

## **“Shake-and-Shoot”: A Rapid Solvent Extraction Process for PCBs and TPH – 11375**

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### **ABSTRACT**

The rapid solvent extraction process, also known as the “shake-and-shoot” extraction, offers an innovative, efficient, and time-saving option to prepare soil samples for high-quality screening that prevents radiological contamination from leaving a radiologically-impacted remediation site. Shipping, handling, and disposing of potentially radiologically-impacted soil samples may pose health and safety risks, invoke regulatory requirements, create logistical challenges, and increase costs. Field chemists conducted the shake-and-shoot extraction in a laboratory field trailer. Performing the extraction onsite eliminated a laboratory preparation step. Approximately 600 soil samples were collected, extracted, and screened in less than 6 weeks. To validate that samples were free of radioactivity, sample extracts were radiologically-screened prior to being delivered to the local offsite laboratory.

At remediation sites, soil samples collected for site characterization and remediation efforts are commonly shipped to offsite laboratories for extraction and analysis. If a site is potentially impacted with radiological contaminants, these soil samples may also be potentially radiologically-impacted. The shake-and-shoot extraction was implemented during a time-critical removal action to produce laboratory screening results that were used to determine the final removal action excavation boundaries. Shake-and-shoot was used to extract organic contaminants of concern (COCs), specifically polychlorinated biphenyls (PCBs) and total petroleum hydrocarbons (TPH), into a nonpolar solvent, which allowed for radioactivity-free samples to be shipped offsite for analysis.

Using nonpolar (hydrophobic) solvents to extract organic contaminants from soil samples is an integral part of the U.S. Environmental Protection Agency analytical methodology that is commonly used by government-certified analytical laboratories for environmental analyses. The shake-and-shoot rapid screening process uses trimethylpentane (TMP), a very hydrophobic organic solvent, to extract PCBs and TPH from soil samples in the field. Because radiochemistry salts will not dissolve in nonpolar solvents, the salts will remain in the soil matrix and the solvent extract can be transported to a local offsite nonradiologically-licensed laboratory for rapid screening for PCBs and TPH. The method also includes adding anhydrous sodium sulfate during the extraction phase to bind up any water or water soluble compounds in the soil/sediment sample extracts. This common laboratory practice creates hydrophobic conditions in the sample that drive organic compounds (i.e., PCBs and TPH) into the TMP while water and other inorganic compounds (including radiochemistry salts) stay bound in the hydrophilic soil with the sodium sulfate.

### **INTRODUCTION**

A time-critical removal action to address soil and sediment contaminated with polychlorinated biphenyls (PCBs) and total petroleum hydrocarbons (TPH) is being conducted at a federal site located in San Francisco, California. The site has been determined to be radiologically impacted. Soil sampling was needed to refine the vertical and lateral boundaries for the excavation of PCB and TPH contaminated soil. Field test kits may be used for fast screening data but have several drawbacks which include giving false

positives/negatives, providing only quantitative results, and being affected by moisture in soil and the presence of other compounds. As an alternative to field test kits and to allow for rapid screening of soil and sediment samples from the site at an offsite laboratory without offsite transport of radiological materials, a rapid solvent extraction procedure was developed. It is also known as the “shake-and-shoot” extraction. A series of bench scale tests based on chemical solubility principles were conducted to identify a nonpolar solvent that will extract organic compounds from soil without mobilizing any other material. The use of nonpolar solvents to extract organic contaminants from soil samples is an integral part of U.S. Environmental Protection Agency (EPA) analytical methodology that is commonly used by government-certified analytical laboratories for environmental analyses. Because radiochemistry salts do not dissolve in nonpolar solvents, they remain in the soil matrix and only the solvent extract is transported offsite. Field chemists conducted the extraction in a field laboratory trailer at the site. Sample extracts were radiologically screened for surface contamination and radioactivity in the sample matrix prior to being taken to the local offsite laboratory.

### **Chemical Basis for Method**

The chemical principles of the shake-and-shoot extraction are the same as used for EPA analytical methods for environmental analyses: use of a selective solvent specific to the contaminant to extract it from a complex matrix (i.e., soil or water). A previous report further supports the position that organic contaminants can be chemically separated from radiochemistry salts based on chemical solubility principles. Swann et al. evaluated the presence of naturally-occurring radioactive materials (NORM) associated with waste fluids (brine) and scale produced during oil field operations. They used an isolation and purification technique to extract NORM, which contained radium-226 (Ra-226) and radium-228. These isolation and purification techniques applied organic solvents (toluene and acetone) to remove oil and oily sludge from the scale and to dry the samples before analysis. They found that dissolution of radium salts was only accomplished using concentrated nitric acid. This purification technique leaves behind the radium sulfate present in the barite scale, while removing the interfering organic material (Swann et al, 2004). The Swann et al. study provides additional evidence for chemical basis of the shake and shoot extraction.

For the federal site in San Francisco, the organic COCs (PCBs and TPH) were extracted from the soil matrix via a method that had been tailored through laboratory tests. Several different solvents were evaluated, including hexane and trimethylpentane (TMP), which is a nonpolar (very hydrophobic) organic solvent. The final method included adding anhydrous sodium sulfate to TMP during the extraction phase. Using anhydrous sodium sulfate to draw off water in soil or sediment prior to solvent extraction is a common laboratory procedure. Creating the hydrophobic condition forces the organic components (i.e., PCBs and TPH) into the TMP, leaving water and other inorganic compounds (including radiochemistry salts) bound in the hydrophilic/soil phase with the sodium sulfate.

### **Radionuclides of Concern**

The radionuclides of concern at the federal site in San Francisco are Ra-226, cesium-137 (Cs-137), and strontium-90 (Sr-90). The chemical properties of radium are similar to other alkaline earth elements, particularly barium and calcium. Radium exists in only the +2 oxidation state in solution and does not easily complex in water (Ames and Rai, 1978). Radium sulfate is extremely insoluble salt in water at standard conditions (i.e., 20 °C and 1 atm) and its solubility is around  $2 \times 10^{-8}$  grams per cubic centimeter.

During the development of the shake-and-shoot extraction method, solubility reference data were reviewed for chemical and physical properties of the inorganic and organic compounds. Table 1 provides information regarding radiochemistry salts that could potentially be present at the site.

**Table 1. Radiochemistry Salt Solubility Characteristics**

<b>Compound</b>	<b>Soluble In</b>	<b>Insoluble</b>
Radium sulfate (RaSO <sub>4</sub> )	Concentrated nitric acid	Organic, nonpolar solvents
Strontium sulfate (SrSO <sub>4</sub> )	Concentrated hydrochloric acid or sulfuric acid	Alcohols
Cesium chloride (CsCl)	Water, methanol	Acetone

Reference: Frame, 2007.

## **FIELD PROCEDURES**

### **Soil Extraction Procedures**

Soil samples were collected using direct push drilling techniques and hand augers, and then the soil extraction procedure was implemented. First, an aliquot of the soil sample was transferred to a clean, glass vial (Figure 1). Sodium sulfate was added and mixed with the soil until homogenous. For quality control/quality assurance purposes, a field blank and each sample were spiked with a surrogate compound. The extract solvent, TMP, was added to the vial, and then it was shaken vigorously. After shaking, the vials were left to settle on the bench to separate the layers. The TMP (top) layer was transferred to a laboratory vial for shipment to the offsite laboratory.

### **Radiological Procedures**

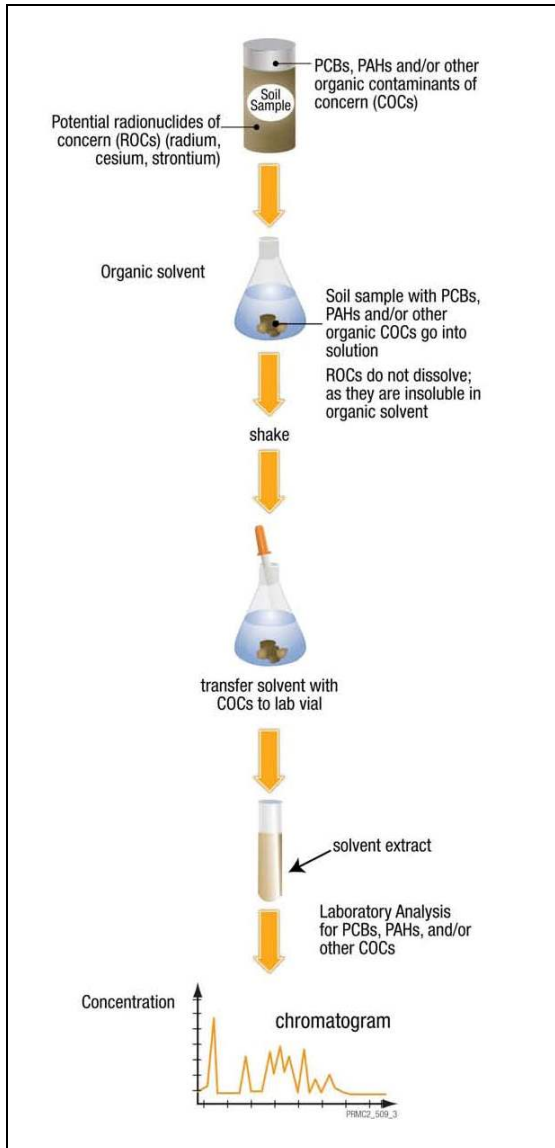
Ten percent of the shake-and-shoot extracts were submitted to an onsite radiological laboratory for gamma spectrometry analyses. Gamma spectrometry results were used to verify that the shake-and-shoot extraction procedure was not mobilizing radiological species, if present, from the soil sample to the extract. Onsite laboratory gamma spectroscopy provided qualitative assessment for the presence or absence of Ra-226 and Cs-137 in the shake-and-shoot extracts. Sr-90 is a beta emitter and could not be analyzed onsite using this method. Historical soil sampling at the site has established that Sr-90 contamination is only present in the soil when Cs-137 contamination is also present. By procedure, if Cs-137 was detected above the site-specific action level, then the sample was sent to an offsite laboratory for Sr-90 analysis.

Gamma spectroscopy reports were generated and presented the isotopic identification, not quantification, of the extract samples. An empty glass vial used to collect the liquid extract sample was counted to determine the isotopic contribution to the spectrum from natural background isotopes within the materials of the vial. The gamma spectroscopy results from extract samples were compared to the empty glass vial results to qualitatively determine if Ra-226 or Cs-137 was present in the liquid extract samples.

Smear sampling is a method of determining the removable contamination on a surface. Smear sampling surveys provide quantitative measurement of the removable gross alpha and gross beta contamination on a surface. Smear samples were collected from each sample vial to verify that no removable contamination was present on the exterior of the vials to ensure safe handling. The smear samples were analyzed in the field laboratory trailer using a Ludlum Model 3030 low-background sample counter and compared to radiological release criteria for removable contamination on surfaces presented in Table 2.

**Table 2. Radiological Release Criteria**

Radionuclide	Type of Radiation	Half-life (years)	Surfaces (disintegrations per minute/100 square centimeters)	
			Removable	Total
Strontium-90	beta	28.78	200	1,000
Cesium-137	beta, gamma	30.1	1,000	5,000
Radium-226	alpha, gamma	1,599	20	100



**Figure 1**

## RESULTS AND DISCUSSION

Approximately 600 soil samples were collected, extracted, and screened in less than 6 weeks. Radiological screening for removable and total contamination verified that no radiological contamination in excess of release limits was present on sample vials following the shake-and-shoot extractions.

To validate that samples were free of radioactivity, 10 percent of the sample extracts were radiologically-screened prior to being delivered to the local offsite laboratory. All samples were qualitatively determined to not contain Ra-226 or Cs-137, verifying that any radiological salts potentially present in the soil were not mobilized into the extracts during the solvent extraction process. It must be noted that the laboratory data does not confirm that radiological salts were present in the soil sample because the soil sample was not analyzed for radioactivity prior to and after the shake-and-shoot extraction. Subsequent gamma spectroscopy of soil samples from excavation spoils has confirmed that Ra-226 and Cs-137 are present in the site soils above the site-specific release limits.

This extraction procedure was implemented to achieve high quality screening data in a short amount of time. Because the site is radiologically-impacted, any soil samples collected at the site were considered potentially radiologically-impacted. Shipping, handling, and disposing of potentially radiologically-impacted soil samples may pose health and safety risks, invoke regulatory requirements, create logistical challenges, and increase costs. If a soil sample is potentially radiologically-impacted, it must be sent to a radiologically-licensed laboratory. (Because this is a federal site, all laboratories must be accredited by the Department of Defense Environmental Laboratory Accreditation Program.) Approved radiological laboratories are located out of state and would have required at least one day for transportation.

The shake-and-shoot method was an efficient, time-saving, and innovative option for preparing samples for screening in a local laboratory. The laboratory results were received within 48 hours of sample submission. The results were processed and the vertical and lateral excavation boundaries were refined and ready for client presentation within 2 weeks after sampling was completed.

## REFERENCES

Ames, L.L. and Rai, D, 1978, *Radionuclide Interactions with Soil and Rock Media*. EPA 520/6-78-007. Las Vegas, Nevada: U.S. Environmental Protection Agency, Office of Radiation Programs.

Frame, Paul. 2007. *Radioluminescent Paint*. Oak Ridge Associated Universities, Oak Ridge, Tennessee. Last updated October 18. <<http://www.ornl.gov/ptp/collection/radioluminescent/radioluminescentinfo.htm>> (December 7, 2010).

Swann, C., Matthews, J., Ericksen, R., and Kuszmaul, J. 2004. *Evaluations of Radionuclides of Uranium, Thorium, and Radium Associated with Produced Fluids, Precipitates, and Sludges from Oil, Gas, and Oilfield Brine Injections Wells in Mississippi*. U.S. Department of Energy Award Number DE-FG26-02NT 15227. March.