Technical Notes for EPA Method 903.0 – *Alpha Emitting Radium Isotopes in Drinking Water*

1. Scope and Application

This method is sometimes colloquially referred to as "Total Radium." This unfortunate practice causes confusion regarding its applicability. It is a screening method only for drinking water samples for only one isotope of radium, ^{226}Ra. The results generated provide an upper bound on the concentration of ^{226}Ra present in a sample.

The coprecipitation technique used separates all radium isotopes present because all radium isotopes are chemically equivalent. The separated radium is then alpha-counted. In addition to ^{226}Ra, any alpha-emitting isotopes of radium present, such as the shorter-lived ^{224}Ra and ^{223}Ra, and their progeny, will contribute to the total alpha counts measured. For this reason, Method 903.0 results are at least equal to — but often exceed — the actual ^{226}Ra concentration of the sample.[1] Thus, when Method 903.0 generates a result below 5 pCi/L, it is safe to conclude that the ^{226}Ra concentration of the sample is below or equal to 5 pCi/L.

Much of the confusion about the applicability of this method is due to the misunderstanding about its ability to measure ^{228}Ra. In spite of its common name, "Total Radium," this method is sensitive only to alpha-emitting radium and cannot provide any usable information about ^{228}Ra, which is a low-energy beta-emitter. Approved methods for ^{228}Ra, such as EPA Method 904.0[2], must be used to determine the ^{228}Ra concentration of a sample, which is then summed with the ^{226}Ra concentration from a second method such as EPA 903.0 or 903.1 to demonstrate compliance with the combined ^{226}Ra + ^{228}Ra maximum contaminant level (MCL) requirement in drinking water.[3]

This method is also unsuitable for screening measurements for ^{223}Ra or ^{224}Ra because it non-conservatively underestimates the activity of these short-lived isotopes. There are two reasons for this:

- It does not account for their decay, and
- Calibrations and ingrowth correction factors assume that ^{226}Ra is the only isotope of radium present.

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

[1] This frequently causes problems during performance testing (PT) of method 903.0 because ^{228}Ra frequently is present in the PT samples and its progeny ^{224}Ra is also present, resulting in a high bias. This indicates, however, that the screening method is working as it should. Unfortunately, PT study acceptance criteria do not reflect this fact, and the test samples are given the misleading evaluation of' "not acceptable." See Section 4 of this note for further discussion about the rationale for delaying the sample count to minimize positive bias from shorter-lived, interfering ^{223}Ra and ^{224}Ra that also decay by alpha emission.

[2] See 40 CFR 141.25(a) for other approved methods for compliance testing for ^{228}Ra in drinking water.

[3] For details, including guidance on substituting gross alpha results for ^{226}Ra, see "Implementation Guidance for Radionuclides," U.S. EPA Office of Ground Water and Drinking Water, EPA 816-F-00-002, March 2002.

requirements listed in Method 903.0. At the time of this writing, the interim MCL for ^{226}Ra has been replaced with an MCL for "Combined ^{226}Ra/^{228}Ra" of 5 pCi/L. The Required Detection Limit (RDL) for ^{226}Ra is 1 pCi/L.

As with any radiochemical method, the detection limit is a function of sample size, count time, detector efficiency, chemical yield, and detector background. Using a commercially available, low-background gas-flow proportional counter with nominal alpha backgrounds below 0.2 cpm and detection efficiencies of 0.2, RDLs of 1 pCi/L can be met easily with a 1.0 liter sample in a count time of under 2 hours. For this method, there is an additional consideration called the "ingrowth factor." Within hours of separation, ^{226}Ra decays to form significant quantities of three additional short-lived alpha emitters. These alpha emitters produce responses in the detector that are indistinguishable from ^{226}Ra. If these progeny are allowed to ingrow prior to counting, the net effect will be an improvement in the detectability. An ingrowth factor of up to 4 can be achieved if the sample is allowed to ingrow for about 21 days.

Details of the Detection Limit (DL) calculation are discussed in Section 9 of these notes.

2. Summary of the Method

The methodology used for the analysis of radium isotopes uses the fundamental techniques of coprecipitation (barium and lead sulfate), complexation (ethylenediamine tetraacetic acid, "EDTA"), and masking (acetic acid and EDTA). Lead, barium, and radium are precipitated using sulfuric acid. The precipitate is washed, then redissolved using EDTA. The radium is selectively coprecipitated from this solution using ammonium sulfate and acetic acid. The precipitate is washed, dried, weighed to determine chemical yield, and then alpha-counted using a gas-flow proportional or alpha scintillation counter. Although the original method specifies an internal (windowless) gas flow proportional counter, the GPC instruments with windows currently in use provide acceptable results and MDC values commensurate with the legal requirements. A summary of the method is displayed in Figure 1 on the next page.

3. Sample Handling and Preservation

Method 903.0 references the preservation technique outlined in Method 900.0 (*Gross Alpha and Gross Beta Radioactivity*). The rationale for the preservation technique is outlined here as well. Acid preservation is extremely important for drinking water samples because there are several metal contaminants (including radionuclides) that may precipitate unless the pH is reduced below 2.0. This pH is important because it helps to minimize both adsorption onto container walls and precipitation in the sample container during sampling, shipment, and storage. In Section 4 of the method, the recommendation is to add 15 mL of 1 N nitric acid per liter of sample at the time of collection. However, based on the characteristics of the water source, adding acid to a pH of 2 alone may not be sufficient to dissolve all materials in the sample.

Samples that are older than five days from sampling and have not been preserved are not acceptable for analysis because there is a significant likelihood that radium has been lost to the

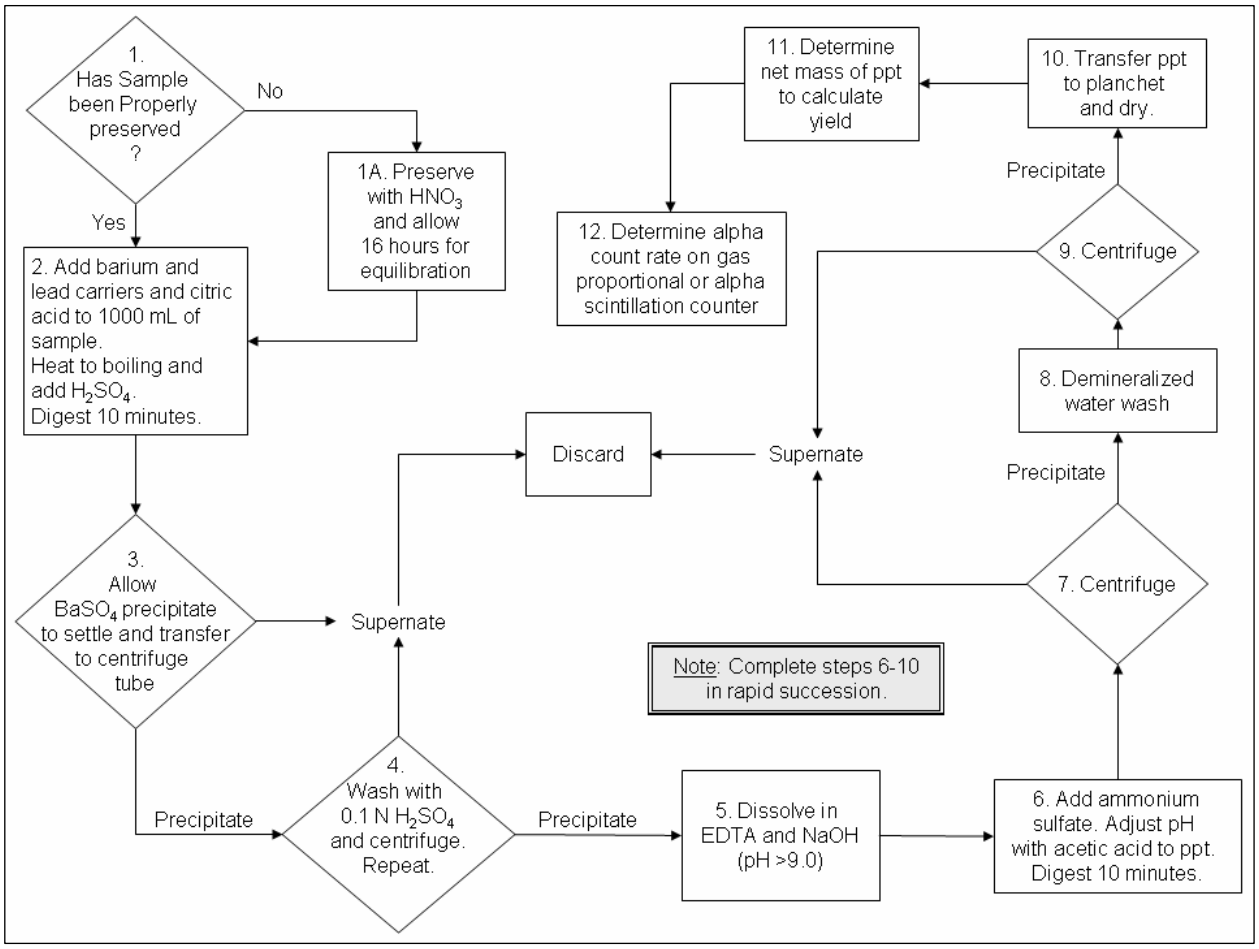

Figure 1. Method 903.0 Process Flow Diagram

container walls. If the sample is received unpreserved and it is less than five days since sampling, then preservation is implemented followed by a 16-hour waiting period prior to beginning the method. This is to ensure that the H^+ ions in the sample have sufficient time to replace any adsorbed radium ions and to ensure that the radium present has had the opportunity to be dissolved.

4. Interferences

The method discusses possible interference from samples with naturally occurring barium. If there is reason to suspect that a sample may contain sufficient barium to bias yield measurements using the 32 mg of Ba^2 prescribed by the method[4], the native barium content of the preserved sample can be determined using atomic emission spectroscopy or an equivalent spectroscopic technique that will determine barium to a concentration of 1 ppm. The mass of barium added to the sample can then be adjusted to account for barium contained in the sample aliquant.

[4] For example, it may be noted that chemical yields significantly exceed routinely observed levels (or 100%), indicating that a second source of barium must be present somewhere in the process.

Method 903.0 does not describe how to calculate the yield for radium, although Section 6 of the method addresses standardization of the barium carrier solution. Consult Section 9 of these notes for a calculation that can be used to determine chemical yield.

Interference from short-lived, naturally occurring isotopes of alpha-emitting radium, ^{224}Ra (half-life = 3.66 days) and ^{223}Ra (half-life = 11.4 days), can be minimized by delaying the counting of the sample. The degree of minimization of interfering alpha activity depends upon the time elapsed between separation and counting. By waiting two weeks, the activity of ^{224}Ra and ^{223}Ra (and their respective decay progeny) will be reduced by 90% and 57% of their original values, respectively. After three weeks, the reduction is 97% and 71%, respectively. Because after two to three weeks the ^{226}Ra progeny nearly quadruple the total alpha response, ^{226}Ra will be the overwhelming contributor to the alpha counts detected. Although the only truly radionuclide-specific method for ^{226}Ra is the de-emanation technique, Method 903.0 is generally regarded as being radionuclide-specific for ^{226}Ra when counting is delayed for two or more weeks.

In addition to the possibility of interference from naturally occurring barium and short-lived radium isotopes, any other alpha-emitting radionuclides that are not removed during chemical separations will contribute to the total activity determined by gas proportional counting. Thus effective chemical separations are extremely important as there would be no way to determine if other non-radium alpha emitters were present.

5. Apparatus

Current gas-flow proportional counters have alpha backgrounds of less than 0.2 cpm.

Glassware and glass desiccators are the generic terms used in this method for labware used for processing the samples. Labware may be made of plastic or glass, and the desiccators made of any suitable material.

6. Reagents

Solutions of lead, barium, and EDTA are commercially available. It is may be acceptable for the laboratory, following its procedures, to dilute such a solution to the concentration stipulated by the method.

If a primary standard solution of barium chloride can be purchased, it may be diluted to the proper concentration and used. The equivalent mass of barium sulfate per mL of added carrier may then be calculated using the gravimetric factor.

The exact concentration of the barium in the barium chloride carrier solution must be known because it is used for chemical yield determinations. Each time a new barium carrier solution is made or purchased, the solution must be standardized to determine its concentration in mg $BaSO_4$ per mL of barium carrier. The barium solution is standardized by precipitating $BaSO_4$ as described in Step 6.4. The standardization is to be performed in at least triplicate, and the average value used as the standardized concentration in mg $BaSO_4$ per mL of carrier solution.

There is no stated acceptance criterion for the acceptable spread of values for the barium solution standardization. It is recommended that the laboratory develop its own acceptance criteria for the repeatability of these measurements. Since this is a gravimetric determination the relative standard deviation should be on the order of about 0.5–2% because of the small mass of barium involved. The uncertainty associated with this measurement should be included in the total propagated uncertainty of the final analytical result. In addition, the laboratory should include shelf lives for the barium chloride solutions that are based on laboratory developed stability studies.

7. Calibrations

The efficiency of each detector used is determined by counting a standard containing a known quantity of ^{226}Ra, traceable to NIST, which is precipitated with an amount of $BaSO_4$ equivalent to that used in the analytical process. Matching the calibration standard to the sample allows one to most accurately reproduce the efficiency of the sample. Ideally, the sample and the calibration standard used to determine efficiency will contain the same target nuclide (^{226}Ra) in the exactly the same mass of precipitate. This is important since the mass of barium sulfate present determines the degree of sample self-absorption which significantly affects the efficiency with which alpha particles are detected.

Some methods employ self-absorption corrections that adjust the efficiency to account for differences self-absorption resulting from variable precipitate masses (e.g., Method 900.0). Method 903.0, however, only uses a single point efficiency calibration. This will affect the accuracy of results if chemical yields fall significantly below the 100% point modeled by the calibration standards. Consider a sample with a chemical yield on the order of 40%. With a significantly lower mass of precipitate, the effect would be less self-absorption, a higher apparent count rate and a high result bias. If one needed to accurately know exactly how much ^{226}Ra is in the sample, this would be of great concern. As a screening test for drinking water compliance, however, the high bias is conservative from a regulatory standpoint.
The equation shown in the method for efficiency,

$$E,(cpm/dpm) = \frac{(net\ count\ rate\ of\ sample)}{(activity\ of\ ^{226}Ra\ added\ in\ dpm)\times(ingrowth\ factor)}$$

takes into account the ingrowth of radium progeny. The ingrowth factor in the denominator compensates for the number of decays of progeny atoms per decay of ^{226}Ra. This factor varies from 1, at the point separation where no progeny are present, to 4 at full ingrowth (approximately 21 days). Section 9.2 of the method contains a look-up table for these factors. Also see Section 9 of these notes for further discussion about the ingrowth factor.

8. Procedure

The usual sample size for this method is about 1 liter. The sample is reduced to a manageable size by coprecipitating the radium isotopes with barium and lead sulfates. Citric acid is added to form a soluble complex with lead. Radioactive lead isotopes (^{210}Pb, ^{212}Pb and ^{214}Pb) also are

precipitated in this first step. After allowing the precipitate to settle, the supernatant solution is discarded and the precipitate is washed with two portions of 0.1 N sulfuric acid. The supernatant solution from the washings is also discarded. The purpose of this wash is to remove other radionuclides and metals from the precipitate. Dilute sulfuric acid is important since it maintains the insolubility of the barium/radium sulfates and minimizes resuspension (peptization) of the precipitate that would be difficult to centrifuge.

The precipitate is then dissolved in basic EDTA solution. Although the method does not state what the exact final pH should be, it says that NaOH is added "…until dissolution is complete."[5] EDTA forms complexes with barium, lead and radium, so all three metals are dissolved as the EDTA complex. The barium and radium sulfates are selectively reprecipitated using ammonium sulfate and acetic acid. The acetic acid has two functions:

- Acetic acid lowers the pH to the point where EDTA is in its least ionized form and no longer effectively complexes barium and radium.
- The acetate ion helps mask lead so it will not precipitate.

As Ba and Ra are released from the EDTA complex, they can precipitate with the sulfate ion present in solution. Lead remains in solution as a soluble Pb-EDTA complex and does not precipitate. If the pH falls too far below 4.5, the fraction of lead released from its complex increases and will coprecipitate with $Ba/RaSO_4$.[6] This will result simultaneously in a positive bias in results (because the polonium progeny of ^{212}Pb are alpha emitters) and in a negative bias (because enough lead may be present to bias the chemical yield high).

Ammonium sulfate is used instead of sodium sulfate because the ammonium and acetate ions will create an electrical double layer on the barium sulfate, which will volatize easily during the drying process. The use of ammonium sulfate for precipitation minimizes the mass of sodium (from sodium sulfate) that would be retained in the secondary electrical double layer, which would increase the mass of the precipitate and would result in a non-conservative value (low) for radium isotopes by increasing the apparent yield.

The processing of the sample *should not* be delayed after the precipitation because the ingrowth of radium progeny will have begun, and losses of the progeny may occur when the precipitate is washed, leading to low results. The final precipitate is washed with demineralized water and transferred with a minimal amount of liquid to a tared planchet.

The planchet with precipitate is then dried to eliminate the electrical double layer and water, taking care to minimize volatilization of radon and its progeny present in the precipitate by drying the planchet as close to the precipitate separation time as possible. The longer the drying step is delayed, the greater chance of losing significant quantities of ^{222}Rn. Loss of ^{222}Rn and its progeny would give the result a low bias, which is not conservative.

[5] Although too much NaOH will not harm the process, it will require that more acetic acid be added in subsequent steps to precipitate barium sulfate.

[6] This is a commonly encountered problem when running this method. Standard Methods 7500-Ra-B utilizes an acid-base indicator at this step, bromcresol green, to monitor the pH and minimize the risk of adjusting the pH too low.

The half-life of ^{222}Rn is 3.8 days. It will achieve ~98% of full secular equilibrium at 21 days. However, we can calculate the exact ingrowth factor (how many alphas will be emitted per alpha of ^{226}Ra) using the Bateman Equations. An abbreviated table of this ingrowth factor is shown in Section 9.2 of the method.

9. Calculations

Activity is calculated by counting the final sample test source — the barium sulfate precipitate — in a gas flow proportional counter.

When the method was originally written, alpha spectrometric detectors were not available commercially. However, the use of an alpha spectrometric detector may provide a good means of quality checking the purity of the precipitate, because the analyst will be able to identify the levels of other contaminating alpha emitters that may be present.

An equation that can be used for calculating the yield is:

$$Y,\ ^{226}Ra = \frac{\left(M_{p+s} - M_p\right)}{\left(mL_{std} \times C_{std} \times GF\right)}$$

Where:

Y	=	the chemical yield factor based on the mass of barium sulfate
M_{p+s}	=	mass of the dried precipitate and planchet, mg
M_p	=	mass of the clean, dry planchet, mg
mL_{std}	=	mL of the standardized barium solution
C_{std}	=	the concentration of barium in the standard solution, mg/ml
GF	=	the gravimetric factor for the mass of barium sulfate per mass of barium (233.4/137.34) = 1.69943, dimensionless)

> Note that if the laboratory has standardized the barium sulfate solution to units of mg $BaSO_4$ per mL, the GF value is 1.0.

If native barium is present in the sample, the mass contributed would be:

Barium sulfate (due to Native Ba) = Sample volume × [Ba, mg/L] × GF

This would be added to the value for C_{std} in the denominator of the equation above to get the total barium in the initial solution.

The ingrowth factor in the denominator of the activity, uncertainty and efficiency equations reflects the total number of alpha decays occurring in the sample test source per decay of ^{226}Ra. The number of alpha particles emitted by decay progeny, relative to ^{226}Ra, at a given time following separation may be calculated using the Bateman equations. They are summed and added to one (1) - ^{226}Ra emits one alpha particle per decay. Thus the ingrowth factor varies

from 1 at the point separation, when only ^{226}Ra and no progeny are present, to 4 at full ingrowth when ^{226}Ra supports three alpha-emitting progeny.

The ingrowth factor look-up table in section 9.2 of the method provides factors that account for ingrowth of the progeny of ^{226}Ra into the source. This factor is sometimes approximated to within 1% of the values listed in the table using the relationship:

$$\text{I, i}\textit{ngrowth factor} = 1 + \left[3 * \left(1 - e^{-\lambda t}\right)\right]$$

Where:

λ = decay constant for ^{222}Rn, (1.256×10^{-4} min^{-1})
t = time elapsed between separation and the midpoint of the sample count (min)

The definition of the detection limit (DL) in the current version of 40CFR141.26 translates into the following equation:

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

Where:

t_s = time of the measurement used to accumulate the sample count
t_B = time of the measurement used to accumulate the background count
R_B = background count rate
V = volume of the sample aliquant
ε = detection efficiency for alpha particles from ^{226}Ra and progeny
Y = factor for chemical yield correction
I = ingrowth factor

This specific equation is not noted in the method, nor is it identified in the *Code of Federal Regulations* (CFR). It has been derived solely from the description in the CFR. A laboratory can use this equation to verify that typical parameters for their method (i.e., detector backgrounds, count times, volumes, efficiencies, chemical yields and ingrowth factors) will produce results that reliably satisfy required detection limits (RDLs). This equation can also be used to demonstrate a sample measurement has met the RDL. If these estimates prove to give values that are above 1 pCi/L as an RDL, the most effective means to get the analysis to that level is to increase the sample volume. Doubling the volume decreases the DL by 2, while increasing the count time does not have as significant an effect; doubling the count time decreases the RDL by ~$(2)^{½}$, a factor of 1.4.

The method as written does not provide an equation to calculate the counting uncertainty associated with each sample. Generally speaking the counting uncertainty is the principal contributor to the total uncertainty of the analysis for an individual sample where the ^{226}Ra concentration is at or below the value of 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:

$$U, at\ 95\%\ confidence = \frac{1.96\sqrt{\frac{R_s}{t_s} + \frac{R_B}{t_B}}}{2.22 \times \varepsilon \times V \times Y \times I}$$

Where U is the counting uncertainty in units of pCi/L and the other symbols have the definitions as previously noted.[7]

10. This section deals with the precision and accuracy of the method as determined by laboratories participating in an inter-comparison studies of blind PT samples from 1977 to 1979. However, no specific information is provided in the method regarding quality control samples to be used for this analysis or the batch size that is acceptable.

    Quality control (QC) requirements and acceptance criteria appropriate to EPA Method 903.0 are presented in Chapter VI of the *EPA Drinking Water Certification Manual* (see Reference 6) and address QC requirements specific to compliance monitoring of drinking water samples. The certification manual should be consulted for complete details.

References

1. ANSI N42.14-2004, "Calibration and Use of Germanium Spectrometers for the Measurement of Gamma-Ray Emission Rates of Radionuclides."
2. ASTM D7282-06, "Standard Practice for Set-up, Calibration, and Quality Control of Instruments Used for Radioactivity Measurements."
3. U.S. Environmental Protection Agency (U.S. EPA), 2002. *Implementation Guidance for Radionuclides*, Office of Ground Water and Drinking Water, EPA 816-F-00-002, March.
4. MARLAP. "Multi-Agency Radiological Laboratory Analytical Protocols Manual." Volumes 1 – 3. Washington, DC: EPA 402-B-04-001A-C, NUREG 1576, NTIS PB2004-105421. (July 2004). Available at www.epa.gov/radiation/marlap/index.html.
5. Standard Methods for the Examination of Water and Wastewater, American Public Health Association, Washington, DC. Available at www.standardmethods.org.
6. U.S. Environmental Protection Agency (U.S. EPA), 2005**.** *Manual for the Certification of Laboratories Analyzing Drinking Water Criteria and Procedures Quality Assurance* (5th Edition). Office of Ground Water and Drinking Water, EPA 815-R-05-004, January. Available at http://www.epa.gov/safewater/methods/laboratorycertification.html.

[7] For methods with very low counts, such as alpha counting, MARLAP Section 19.5.2.2 recommends adding one count each to the gross counts and the background counts when estimating the uncertainty of the net count rate. Thus, the equation for the counting uncertainty would be:

$$U,\ at\ 95\%\ confidence = \frac{1.96\sqrt{\frac{R_s}{t_s} + \frac{1}{t_s^2} + \frac{R_B}{t_B} + \frac{1}{t_B^2}}}{2.22 \times \varepsilon \times V \times Y \times I}$$

This addresses negative bias in the estimate of uncertainty and prevents calculating zero uncertainty when zero total counts are observed in the sample and background counts.