

From: "pshebell" <pshebell@mail.eml.doe.gov>
To: <jxd3@nrc.gov> — J-C. Dehmel - NMSS
Date: 02/24/2003 12:25PM
Subject: revision

Jean-Claude, — NMSS

Attached is a revision of one of the reports. I had one of our radiochemist review it. One of the comments or suggestion is the idea of filtering a solublized sample and checking the filter for hot particles. Apparently the lab has some experience with this technique for Sr-90 hot particles.

I will be doing some DHS activities tommorrow and Wednesday. I'll be checking my e-mail, so if you have any immediate concerns or comments you can e-mail them to me.

Regards,

Peter Shebell, Physicist
Environmental Sciences Divison
Environmental Measurements Laboratory
201 Varick St 5th Floor
New York, NY 10014-4811
Voice: (212) 620-3568
email: peter.shebell@eml.doe.gov

J-257

Sampling, sample preparation, radiochemical analysis for radionuclides associated with heterogenously distributed contamination.

Draft Letter Report

**Prepared by
Peter Shebell**

Jean-Claude Demhel, NRC Lead Health Physicist

**U.S. Dept. Of Energy
Environmental Measurements Laboratory**

February, 2003

**Prepared for
Office of Nuclear Material Safety and Safeguards
Division of Waste Management
Decommissioning Branch
Facilities Decommissioning Section
U.S. Nuclear Regulatory Commission
Washington, DC 20555
NRC JOB CODE J5402**

Introduction

The purpose of this brief report is to discuss a few key issues associated with sample collection, sample preparation and radiochemical analysis of radionuclides associated with heterogeneously distributed contamination. Issues regarding sample design for heterogeneously distributed contamination will not be addressed. References are provided so that more detailed information may be obtained.

Sample collection

Previous reports on sampling for heterogeneously distributed contamination, i.e., hot spot and hot particles, have advocated the use of scanning techniques as the only effective approach to the problem. However, scanning data should always be supplemented with media samples that are analyzed in a fixed laboratory using approved or appropriate radioanalytical techniques, so-called analytical data. It should be noted that comparisons of field data and analytical data can be problematic, especially if the contamination is heterogeneous. Therefore, analytical data should be used to determine information that cannot be determined by using field methods (e.g. isotopic information that could be used to establish surrogates).

The challenge of sample collection for heterogeneously distributed contamination deals primarily with representativeness. By definition, a representative sample must, in this case, exhibit the average concentration, to a specified degree of accuracy, over an area or volume. Unfortunately, there may not be any way to know or estimate the degree of heterogeneity that could be used to develop a sampling strategy. In this case, the goal of sampling would be to establish bounds or a worst case scenario. Also, the approach should not be prescriptive. Instead, the approach should be interrogative, with ability to modify the sampling strategy as more information from the characterization process becomes available. This idea of using real-time, field generated data to support real-time decision-making to manage the uncertainty associated with site characterization has been addressed by the EPA and is referred to as the Triad Approach (Crumbling et al. 2001). It is an outgrowth of the DQO process and elements of it are reflected in MARSSIM. It is mentioned here because the Triad Approach provides a frame work that combines the use of novel field screening techniques (e.g., FIDLER, AXISS, SCM/SIMS, etc.) and traditional sampling, with laboratory analysis, to manage the uncertainty associated with analytical and sampling errors that are connected with site characterization.

Sample Preparation

Most samples that are collected cannot be assayed directly but must be converted to a more suitable form. One of the first steps in that process involves homogenization. The degree of processing required to achieve some level of homogeneity is largely a function of the form of the sample (e.g., sediment, soil, rock) and the desired degree of reproducibility, which is a function of the size of the sub-sample that is required to perform the analysis. For example, the analysis of gamma-emitting fission products in sediment using gamma-ray spectrometry needs almost no processing. This is because sediment usually consists of fine particles and the amount needed for gamma-ray spectrometry can be a significant fraction of the sample collected (i.e., a large sub-sample). However, if the analytical method involves Inductively Coupled Plasma Mass

method
the
steps
explain
have a
top

Spectrometry, then only a few micrograms out of a much larger sample (~10 - 20 grams) are required. In this case, the small sub-sample increases the chance for error and it is therefore essential that the sample is well-homogenized. Moreover, if the sample consists of hot particles, then a significant amount of grinding and blending will be necessary to reduce (not eliminate) the uncertainty associated with sub-sampling. Standard practices for soil sample preparation may be found in ASTM C999-90 (ASTM 1990). Clearly, if hot particles are an issue, then techniques such as ICP-MS should be avoided. The canonical work on sampling theory and practice is attributed to Pierre Gy and is summarized in Pitard (1993). A more concise treatment may also be found in MARLAP (ref).

Once sample has been sufficiently homogenized, then chemical treatment on the sample begins with the addition of a tracer, which is used to make corrections (for losses) on the target analyte. Several other steps are necessary before a activity measurement can be performed. These steps include: conversion of contaminates into acid soluble form (dissolution), radiochemical separation, purification and source preparation. Of special note is the dissolution of refractory plutonium (di)oxide (PuO_2), which is a common form of plutonium in spent fuel. If the dissolution of refractory PuO_2 is not done correctly, it can be a source of significant error when analyzing samples that could contain fuel fragments. It should be noted that the recoveries that might be associated with a given technique could be very good, but misleading in the case of Pu. This is because the tracer is not same chemical form, often Pu-nitrate (Eriksson 2002). Leaching methods using a Aqua Regia (a mixture of nitric and hydrochloric acid) can leave as much as 40% of Pu activity undissolved, and the use of hydrofluoric acid can leave up to 50% (Croudance et al. 1998). However, a mixture of hydrofluoric and nitric acid has been successful in extracting PuO_2 from environmental samples (Montero Rubio et al. 2000). These total dissolution methods use very small samples size (~ at most a few grams), which again can be problematic for heterogeneous contamination. Again, if hot particles are suspected, then it might be a good idea to filter the solution after the dissolution step and screen the filter for activity. If activity is found, then one could use autoradiography to confirm the presence of hot particles.

Stent
than
Aqua
Regia

Radiation Measurement

There are two basic approaches to determining activity: atom counting and decay counting. For low specific activity radionuclides ($T_{1/2} > 1000$ yrs), one method involves atom counting using Inductively Coupled Plasma Mass Spectrometry. This technique is very sensitive and can detect elements at the parts-per billion and parts per trillion level (in some instances parts per quadrillion). This sensitivity makes it ideal for trace analysis. But given our earlier comments, is probably not the best method for the analysis of hot particles. Fortunately, many transuranic isotopes decay by alpha and therefore alpha spectrometry can be used, providing both quantitative and qualitative information about the nuclides in the sample. Quantitative determination using alpha spectrometry presents its own problems mainly due to the nature of alpha particles. Because alpha particles interact strongly with matter, alpha spectrometry sources must be very thin. Also, the counting geometry should be optimized to ensure good separation among the alpha peaks.

SV12
add
TC99

It should be noted that given some of the challenges associated with the radioanalytical techniques for transuranics (e.g. refractory Pu), the service laboratory must have a measurement quality assurance (MQA) program. The minimum requirements necessary to maintain a viable measurement assurance program by a radioassay laboratory may be found in ANSI N42.23-1996 (ANSI 1996). It is essential that radioassay laboratory that is performing the analysis participate in a MQA assessment program. The laboratory should have acceptable or satisfactory performance for the radionuclides and matrices associated with the site characterization in question.

For a more complete listing of standard laboratory methods and instruments see the NUREG-1575 (NRC 1997), and for specific radiochemical techniques consult the EML procedures Manual (DOE 1997) .

Conclusion

For hot particles and heterogeneous contamination, samples must be well homogenized. Also, avoid techniques that use very small sample sizes. Use gamma ray spectroscopy when possible. If radiochemistry has to be done, be sure to use the appropriate techniques for the given analytes and matrices and that the laboratory performing the analysis participates in an MQA assessment program. The laboratory should have acceptable performance for the radionuclides and matrices associated with the site characterization in question

References

American National Standards Institute (ANSI). American National Standards Measurement and Associated Instrument Quality Assurance for Radioassay Laboratory, New York, ANSI N42.23-1996: 1996

American Society for testing and Materials (ASTM) C 999-90 Soil Sample Preparation for the Determination of Radionuclides, West Conshohocken, PA,1990

Croudance I., P. Warwick, R. Taylor, S. Dee, J. Milton, J-S Oh, Borate Fusion Followed by Ion-Exchange/Extraction Chromatography for Rapid Determination of Pu and U in Environmental Materials, *Radioact. Radiochem*, 9 (3), pp. 41-48, 1998

Crumbling D.M., C. Groenjes, B. Lesnik, K. Lynch, J. Shockley, J. van Ee, R.A. Howe, L.H. Keith, and J. McKenna, Managing Uncertainty in Environmental Decisions: Applying the Concept of Effective Data at Contaminated Sites Could Reduce Costs and Improve Cleanups, *Environmental Science & Technology*, 35 (9), pp. 404A-409A, 2001

Department of Energy, EML Procedures Manual, HASL-300, 28th ed. 1997

Eriksonn, M.. On Weapons Plutonium in the Arctic Environment (Thule, Greenland), Risø-R-1321(EN), Risø National Laboratory, Roskilde, Denmark, April 2002.
<<www.risoe.dk/rispubl/NUK/ris-r-1321.htm>>

Montero Rubio, M. P., A. Sanchez Martin, M. T. Vazquez Crespo, J. L. Murillo Gascon,
Analysis of plutonium in soil samples, Appl. Radiat. Isot., 53 pp. 259-264, 2000

NUREG-1575, "Multi-Agency Radiation Survey and Site Investigation Manual (MARSSIM),"
Washington D.C.: Nuclear Regulatory Commission, December 1997.