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ABSTRACT

The equations necessary for determining the plutonium and ^{241}americium content of samples from alpha- and gamma-counting data are presented. Corrections for alpha absorption, background, detector efficiency, and coincident alpha counts are all considered. An empirical determination of the alpha-specific activity for different types of plutonium based on historical data is presented. Finally, a program written in the Visual Basic language to perform these calculations is also described.

INTRODUCTION

The Analytical Chemistry Group's Radiochemistry Team at Los Alamos National Laboratory (LANL) is responsible for certifying liquid waste for disposal and for determining the plutonium and ^{241}americium (hereafter americium) content of samples for programs, i.e., defense and heat source programs. To ensure quality and to expedite reporting results, a FORTRAN program was written in 1960 to perform data calculations and prepare final reports for customers. More recently, in 1993, G. Matlack wrote the program RC.EXE using Quick Basic. Other programs by D. Vance (Menu129.EXE, Quick Basic, 1995), P. Brug (Rad Calc for Windows,Visual Basic, 1995), and J. Willerton and A. Wong (Rad Calc II, Visual Basic, 1996) were written to meet new customer needs and to improve the quality of the programs.† Rad Calc II was the first attempt to replace all of the above calculation programs by combining them in a single window-based program. Rad Calc III was designed to improve the calculation programs

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† The programs written before Rad Calc III were not formally documented.

that support the Radiochemistry Team. The purpose of this report is to document the equations and methods used in this latest radiochemistry calculation program.

Waste Disposal Certification

Aqueous waste solutions from the LANL Plutonium Facility (TA-55) are analyzed for alpha activity and certified before the liquids are discharged to the Waste Water Treatment Plant at TA-50. The task of determining the alpha activity of these waste solutions involves determining the gross alpha count rate for an aliquot of the waste sample using a gas proportional counter or a liquid scintillation counter. Corrections for detection efficiency, background, and any dilutions are made; the count rate is converted to curies; and the alpha activity of the waste solution in curies per liter is reported. The final step is to compare this activity with the disposal limit of the appropriate waste stream. The disposal limits for industrial, acidic, and caustic waste lines are 5.0×10^{-7}, 6.0×10^{-5}, and 4.5×10^{-3} Ci/L, respectively [1].

Plutonium and Americium Determinations

The Rad Calc III method for determining a sample's plutonium and/or americium content involves direct alpha and/or gamma measurements. The basis of the analysis is the simple equation

$$\alpha = BR \times \frac{\ln 2}{t_{1/2}} N \quad ,$$

where

α	=	the alpha emission rate,
BR	=	the alpha branching ratio, and
N	=	the number of atoms with half-life, $t_{1/2}$, along with an analogous equation for gamma emission.

Samples consisting only of plutonium are relatively simple to analyze, because a determination of the plutonium content only requires solving the above equation for N. In practice, it is more complicated because the constituent isotopes of plutonium each

have a different half-life and their mass abundance varies with material type. This complication is discussed below in the paragraphs on determining specific activity in the Calculations section.

Samples consisting of only americium are straightforward because their analysis only requires solving a single equation for the americium content. In the case of americium, however, the analog equation for the gamma count rate rather than the alpha equation is used because emission of the 59.5-keV gamma is a distinctive signature of americium.

Mixtures containing both americium and plutonium add the complication that the alpha count rate has contributions from both actinides as does the gamma count rate. Therefore, to determine the sample's composition, one must measure both the total gamma and total alpha count rates and solve the two equations simultaneously for the plutonium and americium concentrations. In such an instance, one must use care to ensure that the plutonium contribution to the gamma count rate has been determined by the same type of detector as the one used in the analysis. Because of the drastic difference in resolution between a germanium and sodium iodide detector, the width of the acceptance window around the americium 59.5-keV gamma ray is generally quite different from that of the sodium iodide detector, resulting in different contributions from plutonium to the total gamma count rate measured in the different detectors. The Radiochemistry Team has chosen to use automatic sodium iodide detectors rather than germanium detectors for routine analyses because the former are less expensive, easier to maintain, and were available earlier than germanium detectors.

The analysis described herein and incorporated in Rad Calc III assumes that the alpha and gamma activity of a sample results solely from the presence of plutonium and/or americium. Consequently, this method is not applicable to samples containing significant amounts of uranium or other radionuclides.

The equations for the waste alpha activity and plutonium and americium concentrations are presented in the Calculations section following descriptions of the various corrections in the count rates that must be taken into account. The Rad Calc III section then discusses a number of the useful although not inherently critical features of the current radioanalysis calculation program.

CALCULATIONS

Background and Efficiency Corrections

Several corrections must be made in the count rates before they can be used to calculate anything meaningful. The two most obvious of these are the detector background and efficiency corrections. The background correction simply involves measuring the background count rate for a particular detector and subtracting the current background count rate from the measured count rate.

In principle, the detector efficiency correction converts the number of detected counts to the number of emitting events that occurred during the counting interval. Therefore, the efficiency correction consists of dividing the count rate by the detector efficiency after the background has been subtracted. For historic reasons, the efficiency correction used in these applications converts the number of detected alpha or gamma counts to americium disintegrations rather than the number detected per alpha or gamma emission. Therefore, the efficiency corrections implicitly incorporate the americium branching ratio. To compensate for this, the plutonium-specific activities used in these calculations implicitly contain the plutonium-to-americium branching ratios, and the americium-specific activities omit the americium branching ratio. Because the americium branching ratio for alpha emission is 100%, the implicit factor reduces to the plutonium branching ratio, and consequently the plutonium-specific activity for alpha emission is what one would expect. However, the plutonium-specific activity for gamma emission used in these calculations and described throughout this text contains the ratio of the plutonium-to-americium branching ratios for gamma emission. Although this approach may confuse some readers, it is used because these procedures and empirical specific activities were developed before the plutonium and americium branching ratios were known precisely. The equations contained herein allow the branching ratios to be combined with other things as measurable quantities, thus avoiding the explicit use of what were at the time uncertain constants.

Coincidence Correction

Perhaps a less obvious but necessary correction is the coincidence correction of the alpha counter. This correction is based on the fact that when two alpha particles reach the gas proportional counter at the same time or the second one arrives before the electron avalanche has been quenched, the two events are recorded as a single event. Because the probability of these coincident events increases with count rate, the importance of this correction also increases with count rate. Commercially available automatic alpha counters incorporate such a correction themselves but the correction must be applied to the manual alpha counters that were designed and built at Los Alamos [2].

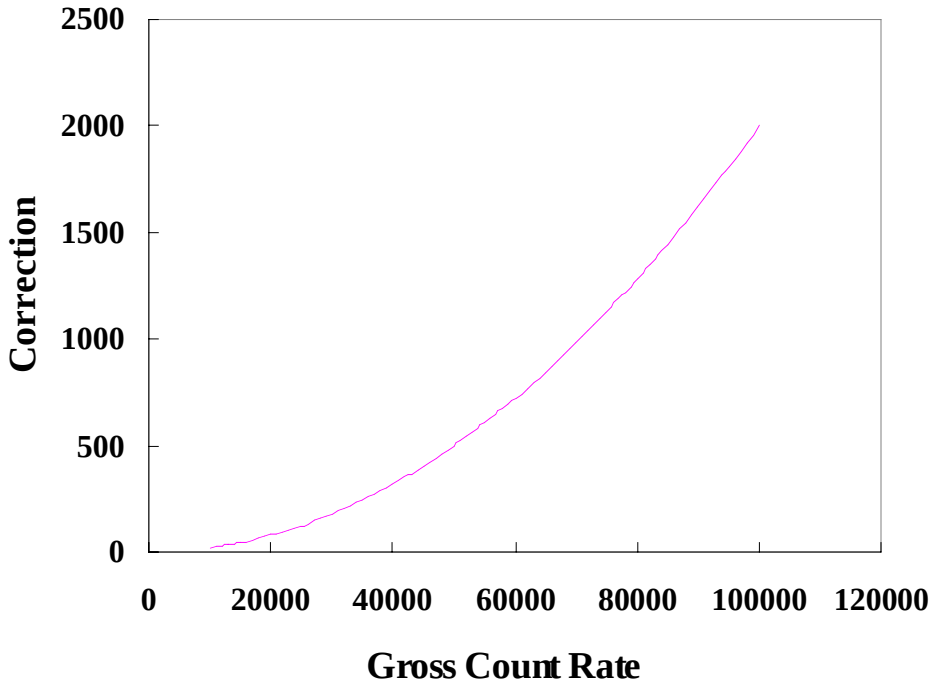

Figure 1. Measured coincidence correction needed for manual alpha counters of the LANL design [2].

Experiments with split sources have shown[‡] that for count rates below 10,000 counts per minute (cpm) no coincidence correction is needed because it would represent a correction of much less than 0.5%. The following equation, which is displayed as the curve in Figure 1, represents the fit to the determined coincidence corrections and is used to correct count rates for coincidence.

$$CAVGA_{(cpm)} = AVGA_{(cpm)} + \left(\frac{AVGA_{(cpm)}}{100{,}000} \right)^2 \times 2000 \quad ,$$

where

CAVGA	=	the coincidence-corrected count rate and
AVGA	=	the average alpha count rate before coincidence correction.

Absorption Correction

Alpha particles have very short ranges, and virtually any substance between the alpha-emitting atom and the detector will cause enough absorption of alpha particles to require a correction. Alpha counting involves placing an aliquot of the sample on a plate, allowing the solvent to evaporate, and then counting the alpha activity emitted by the residue. In the case of samples with dissolved salts or inhomogeneous suspensions, the residue on the plate can be sufficient to absorb some of the alpha particles before they can be detected. Experimental data [3] show that the percent of alphas absorbed by the salt, ABS, follows the equation

$$ABS = -0.0008 \times SALT^2 + 0.1774 \times SALT \quad ,$$

where SALT denotes the residue on the plate in micrograms.

Figure 2 displays this relationship between alpha absorption and the amount of salt residue left after evaporation. The measured alpha count rates are corrected for alpha

[‡] Private communication with George Matlack and John Blackadar in fall of 1999.

absorption caused by the salt deposit. The amount of salt is determined through visual comparison with plates having standard salt loadings. The percent of alphas absorbed is converted to a decimal and then subtracted from 1 in the plutonium determination equations below to determine the fraction of alphas that are transmitted through the salt layer on the plate.

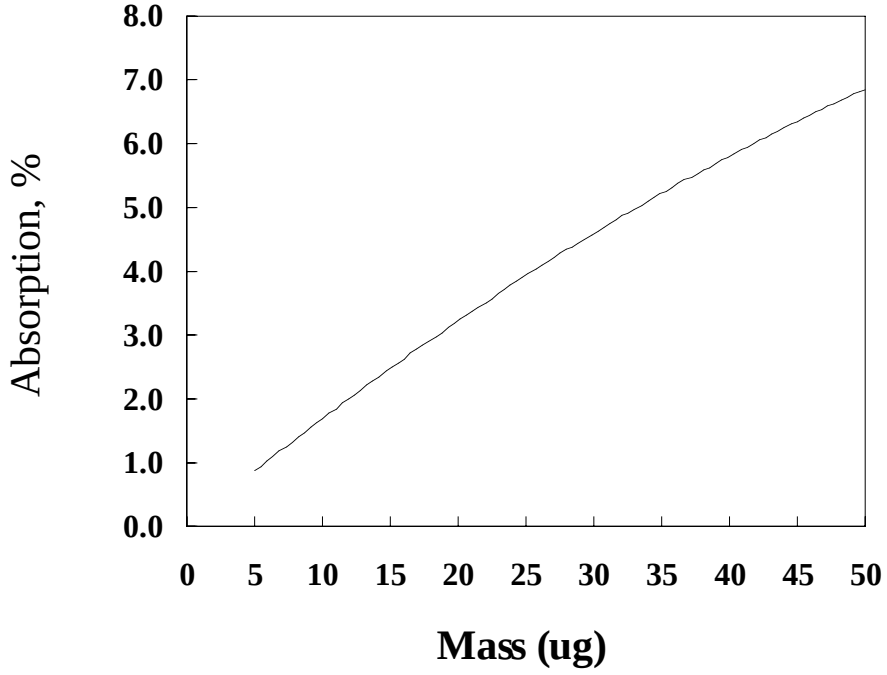

Figure 2. Measured absorption of alpha particles as a function of amount of salt residue [3].

Determining Specific Activity

As mentioned above, the process for obtaining the value for plutonium- (alpha-) specific activity is somewhat complicated. If the plutonium's isotopic composition in the sample is known, the alpha-specific activity of plutonium may be calculated directly as described in the Rad Calc III section below. However, more often, the isotopic composition is not well known and an alternate approach to determining the specific activity must be sought. Figure 3 shows the alpha-specific activity of 223 samples of plutonium obtained from 1975 to 1978. The alpha-specific activity was calculated based

on mass spectrometry data. The following second-order polynomial (shown as the curve in the figure) represents the best fit to the data.

$$SAPA = 4.0156 \times 10^{8} \times (\%Pu240)^{2} + 2.0005 \times 10^{7} \times (\%Pu240) + 1.51791 \times 10^{11} ,$$

where the alpha-specific activity of plutonium in disintegrations per minute per gram (dpm/g), SAPA, is based on the percent of ^{240}Pu in the plutonium [4]. The percent of ^{240}Pu in these samples ranged from 5.1% to 9.2%. Although there is some scatter in the data, the curve does a remarkable job of reproducing the alpha-specific activity of plutonium without knowing complete information on the isotopic composition of each individual plutonium sample. Although the isotopic content of each sample depends on the reactor irradiation conditions under which the plutonium was produced and the age of the plutonium sample, an estimate of the percent ^{240}Pu is generally available.

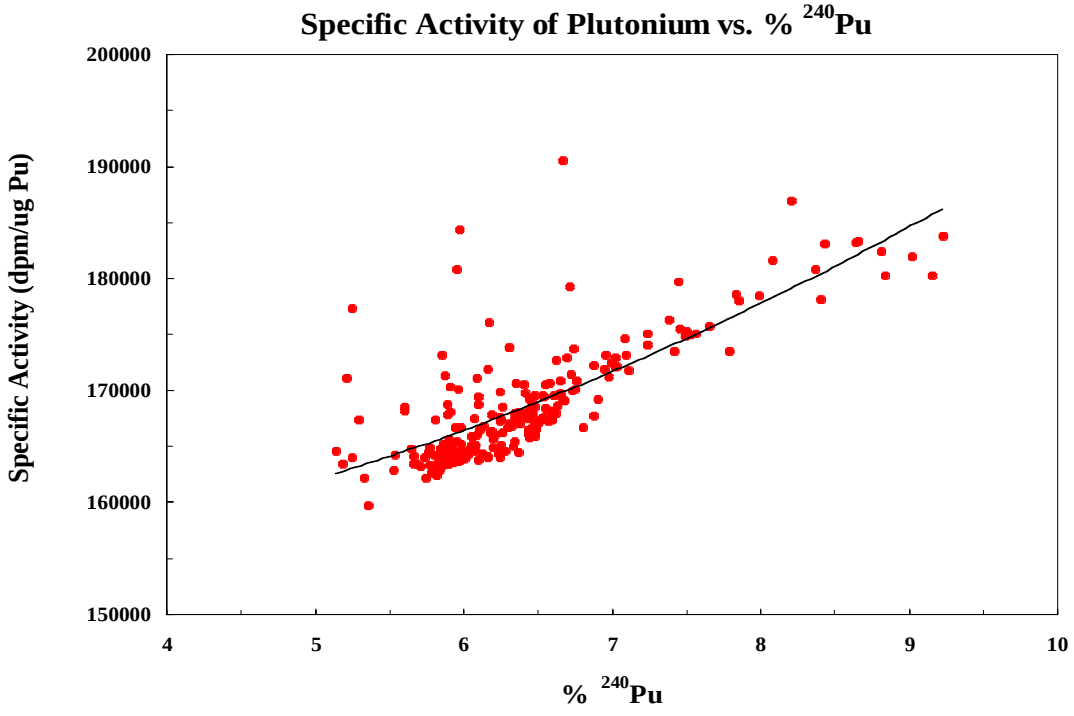

Figure 3. Alpha-specific activity of plutonium samples from 1975 to 1978 (points) and a fit to these data (curve) [4].

To the above data set, 56 additional samples from 1995 with percent ^{240}Pu ranging from 5.7% to 12.4% were added, and the combined data set was fit with another second-order polynomial. The resulting equation was compared with the first and found to agree to within 1% for values of ^{240}Pu ranging from 4.7% to 9%. Because of the limited amount of sample data containing high percentages of ^{240}Pu, Rad Calc III will not use the above equation for samples containing more than 10% ^{240}Pu. Even with the uncertainty introduced by this procedure, the total uncertainty in the final plutonium or americium concentration is estimated to be less than about 5%.

The corrected count rates used in the following equations are obtained by applying the above corrections. First, the coincidence correction is applied (when necessary), then the background correction is made (when necessary), and finally the detection efficiency correction is applied to the counting data.

Waste Disposal Calculation Equation

The alpha activity of aqueous waste samples, which is needed for determining the appropriate means of disposal, is calculated according to

$$WA = AVGA \times \frac{1}{DA \times 10^{-6}} \times DF \times \frac{1}{2.22 \times 10^{12}_{(dpm/Ci)}} \ ,$$

where

WA = waste activity in curies per liter.

AVGA = average corrected (coincidence, background, and efficiency) alpha count rate in disintegrations per minute.

DA = the size of the counted aliquot in microliters.

DF = the dilution factor = $\frac{DV}{AL \times 10^{-3}}$,

where

DV = dilution volume in milliters
AL = undiluted sample aliquot size in microliters.

The final term in the above equation is the factor that converts the count rate to curies. In cases where the waste sample need not be diluted, the dilution factor is simply omitted from the equation.

Plutonium Only (No Americium) Determination Equations

The corrected alpha count rates can also be used to calculate the plutonium concentration and total plutonium for samples containing no americium when the following equations are used:

$$CPu = \frac{AVGA}{1 - \frac{ABS}{100}} \times \frac{1}{DA \times 10^{-6}} \times DF \times \frac{1}{SAPA} \ ,$$

$$TPu = CPu \times TSV \times 10^{-3} \ ,$$

$$Pu = \frac{TPu}{SM \times 10^{-3}} \ ,$$

where

CPu	=	concentration of plutonium in grams per liter.
ABS	=	percent of absorption due to salt.
SAPA	=	specific activity constant for plutonium alpha based on percent ^{240}Pu or plutonium S.A. entered by the user in disintegrations per minute per gram.
TPu	=	total amount of plutonium in grams.
TSV	=	total sample volume in milliliters.
Pu	=	total amount of plutonium in sample in grams per gram.
SM	=	sample mass in milligrams.

Other variables are as defined previously. The dilution factor is again equal to 1 if no dilution is made.

Americium Only (No Plutonium) Determination Equations

The following equations calculate the americium concentration and total americium in samples that have no plutonium using gamma-counting data that have been corrected for detection efficiency:

$$CAm = \frac{1}{AT \times 10^{-3}} \times \frac{AVGG}{SAAG} \times DF \ ,$$

$$TAm = CAm \times TSV \times 10^{-3} \ ,$$

$$Am = \frac{TAm \times 10^{6}}{SM \times 10^{-3}} \ ,$$

where

CAm	=	concentration of americium in grams per liter.
AT	=	the size of the aliquot counted in the tube in milliliters.
AVGG	=	average corrected (efficiency) gamma count rate in disintegrations per minute.
SAAG	=	specific activity constant for americium gamma = 7.61×10^{12} disintegrations per minute per gram.
TAm	=	total amount of americium in grams.
Am (ppm)	=	total amount of americium in sample in micrograms/gram.

Other variables are as defined previously. Again, the dilution factor is equal to 1 in cases where no dilution is needed.

Plutonium and Americium Determination Equations

The following equations are used for samples containing both plutonium and americium. As discussed in the Introduction, they arise from simultaneously solving equations for the total gamma and total alpha count rates.

$$CPu = DF \times \frac{\frac{AVGG}{(AT \times 10^{-3}) \times SAAG} - \frac{AVGA}{(1 - \frac{ABS}{100}) \times (DA \times 10^{-6}) \times SAAA}}{\frac{SAPG}{SAAG} - \frac{SAPA}{SAAA}} \quad ,$$

$$TPu = CPu \times TSV \times 10^{-3} \quad ,$$

$$Pu = \frac{TPu}{SM \times 10^{-3}} \quad ,$$

$$CAm = DF \times \frac{\frac{AVGG}{(AT \times 10^{-3}) \times SAPG} - \frac{AVGA}{(1 - \frac{ABS}{100}) \times (DA \times 10^{-6}) \times SAPA}}{\frac{SAAG}{SAPG} - \frac{SAAA}{SAPA}} \quad ,$$

$$TAm = CAm \times TSV \times 10^{-3} \quad ,$$

$$Am = \frac{TAm \times 10^{6}}{SM \times 10^{-3}} \quad ,$$

$$\%Am = \frac{CAm \times SAAA}{\frac{AVGA \times DF}{(DA \times 10^{-6})}} \times 100 \quad ,$$

where

SAAA, SAPG	=	specific activity constants:
AAA (for Am alpha)	=	7.61 x 10^{12} disintegrations per minute per gram.
SAPG (for plutonium gamma)	=	1.51 x 10^{8} disintegrations per minute per gram.
%Am	=	percent of total alpha activity from ^{241}Am.

Other variables are as defined previously. As was true for the above equations, the dilution factors are equal to 1 in cases where no dilution is made. It is worth reiterating that the above specific activity constant for plutonium gamma (SAPG) is applicable only to sodium iodide detectors set to measure the 59.5-keV americium gamma ray transition (~40 to 80 keV).

Plutonium extractions using TTA (2-thenoyltrifluoroacetone) in which the plutonium is separated from the americium in solution are calculated as separate analyses. The volume of the organic solvent (the phase containing the extracted plutonium) is used as the dilution volume for the plutonium in the above plutonium by dilution equations. The aqueous phase is treated as an americium by dilution analysis using the equations given above.

RAD CALC III

The program Rad Calc III was developed to perform the above calculations, to submit the results to the LANL Laboratory Information Management System (LIMS), and to provide hard-copy output of the analytical results for the sample's submitter. Rad Calc III is written in the Visual Basic 4.0, 16-bit development language and uses customized data entry and results screens and the code necessary to support the forms and perform the required operations.

In addition to the radiochemistry calculations and file management functions, such as saving, printing, and opening files, which constitute most of the program's computer code, several peripheral features are included. The most important of these is the feature that allows the program to submit the results directly to the LIMS. This feature writes the results to a comma-separated variable file that conforms to the current LIMS radiochemistry template for the particular type of analysis being performed. After the reviewer submits the proper LIMS user name and password, the file is transferred to the LIMS for processing.

Another useful feature of the program is the ability to calculate the alpha-specific activity of plutonium when the isotopic composition of the sample is known. This module uses the mass percents of each isotope of plutonium entered by the user to

calculate a mass-weighted average of the alpha-specific activities for each of the plutonium isotopes. The alpha-specific activities for each isotope are calculated according to the following equation:

$$SA = \frac{\ln(2) \times N_A}{t_{1/2} \times M} \times BR \ ,$$

where

SA = the alpha-specific activity of the isotope,
N_A = Avogadro's number,
$t_{1/2}$ = the isotope's half life [5],
M = the atomic mass of the isotope [6], and
BR = the alpha branching ratio for the isotope (in most cases 100%).

Calculation of the alpha-specific activity in this way is more accurate than the estimation of the specific activity using historic data described above in the Calculations section.

Rad Calc III also contains a module that determines whether a measured value that does not appear to be consistent with other measurements of the same quantity can be discarded with 90% confidence. This calculation uses the Q test described by Dean and Dixon [7]. The ratio of the difference between the questioned value and the value closest to it (the gap) to the difference between the minimum and maximum values in the data set (the range) is calculated. This ratio is then compared with the standard Q value for the number of observations in the data set at the 90% confidence level. When the ratio is greater than the standard value, the program returns "Yes," indicating that the questioned value may be discarded; otherwise, it returns to "No."

CONCLUSIONS

We have described simple algebraic expressions to correct for the absorption of alpha particles in salt residue, the count-rate-dependent coincidence of alpha particles in manual alpha counters, and the estimation of the alpha-specific activity of plutonium in samples for which complete isotopic information is not available.

We have also discussed the program, Rad Calc III, which performs the repetitive and complicated calculations necessary to determine the alpha activity of waste samples and the plutonium and americium concentrations of samples containing either or both actinides. The analysts need only enter the sample information (sample ID, date, comments, etc.), the sample preparation information (sample volumes, dilution volumes, etc.), the counting information (volume counted, count rate, amount of salt, etc.), and the detector information (efficiency and background). Rad Calc III uses the entered data to determine all necessary information, or it prompts the analyst to enter any necessary information that has not been supplied. After completing the calculations and approving the results, a reviewer can submit the results directly to LIMS.

ACKNOWLEDGMENTS

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