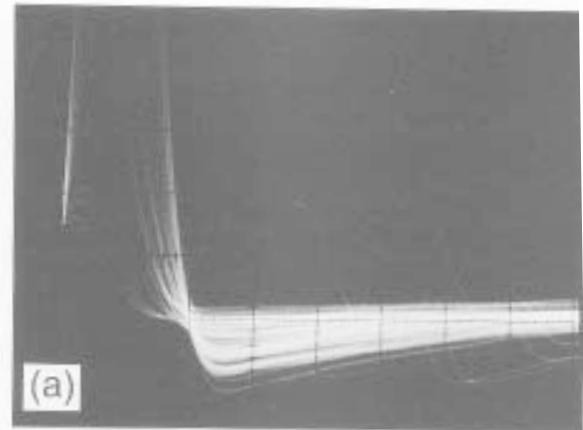
Figure 5. Examples of (a) undershoot or under-compensated; (b) optimum adjustment; and (c) overshoot or overcompensated

(j) Ensure that the peak is a symmetrical singlet and not skewed. Non-symmetry of the peak is the product of a poor pole-zero adjustment. A noisy baseline will affect the resolution creating peak broadening.

(k) If the gain settings are correct, the caesium-137 peak at 661.1 keV should be at channel 1324 and the 1332 keV peak of cobalt-60 at channel 2664 for a 4096 channel system.

5. CALIBRATION PROCEDURES

5.1 Counting geometry

It is important to select a counting geometry that maximises the detector counting efficiency. Although basic physics suggests that the optimum geometry is a point source, in practice this is not feasible. A compromise geometry must be selected to satisfy the following criteria:

(a) The sample container must be readily available from commercial suppliers at a realistic price.

(b) The dimensions must allow the container to sit squarely on top of, or over in some cases, the detector end-cap, such that there is no overlap.

(c) There is sufficient sample available to **fill** the container

(d) The container should not be so large that it requires vast quantities of wet sample to be processed in order to fill it.

Warning: For every type of sample container used it is necessary to produce a full calibration. As this is very time consuming some laboratories tend to use a liquid calibration for all geometries; this practice can lead to additional errors of over 10% being introduced and should be avoided.

In practice detector crystal dimensions do not vary by much from one manufacturer to another. DFR have standardised on the following containers:

1. Liquids

    a) 75 ml plastic pot with snap top lid
    b) 300 ml plastic pot with snap top lid
    c) 500 ml plastic bottle

2. Solids

    a) **Disc** 5 cm diameter 1 cm thick
        20 - 34 g (depending upon density)

    b) **Tub** 8 cm diameter, 5 cm height
        (chocolate spread tub)

        200 g
        287 g
        462 g

5.2 Calibration

5.2.1 Introduction

The essential requirements of a calibration are to establish an energy / efficiency / resolution relationship. This is most conveniently achieved using a commercially available mixed source standard (QCY 48) dispersed evenly throughout the calibration material. The standard should contain radionuclides covering the whole gamma energy range. Complete dispersion is not easy to achieve as it is difficult to produce a totally homogeneous sample without incurring some losses en-route, however it is important to ensure that the calibration sample reflects accurately the density of the samples to be measured. Although dispersion in liquids is much easier these should not be used as substitutes for solids.

The following instructions for calibrating the counting system are based upon the assumption that the user has access to a computer-controlled system. If this is not the case then peak areas, efficiencies, activities, etc. can be calculated by hand but this is an exceedingly arduous task.

When counting low-level environmental samples, it is important to make allowances for the background contribution to the gross count. Careful measurements should therefore be made of:

    a) the environmental background arising from the shield and its surroundings, and

    b) any additional effects of the blank material used in the calibration.

Containers of the same type as those used for the samples should be filled with blank material and counted for not less than four times longer than that required for the least active sample. These data are stored in the system memory and are used to correct the sample counts at a later stage.

5.2.2 Sum-coincidence effects

Before commencing any calibration it is important to understand and correct for the effects of sum-coincidences.

Coincidence summing occurs for radionuclides emitting two or more photons in sequence within the resolving time of the spectrometer. If a coincidence photon is also detected, a sum pulse is recorded leading to the loss of the event from the full energy peak of the first photon. The probability for such summing effects increases with increasing total efficiency, e.g. with decreasing source-detector distance, but is independent of count rate. Corrections can be omitted only in the

special case where a sample is measured relative to a standard of the same radioactive nuclide in the same geometry. A simple and effective solution to eliminate this effect is to position the sample at least 10 cm from the detector surface, unfortunately this not only reduces the sum-coincidence effect but also considerably reduces the detector efficiency. A compromise of 1 cm is considered reasonable for normal environmental samples.

5.3   Computer-assisted calibration

(i)   Carefully select the counting geometry, choose one container to carry out the initial calibration. (sub-section 5.4, note (l)).

(ii)   Fill the container with the prepared reference material (sub-section 5.4, note (m)) and double wrap with protective film.

(iii)   Place the container on the detector in such a way that the position can be reproduced for any other sample (sub-section 5.4, note (n)).

(iv)   Acquire a spectrum for sufficient time to produce at least 10^4 counts for each peak of interest (sub-section 5.4, note (m)).

(v)   Input reference source data according to manufacturers' instructions. Then, using the spectral output, calculate the position of each peak and each peak efficiency (sub-section 5.4, note (o)).

(vi)   Plot an efficiency/energy relationship.

(vii)   Using recognised mathematical principles smooth the curve to eliminate any points which cause irregularities (sub-section 5.4, note (p)).

(viii)   Recalculate efficiency values using the smoothed data from (vii) above (sub-section 5.4, note (q)).

(ix)   Follow the manufacturers' protocol and input the new efficiency values, from (viii) above (sub-section 5.4, note (r)).

(x)   Repeat the calibration for any other geometry or density (sub-section 5.4, note (s)).

(xi)   Fill a container of the same geometry with blank material and count for at least four times the counting period used for the least active samples (sub-section 5.4, notes (t) and (u)).

(xii)   Store this background spectrum for subsequent use in the calculation of the activity of samples.

(xiii)   In an identical container to that used in the calibration, count a sample of known radioactive content for sufficient time to accumulate statistically valid counts in each peak of interest (sub-section 5.4, note (v)).

(xiv)   Using the efficiency curve already obtained, calculate the activity in the sample in recognised units e.g. Bq l^{-1} or Bq kg^{-1} (sub-section 5.4, note (w)).

(xv)   Compare answers with those given for the known sample. Accept those that fall within +/- two standard deviations of the correct result. If errors greater than this exist, carry out an investigation and carefully check calibration data.

5.4   Notes

(l)   Choose the container which is likely to be most frequently used. Have in mind the cost and availability of supplies.

(m)   See also sub-section 6.1.

(n)   The use of a former is recommended.

(o)   It is assumed that a radionuclide library resides within the computer memory.

(p)   Any points within the statistical limits may be smoothed. Others outside require careful checking before proceeding further. Figure 6 shows a typical calibration for an HPGe detector.

(r)   **These values are only valid for this geometry, all other geometries require a new calibration**.

(s)   Some software systems allow a single calibration to be used in conjunction with factors which relate one geometry or density to another.

(t)   The blank should consist of material at least of the same matrix composition as the sample but without detectable radioactive content.

(u)   Count for not less than 24 hours.

(v)   The known sample may be a reference material or reference standard, preferably with the same matrix composition as the sample.

(w)   The efficiency curve and the other related data such as peak search programs etc. are assumed to be in the computer memory.
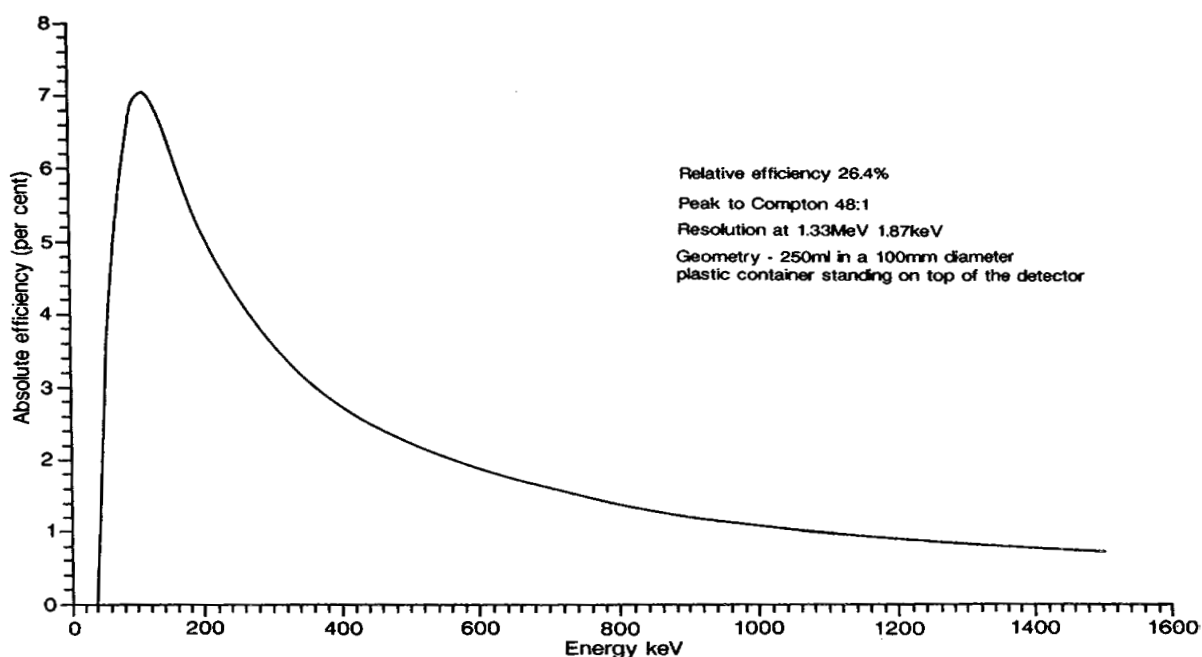
Figure 6. Efficiency versus energy calibration for a typical HPGe detector

The text within the figure reads:

Relative efficiency 26.4%

Peak to Compton 48:1

Resolution at 1.33MeV 1.87keV

Geometry - 250ml in a 100mm diameter
plastic container standing on top of the detector

6. SAMPLE COUNTING

6.1 Introduction

In comparison to calibrating the instrument, counting the sample is relatively simple. On the Canberra system there is a facility to run a small job stream called 'set-up'. This allows the operator to input such details as, sample identification, collection date (for half-life calculations), sample weight and other data required for activity calculations.

Other criteria such as sensitivity, energy tolerance, half-life ratio etc. are preset by the manufacturer but may be altered as desired. If for example a sample activity is close to background then the operator may wish to change the peak search sensitivity in order to enhance those peaks arising from the sample as distinct from those from the background this he would do by changing the sensitivity control.

The activity of identified radionuclides is calculated by using previously inputted calibration data which takes into account background contributions, interferences, half-lives, etc. These calculated data must then be examined by a skilled analyst before they may be used elsewhere as they are values interpreted by the software and occasionally give rise to anomalies.

There are however still some important points that must be considered before the actual sample counting takes place:

a) The position of the sample on the detector is critical, it must be placed in exactly the same position as the calibration sample, this can be ensured by the use of a jig.

b) Care should be taken to ensure that the Analogue to Digital Converter (ADC) dead-time does not exceed 5%, if this is not possible then the sample volume should be reduced to an alternative (calibrated) geometry until a reasonable dead-time is achieved. Some specially designed ADCs are able to cope with high count-rates, check before use.

c) Ensure that the sample container is filled to the same volume as for the calibration.

6.2 Sample counting procedure

(i) Count the sample in an appropriate geometry for sufficient time to ensure that the precision with which individual radionuclides are measured meets analytical requirements. For low level environmental samples this can only be achieved by counting for considerable lengths of time — typically 55 000 seconds and occasionally much longer.

(ii) If a preset counting time has not been selected, stop counting when sufficient counts have been obtained in all peaks of interest.

(iii) Use calibration data to calculate activity concentrations, or limits of detection as described in section 7.

6.3 Analysis of spectra

Several software packages have been written in DFR for the Canberra system to account for such problems as interference of one photo peak upon another and the grow-in of daughters e.g. Zr/Nb. Such problems as this are often not considered by the manufacturers.

6.4 Computer-assisted analysis

Spectral information is fed into a computer where a comparison is made between the peak position and its corresponding energy. Having established this relationship, the computer then compares the gamma peak energies with those contained within the library and identifies those radionuclides which fall within tolerance limits previously specified in the computer set-up programme. A comparatively wide tolerance limit is often specified (about 2 keV) to allow for drift in peak positions. Providing that the photon peak fits within the tolerance then it is accepted for further computation.

Identified radionuclides are quantified in terms of count rate and converted into activity concentration (Bq l^{-1}) using counting efficiency, decay data and sample volume.

7. LIMITS OF DETECTION

There are many instances when it is very important to define a detection limit for certain radionuclides. This limit, known also as the minimum detectable emission rate or minimum detectable activity (MDA), will depend upon the sample composition, the energy of the radiation, the source to detector distance, the detector efficiency, the background and the counting time available. To quote MDAs it is necessary to define all these criteria. All MDA values quoted by DFR are based upon standard counting times of 55 000 seconds using a 300 ml tub counted on an 'average' efficiency detector.

MDAs calculated within DFR are all based upon the paper 'Limits for Qualitative Detection and Quantitative Determination - Applications to Radiochemistry' (Currie, 1968). Currie's work has been extended (Dutton, 1982) to cover simple aspects of gamma spectrometry.

Dutton defined two values based upon a net zero (background) distribution:

(a) MACC – a minimum activity based on a critical count, such that the analyst can say that above this critical level there is a probability < p of the result coming from the net zero signal distribution:

$$MACC = Fk\sqrt{2B}$$

where F is the factor converting counts to activity, k is the probability, and B is the number of counts in the peak continuum; and

(b) MDA – a minimum detectable activity – this is the amount of activity that must be present such that there is a probability < P1 of saying that there is not any activity when there is and there is a probability, P2 of saying there is activity present when there is not. Dutton suggests that if the probability P1 = P2 then :

$$MDA = F \times 2k \times \sqrt{2B}$$

The use of p < .05 as the requirement for making an incorrect judgement results in :

$$MACC\ (p<.05) = F \times 1.645\ \sqrt{2B} = F \times 2.33\ \sqrt{B}$$

$$MDA\ (p<.05) = F \times 3.29\ \sqrt{2B} = F \times 4.66\ \sqrt{B}$$

All results published by DFR use the MDA criterion shown above.

8. QUALITY ASSESSMENT

8.1 Introduction

No analytical system can be considered complete unless it encompasses a well thought out quality assessment scheme. Quality assessment consists of two elements:

1) Quality control   2) Quality assurance.

Quality control is defined as:

'Those operations undertaken in the laboratory to ensure that the data produced are generated within known probability limits of accuracy and precision'.

Note that nothing is said about the actual level of accuracy or precision, only that they are known to a certain level of confidence.

Similarly, quality assurance is defined as:

'An overall system of events whereby the laboratory can assure clients that it is generating data of proven and known quality'.

Quality assurance depends primarily on a documented system of procedures, which are designed to meet the following objectives:

1) To demonstrate that the quality control operations are in fact being carried out.

2) To assure accountability of the data, i.e., that the data reported do in fact represent analyses on the sample as submitted or collected. In other words, to show that there are safeguards against sample mix-up.

3) To assure traceability of reported data. Each result reported should be easily traceable to the analyst who ran the test, the method used, the raw data collected, the instrument used, its condition, and the status of the quality control system at the time the sample was run.

4) To show that reasonable precautions are being taken to prevent the possibility of falsification of data.

8.2 Quality control

The calibration technique has already been discussed earlier in section 5. During that procedure a traceable 'multipeak' gamma emitter was used to establish the efficiency versus energy relationship and the resulting graph was drawn. This relationship is very important in the calculation of activity, as too are other instrumental parameters such as peak position and resolution. The laboratory operates a system whereby these important parameters can be monitored on a regular basis.

8.2.1 Quality control in sample preparation

As sample preparation is so important it is necessary to to check the preparation process on a regular basis. A sample of large volume is divided into two aliquots, the first aliquot is processed normally through to the results stage, the second is then processed by another person who played no part in the preparation of the initial sample. Once again the sample passes through the system, but on this occasion particular care is taken to ensure that all equipment is thoroughly cleaned before use. The results are then plotted on a control chart and studied statistically to establish if any changes have taken place.

Remedial action dependant upon the degree of error, is instigated if the statistical limits are exceeded.

8.2.2 Quality control in sample counting

Sample quality control (QC) is maintained in two ways:-

(i) A traceable source of Am-241, Cs-137 and Co-60 as mixed radionuclides in a solid source is counted every second day (weekends excluded) for 2000 seconds. The data provides immediate information on **peak position, resolution and efficiency,** thus allowing the analyst to make adjustments where necessary. Naturally if an adjustment is made then the QC sample is recounted to ensure that the

counting parameters have returned back to their correct position. All QC data is retained and subjected to a vigorous statistical analysis, control charts are plotted and used to assess any long term drift. Clear and concise notes are kept regarding all changes together with the signature of the analyst responsible for sanctioning the action.

(ii) Arguably the most important part of any analytical scheme is the answer it produces. A good QC scheme should contain some means whereby one can assess the reproducibility of the answer itself. **'Does the system give the same answer today as it gave yesterday?'** is the question that should be posed.

To address this problem a moderately active environmental sample of sediment is counted approximately two times per month on every detector. The results are tabulated and again analysed statistically to see if there are any deviations from the mean.

This sample is particularly good as it enables the analyst to not only assess the reproducibility between detectors but also to check the software to see how well it copes with such things as grow-in, interference, decay etc. It is important to ensure that the sample does not become too low in terms of its radioactive content as this will place abnormal strains on the software that would not be encountered under normal circum- stances. The objective is to have a sample representative of the normal sample regime, that includes a good variety of radionuclides as well as a reasonable level of activity.

Finally, a sample made from the mixed radionu- clide standard QCY 48 is counted when it is available from Amersham. This is used to check whether the efficiency calibration is still valid.

8.3 Quality assurance

Upon receipt, sample details such as site, station, species, collection date etc. are entered into the labora- tory sample data management system (LSDM). These data are then compared to the schedule for that year and any predetermined analysis requirements will be automatically added to the sample records. If however a particular sample is not scheduled then it is necessary to enter analysis codes before the sample can progress further. At this point a unique laboratory sample identifier is allocated (LSN), this number will accom- pany the sample throughout the whole analytical process.

At the counting stage the analyst enters the LSN into the management system in order to retrieve the sample details and the analysis codes. This enables the analyst

to confirm that this is the correct sample and that the details correspond. One further check is to ensure that the correct counting geometry and efficiency tables are allocated. When the analysis is complete the results and the sample details are screened by at least two analysts and then transferred to the LSDM for further use by the customer.

Like all modern computer systems there is a complex security screening of all users. The system in use at DFR prevents all unauthorised entry and will not allow any person to change a result without permission. All authorised changes are recorded together with the date of change.

Acknowledgement

Some of the material reproduced here is that given in the booklet 'Determination of Radioactivity in Water by Multinuclide Gamma Ray Spectrometry 1989: Methods for the Examination of Waters and Associated Materials' published by Her Majesty's Stationery Office, London.

9. REFERENCES

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APPENDIX 1. Properties of gamma rays

There are several possible interaction processes attributed to the passage of gamma rays through matter, but only three play a major role in radiation measurements: *photoelectric absorption, Compton scattering, and pair production*. All of these processes lead to either partial or complete transfer of the gamma ray photon energy to electron energy. They usually result in sudden or abrupt changes in the gamma photon history, in that the photon either disappears entirely or is scattered in an alternative direction.

Photo electric effect: In this case all the energy of an X- or gamma photon undergoes interaction with an absorber atom in which the photon completely disappears. In its place, an energetic *photoelectron* is ejected by the atom from one of its quantum shells. The photoelectric process is the predominant mode of interaction for gamma rays (or X-rays) of relatively low energy. The process is also enhanced for absorber materials of high atomic number Z. This is an important phenomenon which must be considered when selecting the shielding material at a later stage.

Compton scattering: This effect takes place between the incident gamma ray photon and an electron in the absorbing material. It is most often the predominant interaction mechanism for gamma ray energies typical of radioisotope sources. In Compton scattering, the incoming gamma ray photon is deflected through an angle with respect to its original direction. The photon transfers a proportion of its energy to the electron (assumed to be initially at rest), which is then known as a *recoil electron*. Because all angles of scattering are possible, the energy transferred to the electron can vary from zero to a large fraction of the gamma ray energy.

Pair production: Provided that the gamma ray energy exceeds twice the rest mass energy of an electron (1.02 MeV), it is possible that in the intense electric field close to a charged particle an energetic gamma photon may be converted into a positron-electron pair, each having half of the available energy (0.51 MeV).

Thus all three interactions result in the loss of photon energy to atomic electrons.

APPENDIX 2. Quantities, symbols and units

Given below are the quantities, symbols, units and abbreviations used in this document.

Quantity	Symbol	Unit	Abbreviation
Activity	A	bequerel	Bq
Activity at time t	A(t)	bequerel	Bq
Volume	V	litre	l
Activity concentration	C	bequerels per litre	Bq l^{-1}
Half life	$t_{1/2}$	seconds	s
Decay constant	λ	reciprocal seconds	s^{-1}
Counting efficiency	e	counts per bequerel	Cts Bq^{-1}
Transition probability (abundance)	P_E	fractional proportion	
Counts per second	cps	reciprocal seconds	s^{-1}

Decay constant $\lambda = \ln 2/t_{1/2} = 0.693/t_{1/2}$

APPENDIX 3. Hazards

A3.1 Hazards to the operator

Appropriate precautions must be taken when handling radioactive substances. Contamination can be avoided by wearing protective clothing, especially gloves. Inadvertent consumption can be prevented by prohibiting eating or drinking where there is a likelihood of dust particulates or other contaminating substances. Inhalation can be minimised by using fume hoods or similar protection. Direct radiation exposure can be reduced by the use of shielding and minimising the time of proximity. Dosemeters should be worn where necessary. Details of the regulatory control, and guidance on the use of radioactive substances, are laid down in the Radioactive Substances Act (Gt Britain - Parliament, 1960) and the Ionising Radiations Regulations (Health and Safety, 1985).

High voltages are employed in parts of the equipment used for gamma spectrometry; care should be exercised when carrying out servicing or adjustments. If at all possible servicing must only be carried out by an authorised engineer.

Liquid nitrogen is used as a coolant (BP -196°C). Appropriate protective clothing including specialist gloves and full face protection must be worn when handling this material and adequate ventilation must be provided at all times. Care is also needed to ensure that ice does not block either the filling tube or the exhaust vent of the detector cryostat; bursting can result from blockage.

A3.2 Hazards to equipment

Germanium detectors are operated under liquid nitrogen temperatures. They must be kept permanently cooled whilst in use and connected to an alarm system which triggers when the nitrogen level falls below the recommended value. The detector must be cooled with liquid nitrogen for some 6 hours before applying bias and high voltages. Care must be taken to ensure that the polarity of the high voltage supply is correct before switching on, otherwise **irreversible damage** to the detector will occur. The high voltage must be applied by increasing slowly over a period of several minutes.

Samples must be enclosed to avoid contamination of the detector. This may be simply achieved by covering the detector with a thin polythene bag. An exposed pre-amplifier must not however be covered as it will be damaged by the formation of condensation.

A3.3 References

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