

## Technical Notes for EPA Method 906.0 — *Tritium in Drinking Water*

### 1 Scope and Application

The method applies to the determination of tritium as either  $^3\text{HOH}$  or  $^3\text{H}_2\text{O}$ . This is because the techniques used to isolate tritium in the sample rely on the presence of tritium as part of the water molecule. If the chemical form of tritium in the sample is not known, additional techniques of chemical treatment may be required to assess the total tritium content.

Note that the National Interim Primary Drinking Water Regulations (NIPDWR) requirements referenced in the method's scope are obsolete. Current requirements for drinking water compliance testing found in the most recent revision of 40 CFR 141 supersede the requirements listed in Method 906.0. At the time of this writing, the Maximum Contaminant Level (MCL) for tritium is 20,000 pCi/L. The Required Detection Limit (RDL) for tritium is 1,000 pCi/L.

### 2 Summary of Method

Tritium is an isotope of hydrogen. Thus, it reacts identically to any other hydrogen atom or ion. In an aqueous solution, the ionization of water is described by the following equilibrium,



At 25 °C, the amount of hydrogen ion,  $\text{H}^+$ , dissociated at any given time has the value

$$K_w = [\text{H}^+][\text{OH}^-] = 1 \times 10^{-14} \quad (2)$$

Although the value of  $K_w$  is low, the kinetics of ionization are very rapid. This means that ionically bound tritium is very labile and is being exchanged constantly with different water molecules. Sample preparation and radionuclide separation techniques for tritium analysis are the same as that for water comprised only of stable hydrogen isotopes ( $^1\text{H}$  and  $^2\text{H}$ ). For this reason, at concentrations of tritium anticipated in any samples taken from the environment, it is unlikely that any discrete molecules of  $^3\text{HO}^3\text{H}$  would exist.

The method's schematic is depicted in Figure 1. The sample is treated with sodium hydroxide and potassium permanganate. This alkaline permanganate solution does the following:

- Oxidizes most organic material that occurs in drinking water samples to carbon dioxide and water. In the alkaline medium carbon dioxide is converted to non-volatile carbonate.
- Oxidizes iodines and other halogens to a non-volatile oxidation state (e.g.,  $\text{IO}_3^-$ ).
- Converts any potentially volatile metal radionuclides (Po, Pb, etc.) to non-volatile hydroxides.

These chemical reactions are important so that tritium is effectively separated from other radionuclides using distillation. Traces of radionuclides like  $^{131}\text{I}$  or  $^{14}\text{C}$  can interfere with tritium analysis because both are low-energy beta emitters and will provide response in the tritium

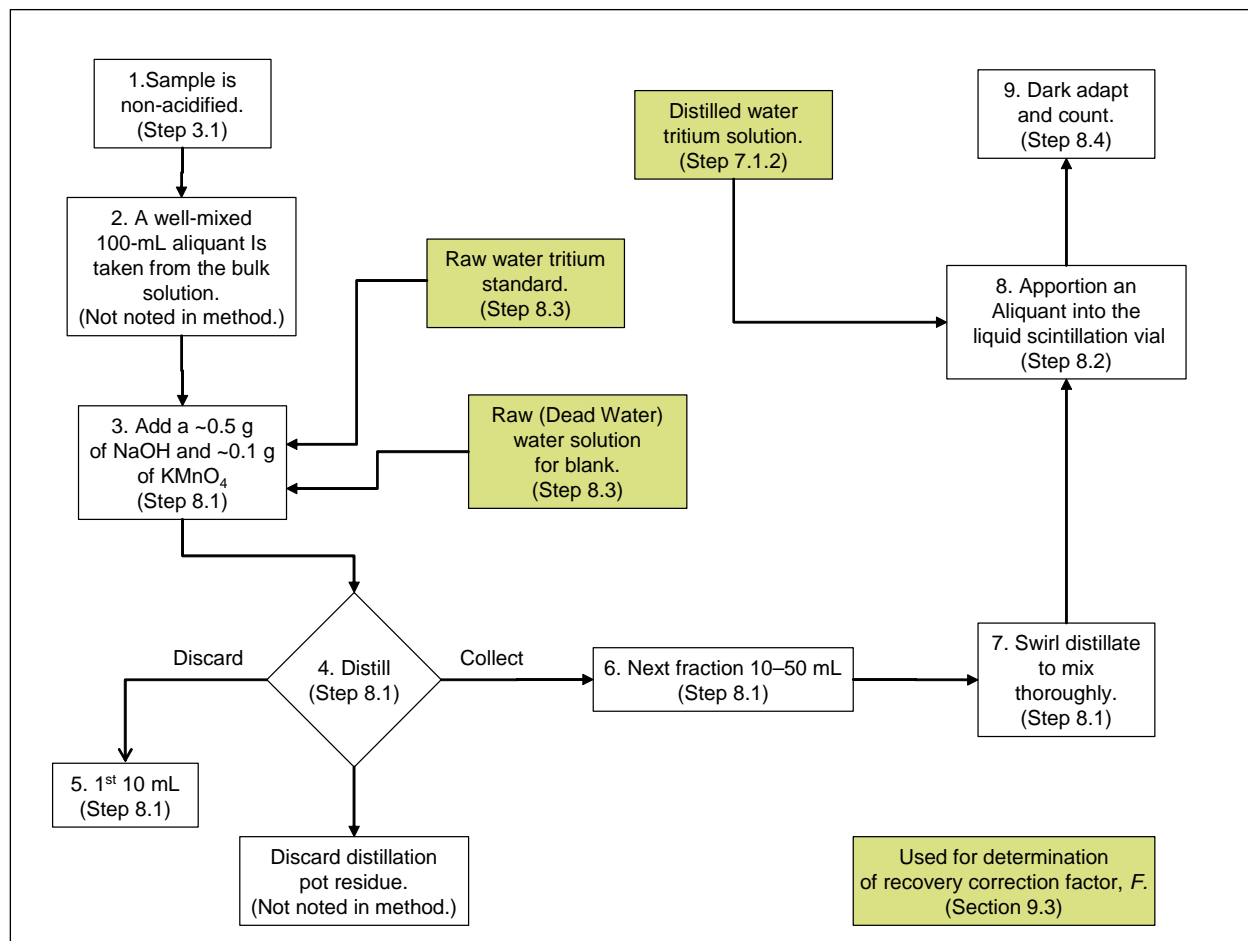


Figure 1 — Method 906.0 analytical schematic

region for liquid scintillation analysis. Any  $^{131}\text{I}$  present, like stable iodine, will be oxidized to a non-volatile form,  $\text{IO}_3^-$ . Any  $^{14}\text{C}$  will be oxidized to  $\text{CO}_2$ , stabilized as non-volatile carbonate ions in the alkaline solution, and retained in the distillation pot. Radioactive metal ions are converted to the oxides or hydroxides in the basic, oxidizing medium and are retained in the distillation pot.

A 100-mL aliquant is distilled to ensure that sufficient sample is available for liquid scintillation analysis. Following the addition of the permanganate, a simple distillation is performed. The first 10 mL fraction of the distillate is discarded. This may contain dissolved gases and low-boiling-point organic materials that volatilize prior to being oxidized by the permanganate. Dissolved gases that can interfere with liquid scintillation analysis of tritium include the naturally occurring radon isotopes and organic compounds containing  $^{14}\text{C}$ . Although the radionuclides of radon,  $^{220}\text{Rn}$ ,  $^{219}\text{Rn}$ , and  $^{222}\text{Rn}$  are alpha emitters, they rapidly decay to progeny that are low-energy beta emitters. Discarding the first fraction eliminates these potential interferences.

Another reason for allowing at least 10 mL to distill is that all of the interior glass surfaces of the distillation apparatus become equilibrated with the tritium bearing solution. This minimizes the

amount of adsorbed water on the surfaces from previous samples or cleaning of glassware that could dilute or contaminate the sample.

The next 50 mL fraction is collected. The method states that this fraction should be mixed thoroughly. The rationale behind this is that <sup>3</sup>HOT and HOH may fractionate during the distillation process since they have slightly different boiling points. Mixing thoroughly is accomplished by simply swirling the distillate so that tritium is uniformly distributed.

Tritium has a half-life of 12.32 years. It undergoes ~0.5% decay in about 30 days. Because the decay time for drinking water samples is limited by the specified holding time of six months, the maximum radioactive decay for tritium in a sample should not exceed 3%. Although this results in a small decay correction for most samples, it will affect the activity of the standards used for calibrating the liquid scintillation counter and preparing quality control samples more significantly.<sup>1</sup> The analyst should ensure that the tritium standards are routinely corrected for radioactive decay, using Equation (3).

$$A = A_0 e^{-\lambda t} \quad (3)$$

where:

- $A$  = Activity on the date of the measurement
- $A_0$  = Activity on the standard reference date
- $\lambda$  = Decay constant,  $0.6931 / (5000 \text{ d}) = 1.386 \times 10^{-4} \text{ d}^{-1}$
- $t$  = Elapsed time between activity reference date/time and date/time of the count in days.

### 3 Sample Handling and Preservation

The method identifies that the sample for tritium should be taken in its “natural state” and not acidified. This is because there is no need to stabilize the tritium in the sample analogous to the acid preservation applicable for other radionuclides that precipitate at elevated pH. Samples that are to be held for a significant amount of time have been refrigerated or frozen to minimize biological growth.

The statement in the method about not acid-preserving samples has led to misunderstanding regarding the effect of acid preservation on the technique. First of all, although the method says that samples “should not” be acidified, preserving samples with acid will not interfere with the technique and acid preserved samples that are analyzed following the method *will* produce valid results. This is because acid present in the concentrations used for sample preservation (15 mL/L) will be neutralized by the addition of excess NaOH prior to distillation. A second misconception regards the diluting of the hydrogen content of samples by adding acid. When samples are preserved with acid to a pH of 2, the amount of hydrogen added is so small relative to the total amount of hydrogen present that it does not significantly change its concentration in

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<sup>1</sup> This is because standards are only used up over long periods of time like 5-6 years. During that time period measurable decay (up to ~30%) does occur.

the sample by more than about 0.2 %. In fact, this is much smaller than the 1.5 % volumetric dilution that occurs when 15 mL of acid is added to approximately 1 L of sample.<sup>2</sup>

A regulatory hold time of 6 months is specified in Table VI-2 of the *Manual for the Certification of Laboratories Analyzing Drinking Water*.<sup>3</sup>

#### 4 Interferences

Tritium is a naturally occurring radionuclide as well as one that is artificially produced. Tritium is naturally produced in the atmosphere by cosmogenic processes. Nuclear weapons testing during the 1950s through the 1980s significantly contributed to surface water concentrations of tritium. Nuclear power plants, Department of Energy sites, and facilities that use tritium in their manufacturing process (e.g., exit signs, gun sights, and wrist watches), and waste sites may have measurable amounts of tritium in their discharge. During the past decade the concentration in surface waters not in the flow of a direct discharge have average values between 10 and 60 pCi/L.

Method 906.0 specifies that the tritium content in the water used to determine the background activity subtracted from sample counts should be less than the minimum detectable activity (MDA). The concentration of tritium present in environmental waters depends on several factors such as rainfall, sunspot activity, and dilution or contamination from other sources. Thus, it is important to identify water that has negligible concentrations of tritium to be used for determining backgrounds and for performing dilutions of tritium standards and samples. Water sources that have been isolated from the normal hydrosphere for tens of years or more, such as deep wells or aquifers, will have concentrations of tritium that are much lower, because the tritium originally in these sources will have decayed. These sources are colloquially referred to as “dead water” because they have very low concentrations of tritium ( $\ll 10$  pCi/L). See Section 6 of this technical note for further discussion of dead water.

Toluene- or dioxane-based cocktails are no longer commonly used for analysis of tritium. Cocktails that are commercially prepared have shorter times for dark adapting than the older cocktails: usually between 15 and 45 minutes. However, each user should determine the length of time that their instrument and cocktail system need for dark adaption. The dark adaption process allows for other sources of fluor excitation, unrelated to the radioactivity measurement, to undergo their normal decay process. These sources include primarily fluorescence (room lighting and sunlight causing short term excitation of the fluor) and chemiluminescence (a chemical reaction between something in the sample and the fluor leading to fluor excitation).

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<sup>2</sup> Samples for many radionuclides are preserved by adding 15 mL of nitric acid per liter of sample, resulting in a dilution factor of about 0.015, or 1.5%. The effect this dilution, however, is generally ignored. In contrast, when adding 15 mL of concentrated nitric acid, or 0.24 moles/L of  $H^+$ , to approximately one liter of sample that already contains about 111 moles/L of exchangeable  $H^+$  [ $2 \text{ moles } H^+/\text{mole } H_2O$ ]  $\times$  [ $55.6 \text{ moles } H_2O/L$ ] will result in a change in the hydrogen concentration on the order of of about 0.002, or 0.2%.

<sup>3</sup> U.S. Environmental Protection Agency (U.S. EPA), 2005. *Manual for the Certification of Laboratories Analyzing Drinking Water Criteria and Procedures Quality Assurance* (5<sup>th</sup> Edition). Office of Ground Water and Drinking Water, EPA 815-R-05-004, January. Available at <http://www.epa.gov/safewater/methods/laboratorycertification.html>.

Although chemiluminescence is rare in distilled samples, it is possible. Many instruments have luminescence monitors that allow assessing the results of each count for photo- or chemiluminescence. Suspected photo- or chemiluminescence also may be evaluated by conducting a time study (several counts over varying amounts of dark adapt time) or a quench study (attempting to add a chemical which will terminate the chemical reaction in a shorter time frame).

Another advantage of commercially prepared cocktails currently in use is that their flashpoints are greater than 140 °F, and they are not “listed” hazardous wastes.

Users should be aware that instrument response and backgrounds may vary significantly from lot to lot and from bottle to bottle of cocktail. Many quality programs require a recalibration for efficiency and new background measurements when use of a new lot of cocktail is initiated. When a new lot or bottle of cocktail is opened, comparing quench curve and backgrounds to historical data may show potential differences in the efficiency or background count rates that would require a new calibration or background measurement.

## 5 Apparatus

The distillation apparatus is a simple still that does not incorporate a thermometer for monitoring the distillate temperature. Thus, it is not possible to ensure that the distillate is pure water, an azeotropic mixture of water and another substance, or if dissolved salts are driving up the boiling point of the system. If azeotropic mixtures are present, or if the solution has a boiling point significantly different from 100 °C, the distillate produced may contain impurities. Due to the nature of the matrix, this is not generally a significant concern for drinking water samples.

In Section 7, the method refers to the addition of a “boiling chip,” which is identified in Section 5 as part of the distillation apparatus. The purpose of this material is to promote smooth boiling of the solutions without “bumping.” Bumping occurs when water superheats at the bottom of the distillation flask due to lack of formation of nucleate steam bubbles. The superheated liquid very rapidly turns to vapor, forming a large bubble that pushes the liquid above it into the condenser and over to the receiving flask. If this occurs, the entire apparatus should be cleaned thoroughly and the distillation started again. Commercially available materials that promote smooth boiling are sold under several different names and are acceptable substitutes for a “boiling chip.”

Liquid scintillation vials made of natural silica based materials have some <sup>40</sup>K as an impurity (on the order of 0.3 % by weight potassium). Because <sup>40</sup>K is a beta emitter, it will add to the instrument background. Thus, low-potassium-glass liquid scintillation vials (usually less than 0.15% by weight potassium) are recommended if glass is used. Normal glass vials may be used for this purpose, but higher backgrounds will make it more difficult to achieve the RDL of 1,000 pCi/L (e.g., longer count times).

Plastic vials may be used with cocktails because organic solvents that react with plastics have been eliminated from the plastic formulation. The plastic vials contain no naturally occurring radionuclides and provide very good translucence to the emissions of the fluors contained in the cocktail. The drawback of using plastic vials is that they can carry a static charge. The release of

the static charge can lead to chemiluminescence or photomultiplier tube response (due to the light emitted by the discharge), elevating the apparent sample activity yielding Type I errors.

## 6 Reagents

Reagent grade sodium hydroxide and potassium permanganate are acceptable for use as their content of any volatile radioactive materials (that is anything that will distill with water) will be nil.

Method 906.0 specifies that the tritium content in the water used to determine the background activity subtracted from sample counts should be less than the MDA. While the method specified an RDL of 1,000 pCi/L (see Section 9 of this technical note for the calculation of the RDL), most modern liquid scintillation counters are equipped with sufficient shielding and electronics for minimizing background such that MDAs of 200-400 pCi/L, and below, can readily be achieved. When this method was written, significantly higher levels of tritium were present in environmental and drinking waters due to atmospheric testing of nuclear weapons. Since the 1980s, when atmospheric testing was terminated, the levels of tritium in the environment have been approaching pre-testing concentrations. The sensitivity of liquid scintillation counters has improved significantly over the intervening years and detection limits of 400 pCi/L and below can now be readily achieved. At the lower concentrations being measured today, very significant Type II (negative) bias can occur if the background water contains significant amounts of tritium activity. Figure 2 shows the negative bias introduced to measurement results as a function of varying tritium concentration in the water samples. In samples containing 400 pCi/L, background water containing 50 pCi/L of tritium will introduce approximately a 13% bias. This bias decreases as sample concentration increases.

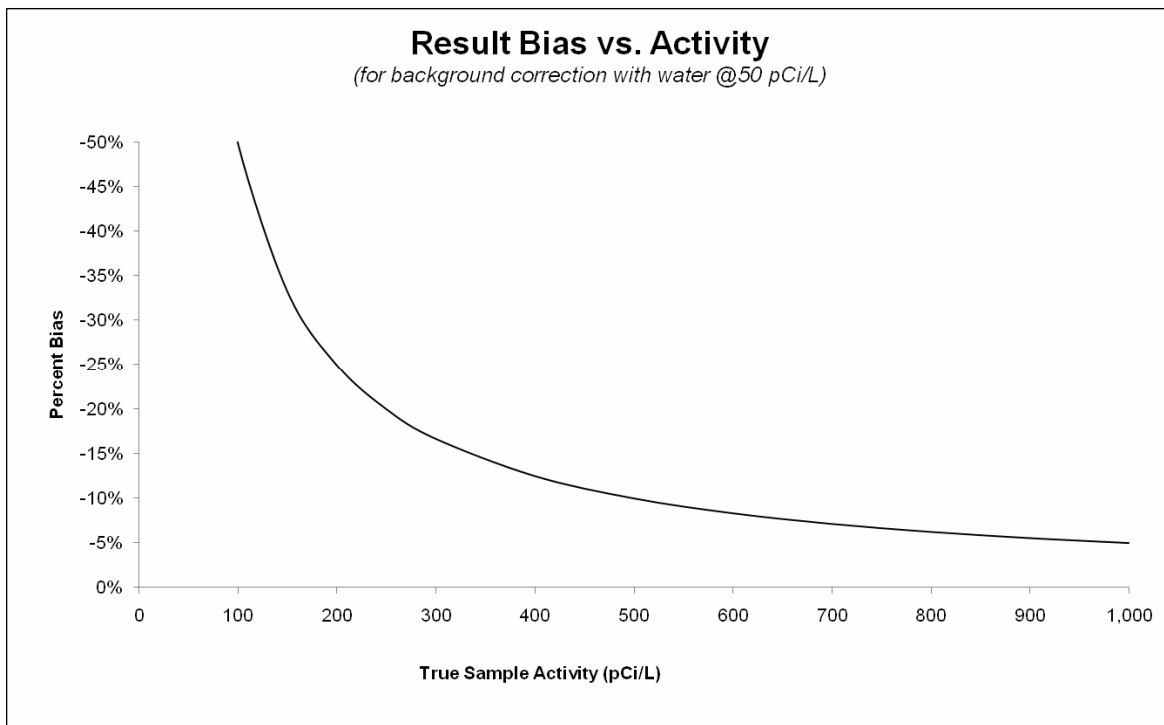


Figure 2 — Tritium concentration bias using water with naturally occurring levels of tritium

## 7 Calibrations

Tritiated water (HOT) and normal water (HOH) have slightly different boiling points. The boiling point of tritiated water is slightly higher and can lead to a small degree of fractionation during the distillation process. The laboratory needs to perform a calibration of their distillation process to account and correct for this fractionation. Although hydrogen has two stable isotopes ( $^1\text{H}$  and  $^2\text{H}$ ), these isotopes are difficult to measure and cannot be readily used as tracers to determine the degree of fractionation, or “recovery<sup>4</sup>,” which occurs during the distillation process. Instead, standards containing known activity of tritium are used to generate an indirect “recovery correction factor” that is applied to sample results to correct for fractionation. Four separate solutions are used to make this determination:

- a. Dead Water
- b. Distilled Dead Water
- c. Raw Water Tritium Standard Solution, and
- d. Distilled Water Tritium Solution.

The Dead Water used should contain tritium in concentrations less than the MDA and ideally low enough that it will not introduce significant bias into low activity sample results. Distilled Dead Water is prepared by distilling a source of dead water in accordance with the steps in Section 8 of this method.

The third solution described in this section is a Raw Water Tritium Standard Solution that is prepared by diluting a purchased tritium standard with low tritium water (dead water) that *has not* been distilled. The method suggests a concentration of the standard to be used, but does not state how much of the standard should be added to this solution. Best practices should ensure that enough activity has been added to produce enough counts to minimize the overall uncertainty of the measurement. Frequently a goal of 1% relative uncertainty is set. When calculating the amount of standard to be used, it is important to remember that only 4–8 mL of the resulting solution will be taken for counting. Using 2.5 mL of 1,000 dpm/mL tritium standard generally would provide 10,000 net counts in a reasonably brief counting interval.

A fourth solution, Distilled Water Tritium Solution, is made similar to the third except that the *Distilled Dead Water* is used to dilute the purchased tritium standard to the same concentration as the Raw Water Tritium Standard Solution. This solution is the Distilled Water Tritium Standard. These last three solutions are used to determine the “recovery correction factor” for tritium, identified as “*F*” in Section 9.3.

### NOTE

Laboratory personnel should be careful not to leave the “dead water” container open for extended periods of time because the water vapor in the atmosphere has higher levels of tritium in it than the dead water and will equilibrate rapidly with the dead water, raising the background activity of the dead water.

<sup>4</sup> The current terminology for this is not recovery but “yield.” The yield is a sample-specific correction accounting for isotopic losses of radioactive elements during the chemical separation process.

Three separate aliquants of the “Raw Water Tritium Standard Solution” are distilled according to the procedural steps in Section 8. The distillate fractions for these separate aliquants are then prepared individually for liquid scintillation counting.

The “Distilled Water Tritium Solution” is directly aliquanted into three separate liquid scintillation vials with the appropriate quantity of cocktail. No distillation is performed.

Three separate aliquants of the raw dead water are distilled according to the steps in Section 8, and prepared for liquid scintillation counting in the same fashion as the other standards. This is the *blank solution* used for the determination of background in the recovery correction factor equation that is discussed below in Section 9.

The recovery correction factor should only need to be determined once, unless the following conditions occur:

- The type of distillation apparatus being used changes.
- The concentration of tritium in the dead water changes.

## 8 Procedure

As described earlier, solid sodium hydroxide and solid potassium permanganate are added to a 100- mL aliquant of sample. Both reagents are added as solids so as not to contribute additional water to the sample which would dilute the tritium concentration.

The Figure of Merit (FOM) is used to determine the optimum counting region for tritium using Equation (4):

$$\text{FOM} = (\text{Efficiency})^2 / (\text{Background cpm}) \quad (4)$$

A tritium standard and a background sample are each counted in the exact configuration to be used for samples (i.e., distilled water in the same type of vial and cocktail, the same volume of sample, the same sample-to-cocktail ratio, and the same instrument settings). Beginning with a range of channels that is wider than the actual tritium peak, the efficiency, the background cpm and the FOM are calculated for successively narrower energy regions until a maximum in the FOM is obtained. This energy region is the optimum counting region for tritium.

## 9 Calculations

*Note: Method 906.0 does not include the correction factor for decay between the date of collection (or other specified reference date) and the date of the count included in these formulas.*

9.1 Tritium concentration,  $A$  (pCi/L), is calculated using Equation (5):

$$A = \frac{(C - B) \times 1000}{2.22 \times E \times V \times F \times DF} \quad (5)$$



where:

$C$	=	Gross count rate of the sample, cpm
$B$	=	Background count rate as determined with dead water, cpm
$E$	=	Detector efficiency, dimensionless quantity
$V$	=	Volume of distilled sample transferred to the scintillation vial in mL
$F$	=	Recovery (yield) correction factor, dimensionless quantity
$DF$	=	Decay correction factor, dimensionless quantity
2.22	=	Conversion from dpm to pCi

9.2 The counting efficiency,  $E$  (dimensionless), is determined as follows. The Distilled Water Tritium Solution is used for this purpose along with the distilled dead water for the blank solution. The efficiency is then calculated as:

$$E = \frac{D - B}{G} \quad (6)$$

where:

$D$	=	Distilled Water Tritium Solution count rate, cpm
$B$	=	Distilled Dead Water count rate, cpm
$G$	=	Theoretical decay corrected activity of the Distilled Water Tritium Solution, dpm

### Quench Curve Preparation:

Detection efficiency varies with the measured value of the quench indicating parameter of the sample. Although a relatively narrow range of quench is routinely observed for distilled drinking water samples, it is still important to calibrate across the full range of quench values, and thus the full range of detection efficiencies, that will be encountered in analysis. This is accomplished by preparing a quench curve. A quench curve consists of a series of quench standards (usually 7 or more) each containing the same known amount of standard  $^3\text{H}\text{O}\text{T}$  and varying levels of quench agent. The quench is produced by adding incremental amounts of a suitable quenching agent. The ideal quench agent would be the same as the source of quench present in samples. This is not usually practical, as the source of sample quench is usually not known. More frequently, surrogate quenching agents, such as Eriochrome Black T or nitromethane, are used. The best quenching agents produce a significant degree of quench with a minimum volume of the agent, and thus provide a better match between the geometry of samples and the quench standards. The quench standards are then counted long enough to minimize uncertainty (e.g., 10,000 net counts with a negligible amount of background counts), and observed efficiency values plotted against the measured quench. This plot can then be used to determine the efficiency of samples based on quench measured by the instrument.

Instruments often have on-board utilities that support acquisition and calculation for quench curves.

9.3 The recovery correction factor,  $F$  (dimensionless), is determined using the equation stipulated in the method:

$$F = \frac{(L - B)}{M(\times E)} \quad (7)$$

where:

- $L$  = Distilled Water Tritium Solution activity, cpm
- $B$  = Distilled Dead Water count rate, cpm
- $M$  = Activity of the Raw Water Tritium Standard solution (before distillation), dpm
- $E$  = Efficiency as determined in Equation (6) (cpm/dpm)

9.4 The counting uncertainty at the 95% confidence interval,  $U$  (pCi/L), is determined using the equation stipulated in the method:

$$U \text{ at } 95\% \text{ confidence} = \frac{1.96 \times \sqrt{(C/t_c + B/t_b)} \times 1000}{2.22 \times E \times V \times F \times DF} \quad (8)$$

where:

- $t_c$  = count time for the sample (min)
- $t_b$  = count time for the background (min)

#### 9.5 Detection Limit

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,  $DL$  (pCi/L), translates into the following equation:

$$DL = \frac{\frac{1.96^2}{2t_s} \times \left[ 1 + \sqrt{1 + \frac{4t_s^2}{1.96^2} \times B \times \left( \frac{1}{t_s} + \frac{1}{t_b} \right)} \right]}{2.22 \times E \times V \times F \times DF} \quad (9)$$

where:

- $B$  = background count rate, cpm
- and other factors are as noted above.

9.6 The decay correction factor,  $DF$  (dimensionless), is determined using

$$DF = e^{-\lambda t} \quad (10)$$

where:

- $DF$  = Decay correction factor  
 $\lambda$  = Decay constant,  $0.6931 / 5000 \text{ d} = 1.386 \times 10^{-4} \text{ d}^{-1}$   
 $t$  = Time between sample date/time and start of counting date/time, days

## 10 Precision and Accuracy

The original data in the method identifies the statistical evaluation for solutions at 7 pCi/mL (7,000 pCi/L) and for 300 pCi/L (a typographical error exists in the original document indicating 300 pCi/mL). The method states that there was no measurable bias at 7,000 pCi/L. As shown in Figure 1, for 300 pCi/L in natural water the bias of measurement would be about 15%, whereas when dead water is used the uncertainty reported in the original method is only about 9%. There is no indication in the method of what the actual dead water concentration of tritium was, but it was certainly lower than the 50 pCi/L used to generate Figure 2.