

Preparation and Testing of Soil Standards Containing Known Activities of Homogeneously Distributed Radionuclides.

David S. Sill
Radiological and Environmental Sciences Laboratory
U.S. Department of Energy

The only unequivocal way to determine the accuracy of a laboratory's procedures and to demonstrate this capability to others, is by analysis of samples containing accurately known quantities of radionuclides¹. If a particular analyst obtains the known value within the statistics of the measurement at the confidence level, precision and sensitivity required, the analysis is correct. If any other value outside those limits is obtained, the analysis is incorrect. It makes no difference what precision was obtained on replication or what others obtained on the same sample. Most QA programs refer vaguely to analysis of standards but with little emphasis on what those standards are or where they come from.

The proper preparation and use of soil standards containing accurately known quantities of radionuclides continues to be one of the most important aspects of determining the accuracy and reliability of radiochemical procedures and is fundamental in maintaining QC in the laboratory.

The analytical procedure can never produce experimental results that are more accurate than the accuracy of the standards used in the calibration and testing of the method. It is extremely important that the reference values for the standard represent the actual activities of the radionuclides that are in the particular sample. If the reference value is biased, as is often the case, erroneous conclusions about the quality of the particular method or operator being tested will be made.

This paper will discuss some of the common problems encountered in the preparation and use of soil standards, common QC practices being used today, and laboratory QC in general.

Preparation of Standard Material vs. Evaluation of Method Performance. It is extremely important to keep the validation of the radiochemical procedure, using a certified standard, separate from the verification of a standard using a certified chemical procedure. Otherwise, a condition exists that is similar to the situation of trying to solve a single equation that contains two variables: If an incorrect result is obtained it is impossible to determine whether the problem is associated with the standard or with the analytical procedure. This seems elementary but occurs all the time: a standard is sent out to evaluate performance, the results are widely dispersed, and the conclusion becomes one of an inhomogeneous sample. Why then was the standard sent out in the first place?

In order to evaluate the performance of a radiochemical procedure, the reference value of the standard being used must be unquestionably accurate so that the analytical value obtained can be compared and an evaluation made based on performance of the procedure. Conversely, once a radiochemical procedure has been shown to give accurate and reliable results, the procedure can be used to analyze a sample or standard and the results obtained should be trusted. If the results obtained from this "certified" procedure are outside the statistics of the measurement, the sample or standard is inhomogeneous at that particular sample size. Inhomogeneity of a sample should never be mistakenly equated to poor performance of the chemical procedure.

It is important not to deviate from these concepts and erroneously assign blame for an inhomogeneous "standard" to the chemical procedure, or fault a truly qualified standard when using an unreliable chemical procedure.

Duplicates. Many laboratories depend heavily on duplicate analyses to assess the quality of the analytical results. Even when agreement among results is good, duplicates only indicate precision, not accuracy. When agreement among the results is poor, the analyses still cannot be held responsible because the sample could be inhomogeneous, a very common occurrence. There are many examples in the literature that show highly precise results that are extremely inaccurate.

Interlaboratory Comparisons. Analytical results from different laboratories are widely used in round-robin testing of a given procedure, or in determining a consensus value for an analyzed standard. If the results from a large number of laboratories are in very poor agreement, it is evident that not all of the results can be correct or the standard is inhomogeneous. Part of the problem can be caused by the difference in the precision with which the measurements were made, primarily due to not specifying a common sample size and counting time to be used for the particular level of activity present. The results themselves cannot be in any better agreement than the uncertainty in the measurements will permit. Although many of the results may be statistically identical, there is little consolation to be derived from this fact in determining the "reference value" for the sample because of the large standard deviations of the individual measurements. The uncertainty of the reference value derived in such a way will always be larger than uncertainties derived from dilution of known standards.

Spiked Standards. For some reason that I can't understand, there appears to be a belief that there is something synthetic and unnatural about spiking a natural matrix (soil) homogeneously with a known activity of a radionuclide; compared to a natural matrix standard that had an unknown amount of the same radionuclide deposited randomly and inhomogeneously.

The term "spiked standard" is meant to refer only to the method used to incorporate the radionuclide of interest into the natural matrix and does not infer anything synthetic, artificial or inferior in any other way to those designated by the term "natural matrix standard". There is little disagreement that radioactive tracers can be purified to almost any extent desired and can be standardized accurately by the National Institute of Standards and Technology (NIST) or a commercial vendor that is traceable to NIST. From this certified standard, appropriately sized aliquots can be taken to give the desired activity that ensures the proper precision is obtained for the measurement. Accordingly, the concentration of a given radionuclide in the spiked standard will be that calculated from the activity added divided by the mass of the soil provided only that the following apply: that contamination is avoided, that activity indigenous in the soil is negligible or can be corrected for, and that the activity added is homogeneously distributed throughout the matrix. Because the first two provisions can be easily satisfied for soil standards, sample homogeneity becomes the most important consideration in establishing that the calculated value for the standard can be obtained among different aliquots of the standard. Consequently, proof of accuracy for a given sample size follows logically from proof of homogeneity by replicate analyses of individual aliquots by procedures of the highest precision.

When prepared as described, spiked standards possess many advantages over natural matrix standards. They can be prepared with any nonvolatile radionuclide at any level of activity desired in any type of sediments of any "real-world" composition. They can be designed to be homogeneous at virtually any sample size or sensitivity desired. The reference activity of each radionuclide present is based on a calculated value and has nothing to do with analysis of the sample. This method assures that no bias from the analytical measurements is introduced into the

reference value. Spiked soils can be made to possess many of the characteristics expected to be encountered in the real world, particularly with respect to chemical composition. They can be used to check fundamental properties of chemical procedures such as complete dissolution of refractory compounds and isotopic exchange with tracers². They also can be diluted with one another much like liquids and combined with other solids to produce standards having an infinite variety of compositions and concentrations.

Aliquots of either single standards or mixtures of several standards can be analyzed as desired to provide unequivocal quality control in the laboratory at any desired frequency without assistance or participation by others. Because of the large number of combinations of standards and diluent soils possible, the analyst need never be required to analyze a sample with the same radiochemical profile or level of activity a second time, eliminating any possible bias due to having analyzed this same sample previously. If a composite sample is made of more than one standard, or a dilution of a single standard with blank soil, the results cannot be biased unconsciously in favor of the correct result.

Natural Matrix Standards. Several problems have been identified repeatedly over many years with the use of natural matrix materials as standards for radiochemical analysis. Perhaps the most serious one is that soils and other materials contaminated with radionuclides from natural processes must be analyzed to determine the activity present of each radionuclide of interest to be used as the reference value for the standard. This is usually done by some type of round-robin program which almost always produces results that are scattered far more than the statistics of the measurement will allow. To introduce a large uncertainty or inaccuracy into the reference value of a standard from the analytical procedures used in its standardization is simply not acceptable in a standard whose very purpose is to detect inaccuracies in the performance of both the analytical procedures used by others and the analyst doing the work. It is evident that there is a pressing need for standards of known content against which all analytical results can be compared rather than against values which are themselves determined by analyses.

Natural matrix standards are frequently inhomogeneous at sample sizes routinely encountered in the laboratory. This is particularly likely with the transuranium elements and other radionuclides that are of relatively high specific activity. Some samples cannot be homogenized even with extensive grinding and blending because of a fundamental particle problem³. The latter term is meant to refer not merely to the fact that particles are present, but that the particles present are so small that they cannot be further subdivided significantly, yet are still large enough that the radioactivity of a single particle can be detected easily under the conditions being used.

Testing of Real World Conditions. A proper standard must test the ability of both the analytical procedure and the analyst to handle the worst problems likely to be encountered in the real world⁴. Too often soil standards that are used to test the determination of plutonium only contain the element in a soluble form. This does little to prove that the chemical procedure will work satisfactorily on anything other than soluble plutonium compounds, when in fact most plutonium compounds encountered in the environment are very insoluble if not refractory in nature. This conditional performance is usually overlooked and an overall assumption is made that the procedure will perform equally well on any sample. Other leaching procedures stipulate that they are only intended to be used for the determination of the acid soluble form of plutonium. In some cases the procedures themselves convert the relatively soluble form to an insoluble refractory type oxide by heating. If the standard does not test the specific conditions needed to be tested the data produced will be unreliable at best.

Selection of Proper Activity. It is desirable and necessary that standards be available at more than one activity level for each radionuclide of interest. To determine the real precision and accuracy of which a procedure is capable with any reasonable sensitivity, the sample must contain enough activity to keep the statistical uncertainties in the measurements at an acceptably low level. Otherwise, one cannot know whether widely dispersed results are caused by poor chemistry or poor statistics of measurement.

In order to determine the sensitivity of the procedure, and to verify the detection limits claimed are being achieved, the activity present should not be more than about two or three times the stated detection limit for the conditions used. A net positive signal must be obtained from the sample to show that chemical procedure is adequate to separate the minimum detectable quantity of the radionuclide from the background and to ensure that a statistically positive result is obtained. Blanks cannot be used for this purpose because they only show that the analyte of interest was not detected, a conclusion equally possible from a complete failure of the chemical dissolution, separations, or instrument malfunction.

Conclusions. There is an abundance of documented experimental evidence that much of the current analytical data being generated in the determination of most radionuclides in soil containing refractory and siliceous materials is inaccurate. A large part of the problem is caused by incomplete sample dissolution and poor chemistry used in the analytical procedures, and poor performance on the part of some of the individual analysts. Another large part of the problem derives from inadequate planning of the analyses to ensure that the sample size and counting time used will produce a statistically valid result at the concentration of the radionuclide present. Routine analyses of solid standards of known activity would permit each individual analyst to assess his own performance on a continuing basis without assistance from others, and would result in much better quality control than can be obtained using weaker criteria such as replication of analyses or comparison with the results of others. The standards must be homogeneous, be free of significant biases introduced by other analyses, contain levels of activity appropriate to the sensitivity and precision desired, and contain the main problems to be encountered in the real world. Standards prepared determinately by spiking natural matrix materials having a chemical composition similar to that of the samples to be measured fill QC requirements better than materials with the radionuclides of interest already in place by natural means.

The data in the two tables below demonstrates the precision and accuracy that is achievable in preparing spiked standards.

High level standard used to check homogeneity on small sample sizes (10mg to 100mg)

Sample	Pu-239	Pu-238	Am-241	Sr-90
Q0651A	42.3 ± 1.7	30.0 ± 1.4	20.7 ± 1.0	5.3 ± 0.2 E2
Q0651B	43.3 ± 1.8	30.1 ± 1.3	19.4 ± 0.9	5.3 ± 0.2 E2
Q0651C	43.9 ± 1.8	29.5 ± 1.3	21.4 ± 1.0	5.3 ± 0.2 E2
Q0651D	42.1 ± 1.8	29.5 ± 1.3	21.1 ± 1.0	5.3 ± 0.2 E2
Q0651E	43.2 ± 1.8	28.6 ± 1.3	19.2 ± 0.9	5.4 ± 0.2 E2
Q0651F	41.0 ± 1.7	27.5 ± 1.2	19.5 ± 0.9	5.3 ± 0.2 E2
<hr/>				
Mean:	42.6 ± 1.0	29.2 ± 1.0	20.2 ± 1.0	5.3 ± 0.1 E2
Known:	43.1 ± 0.2	29.0 ± 0.1	20.8 ± 0.1	5.40 ± 0.05 E2

1 kg Spiked Individual Sample Size 100 mg Activities in pCi/g

Final blended standard for routine use. Lower activity level.

Sample	Pu-239	Pu-238	Am-241	U-234	U-238
#10	1.39 ± 0.05	0.76 ± 0.05	0.18 ± 0.04	4.17 ± 0.16	1.18 ± 0.07
#26	1.37 ± 0.05	0.76 ± 0.05	0.18 ± 0.04	4.20 ± 0.17	1.11 ± 0.07
#53	1.29 ± 0.05	0.76 ± 0.05	0.16 ± 0.04	4.25 ± 0.18	1.12 ± 0.08
#77	1.26 ± 0.05	0.77 ± 0.05	0.16 ± 0.04	4.16 ± 0.08	1.12 ± 0.08
#92	1.25 ± 0.05	0.78 ± 0.05	0.18 ± 0.04	4.35 ± 0.08	1.17 ± 0.08
#129	1.33 ± 0.05	0.79 ± 0.05	0.19 ± 0.04	4.27 ± 0.15	1.15 ± 0.08
<hr/>					
Mean:	1.32 ± 0.06	0.77 ± 0.01	0.18 ± 0.02	4.23 ± 0.08	1.14 ± 0.03
Known:	1.30 ± 0.02	0.745 ± 0.011	0.177 ± 0.003	4.27 ± 0.10	1.10 ± 0.03

52.3 kg Spiked

Sample Size 1 g

Activities are in pCi/g

References:

- 1) C.W. Sill, D.S. Sill, Soild Standards for Quality Control in Radiochemical Analysis, *Radioactivity & Radiochemistry*, Vol 6, No.2, 1995, p28-39
- 2) C.W. Sill, D.S. Sill, Sample Dissolution, *Radioactivity & Radiochemistry*, Vol 6, No.2, 1995, p8-14
- 3) C.W. Sill, Some Problems in Measuring Plutonium in the Environment, *Health Physics*, Vol 29, 1975, p619-626
- 4) D.S. Sill, C.W. Sill, Simultaneous Determination of the Actinides in Small Environmental Samples, *Radioactivity & Radiochemistry*, Vol 5, No.2, 1994, p8-19