Designation: D 3649 – 98a

An American National Standard

Standard Practice for
High-Resolution Gamma-Ray Spectrometry of Water[1]

This standard is issued under the fixed designation D 3649; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This practice covers the measurement of gamma-ray emitting radionuclides in water by means of gamma-ray spectrometry. It is applicable to nuclides emitting gamma-rays with energies greater than 20 keV. For typical counting systems and sample types, activity levels of about 40 Bq are easily measured and sensitivities as low as 0.4 Bq are found for many nuclides **(1)**.[2] Count rates in excess of 2000 counts per second should be avoided because of electronic limitations. High count rate samples can be accommodated by dilution or by increasing the sample to detector distance.

1.2 This practice can be used for either quantitative or relative determinations. In tracer work, the results may be expressed by comparison with an initial concentration of a given nuclide which is taken as 100 %. For radioassay, the results may be expressed in terms of known nuclidic standards for the radionuclides known to be present. In addition to the quantitative measurement of gamma radioactivity, gamma spectrometry can be used for the identification of specific gamma emitters in a mixture of radionuclides. General information on radioactivity and the measurement of radiation has been published **(2,3)**. Information on specific application of gamma spectrometry is also available in the literature **(4)**. See also Practice D 1066, Test Method D 1943, Practice D 3084, Practice D 3085, Practices D 3370, and Method E 181.

1.3 *This standard does not purport to address the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitation prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 1066 Practice for Sampling Steam[3]
D 1129 Terminology Relating to Water[3]
D 2777 Practice for Determination of Precision and Bias of Applicable Test Methods of Committee D–19 on Water[3]
D 3085 Practice for Measurement of Low Level Activity in Water[4]
D 3370 Practices for Sampling Water from Closed Conduits[3]
D 3648 Practices for Measurement of Radioactivity[3]
E 181 General Methods for Detector Calibration and Analysis of Radionuclides[5]

3. Terminology

3.1 *Definitions*—For definitions of terms used in this practice, refer to Terminology D 1129. For terms not defined in this practice or in Terminology D 1129, reference may be made to other published glossaries **(5)**.

4. Summary of Practice

4.1 Gamma ray spectra are measured with modular equipment consisting of a detector, an analyzer, memory, and a permanent data storage device.

4.2 Lithium-drifted germanium, Ge(Li), or high-purity germanium (HPGe) detectors, p-type or n-type, are used for the analysis of complex gamma-ray spectra because of their excellent energy resolution. These germanium systems, however, are characterized by high cost and require cooling with liquid nitrogen.

4.3 In a germanium semiconductor detector, gamma-ray photons produce electron-hole pairs. The charged pair is then collected by an applied electric field. A very stable low noise preamplifier is needed to amplify the pulses of electric charge resulting from gamma photon interactions. The output from the preamplifier is directly proportional to the energy deposited by the incident gamma-ray. These current pulses are fed into an amplifier of sufficient gain to produce voltage output pulses in the amplitude range form 0 to 10 V.

4.4 A multichannel pulse-height analyzer is used to determine the amplitude of each pulse originating in the detector, and accumulates in a memory the number of pulses in each amplitude band (or channel) in a given counting time. Computerized systems with stored programs and interface hardware can accomplish the same functions as hardwired multichannel analyzers. The primary advantages of the computerized system

---

[1] This test method is under the jurisdiction of ASTM Committee D-19 on Water and is the direct responsibility of Subcommittee D19.04 on Methods of Radiochemical Analysis.

Current edition approved July 10, 1998. Published March 1999. Originally published as D 3649 – 78. Last previous edition D 3649 – 98.

[2] The boldface numbers in parentheses refer to the list of references at the end of this test method.

[3] *Annual Book of ASTM Standards*, Vol 11.01.

[4] *Discontinued*—See 1988 *Annual Book of ASTM Standards,* Vol 11.02.

[5] *Annual Book of ASTM Standards*, Vol 12.02.

include the capability of programming the multi-channel analyzer functions and the ability to immediately perform data reduction calculations using the spectral data stored in the computer memory or mass storage device (**6**). For a 0 to 2-MeV spectrum, two thousand or more data points are needed in order to fully utilize a germanium detector's excellent energy resolution.

4.5 The distribution of the amplitudes (pulse heights) of the pulses can be separated into two principal components. One of these components has a nearly Gaussian distribution and is the result of total absorption of the gamma-ray energy in the detector. This peak is normally referred to as the full-energy peak or photopeak. The other component is a continuous one lower in energy than that of the photopeak. This continuous curve is referred to as the Compton continuum and is due to interactions wherein the gamma photons lose only part of their energy to the detector. These two portions of the curve are shown in Fig. 1. Other peaks, such as escape peaks, backscattered gamma rays or X rays from shields, are often superimposed on the Compton continuum. Escape peaks will be present when gamma-rays with energies greater than 1.02 MeV are emitted from the sample (**7**). The positron formed in pair production is usually annihilated in the detector and one or both of the 511–keV annihilation quanta may escape from the detector without interaction. This condition will cause single or double escape peaks at energies of 0.511 or 1.022 MeV less than the photopeak energy. In the plot of pulse height versus count rate, the size and location of the photopeak on the pulse height axis is proportional to the number and energy of the incident photons, and is the basis for the quantitative and qualitative application of the spectrometer. The Compton continuum serves no useful purpose in photopeak analysis and must be subtracted when peaks are analyzed.

4.6 If the analysis is being directed and monitored by an online computer program, the analysis period may be terminated by prerequisites incorporated in the program. If the analysis is being performed with a modern multichannel analyzer, analysis may be terminated when a preselected time or total counts in a region of interest or in a specified channel is reached. Visual inspection of a cathode-ray tube (CRT) display of accumulated data can also be used as a criterion for manually terminating the analysis on either type of data acquisition systems.

4.7 Upon completion of the analysis, the spectral data are interpreted and reduced to include activity of Bq (disintegration per second) or related units suited to the particular application. At this time the spectral data may be inspected on the CRT to identify the gamma-ray emitters present. This is accomplished by reading the channel number from the *x*-axis and converting to gamma-ray energy by multiplying by the appropriate keV/channel (system gain). If the system is calibrated for 1 keV per channel with channel zero representing 0 keV, the energy will be equal to the channel number. In some systems the channel number or gamma-ray energy in keV can be displayed on the CRT for any selected channel. Identification of nuclides may be aided by catalogs of gamma-ray spectra and other nuclear data tabulations (**8**).

4.7.1 Computer programs for data reduction have been used extensively although calculations for some applications can be performed effectively with the aid of a desk-top or pocket calculator (**8**). Data reduction of spectra taken with germanium spectrometry systems is usually accomplished by integration of the photopeaks above a definable background (or baseline) and subsequent activity calculations using a library which includes data such as nuclide name, half-life, gamma-ray energies and associated abundance (or branching ratios) (**9**).

5. Significance and Use

5.1 Gamma-ray spectrometry is of use in identifying radionuclides and in making quantitative measurements. Use of a semiconductor detector is necessary for high-resolution measurements.

5.2 Variation of the physical geometry of the sample and its relationship with the detector will produce both qualitative and

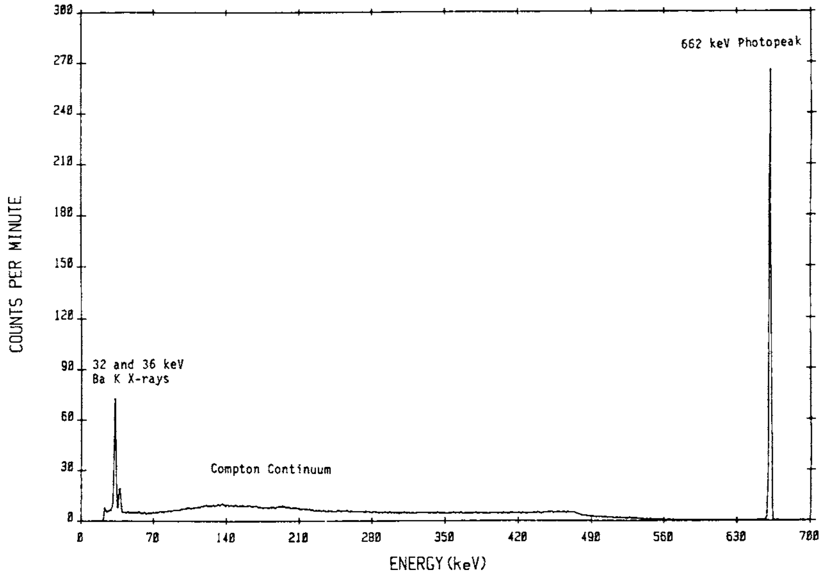

FIG. 1 Cesium-137 Spectrum

quantitative variations in the gamma-ray spectrum. To adequately account for these geometry effects, calibrations are designed to duplicate all conditions including source-to-detector distance, sample shape and size, and sample matrix encountered when samples are measured.

5.3 Since some spectrometry systems are calibrated at many discrete distances from the detector, a wide range of activity levels can be measured on the same detector. For high-level samples, extremely low-efficiency geometries may be used. Quantitative measurements can be made accurately and precisely when high activity level samples are placed at distances of 1 m or more from the detector.

5.4 Electronic problems, such as erroneous deadtime correction, loss of resolution, and random summing, may be avoided by keeping the gross count rate below 100 000 counts/min and also keeping the deadtime of the analyzer below 5 %. Total counting time is governed by the radioactivity of the sample, the detector to source distance and the acceptable Poisson counting uncertainty.

6. Interferences

6.1 In complex mixtures of gamma-ray emitters, the degree of interference of one nuclide in the determination of another is governed by several factors. If the gamma-ray emission rates from different radionuclides are similar, interference will occur when the photopeaks are not completely resolved and overlap. A method of predicting the gamma-ray resolution of a detector is given in the literature **(10)**. If the nuclides are present in the mixture in unequal portions radiometrically, and if nuclides of higher gamma-ray energies are predominant, there are serious interferences with the interpretation of minor, less energetic gamma-ray photopeaks. The complexity of the analysis method is due to the resolution of these interferences and, thus, one of the main reasons for computerized systems.

6.2 Cascade summing [6] may occur when nuclides that decay by a gamma-ray cascade are analyzed. Cobalt-60 is an example; 1172 and 1333-keV gamma rays from the same decay may enter the detector to produce a sum peak at 2505 keV and cause the loss of counts from the other two peaks. Cascade summing may be reduced by increasing the source to detector distance. Summing is more significant if a well-type detector is used.

6.3 Random summing is a function of counting rate and occurs in all measurements. The random summing rate is proportional to the total count squared and the resolving time of the detector. For most systems random summing losses can be held to less than 1 % by limiting the total counting rate to 1000 counts/s. Refer to Method E 181 for more information.

6.4 The density of the sample is another factor that can effect quantitative results. Errors from this source can be avoided by preparing the standards for calibration in solutions or other matrices with a density comparable to the sample being analyzed.

7. Apparatus

7.1 *Gamma Ray Spectrometer*, consisting of the following components:

7.1.1 *Detector Assembly*:

7.1.1.1 *Germanium Detector*—The detector shall have a volume of about 50 to 150 cm^3, with a full width at one-half the peak maximum (FWHM) less than 2.2 keV at 1332 keV, certified by the manufacturer. A charge-sensitive preamplifier using low noise field effect transistors should be an integral part of the detector assembly. A convenient support shall be provided for samples of the desired form.

7.1.1.2 *Shield*—The detector assembly shall be surrounded by an external radiation shield made of massive metal, equivalent to 102 mm of lead in gamma-ray attenuation capability. It is desirable that the inner walls of the shield be at least 127 mm distant from the detector surfaces to reduce backscatter. If the shield is made of lead or a lead liner, the shield must have a graded inner shield of 1.6 mm of cadmium or tin lined with 0.4 mm of copper, to attenuate the 88-keV Pb X rays. The shield must have a door or port for inserting and removing samples.

7.1.1.3 *High Voltage Power/Bias Supply*—The bias supply required for germanium detectors usually provides a voltage up to 5000 V and 1 to 100 μA. The power supply shall be regulated to 0.1 % with a ripple of not more than 0.01 %. Line noise caused by other equipment shall be removed with rf filters and additional regulators.

7.1.1.4 *Amplifier*—An amplifier compatible with the preamplifier and with the pulse-height analyzer shall be provided.

7.1.2 *Data Acquisition and Storage Equipment*:

7.1.2.1 *Data Acquisitions*—A multichannel pulse-height analyzer (MCA) or stand-alone analog-to-digital-converter (ADC) under software control of a separate computer, performs many functions required for gamma-ray spectrometry. An MCA or computer collects the data, provides a visual display, and outputs final results or raw data for later analysis. The four major components of an MCA are; the ADC, the memory, control, and input/output. The ADC digitizes the analog pulses from the detector amplifier. These pulses represent energy. The digital result is used by the MCA to select a memory location (channel number) which is used to store the number of events which have occurred with that energy. Simple data analysis and control of the MCA is accomplished with microprocessors. These processors control the input/output, channel summing over set regions of interest, and system energy calibration to name a few examples.

7.1.2.2 *Data Storage*— Because of the use of microprocessors modern MCAs provide a wide range of input and output (I/O) capabilities. Typically these include the ability to transfer any section of data to one or more of the following; terminal, line printer, cassette tape, floppy or hard disk, *x-y* plotter, and to computer interfaces by means of a serial or parallel port.

8. Sampling

8.1 Collect the sample in ccordance with Practices D 3370.

8.2 Preserve the sample in a radioactively homogeneous state. A sample can be made radioactively homogeneous by the addition of a reagent in which the radionuclides or compounds

---

[6] Refer to *Annual Book of ASTM Standards*, Vol 12.02 on Nuclear, Solar, and Geothermal Energy for more information on this subject.

of the radionuclides present would be soluble in large concentrations. Addition of acids, complexing agents, or stable chemically–similar carriers may be used to obtain homogenity. Consideration of the chemical nature of the radionuclides and compounds present and the subsequent chemistry of the method shall indicate the action to be taken.

9. Test Specimens

9.1 *Containment*—Sample mounts and containers must have a convenient reproducible geometry. Considerations include commercial availability, ease of use and disposal, and the containment of radioactivity for protection of the working environment and personnel from contamination. The evaporation of liquid samples to dryness is not necessary and liquid samples up to several litres may be used. However, samples that have been evaporated to dryness for gross beta counting can also be gamma counted. Massive samples may cause significant self-absorption of low-energy gammas and degrade the higher-energy gammas. Therefore, it is important to calibrate the detector with standards of the same geometry and density. A beta absorber consisting of about 6 mm of aluminum, beryllium, or plastic may be used for samples that have a significant beta activity and high beta energies.

10. Calibration and Standardization

10.1 *Overview*—Put the instrumentation and detector into operation according to the manufacturer's instructions. Initial set-up includes all electronic adjustment to provide constant operating conditions consistent with the application and life expectancy of the calibrations. The analog-to-digital converter gain and threshold, amplifier gain and zero-level, and detector high voltage, or bias must be adjusted to yield an optimum energy calibration, usually 1 keV, or less, per channel (0.5 keV/channel is recommended). Modern commercial equipment is capable of linearity to the extent that the energy may be interpreted by the operator directly to the nearest 0.5 keV simply by reading the channel number of the highest channel in a peak and using the energy calibration data to calculate the energy of the peak. The energy calibration is usually accomplished with radioactive sources covering the entire range of interest. Subsequent efficiency calibrations and source analyses are performed with the same gain settings and the same high voltage setting. Efficiency calibrations are obtained by placing an appropriate volume of a radionuclide standard solution containing 100 to 10 000 Bq in a container and placing the container on the detector or in the well.

10.2 *Procedure*:

10.2.1 *Preparation of Apparatus*:

10.2.1.1 Follow the manufacturer's instructions, limitations, and cautions for the setup and the preliminary testing for all of the spectrometry equipment to be used in the analysis. This equipment would include, as applicable, detector, power supplies, preamplifiers, amplifiers, multichannel analyzers, and computing systems.

10.2.1.2 Place an appropriate volume of a standard or a mixed standard of radionuclides in a sealed container and place the container at a desirable and reproducible source-to-detector distance. The solution should provide about 100 counts/s in the peaks of interest and be made up of standard sources traceable to a nationally certified laboratory. In all radionuclide measurements, the volumes, shape, physical and chemical characteristics of the samples, standards and their containers must be as identical as practicable for the most accurate results. If precipitates or residues are to be analyzed, then the standards must be evaporated on the same type of mount as the sample.

10.3 *Energy Calibration*:

10.3.1 The energy calibration (channel number of the multichannel analyzer versus the gamma-ray energy) of the detector system is accomplished at a fixed gain using standards containing known radionuclides. The standards should be in sealed containers and should emit at least four different gamma-ray energies covering the range of interest, usually 50 keV to 2000 keV in order to test for system linearity. Some commercially available nuclides suitable for energy calibration are the following:

	keV
lead-210	46.5
americium-241	59.5
cadmium-109	88
cerium-141	145
chromium-51	320
cesium-137	662
manganese-54	835
sodium-22	511 and 1275
yttrium-88	898 and 1836
cobalt-60	1173 and 1332
radium-226, equilibrated	186, 352, 609, 1120, and 1765

10.3.1.1 A mixed gamma-ray standard for energy and efficiency calibration is also available (see Fig. 2). This standard can be obtained in solid form in a user-supplied container. The radionuclidic purity of the standards should be verified periodically to ensure against accidental contamination or the presence of long-lived impurities by comparing the observed spectra with the spectra published in the literature (**8**).

10.3.2 A multichannel analyzer shall be calibrated to cover the range of interest. If the range is from 50 to 2000 keV, the gain of the system shall be adjusted until the cesium-137 photopeak, 662 keV, is about one-third full scale. Leaving the gain constant, locate at least three other photopeaks of different energies, covering the same range. Determine and record the multichannel analyzer channel number corresponding to the maximum count rate for each of the four gamma energies. Using rectangular coordinate paper, plot the gamma energy versus the channel number for each of the four gamma-ray energies. A linear relationship will be observed if the equipment is operating properly. Samples should not be analyzed if there is a nonlinear relationship. Calculate the slope and intercept of the line using a least squares calculation. If the spectrometry system is computerized, follow the appropriate manufacturer input instructions for the determination of the slope and intercept. During each day in which the spectrometry system is being used to analyze samples, the above sequence of operation shall be repeated using at least two different gamma-ray energies. If the slope and intercept are essentially unchanged, the energy calibration data remain valid. If an appreciable change in the slope or intercept is evident, the entire calibration procedure must be rerun.

10.4 *Photon Detection Efficiency Calibration*:

10.4.1 Accumulate an energy spectrum using sealed, calibrated radioactivity standards in a desired and reproducible

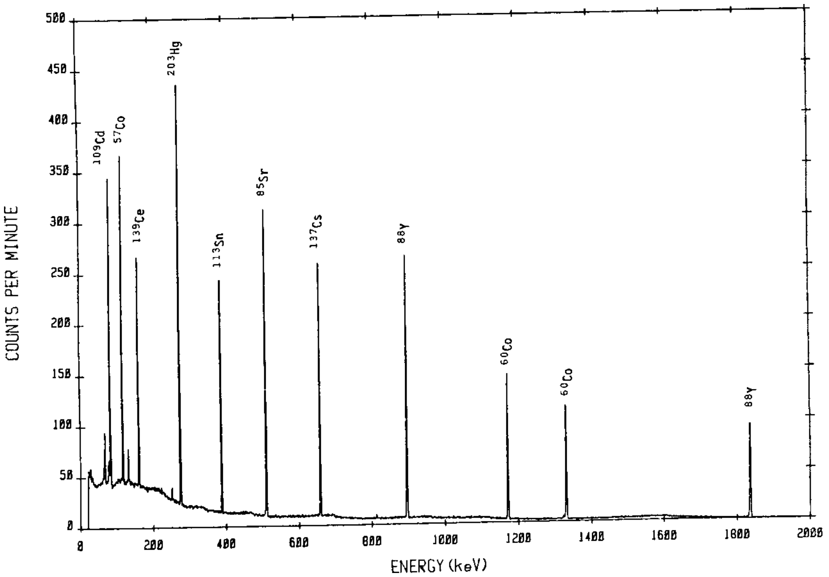

FIG. 2 Mixed Gamma-Ray Calibration Spectrum

counting geometry (see 10.2.1.2). At least 10 000 net counts (total counts minus the compton continuum and ambient background) shall be accumulated in each full-energy gamma-ray peak of interest. Compare the live time of the count to the half-life of the radionuclide of interest. If the live time is greater than 5 % of the half-life, a correction factor must be applied for decay during the count **(8)**.

10.4.2 Correct the radioactivity standard source gamma-ray emission rate for the decay from the time of standardization to the time at which the count rate is measured.

10.4.3 Calculate the full-energy peak efficiency, E_f, as follows:

$$E_f = N_p/N_g$$

where:

E_f = full-energy peak efficiency (counts per gamma ray emitted),
N_p = net gamma-ray count in the full-energy peak of interest (counts/s), and
N_g = gamma-ray emission rate (gamma rays/s). If the standard source is calibrated as to activity, the gamma-ray emission rate is given by:

$$N_g = A \cdot P_g$$

where:

A = number of nuclear decays per second, and
P_g = probability per nuclear decay for the gamma ray.

10.4.4 Many modern spectrometry systems are computerized and the determination of the gamma-ray efficiencies are determined automatically at the end of an appropriate counting interval. Refer to the manufacturer's instructions for specific output requirements.

10.4.5 Plot the values for the full-energy peak efficiency (as determined in 10.4.3) versus gamma-ray energy. The plot will allow the determination of efficiencies at energies for which standards are not available and to show that the algorithms used in computerized systems are providing valid efficiency calibrations. A typical plot is shown in Fig. 3.

10.4.6 Once the efficiencies have been determined, it is unnecessary to recalculate them unless there is a change in resolution, geometry, or system configuration.

11. Sample Measurements

11.1 After the spectrometer system has been set-up, the energy and efficiency calibrations performed, unknown specimens can be measured.

11.2 Following the general concepts of quantitative analytical chemistry, transfer the sample to the specimen container (9.1) and position it in the same manner as was done during system calibration (Section 10).

11.3 Measure the sample for a period of time long enough to acquire a gamma-ray spectrum which will meet the minimum acceptable counting uncertainty.

12. Calculation

12.1 Spectral data obtained with a germanium detector are only corrected for background when these peaks may alter the final results. In many experiments, the background may not affect the results but is still monitored to ensure the integrity of the system. Again, the practice presented here is not the only type but is conducive to available computational hardware and should be used to verify the validity of commercial software.

12.2 The underlying aim of this practice is to subtract the continuum or baseline from the spectral data where it underlies a photopeak of interest. For operator-directed calculations, the choice of the baseline level may be straight-forward. The simplest way, using a plot of the spectral data, is to draw a straight line, using judgement and experience, that best describes the baseline. Then the baseline data can be read directly from the plot and subtracted." Stand-alone" computer programs have accomplished this but are not presented here.

12.3 Photopeaks lying on a sloping baseline or one with curvature will be analyzed, independent of method, with increased uncertainty. Use of data from these peaks should be limited to those cases where there is no other alternative.

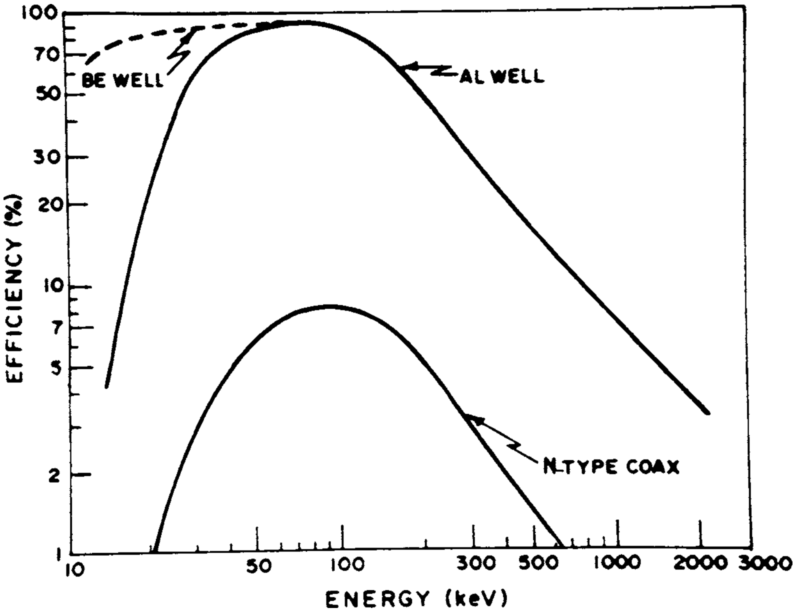

FIG. 3 Efficiency Calibration Plot

Photopeaks that overlap with each other will also increase the uncertainty of the final result. In the case where use of overlapping peaks cannot be avoided, the experimenter may estimate the areas by assuming that the ratio of the peak areas is equal to the ratio of the peak heights. Computer programs separating overlapping peaks with varying degrees of success may be found in the literature **(3, 9, 11)**.

12.4 In order to determine nuclide concentrations the photopeak areas corrected for background and interferences are divided by the count time and efficiency for the energy of the gamma ray being calculated to give gammas per second for the peak of interest. If, as is the case for some nuclides the branching ratio is not accurately known and a direct calibration was made with the same nuclide, the branching ratio and efficiency will be one number that converts counts per second to disintegrations per second for the nuclide and photopeak of interest. If not, the gammas per second are converted to disintegrations per second by dividing the gammas per second by the gammas per disintegration, for the nuclide and photopeak of interest. The results are then corrected for sampling or decay, or both, as demanded by the application. The energies, half-lives, and gammas per disintegration for radionuclides that might be present in water samples are listed in Table 1.