4.5.2 Radiometrology

Ga-01-R

GAMMA RADIOASSAY

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APPLICATION

This procedure is used for the nondestructive measurement of γ-ray emitting radionuclides from a variety of environmental matrices by high resolution germanium (Ge) detector γ-ray spectrometry and NaI(Tl) detector γ-ray spectrometry. It is applicable to nuclides emitting γ-rays with energies > 20 keV for Ge detectors and 50 keV for NaI(Tl) detectors. For typical counting systems and sample types, activity levels of about 40 Bq are easily measured and sensitivities as low as .002 Bq can be achieved for many nuclides. Count rates in excess of 2000 counts sec^{-1} (cps) should be avoided because of electronic limitations. High count rate samples can be accommodated by dilution or by increasing the sample to detector distance.

The procedure is used for either qualitative, 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 standards for the radionuclides known to be present. In addition to the quantitative measurement of γ-ray radioactivity, γ-ray spectrometry can be used for the identification of specific emitters in a mixture of radionuclides. General information on radioactivity and the measurement of radiation has been published. Information on the specific application of γ-ray spectrometry is also available in the literature.

DESCRIPTION OF THE SYSTEM

Gamma-ray spectra are measured at EML with modular equipment consisting of a detector, an amplifier, a pulse-height analyzer, memory, and a permanent data storage device. Lithium-drifted germanium, Ge(Li), or high purity Ge detectors (p-type or n-type) are used for the analysis of complex γ-ray spectra because of their excellent energy resolutions. These Ge detectors, however, are characterized by high cost and require cooling with liquid nitrogen. Thallium activated sodium-iodide crystals, NaI(Tl), can be operated at ambient temperatures and are often used at EML as γ-ray detectors in spectrometer systems. However, their energy resolutions limit their use to the analysis of single nuclides or simple mixtures of a few nuclides.

Upon completion of the γ-ray assay, the spectral data are interpreted and reduced to nuclide activities in Bq (disintegrations 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 γ-ray emitters present. This is accomplished by reading the channel number from the x-axis and converting to γ-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. The channel number or γ-ray energy in keV is usually displayed on the CRT. Identification of nuclides is aided by catalogs of γ-ray spectra and other nuclear data tabulations. Because of the reduced spectral resolution obtained with NaI(Tl) detectors, this technique can only be applied to samples of single nuclides or very simple combinations of nuclides.

Data reduction of spectra taken with Ge spectrometry systems is usually accomplished by integration of the photopeaks above a definable background (or baseline), and by subsequent activity calculations using a library that includes data such as nuclide name, half-life, γ-ray energies and associated abundance (intensity or branching ratios). Computer programs for data reduction of NaI(Tl) detector data have been used extensively at EML. Data reduction of spectra involving mixtures of nuclides is usually accomplished by least-square fitting routines to a library of standard spectra of the individual nuclides acquired under individual conditions.

Variation of the physical geometry of the sample and its relationship with the detector will produce both qualitative and quantitative variations in the γ-ray spectrum. To adequately account for these geometry effects, calibrations are designed to duplicate all sample counting conditions including source-to-detector distance, sample shape and size.

Electronic problems, such as erroneous deadtime correction, loss of resolution, and random summing, may be avoided by keeping the gross count rate below 2000 cps and also by 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.

In complex mixtures of γ-ray emitters, the degree of interference of one nuclide in the determination of another is governed by several factors. If the γ-ray emission rates from different radionuclides are similar, interference will occur when the photopeaks are not completely resolved and overlap. If the nuclides are present in the mixture at markedly different levels of activity, nuclides of higher energies that are predominant can cause serious interferences with the interpretation of minor, less energetic, γ-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.

Cascade summing may occur when nuclides that decay by a γ-ray cascade are analyzed. Cobalt-60 is an example; 1172 and 1333 keV γ-ray from the same decay may enter the detector to produce a sum peak at 2505 keV or a count in the continuum between the individual peaks and the sum peak; thus, causing the loss of counts from one or both of 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.

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 detection system. For most systems, random summing losses can be held to < 1% by limiting the total counting rate to 1000 cps.

The density of the sample is another factor that can affect 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. Another approach is to apply attenuation corrections to all calibration standards and samples based on sample weight, known volume, γ-ray path length and average atomic number of the sample matrix.

APPARATUS

A γ-ray spectrometer consists of the following components:

A. Detector assembly.

1. Germanium detector - The detector should have a volume of at least 50 cm^{-3}, with a full width at one half the peak maximum (FWHM) < 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 should be provided for samples of the desired form. Vertical systems allow the standard/sample to be placed directly on the detector end cap.

2. NaI(Tl) detector - The sodium iodide crystal, activated with about 0.1% thallium iodide, should contain < 5 $\mu g\ g^{-1}$ of K and should be free of other radioactive materials. The crystal should be attached and optically coupled to a multiplier phototube. (The multiplier phototube requires a preamplifier or a cathode follower compatible preamplifier with the amplifier.) The resolution (FWHM) of the assembly for the photopeak of ^{137}Cs should be < 7% for a 75-mm by 75-mm detector.

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

4. High-voltage power/bias supply - The bias supply required for Ge detectors usually provides a voltage up to 5000 V and 1 to 100 µA. NaI(Tl) detectors require a high-voltage power supply of a range of usually from 500 to 3000 V and up to 10 mA to operate the multiplier phototube. The power supply should be regulated to 0.1% with a ripple of not more than 0.01%. Line noise caused by other equipment should be removed with filters and additional regulators.

5. Amplifier - A spectroscopy amplifier compatible with the preamplifier and with the pulse-height analyzer should be used.

B. Data acquisition and storage equipment.

1. Data acquisition - A multichannel pulse-height analyzer (MCA) or stand-alone analog-to-digital converter (ADC) under software control of a separate computer, performs many functions that are required for γ-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. The magnitude of these pulses is proportional to the energy of the photon deposited in the detector. 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, etc.

2. Data storage - Because of the use of microprocessors, modern MCAs provide a wide range of input and output (I/O) capabilities. Typically, these capabilities 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 via a serial or parallel port.

SAMPLE/STANDARD CONTAINERS

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 personnel and working environment from contamination. The evaporation of liquid samples to dryness is not necessary and liquid samples up to 1 L may be used. Massive samples may cause significant self-absorption of low energy γ-rays and may degrade the higher energy γ-rays. A ß absorber consisting of about 6 mm of Al, Be, or plastic may be used for samples that have a significant ß activity and high ß energies.

CALIBRATION AND STANDARDIZATION

This section describes the analysis of mixtures of radionuclides with Ge detectors or single or simple mixtures of radionuclides with NaI(Tl) detectors. If complex mixtures of radionuclides are to be analyzed with NaI(Tl) detectors, refer to page 2 of this procedure.

A. Preparation of apparatus.

Follow the manufacturer's instructions, limitations, and cautions for the setup and the preliminary testing of 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.

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. For environmental analysis, most standards/samples are counted at the detector end cap. The standard should provide about 100 cps in the peaks of interest and should 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.

B. Energy calibration.

The energy calibration (channel number of the MCA versus the γ-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 γ-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: ^{210}Pb, 46.5 keV; ^{241}Am, 59.5 keV; ^{109}Cd, 88 keV; ^{141}Ce, 145 keV; ^{51}Cr, 320 keV; ^{137}Cs, 662 keV; ^{54}Mg, 835 keV; ^{22}Na, 511 and 1275 keV; ^{88}Y, 898 and 1836 keV; ^{60}Co, 1173 and 1332 keV; equilibrated ^{226}Ra, 186, 352, 609, 1120, and 1765 keV. A mixed γ-ray standard for energy and efficiency calibration is also commercially available. This standard can be obtained in solid form in a user supplied container. The radionuclide 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.

A MCA should be calibrated to cover the range of interest. If the range is 50 to 2000 keV, the gain of the system should be adjusted until the ^{137}Cs 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 MCA channel number corresponding to the maximum count rate for each of the four energies. Germanium detectors will have a linear relationship if the equipment is operating properly. Similarly, MCAs and NaI(Tl) detectors being produced today are capable of producing an almost linear energy response. Samples should not be analyzed if this relationship is not obtained. 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 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.

C. Photon detection efficiency calibration.

Accumulate an energy spectrum using sealed, calibrated radioactivity standards in a desired and reproducible counting geometry. At least 10,000 net counts (total counts minus the compton continuum and ambient background) should be accumulated in each full-energy γ-ray peak of interest.

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

Calculate the full-energy peak efficiency Ef as follows:

$$Ef = Np/Ng$$

where

Ef = full-energy peak efficiency (counts per γ-ray emitted),
Np = net γ-ray count in the full-energy peak of interest (cps), and
Ng = γ-ray emission rate (rays sec^{-1}).

If the standard source is calibrated as to activity, the γ-ray emission rate is given by:

$$Ng = A*Pg$$

where

A = number of nuclear decays per second, and
Pg = probability per nuclear decay for the γ-ray.

For Ge detectors, plot the values for the full-energy peak efficiency versus γ-ray energy. The plot will allow the determination of efficiencies at energies for which standards are not available, and will show that the algorithms used in computerized systems are providing valid efficiency calibrations.

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

SAMPLE MEASUREMENTS

After the spectrometer system has been set up, the energy and efficiency calibrations are performed, then the unknown sample can be measured.

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

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

PEAK AREA CALCULATIONS

Spectral data obtained with a Ge 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.

The underlying aim of this procedure 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 straightforward. 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.

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

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 γ-ray being calculated to give photons sec^{-1} 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 cps to Bq sec^{-1} for the nuclide and photopeak of interest. If not, the photons sec^{-1} are converted to disintegrations sec^{-1} by dividing the photons sec^{-1} by the photons per disintegration, for the nuclide and photopeak of interest. The results are then corrected for attenuation or decay, or both.

Canberra Industries MicroSampo Version 2.0 (a commercial software package) is used at EML to perform these calculations.

While the uncertainty due to counting and calibration may represent a significant proportion of the total uncertainty in the measurement, systematic uncertainties should be determined and included in the above calculation. Systematic uncertainties include, but are not limited to, reproducibility of sample position, peak analyses, decay calculations, background subtraction, pulse pile-up, cascade summing corrections, and self-absorption corrections.

ANALYSIS OF COMPLEX MIXTURES OF NUCLIDES WITH NAI(Tl) DETECTORS

Because of the inherent energy resolution of NaI(Tl) detectors, γ-ray peaks in complex mixtures of nuclides may not be separated sufficiently for quantification as outlined above. It may not even be possible to visually locate individual peaks if their energies are similar or their intensity is too low in relation to other γ-rays present in the spectrum. Complex mixtures of as many as 10 to 20 radionuclides can be quantified mathematically with computer programs using linear least squares techniques.

When using these techniques, care should be given to the following parameters.

A. System gain and zero energy channel.

The exact gain and zero energy channel of the spectrometer must be monitored and recorded. If the computer analysis program performs gain and/or baseline (zero energy channel) corrections on sample data, then the library of standards data must be obtained under uniform and precise calibration conditions.

B. Library standards.

The least squares analysis technique is a linear combination of all of the data contained in the standards library. Therefore, the standards library must contain a spectra of every component in the sample; in addition, these spectra must be obtained from the purest radionuclides available.

C. Counting of library standards.

All γ-ray spectra will contain a background component. The activity of the library standards must be high enough so that this background component will be insignificant, even though all computer programs make some kind of a background correction.

The duration of the counting period for the standard library spectra should be long enough to obtain statistically valid data, but it should be short enough so that analyzer gain and baseline drifts are insignificant.

The activity of the library standards should be chosen so that the counting rates of the predominant photopeaks are all about the same.

A very important data evaluation technique to be used with a least squares program is a superimposed plot of the original sample data and the computed spectral data. A plot of residuals (the difference between the original and computed spectra) is also very important. The residuals plot is very sensitive to errors that are caused by omitting radionuclides present in the sample from the library standards.

SAMPLE MEASUREMENTS

After the spectrometer system has been set up, the energy calibrations performed, and individual pulse-height spectra for nuclides expected to be present in samples are obtained, then the unknown specimens can be measured and quantified.

Following the general concepts of quantitative analytical chemistry, transfer the sample to the specimen container and position it in the same manner as was done during system calibration. Measure the sample for a period of time long enough to acquire a γ-ray spectrum which will meet the minimum acceptable counting uncertainty.

COMPUTER CALCULATIONS

WLSQ is an EML least squares Fortran computer program that can be run on a VAX or IBM-compatible PC to resolve complex spectra.

Systematic uncertainties include, but are not limited to: reproducibility of sample position, peak analyses, decay calculations, background substraction, pulse pile up, cascade summing operations, and self-absorption corrections.

The uncertainty obtained from the least squares analysis can be substituted for the uncertainty in counting and should be included to obtain an overall uncertainty of the analysis. The uncertainties obtained from the least squares analysis are the square roots of the diagonal elements of the inverse matrix used to solve the linear set of simultaneous equations representing the sample spectra.

QUALITY CONTROL

The following quality control procedures are required so that the γ-ray spectrometers maintain their energy calibrations. In addition, the systems are to be monitored so that degradation in performance will be noticed as soon as possible.

A. Daily calibration checks.

The energy calibration of each Ge γ-ray detector is determined daily with a mixed nuclide source consisting of ^{241}Am and ^{60}Co.

In order to maintain an energy calibration of 0.5 keV/channel, count the Am-Co source to obtain well-defined peaks. The 59.5 keV γ-ray line from ^{241}Am should fall in channel 119. The 1332.5 keV γ-ray line from ^{60}Co should fall in channel 2665.

If the ^{241}Am and ^{60}Co peaks do not fall in the correct channels, first adjust the DC offset of the amplifier so that the 59.5 keV γ-ray line falls in channel 119. Then adjust the fine gain of the amplifier so that the 1332.5 keV γ-ray line falls in channel 2665.

Recount the Co-Am calibration standard to verify the peak positions and readjust the amplifier if necessary.

The energy calibration of each NaI(Tl) γ-ray detector is determined daily with a nuclide source consisting of ^{207}Bi.

In order to maintain an energy calibration of 10 keV/channel, count the ^{207}Bi source to obtain well-defined peaks. The 570 keV γ-ray line should fall in channel 57. The 1064 keV γ-ray line should fall in channel 106.

If the ^{207}Bi peaks do not fall in the correct channels, first adjust the DC offset of the amplifier so that the 570 keV γ-ray line falls in channel 57. Then adjust the fine gain of the amplifier so that the 1064 keV γ-ray line falls in channel 106.

Recount the ^{207}Bi calibration standard to verify the peak positions and readjust the amplifier if necessary.

B. Weekly efficiency calibration and resolution checks.

Each week the same ^{137}Cs calibration standard is counted, recorded, analyzed, and the date is entered into a permanent data base for each γ-ray spectrometry system.

Count the ^{137}Cs calibration standard in the same manner as unknown samples. Record the data for permanent storage and perform the usual data reduction analysis.

Enter the results of the analysis (Bq) and the resolution of the ^{137}Cs peak (full width at half maximum in keV) in the γ-quality control data base.

Report any deviation from the expected values before samples are analyzed. If remedial action is necessary, the cause and solution of the problem must be recorded in the laboratory logbook. A complete recalibration must be performed if any remedial actions have been taken.