An Analysis of Total Propagated Uncertainties in Analytical Radioactivity Measurements of Environmental Samples

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It is anticipated that future data acquisitions intended for use in radiological risk assessments will require the incorporation of uncertainty analysis. Increasingly, quality assurance specialists, data validators and regulators are aware of the intricacies in computing uncertainties associated with radiochemical determinations. Specific to the environmental management community is the need of a thorough analysis of total propagated uncertainties in radioanalytical chemistry.

In environmental radioactivity measurements, total propagated uncertainties (TPU) encompass uncertainties associated with radiochemistry separations, blank preparation and instrument counting times and methods. The net effect is that equations for TPU can be quite complicated. The Environmental Measurements Laboratory (EML), Analytical Chemistry Division has developed a systematic process to compute uncertainties in constituent components of the analytical procedure as well as the TPU. The equations for computation have also been incorporated into a code for use in the spreadsheet application, QuattroPro™.

Figure 1 is a flow diagram which shows the steps in calculating the sample activity concentration and its uncertainty. Steps I and II require a multistage calculation which is shown by the flow diagram in Figure 2. In α-emitting and β-emitting radionuclides, the sample aliquot activity determination and the calculation of its associated uncertainty is dependent upon the type of recovery method used in the analytical process, the number of counts collected in a given period of time and the detector efficiency. The uncertainty for each stage is determined and the total uncertainty is then propagated to yield the TPU for the analytical process.

Equations for each component are standard equations found in any radioanalytical textbook and its associated uncertainty equations are derived from concepts provided by the International Organization for Standardization (ISO)[1] and also found in ANSI N42.23[2]. Following the development of the standard equations, the total propagated uncertainties for α-emitting (Example 1) and β-emitting radionuclides (Example 2) are discussed.

Example 1. ^{241}Am in Soil - An Analysis of TPU vs. Counting Time

The analysis is for an aliquot of 20g of soil. The ^{241}Am activity is 1.75 Bq/kg. An equal amount of ^{243}Am tracer was added in the analytical procedure for radiochemical recovery method 1 (Figure 2). The detector efficiency is .30 and the tracer recovery is approximately 60%.

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[1]ISO. "Guide to the Expression of Uncertainty in Measurements", 1995.

[2]ANSI N42.23." Measurement and Associated Instrumentation Quality Assurance for Radioassay Laboratories", 1995.

Uncertainties associated with chemical procedures are based on manufacturer specifications for the various types of equipment used .

The variation in relative TPU (also known as coefficient of variation) was ascertained as a function of counting time. Figure 3 shows that as the counting time of the sample is increased from 0.5 to 14 hours, the relative TPU (TPU/ activity) decreases from approximately 38% down to 7% following an exponential form. The greatest change occurs between 0.5 to 3 hours where the relative TPU changes from 38% to 13% . After 3 hours of counting the gains from increased counting time are drastically reduced. Counting beyond 3 hours to 7 hours only brings down the relative TPU from 13% to 10%, a gain of 3% for approximately double the time.

Another analysis of theTPU is illustrated in Figure 4. Much discussion in the analytical community has been centered on the relative contributions to the TPU of laboratory chemical techniques and counting. The results of our analysis show that as counting time increases from 0.5 to 14 hours, the uncertainty from the chemical procedures (referred to as "method error") only changes slightly, from 0.06% to 1.9% of the TPU. For the sample described here and for a counting time of as much as 14 hours the counting uncertainty ("counting error") dominates the TPU. After three hours of counting ,the counting component of the TPU is 99.5% and the TPU relative to the activity is 13%.

Example 2. ^{90}Sr in Water - An Analysis of TPU vs. number of counts

The second example illustrates the dependence of relative TPU on the number of counts collected. The counting interval is held constant at 2 days. The initial analysis is for 0.100 L of water, with 2.0 Bq ^{90}Sr L^{-1}. The recovery of ^{90}Sr is monitored using ^{85}Sr, which is a γ-emitter; this is referred to here as the radiochemical recovery method 2 (Figure 2). The recovery of ^{90}Y is determined gravimetrically. ^{90}Y is counted on a scintillation counter with efficiency of 0.30. The TPU is calculated for increasing number of counts, which corresponds to having samples with increasing activity concentration.

Figure 5 shows the dependence of relative TPU on the number of counts, which is similar to the relationship observed for ^{241}Am in Example 1. As the number of counts increases from 750 to 1500, the change in relative TPU is significant, from 40% to 8%. Beyond 1500 counts the change in relative TPU is minor. For example, if a sample's activity concentration is high enough so that a 0.100 L aliquot results in 5000 counts , the relative TPU approaches 5%.

Figure 6 illustrates contributions to the TPU made by counting statistics as compared to the uncertainties from the chemical procedures. The counting error approaches the method error for an aliquot with approximately 5000 counts.

A discussion of the similarities and the differences between the two examples described here should lead to a better understanding of the significance of the various components of the TPU. The specific details of the relationships have to be detemined for each type of radiochemical analysis and for each laboratory, and then decisions can be made as to the need for calculating and reporting the TPU instead of using the counting uncertainty only.

Steps for Calculation of Sample Activity Concentration and its Uncertainty

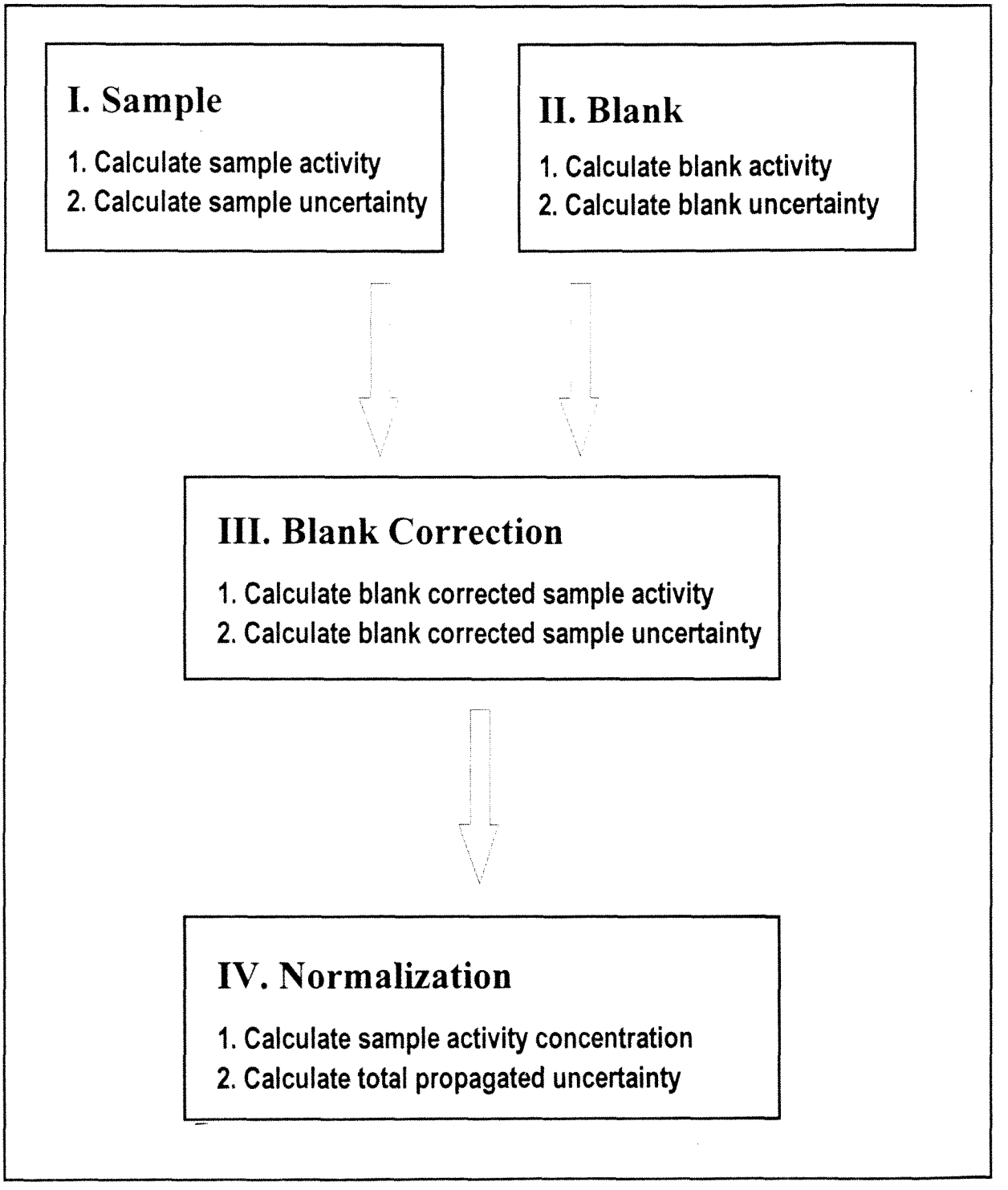

Figure 1

I. Sample Activity Calculations

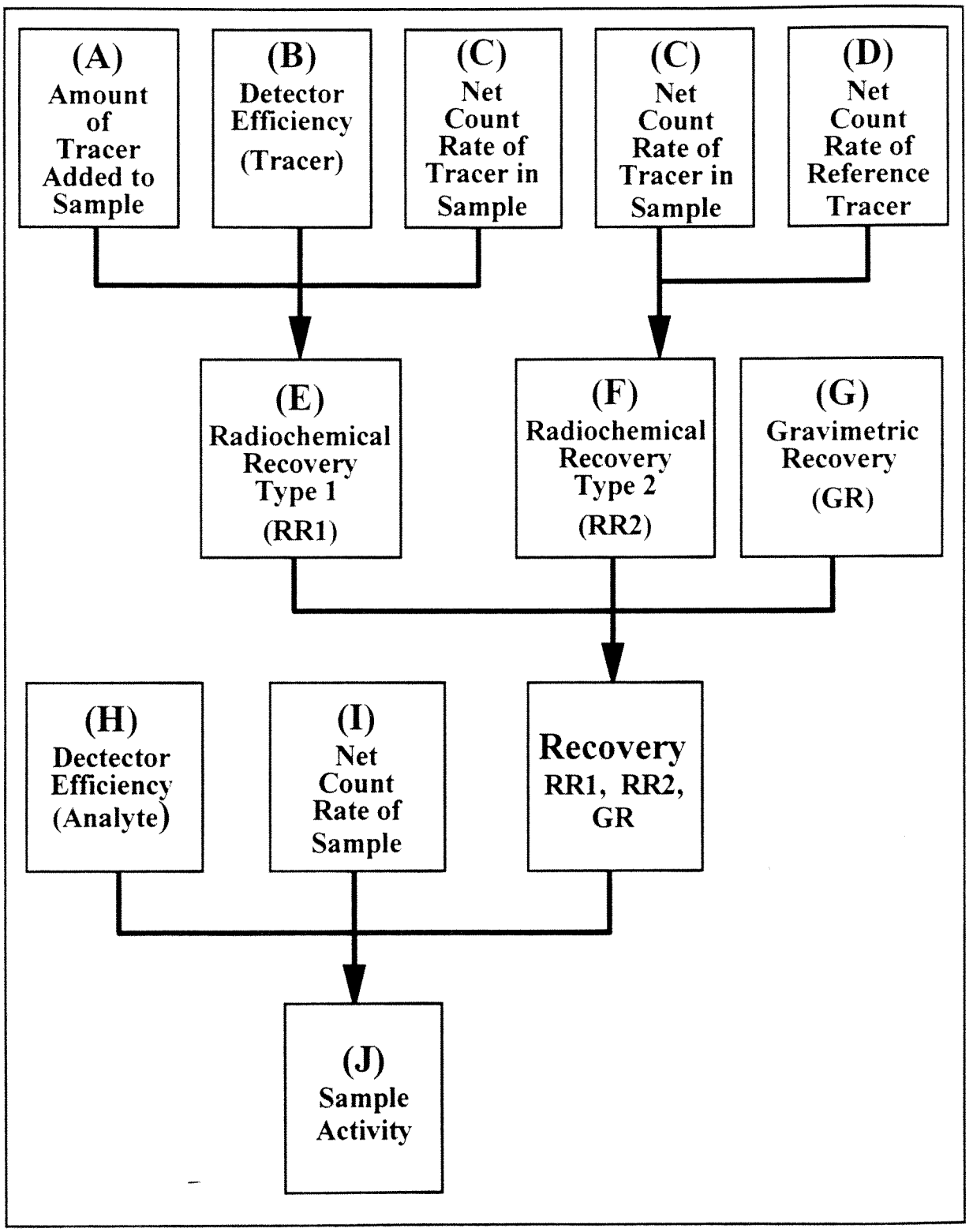

Figure 2

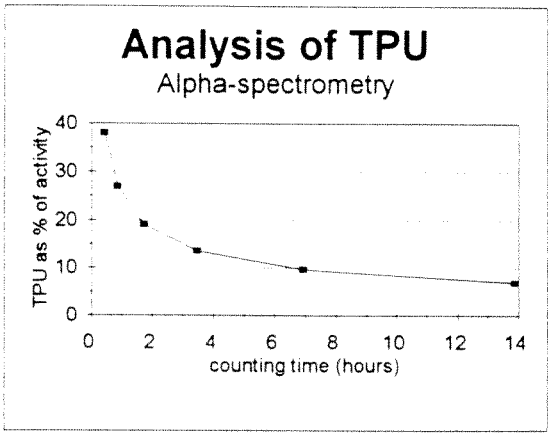

Figure 3

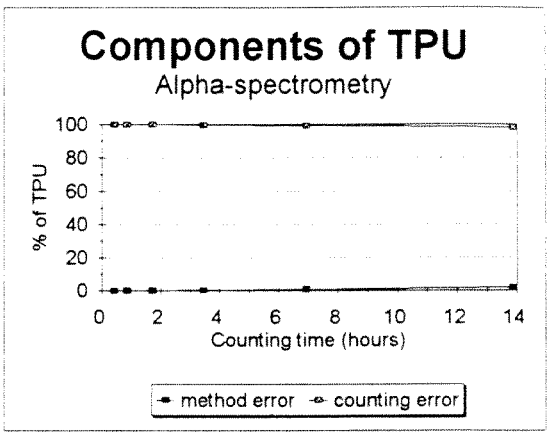

Figure 4

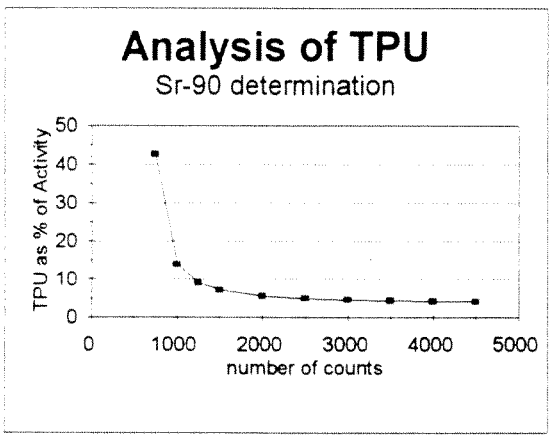

Figure 5

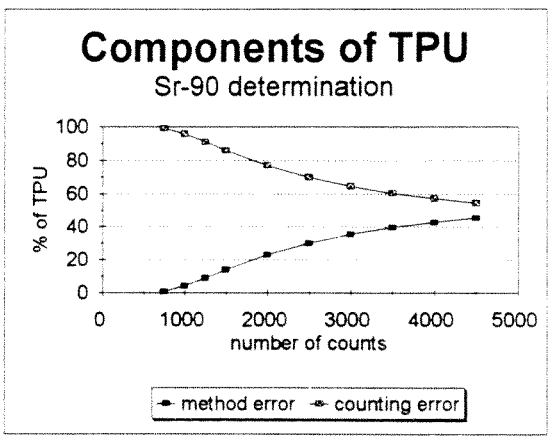

Figure 6