The Use of Uncertainties in Determination of Measurement Variance - 11118

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ABSTRACT

If a result w is a function of several variables, and the variances of the variables are known, then the variance of w is approximately equal to the following expression, where x, y and z are the variables.

$$V_W = (dw/dx)^2 \, V_X + (dw/dy)^2 \, V_Y + (dw/dz)^2 \, V_Z$$

The variances of x, y and z, V_X, V_Y and V_Z equal the square of the standard deviations of x, y and z; i.e., $s_x{}^2$, $s_y{}^2$, and $s_z{}^2$. This paper will compare the variance obtained in this fashion with the variances calculated for various parameters using commercial instrument software packages for gamma spectrometer, alpha spectrometer and gas proportional detector systems.

For these three measurement techniques, the instrument manufacturer's method for determination of peak uncertainty will be verified and incorporated into the propagation of errors calculation to obtain a total propagated uncertainty value.

Total propagated uncertainty values shall be tabulated for several methods and presented as a percentage of established regulatory action levels, if applicable.

INTRODUCTION

The output of radioanalytical measurements typically include a result and an uncertainty. The uncertainty is often expressed as a two sigma uncertainty, such that the result ± uncertainty defines a range of values within which one has 95% confidence that the true value of the measurement falls. The uncertainty

generated by a radioanalytical instrument may only be the so-called counting uncertainty, which is the uncertainty associated with the instrument measurement only and may include uncertainties in instrument variables such as count rate, efficiency, and energy regions of interest.

The overall uncertainty in a result, however, often includes errors in other factors associated with the method such as volume or weight of the sample, tracer volume, tracer recovery measurement, and ingrowth or decay time.   This overall uncertainty is called combined standard uncertainty [1] or U_{std} and can be expressed mathematically using the total propagation of errors equation.

$$V_W \;=\; (dw/dx)^2 \, V_X \;+\; (dw/dy)^2 \, V_Y \;+\; (dw/dz)^2 \, V_Z \qquad\qquad\qquad (Eq.\ 1)$$

Here we are interested in calculating the U_{std} of W. The value of W depends on the variables X, Y, and Z. The quantities (dw/dx), (dw/dy), and (dw/dz) are the partial derivatives of W with respect to X, Y, and Z, respectively, while the terms V_X, V_Y, and V_Z are the variances of X, Y, and Z, respectively.

Uncertainties in factors such as volume or weight of the sample, tracer volume, tracer recovery measurement, can typically be manually entered into the counting instrument so that the instrument may calculate a total propagated uncertainty instead of simply the counting uncertainty.

In this paper, we calculate U_{std} for activities of U-234, U-238 and Th-230 measured by alpha spectroscopy, and of gross alpha (GA) and gross beta (GB) measured by a gas proportional detector system, using the total propagation of errors equation. We will then compare the calculated variances with those generated for the same results by the instrument software programs. The differences in variances and thus in the approaches for calculating variances will be discussed.

DISCUSSION

Alpha Spectroscopy

An Ortec alpha spectroscopy counting system was utilized (Octete ® PLUS)[2]. The uncertainties of three analytes, U-234, U-238 and Th-230 are considered. Attachment A contains the activity equations and tracer recovery equations that are used to construct the total propagation of errors equations.

The activity equation for each analyte contains five variables: gross counts-per-minute, C_{gross} ; background counts-per-minute, C_{bkgnd}; sample volume, V; detector efficiency, E; and fractional recovery of the tracer, R. The fractional recovery equation, in turn, includes four variables, namely the measured tracer activity concentration, the sample volume, the tracer activity concentration added, and the tracer volume added.

For counts-per-minute (cpm), the uncertainties of the background and gross cpm were obtained from randomly selected samples. The uncertainty in the efficiency is provided by the instrument software during the initial calibration for a given detector. Sample volumes are measured with a 250 ml graduated cylinder with 2 ml gradations. The uncertainty in the volume measurement is conservatively estimated to be 40% of a gradation, or 0.8 ml (0.0008 L). The uncertainties in the tracer volumes were obtained from the fixed volume pipette documentation, while the uncertainties in the tracer activity added came from the reference standard certificates which accompanied the tracer when purchased. Finally, a first

approximation of the measured tracer activity uncertainty is provided in the alpha spectrometer raw data but could be calculated in the same manner as the analyte activity uncertainty.

The following uncertainties in Table I are calculated for U-234, U-238 and Th-230 from laboratory control samples (LCS) which are essentially spiked blank samples used to evaluate method accuracy. The uncertainty is simply the square root of the variance. The uncertainty values generated by the Alpha Vision software are also provided. The results indicate that the relative percent differences between the uncertainties are a fairly consistent 20% for both uranium and thorium isotopes, with the alpha spectrometer Alpha Vision software generating the higher value. The author has communicated several times with the instrument manufacturer and they are attempting to assist the author in resolving the discrepancy. It appears that most if not all of the difference may be due to the Alpha Vision software using the two sigma error instead of the one sigma error in the calculation of the efficiency variance term in the TPU equation. When the two sigma error for the efficiency is inserted into the TPU spreadsheet calculation, the RPD values for Th-230, U-234 and U-238 are reduced to 6%, 1.0%, and 0.6%, respectively. The author is continuing to work with the instrument manufacturer until the difference is resolved.

Table I. Calculated TPU Uncertainties and Alpha Vision Generated TPU Uncertainties for U-234, U-238, and Th-230

Analyte	Total Propagated Uncertainty (calculated)	Total Propagated Uncertainty (from alpha spectrometer)	Relative Percent Difference (RPD)
U-234	1.39	1.69	19.5%
U-238	1.34	1.64	20.1%
Th-230	0.84	1.01	18.4%

Gas Proportional Detector

A Protean gas proportional multi-detector counting system (MDS), Model MPC 9604 was utilized [3]. The uncertainties of two analytes, gross alpha (GA) as Th-230 and gross beta (GB) as Sr/Y-90, are considered. Attachment B contains the activity equations and efficiency equations that are used to construct the total propagation of errors equations. Sr/Y-90 is a beta emitter and Th-230 is an alpha emitter. Activity levels of these isotopes are spiked into standard solutions that are used for the efficiency curve solutions as well as the laboratory control sample (LCS) solutions.

The activity equations for GA and GB each contain four variables: gross counts-per-minute, C_{gross} ; background counts-per-minute, C_{bkgnd}; sample volume, V; and detector efficiency, E. The detector efficiency equation, in turn, includes three variables, namely the slope of the efficiency vs. mass curve, the mass of the evaporated or precipitated solid, and the y-intercept.

For counts-per-minute (cpm), the uncertainties of the background and gross cpm were obtained from randomly selected samples. The uncertainty in the efficiency will be determined from a total propagation of errors calculation from the linear efficiency vs. mass curve, using the uncertainties of the mass of evaporated solid and the slope of the curve. Sample volumes are measured with either a 250 ml or 100 ml graduated cylinder. The 250 ml cylinder has 2 ml gradations and the 100 ml cylinder has one ml gradations. The uncertainty in the volume measurement is conservatively estimated to be 40% of a gradation, or 0.8 ml (0.0008 L) for the 250 ml cylinder and 0.4 ml (0.0004 L) for the 100 ml cylinder. From the slope of the mass vs. efficiency curve, we will obtain the uncertainty in the slope. The uncertainty in mass will be the square root of the sum of the squares of the uncertainties of the two weights (empty planchet and planchet with evaporated solid).

The following uncertainties shown in Table II are calculated for LCS samples for GB using EPA Method 900.0 and GA using both EPA Method 7110C and 900.0. The uncertainty values generated by the Protean software are also provided. The results indicate that the differences between the uncertainties are indistinguishable for GA and GB by EPA Method 900.0 and small for GA by 7110C.   While a 5% difference is not great cause for concern, the author is currently investigating the various inputs to see if he can determine the cause of the discrepancy.

Table II. Calculated TPU Uncertainties and Protean Software Generated TPU Uncertainties for Gross Alpha (GA) and Gross Beta (GB)

Analyte	Total Propagated Uncertainty (calculated)	Total Propagated Uncertainty (from alpha spectrometer)	Relative Percent Difference (RPD)
GA (7110C)	0.832	0.876	5.2%
GA (900.0)	0.716	0.715	0.1%
GB (900.0)	0.881	0.880	0.1%

Conclusions

The author calculated total propagated uncertainty (TPU) values for blank spike results for U-234, U-238, Th-230, GA and GB. These values were compared to the TPU values generated by the instrument analysis software programs, namely Alpha Vision (from Ortec/Ametak) for the alpha spectrometer analytes and PIC version 1.3 (from Protean Instrument Corporation) for the GA and GB analytes. The alpha spectrometer analyte TPU values differed by approximately 20% each. The author believes that this may be due to the Alpha Vision using a two sigma uncertainty for the uncertainty in the efficiency since substituting the two sigma uncertainty reduces the differences to small values.

For the gas proportional detector analytes, the differences are quite small so the Protean software is validated for generation of uncertainty values.

Future efforts will be made to compare field sample result uncertainties as well as the uncertainties for Ra-228, Th-228, and Th-232.

References

1. USEPA, "Multi-Agency Radiological Laboratory Analytical Protocols (MARLAP)" EPA 402B-04-001A, July 2004.

2. Ortec/Ametek, "Alpha Vision Software" June 2003.

3. Protean Instrument Corporation, "P1C version 1.3 software for gas proportional multi-detector system" September 2002.

ATTACHMENT A

ALPHA SPECTROSCOPY ANALYTE TOTAL

PROPAGATED UNCERTAINTY EQUATIONS

Isotopic Uranium (U-234 used in the example equations)

$$A_{U234} = (C_{gross} - C_{bkgnd})/(2.22 * V * E * R_{U232})$$
(Eq. 2)

Where: A_{U234} = the activity of U-234

C_{gross} = gross counts per minute (cpm) value for U-234 in sample

C_{bkgnd} = background counts per minute (cpm) value

V = volume of sample aliquot

E = detector efficiency

R_{U232} = U-232 tracer fractional recovery

2.22 = conversion factor (2.22 dpm/pCi)

$$R_{U232} = (A_{U232 measured})(V)/(A_{U232 added to samp})(V_{U232 tracer})$$
(Eq. 3)

Where: $A_{U232 measured}$ = U-232 activity, in pCi/L, measured by alpha spectroscopy

V = volume of sample aliquot, in liters

$A_{U232 added to samp}$ = U-232 activity, in pCi/ml added to the sample

$V_{U232 tracer}$ = volume of U-232 tracer added to sample, in mls

The variance in the activity of U-234, $V_{A(U234)}$ may be represented by the following partial differential equation:

$$V_{(AU234)} = \left(\frac{dA_{U234}}{dC_{gross}}\right)^2 V_{Cgross} + \left(\frac{dA_{U234}}{dC_{bkgnd}}\right)^2 V_{Cbkgnd} + \left(\frac{dA_{U234}}{dE}\right)^2 V_E + \left(\frac{dA_{U234}}{dR_{U232}}\right)^2 V_{RU232} + \left(\frac{dA_{U234}}{dV}\right)^2 V_V$$
(Eq. 4)

Using Equation 2 and solving for the derivative terms, we obtain:

$$V_{(AU234)} = \left(\frac{1}{E * 2.22 * V * R_{U232}}\right)^2 V_{Cgross}$$

$$+ \left(-\frac{1}{E * 2.22 * V * R_{U232}}\right)^2 V_{Cbkgnd} + \left(-\frac{C}{E^2 * 2.22 * V * R_{U232}}\right)^2 V_E$$

$$+ \left(- \frac{C}{E*2.22*V*R_{U232}^2}\right)^2 V_{R_{U232}} + \left(- \frac{C}{E*2.22*V^2*R_{U232}}\right)^2 V_V \qquad \text{(Eq. 5)}$$

Isotopic Thorium (Th-232 used in the example equations)

$$A_{Th232} = (C_{gross} - C_{bkgnd})/(2.22*V*E*R_{Th229}) \qquad \text{(Eq. 6)}$$

Where the definitions of the variables are analogous to those in Equation 2 :

A_{Th232} = the activity of Th-232

C_{gross} = gross counts per minute (cpm) value for Th-232 in sample

C_{bkgnd} = background counts per minute (cpm) value

V = volume of sample aliquot

E = detector efficiency

R_{Th229} = Th-229 tracer fractional recovery

2.22 = conversion factor (2.22 dpm/pCi)

$$R_{Th229} = (A_{Th229measured})(V)/(A_{Th229added\,to\,samp})(V_{Th229tracer}) \qquad \text{(Eq. 7)}$$

Where: $A_{Th229measured}$ = Th-229 activity, in pCi/L, measured by alpha spectroscopy

V = volume of sample aliquot, in liters

$A_{Th229added\,to\,samp}$ = Th-229 activity, in pCi/ml

$V_{Th229tracer}$ = volume of Th-229 tracer added to sample, in mls

The variance in the activity of Th-232, $V_{A(Th232)}$ may be represented by the following partial differential equation:

$$V_{(ATh232)} = \left(\frac{dA_{Th232}}{dC_{gross}}\right)^2 V_{C_{gross}} + \left(\frac{dA_{Th232}}{dC_{bkgnd}}\right)^2 V_{C_{bkgnd}} + \left(\frac{dA_{Th232}}{dE}\right)^2 V_E + \left(\frac{dA_{Th232}}{dR_{Th229}}\right)^2 V_{R_{Th229}} + \left(\frac{dA_{Th232}}{dV}\right)^2 V_V$$

$$\text{(Eq. 8)}$$

Using Equations 6 and 8 and solving for the derivative terms, we obtain:

$$V_{(4Phase)} = \left(\frac{1}{E*2.22*V*R_{TPhase}}\right)^2 V_{C_{gross}} + \left(-\frac{1}{E*2.22*V*R_{TPhase}}\right)^2 V_{C_{bkgnd}} + \left(-\frac{C_{gross}-C_{bkgnd}}{E^2*2.22*V*R_{TPhase}}\right)^2 V_E$$

$$+ \left(-\frac{C_{gross}-C_{bkgnd}}{E*2.22*V*R_{TPhase}^2}\right)^2 V_{R_{TPhase}} + \left(-\frac{C_{gross}-C_{bkgnd}}{E*2.22*V^2*R_{TPhase}}\right)^2 V_V$$

(Eq. 9)

ATTACHMENT B

GAS PROPORTIONAL DETECTOR ANALYTE TOTAL

PROPAGATED UNCERTAINTY EQUATIONS

Gross Alpha (GA)

$$A_{GA} = (C_{gross} - C_{bkgnd})/(2.22 * V * E)$$ (Eq. 10)

Where: A_{GA} = the activity of gross alpha

C_{gross} = gross counts per minute (cpm) value for GA in sample

C_{bkgnd} = background counts per minute (cpm) value

V = volume of sample aliquot

E = detector efficiency

2.22 = conversion factor (2.22 disintegrations per minute (dpm)/picocurie (pCi))

Further, the efficiency, E, may be expressed by the following equation:

$$E = S x M + i$$ (Eq. 11)

Where: E = detector efficiency

S = the slope of the efficiency vs. mass curve

M = the mass of the evaporated or precipitated solid

i = the y-intercept of the efficiency vs. mass curve

The variance in the activity of GA, $V_{A(GA)}$ may be represented by the following partial differential equation:

$$V_{(AGA)} = \left(\frac{dAGA}{dC_{gross}}\right)^2 V_{C_{gross}} + \left(\frac{dAGA}{dC_{bkgnd}}\right)^2 V_{C_{bkgnd}} + \left(\frac{dAGA}{dE}\right)^2 V_E + \left(\frac{dAGA}{dV}\right)^2 V_V$$ (Eq. 12a)

Where $$V_E = \left(\frac{dE}{dS}\right)^2 V_S + \left(\frac{dE}{dM}\right)^2 V_M + \left(\frac{dE}{di}\right)^2 V_i$$ (Eq. 12b)

Using Equations 10 and 12a and solving for the derivative terms, we obtain:

$$V_{(AGA)} = \left(\frac{1}{E * 2.22 * V}\right)^2 V_{C_{gross}} + \left(-\frac{1}{E * 2.22 * V}\right)^2 V_{C_{bkgnd}} \left(-\frac{C}{E^2 * 2.22 * V}\right)^2 V_E$$

$$+ \left(-\frac{C}{E * 2.22 * V^2}\right)^2 V_V$$ (Eq. 13)

Gross Beta (GB)

$$A_{GB} = (C_{gross} - C_{bkgnd})/(2.22 * V * E) \tag{Eq. 14}$$

Where: A_{GB} = the activity of gross beta

C_{gross} = gross counts per minute (cpm) value for GB in sample

C_{bkgnd} = background counts per minute (cpm) value

V = volume of sample aliquot

E = detector efficiency

2.22 = conversion factor (2.22 disintegrations per minute (dpm)/picocurie (pCi))

Further, the efficiency, E, may be expressed by Equation 11 except using the analogous GB efficiency curve characteristics.

The variance in the activity of GB, $V_{A(GB)}$ may be represented by the following partial differential equation:

$$V_{(AGB)} = \left(\frac{dA_{GB}}{dC_{gross}}\right)^2 V_{C_{gross}} + \left(\frac{dA_{GB}}{dC_{bkgnd}}\right)^2 V_{C_{bkgnd}} + \left(\frac{dA_{GB}}{dE}\right)^2 V_{E} + \left(\frac{dA_{GB}}{dV}\right)^2 V_{V} \tag{Eq. 15}$$

Where V_E is defined using Equation 12b and the analogous gross beta efficiency equation variables.

Using Equations 14 and 15 and solving for the derivative terms, we obtain:

$$V_{(AGB)} = \left(\frac{1}{E * 2.22 * V}\right)^2 V_{C_{gross}} + \left(\frac{1}{E * 2.22 * V}\right)^2 V_{C_{bkgnd}} \left(\frac{C}{E^2 * 2.22 * V}\right)^2 V_{E}$$

$$+ \left(-\frac{C}{E * 2.22 * V^2}\right)^2 V_{V} \tag{Eq. 16}$$

ATTACHMENT C

UNCERTAINTY VALUES

Efficiencies and cpm

For counts-per-minute (cpm), the uncertainties of the background and gross cpm were obtained from the instrument raw data from randomly selected samples.

For GA and GB efficiencies, the uncertainty is calculated by solving for V_E in Equation 12b of Attachment B and taking the square root. Please note that there is a GB efficiency and a GA efficiency obtained using a tap water efficiency curve for a given detector using Sr/Y-90 and Th-230, respectively, and a GA efficiency obtained using a iron hydroxide/barium sulfate efficiency curve for Method 7110C.

For the alpha spectrometer efficiency, the uncertainty is that associated with the initial calibration efficiency for a given detector.

Volumes

Volume uncertainties are estimated as 40% of the volume of the smallest gradation on the graduated cylinder used to measure sample aliquots. A 250 ml graduated cylinder is used to measure aliquots for isotopic thorium, isotopic uranium, and GA by 7110C. A 100 ml cylinder is typically used for GA/GB by Method 900.0.

iso-Uand iso-Th: 0.0008 L each (250 ml grad. Cylinder with 2 ml gradations)

GA (900.0): 0.0004 L (100 ml grad. cylinder with 1 ml gradations)

GA(7110C): 0.0008 L (250 ml grad. Cylinder with 2 ml gradations)

GB: 0.0008 L (100 ml grad. cylinder with 1 ml gradations)

The tracer autopipette volume uncertainty is 1.3E-04 mls as per the manufacturer's uncertainty determination for delivery of 100 µLs, or 0.1 mLs.

Table III. Alpha Spectroscopy Uncertainty Values[a]

Analyte	Efficiency (cpm/dpm) X 100	Counts per min[b] (gross/bkgd)	Tracer Volume (mls)	Sample Volume (liters)	Tracer Activity (actual in pCi/ml)	Tracer Activity (measured in pCi/L)
Isotopic uranium	0.50%	0.0042/0.0042	1.3E-04	0.0008	0.76	0.946
Isotopic thorium	0.50%	0.0042/0.0042	1.3E-04	0.0008	1.00	0.992

a. Results from the Maywood LCS sample described in the Discussion section were used. The sample lab ID number is 10-04798

b. Analytes used for the cpm values are U-234 for iso-uranium and Th-230 for iso-thorium

Table IV. Gas Proportional Detector Measurement Uncertainty Values[a]

Analyte	Efficiency	Counts per minute	Sample Volume (liters)
Gross Alpha (7110C)	0.00188 (det. P3D)	19.49/0.040	0.0008
Gross Alpha (900.0)	3.23E-04 (det. P2C)	0.0184	0.0008
Gross Beta (900.0)	2.98E-05 (det. P2C)	40.9/0.026	0.0008

a.Results from the Maywood LCS samples described in the Discussion section were used.
The sample lab ID number is 10-04204 for GA(7110C) and 10-4206 for GA/GB (900.0)