

**Technical Notes for EPA Method 900.0 —
Gross Alpha and Gross Beta Radioactivity in Drinking Water**

1. Scope and Application

- 1.1 The current regulation that stipulates acceptable methods is 40 CFR 141.25 and the limit on gross alpha and gross beta radioactivity is 40 CFR 141.26.
- 1.2 The method is intended to act as a general screening tool to assess if further investigation into activity of specific radionuclides is warranted.

The minimum energy limits of the alpha and beta particles relate to self-absorption of lower energy emissions by the sample itself. Although the method is approved for alpha emitters and mid-to-high energy beta emitters, there are some limitations. Alpha emitters and mid-range energy beta emitters will be significantly attenuated in samples containing dissolved or suspended solids. Thus sample self-absorption calibrations are necessary to minimize bias for these radionuclides. Samples containing radionuclides of maximum beta particle energy less than 100 keV, like ^{63}Ni , ^{210}Pb , ^{228}Ra and ^{241}Pu , cannot be effectively screened using this method. For these low energy beta emitters a screening technique employing liquid scintillation would be much more effective if these radionuclides are of potential concern

- 1.2 Note that the NIPDWR requirements referenced in the method scope have been superseded by recent regulations. Current requirements for drinking water compliance testing are found in the most recent revision of 40 CFR 141. At the time of this writing, the Maximum Contaminant Level (MCL) for Gross Alpha is 15pCi/L and for gross beta is 50 pCi/L with specific cautions for each that are administrative in nature and are outside the scope of this document. The Required Detection Limit (RDL) for gross alpha is 3 pCi/L and for gross beta is 4 pCi/L. The technical derivation of this detection limit is provided in section 9 of this document.
- 1.3 – 1.7 The limit on the total mass of solids that can be deposited on a 2 inch planchet is necessary to minimize corrections for the effects of sample self-absorption of the alpha and beta particles emitted from radionuclides in the sample. This value is 100 mg for gross alpha and 200 mg for gross beta and assumes that the mass is evenly distributed on a 2-inch planchet.

Laboratories should make efforts to assess the maximum volume of water that can be used for this analysis prior to making any radiochemical measurements. This will prevent exceeding the maximum allowable masses saving time and effort by the laboratory staff. No guidance is provided in the method on how to perform this estimate of sample volume. However, two straightforward and easily performed methods are identified here:

- Evaporate an aliquant of the sample into any vessel that can be easily dried and weighed (similarly to how the final drying is performed in the actual analysis). Based on the dried weight calculate a maximum volume that will not exceed 100 mg for gross alpha

analysis. As an example, if 5 mL of water were evaporated yielding 2.5 mg of solids, the maximum volume of water that could be used is $(100 \text{ mg}/2.5 \text{ mg})(5 \text{ mL}) = 200 \text{ mL}$ of sample.

- Using a conductivity meter and a conversion scale for micromhos/cm to ppm (mg/L) CaCO_3 estimate the total solids loading for a given volume in an unpreserved portion of the sample. For example, a certain conductivity meter is calibrated at 1 micromho/cm per 3 ppm of calcium carbonate (0.33 micromho/cm/ppm). A sample having a conductivity of 300 micromho/cm would have a solids loading of 900 mg/L. Thus the maximum volume of sample that could be used would be estimated at 111 mL.

It is important to note that these would only be estimates and that the final determination of the mass would still need to be performed on the aliquant of sample that was evaporated and counted.

It has been established that a volume of water that yields no more than 100 mg of solids may be used to perform gross alpha analysis and for gross beta analysis the limit is 200 mg. The absorption of alpha particles is more significant than for that of beta particles and the value of 100 mg is often the limiting factor in determining how much volume can be used when simultaneous gross alpha beta is performed.

- 1.8 The evaporation technique used in the method does not accommodate those radionuclides that potentially are volatile as nitrates at 105 °C, or those radionuclides that may be volatile (such as tritium, iodine, carbon and technetium).

Some metals form hygroscopic salts with nitric acid that cannot be easily dried prior to their being cooled and counted. The term “hygroscopic” means that the material can readily absorb moisture from the atmosphere. This will be noted when attempting to bring the planchet to constant weight and the weight of the sample continues to increase. In these instances, the planchets may be flamed until a dull cherry red color is imparted to the planchet for a few minutes (this corresponds to a temperature range of 500 °C to about 800 °C). At this temperature, nitrates will usually be converted to oxides that are not hygroscopic. After flaming of the planchet, the final mass on the planchet needs to be re-determined (to correct for sample self absorption) and should not exceed 100 mg.

At 500–800 °C, it is possible to lose some radionuclides regardless of their chemical state or that imparted to the radionuclide by its matrix. Samples containing polonium, lead, and cesium may sustain losses at these temperatures.

- 1.9 Drinking water samples with high levels of solids will prove to be challenging for this technique as the solids will contribute significantly to self-absorption of the alpha and beta particles prior to reaching the detector. An alternate method, *Gross Alpha Screening* (EPA Method 900.1), first precipitates BaSO_4 in an attempt to reduce the amount of soluble salts, and limiting the mass of precipitate. This alternate method however, assumes that the bulk of the alpha emitters are radium related and will coprecipitate with barium. This may not always be the case, and the results of the Methods 900.0 and 900.1 may not give

comparable values. The tables in 40 CFR 141 suggest alternate screening methods for high solids samples that are acceptable (such as SM 7110C).

The alternate method for *Gross Alpha Screening*, 900.1, is meant for total radium isotopes in water with high dissolved solids. Method 900.1 (and others identified in 40 CFR 141) is recommended if the sample has solid loading of >500 ppm.

2 Summary of the Method

The method is very straightforward and does not require any chemical separations. An appropriately sized aliquant of the sample is verified to have a pH less than 2.0, or have its pH adjusted to less than 2.0 using nitric acid. The nitric acid is added to volatilize chlorides during sample evaporation. The sample is reduced in volume to the point where it can be transferred to a stainless steel planchet and evaporated to a dry solid. After verifying that the sample is dry (i.e., at constant weight), it is counted 72 hours after evaporation on a gas proportional counter for gross alpha and gross beta analysis. However, gross beta count can be made any time after planchet preparation. The flow of the overall sample processing is depicted in Figure 1.

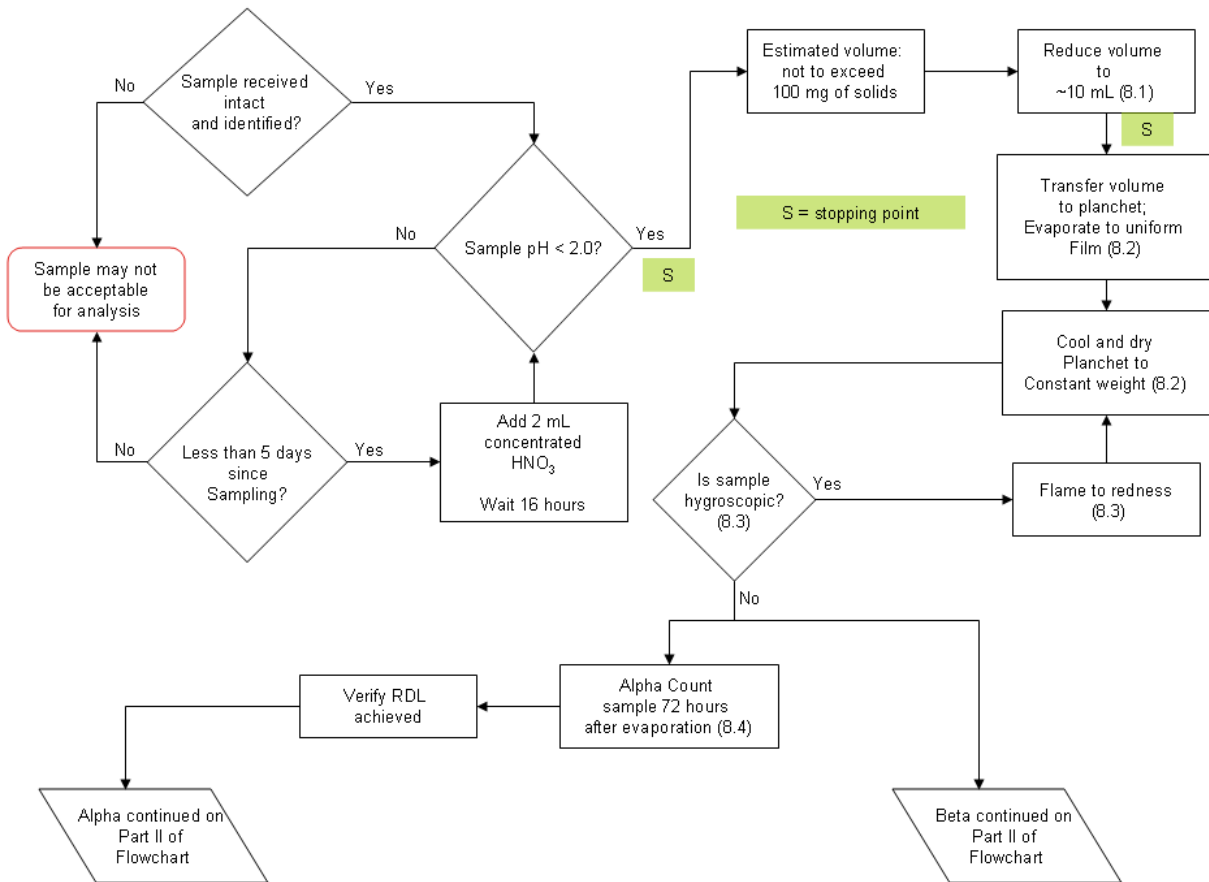


Figure 1a. Sample Processing Flow for Gross Alpha and Gross Beta Analysis

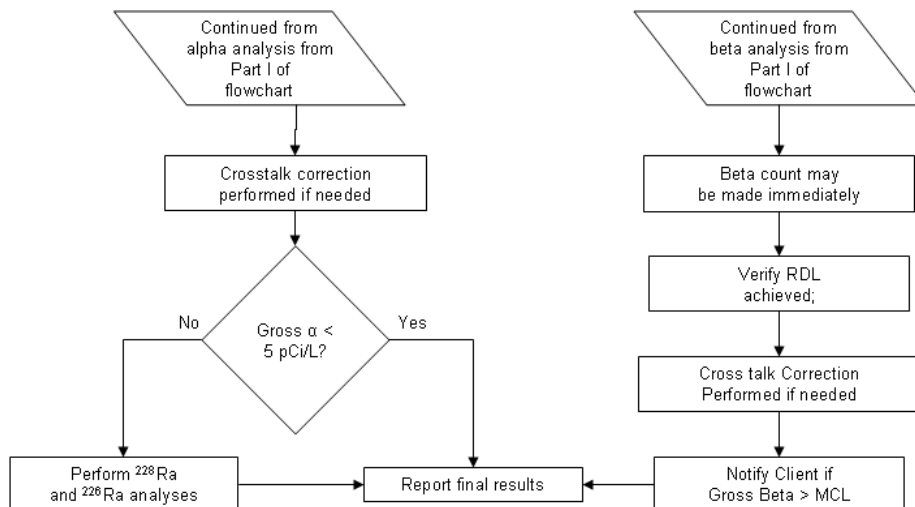


Figure 1b. Sample Processing Flow for Gross Alpha and Gross Beta Analysis (Continued)

The term “constant weight” means that the residue on the planchet must be *dried and weighed* at least *twice*. The temperature of the oven is at 105 °C in order to drive off waters adsorbed onto the surface of the solid residue. Drying at 105 °C neither removes waters of hydration, nor changes the chemical form of potentially hygroscopic salts so they do not readily absorb atmospheric moisture. In between the first and second drying and weighing cycle, the planchet should be placed in a desiccator to cool and prevent re-absorption of water. For many solids, the slope of the self-absorption curve is on the order of 0.2% per milligram of solids. Water will have a smaller self absorption as it has a lower average Z (atomic number) value than any solids. Thus a good estimate of constant weight would be when the change in the mass measured between successive weighings is no greater than 2 mg (less than about 0.4% of self absorption). Should the first two cycles not yield values that are near this weight loss, additional drying and weighing cycles should continue until the value of 2 mg is approached. It is important to note that “constant weight” is determined after samples have been stored in a desiccator. The samples may quickly reabsorb ambient moisture, however, when they are removed from the desiccator for counting. For this reason, if constant weight cannot be achieved by heating at 105 °C, more aggressive heating may be required so that the chemical form of the salt causing the inconstant weight can be altered. This may require that the sample be heated in a flame to about 900 °C (usually considered “cherry red”).

Efficiency curves for alpha and beta activity must be determined based on varying the mass of solids for a given radionuclide activity. This plot of efficiency vs. mass of deposited solids is then used to determine the efficiency for each sample based on its mass of deposited solids. For these efficiency curves it is important to note the following:

- The areal density and mass distribution of the sample should match those of the calibration standards.
- The planchets used for the calibration standards and the samples are *identical* in size, shape and characteristic form (e.g., flat versus ridged bottom).

3 Sample Handling and Preservation

Sample preservation and the verification that this has been successfully achieved are an important requirement to this method. The preservation technique for this method uses enough nitric acid to bring the pH of the sample to less than 2.0. This prevents precipitation of not only the radionuclides but also other metals that may be in the sample that may coprecipitate the radionuclides.

A sample that is received more than 5 days after sampling and does not have a pH less than 2.0 will not be acceptable for analysis. This is because hydroxides of trace metals in the sample, including the radionuclides of interest, can precipitate and irreversibly adhere to the container walls. This would be a loss of analyte prior to analysis leading to a non-conservative estimate of the gross activity.

Simply adding 15 mL of concentrated nitric acid may be insufficient to lower the pH to less than 2.0 for drinking waters that have high concentrations of calcium and magnesium.¹ This volume of added nitric acid also does not account for the sample size; it is assumed the sample size is 1 liter. If your sample size is different the added nitric acid should be proportionally larger or smaller. Even though acid has been added, it is necessary to check the sample pH upon receipt. If not less than 2.0, add acid in 15 mL increments, equilibrate the sample by shaking and check pH again. Once the pH is less than 2.0 the sample must be allowed to equilibrate for 16 hours prior to analysis, and then the pH checked again ensuring it is less than 2.0. The reason for this waiting period is to ensure that all finely suspended materials or surface adsorbed materials have been solubilized. Should more than 30 mL of acid be added to reduce the pH to the appropriate value, consideration should be made for applying a volume correction factor.

The certification manual allows acidification with either nitric or hydrochloric acid. However if HCl is used, nitric acid should be added during the process of sample evaporation to ensure that all chlorides are removed via volatilization. Chlorides if present will rapidly corrode stainless steel planchets causing flowing solids of iron hydroxide, increasing the mass of the residue, and creating significant sample self absorption.

4 Interferences

Moisture associated by the sample residue may interfere with this method. The salts in the dried sample residues are frequently hygroscopic. When these salts absorb ambient moisture, the areal density of the residue, that is the mass of residue per cm² of source surface area, will change. Since the areal density affects the number of alpha or beta particles that reach the detector sensitive area, the accuracy with which the mass is known will limit the accuracy of self-absorption corrections applied to the counting results. Thus, it is important to consider whether the mass of residue as weighed corresponds to that present at the time of counting (see discussion of constant weight in Section 2 above).

¹ 15 mL of 16 M HNO₃ will reduce the pH of 1 liter of unbuffered, demineralized water from 7.0 to 0.6. Thus any chemicals in the water which react with acid will not achieve this low of a pH. Thus it is necessary to check the pH following the acid addition.

The counterpoint, dry samples that have obtained a static charge, may ionize the carrier gas in the gas proportional counting system yielding increased counts above the level of radioactivity that is actually present. Accumulation of static charge may occur when conditions of low humidity (<60% relative humidity) exist in the laboratory. If such conditions exist, the static charge may be successfully removed by connecting a small wire to a grounded metal structure and touching the planchet with the wire before counting.

Modern instruments can perform “simultaneous” alpha and beta counting (also termed “simultaneous counting” or “counting at the beta voltage”). These instruments separate counts into distinct “alpha” and “beta” channels by discriminating between the typical pulse sizes created by alpha and beta particles. Crosstalk² occurs when alpha decays are misclassified as beta counts and stored in the beta channel or when beta decays are misclassified as alpha counts and stored in the alpha channel. Alpha-to-beta crosstalk is generally ranges from one to two orders of magnitude greater than beta-to-alpha crosstalk. Although crosstalk cannot be eliminated when counting on the beta plateau, beta-to-alpha crosstalk can be minimized during set-up of the instrument. The intrinsic crosstalk of the detector can be minimized during instrument set-up by adjusting the alpha and beta discriminators.³ While minimizing crosstalk will also minimize corrections needed for most samples, keep in mind that if there is a significant difference in alpha and beta activities significant crosstalk may still be present. For example a gross alpha measurement of 5 pCi/L and a gross beta of 35 pCi/L may have significant crosstalk of beta into alpha that should be accounted for using crosstalk equations. In cases where unusually high ratios of beta activity to alpha activity are present in samples (e.g., effluents from a nuclear power plant or high levels of beta-emitting contaminants), determining the alpha activity of samples in a separate measurement from the beta by counting on the alpha plateau provides the most effective discrimination against beta-to-alpha crosstalk and the most accurate measurement of alpha activity in samples. Alpha-to-beta and beta-to-alpha crosstalk are accounted and corrected for by calibrating the instrument with standards of the pure alpha or pure beta emitters. The method and calculations for determining crosstalk are further explained in Section 9 of this Technical Note.

5. Apparatus

Ensure that the planchets used for sample preparation are identical to those used for efficiency calibration and background counts.

² In section 9.2.2 of Method 900.0, “alpha amplification factor” is used instead of crosstalk. The term “alpha amplification factor” is no longer used and has been replaced by the term crosstalk. If the beta count rate is significant, a beta-to-alpha channel crosstalk also may occur and may need to be accounted for by similar calculations.

³ Minimizing beta-to-alpha crosstalk to a fraction of a percent (e.g., to ~0.1%) during instrument set-up will minimize the absolute contributions to count activity to the alpha channel from beta activity in the sample. This minimizes the size of the crosstalk correction that is applied and optimizes the accuracy and uncertainty of the measurement. Note that access to discriminators varies by manufacturer and model of the instrument. Consult the operation manual and instrument manufacturer regarding specific capabilities and discriminator set-up of instruments.

6. Reagents

No comments

7 Calibration

The standard traditionally used for alpha activity was ^{241}Am . This standard had several advantages:

- It has a long half-life (432 years) and thus provides a very constant activity source.
- Its first progeny is ^{237}Np also has a long half-life (2.14×10^6 years). This is important because a 5% ingrowth of this alpha-emitting radionuclide will take about 200,000 years. Thus, it will not contribute to the total alpha activity.
- The ^{241}Am has an energy that is in between the naturally occurring radionuclides that are likely contaminants. Thus it provides a response that will be adequately representing either end of the alpha energy range.

Unfortunately ^{241}Am has the distinct disadvantage of having a 59 keV gamma-ray that creates a response in the beta channel.

However in 40 CFR 141, $^{230}\text{Th}^4$ is now recommended for this function since it is not only a long-lived alpha emitter but its energy better mimics the alpha particle energy of naturally occurring radionuclides, such as radium isotopes and their progeny. It also has the disadvantage of a low energy beta component associated with its internal conversion electron at 68 keV, plus miscellaneous low-energy gamma rays.

Because neither ^{241}Am nor ^{230}Th is a pure alpha emitter they both have their disadvantages. Although not permitted for calibration, ^{210}Po , a pure alpha emitter would be the best way to assess the potential crosstalk in the instrument just resulting from alpha.

The required calibration standard for beta channel is $^{90}\text{Sr}/^{90}\text{Y}$ that also has several advantages.

- Both have long half-lives (^{90}Sr is 29 years)
- ^{90}Sr is in secular equilibrium with ^{90}Y (half-life ≈ 2.67 days) in the source and thus the total activity is actually twice that of the documented source activity. The decay product for ^{90}Y is stable ^{90}Zr , thus adding no further activity.
- ^{137}Cs , which has been used at some laboratories as a beta reference, is in secular equilibrium with $^{137\text{m}}\text{Ba}$. The $^{137\text{m}}\text{Ba}$ is a gamma emitter and decays to its stable ground state. Thus there is no additional contribution to the activity.

For ^{90}Sr , it will be necessary to decay correct the standard to the date of the efficiency calibration.

⁴ Except for California, whose regulations require their laboratories to use natural uranium .

There are several suppliers of National Institute of Standards and Technology⁵ (NIST) traceable radioactivity standards. It is no longer required (or recommended) to purchase these standards directly from NIST or any other government agency.

The laboratory's tap water is the recommended matrix for use in preparing the efficiency standards so as to provide a residue matrix which is comparable to that of other drinking water samples to be tested. However, many labs now receive samples from a variety of regional areas where the water composition may be significantly different from their own. This means that the residue matrix and the calibration matrix may not necessarily match too well. A surrogate water matrix similar to one used for commercially available performance test samples may provide a more universal matrix that will be comparable among several laboratories. Another possibility would be to attempt to matrix match the calibration standards to the average concentrations of the common ions contributing to the water samples analyzed (e.g., calcium, magnesium, aluminum, carbonate, chloride, sulfate).

For the alpha self-attenuation curve the method has ²⁴¹Am as the standard. Remember that this is now changed to ²³⁰Th.

Residues for beta analysis can be as high as 200 mg because beta particles are more penetrating than alpha particles. Although beta counting can be performed with solid residues up to 200 mg of solids on a 2-inch planchet, alpha counting must be based on a sample with less than 100 mg of solids. This means that it may be necessary to prepare separate samples for gross alpha and gross beta analyses in order to achieve the required detection limit.

8 Procedure

The actual technique of reducing the volume can have a significant effect on the recovery of material from the samples. Nitric acid forms an azeotropic mixture with water and boils off as the water volume is reduced. Thus, during the process of volume reduction small aliquants of nitric acid should be rinsed down the sides of the evaporation vessel. This ensures three things will occur:

- The acidity of the sample will not decrease during the evaporation process;
- The radionuclides will not dry out on the container walls and be irreversibly adsorbed; and
- Any chlorides contained in the sample will be evaporated during the volume reduction process, because HCl is more volatile than nitric acid.

The method indicates that removal of chloride salts may take place when the sample is at the residue stage. However, removal of chlorides before they form salts on the planchet will prevent considerable problems later on when the final solution is evaporated on the planchet. An indication that not all chlorides have been removed will be a voluminous brown residue that does not appear to belong to the sample. In such cases, the sample should be re-prepared to remove residual chlorides prior to evaporation on the planchet. Evaporated sample residues should be deposited as uniformly on the planchet as possible.

⁵ NIST was formerly the National Bureau of Standards (NBS).

Step 8.4 of the method indicates that the beta counts can be made immediately but that 72 hours of in-growth is required for the alpha count after evaporation onto the planchet. The 72-hour waiting period does not have a very good technical basis. If the presence of ^{224}Ra is not considered, 72 hours (3 days) allows two things to occur:

- Decay of any unsupported progeny of ^{222}Rn , although it is likely that within 8 hours these should be decayed completely.
- Partial ingrowth of ^{222}Rn (and its supported progeny) from ^{226}Ra .

The actual ingrowth for full equilibrium of ^{222}Rn progeny occurs in about 21 days. In this respect the method does not provide the most conservative estimate of the true gross alpha or the gross beta activity.

If ^{224}Ra is present, the issue of ingrowth and decay is significantly more complicated, and is not easily accounted for in the 72-hour timeframe. However laboratories should be aware of the fact that some states impose specific regulations (beyond 40 CFR 141) with regards to ^{224}Ra and its progeny in drinking water.

No requirements exist for when gross beta counting may be performed. The limit for gross beta concentration is based on whether or not a water supply is “deemed vulnerable.” If a water supply has a gross beta value that exceeds the maximum contaminant level (MCL) it may be necessary to perform other analyses (e.g., ^{40}K by gamma spectrometry). However this decision lies with the water supply regulating authority. Thus values for gross beta of greater than the MCL should be communicated to the client so that if speciation of beta emitters is required the laboratory can be told how to proceed.

9 Calculations

The equations for activity calculation are relatively straight forward. The determination of the cross talk factor (alpha amplification factor) and its application to the gross beta activity must be done to accurately determine the final beta activity. It may be possible that high beta activity could lead to beta into alpha crosstalk that would affect the final alpha result. Thus a cross talk correction factor for this should also be determined. The best time to establish these crosstalk factors would be at the time of efficiency calibration and measurement of self-absorption correction factors.

If the alpha activity results in a significant contribution to beta activity due to cross talk (greater than 4% of the total beta activity, or 2 pCi if the sample’s beta activity was as large as 50 pCi) the appropriate correction should be made and this process would be identified in the laboratory’s procedure.

The method as written does not provide an equation to calculate the counting uncertainty associated with each sample measurement. Generally speaking the counting uncertainty is the principal contributor to the total uncertainty of the analysis for an individual sample where the gross alpha or beta concentration is below about 5 pCi/L. The following equation is based on the

generalized formula for counting uncertainty (“error”) shown in Appendix B of the 900 Series method manual and can be used to calculate the *counting* uncertainty for the result:

$$U, \text{ at 95\% confidence} = \frac{1.96 \sqrt{\frac{R_S}{t_S} + \frac{R_B}{t_B}}}{2.22 \times V \times \epsilon}$$

The requirement for detection limit is stated in 40 CFR 141:

For the purpose of monitoring radioactivity concentrations in drinking water, the required sensitivity of the radioanalysis is defined in terms of a detection limit. The detection limit shall be that concentration which can be counted with a precision of plus or minus 100 percent at the 95 percent confidence level (1.96[sigma] where [sigma] is the standard deviation of the net counting rate of the sample.

This definition of the detection limit (DL) in the current version of 40 CFR 141.26 translates into the following equation:

$$DL = \frac{\frac{1.96^2}{2t_s} \times \left[1 + \sqrt{1 + \frac{4t_s^2}{1.96^2} \times R_B \times \left(\frac{1}{t_s} + \frac{1}{t_B} \right)} \right]}{2.22 \times V \times \epsilon}$$

Where:

- t_s = time of the measurement used to accumulate the sample count, minutes
- t_B = time of the measurement used to accumulate the background count, minutes
- R_B = mean background count rate, cpm
- V = sample volume used, L
- ϵ = efficiency and the self absorption correction

The equation for the DL cited above will be used here in an example for determination of gross alpha activity.

Assume a sample volume of 125 mL (V) yields a sample mass of 100 mg. The sample and background count times are both 240 minutes (t_s and t_B). The alpha background count rate is 0.07 cpm (R_B), and the detection efficiency is 0.072 (ϵ). Inserting these values into the equation we get a DL of 2.8 pCi/L. This would meet the required detection limit (RDL) of 3 pCi/L for gross alpha analysis.

In Appendix C of the EPA 900 series procedures manual there is a note that states the maximum recommended count time is 1,000 minutes. If the DL cannot be achieved in that time period a different instrument (i.e., higher efficiency), a larger sample or a different method should be used.