

INTRODUCTION

The Characterization Research Division (CRD), located at Las Vegas, Nevada, of the EPA National Exposure Research Laboratory, develops and evaluates alternative analytical methodologies to support EPA regulations and research efforts. Recently, CRD and its contractor, Lockheed Environmental Systems & Technologies Co., developed methods for speciating mercury in mercury-contaminated soil samples.

Mercury in environmental samples, such as soils and groundwater, is typically measured as total mercury after hot-acid digestion. However, mercury compounds differ greatly in their toxicity and environmental mobility. For example, HgCl_2 is much more toxic and mobile than HgS , which is stable in ore bodies for geologic time periods. Thus, total mercury is a very poor indicator of the toxicological and environmental hazard associated with mercury-contaminated sites.

The toxicity and environmental mobility of different inorganic mercury compounds is closely related to their relative solubilities in aqueous media. Therefore, a sequential extraction procedure, utilizing increasingly powerful aqueous solvents, should permit the separation of mixtures of mercury compounds into operationally defined classes with different potentials for human and ecological exposure. The results of such a speciation should permit a more accurate assessment of the mercury hazard associated with a particular site than is currently provided by determination of total mercury.

This poster describes the development and utilization of a mercury speciation procedure based on sequential extraction.

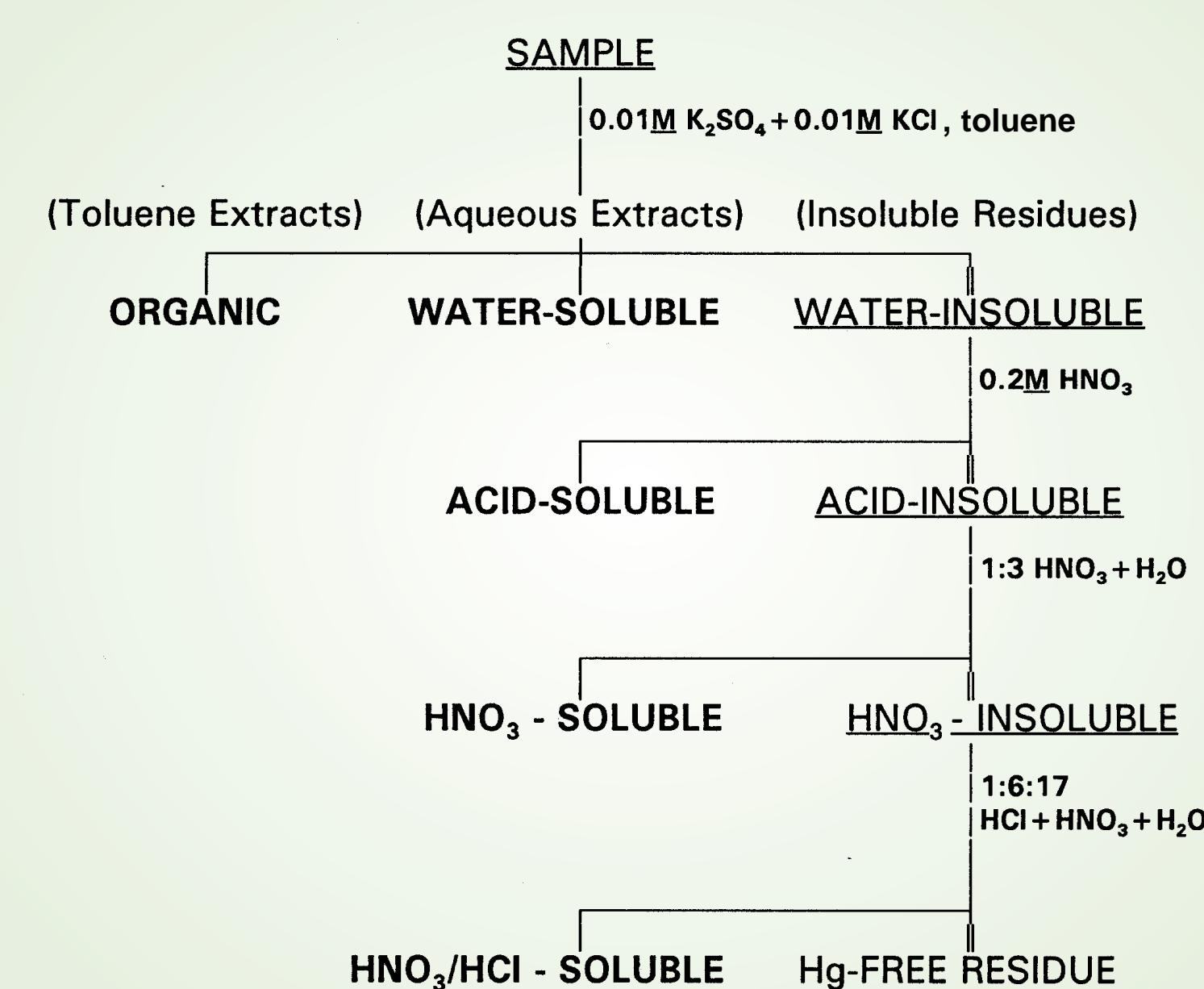
EXPERIMENTAL PROCEDURES AND RESULTS

Determination of Mercury Compound Classes in Soils

Sequential Extraction Procedure.

The sequential extraction procedure developed to separate mercury compounds into different classes is presented in Figure 1. This procedure segregates mercury into five compound classes. These classes, and the more common mercury compounds predicted to be included in each class, are shown in Table 1.

Figure 1. Sequential Extraction Procedure for Speciating Hg Compounds in Soils



Note: Residues are extracted at 95 °C for 30 minutes.

SPECIATION OF MERCURY IN SOILS BY SEQUENTIAL EXTRACTION

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Table 1. Model Compounds used to Develop and Test Mercury Speciation Procedure.

Class of Hg Compound	Model Compound(s)
Organic	$(\text{CH}_3)_2\text{Hg}$, CH_3HgCl , $(\text{C}_6\text{H}_5)_2\text{Hg}$, $\text{C}_6\text{H}_5\text{HgCl}$
Water-Soluble	HgCl_2 , $\text{Hg}(\text{NO}_3)_2$, low HgO^*
Acid-Soluble	high HgO^* , HgSO_4^*
Nitric Acid-Soluble	Hg , $\text{Zn}(\text{Hg})$, $\text{Cu}(\text{Hg})$
Nitric/Hydrochloric Acid - Soluble	HgS , Hg_2Cl_2

*Both HgO and HgSO_4 have limited solubilities in water (~0.1 g/L). Also, the solubilities of ionic Hg compounds depend upon the physical-chemical characteristics of the host soil.

Extraction of Hg Species at High Concentration.

To evaluate the utility of this procedure for speciating mercury at concentrations potentially found at contaminated sites, a standard soil mixture was prepared by fortifying mercury-free sand with a known mass of one of the mercury compounds from each of the classes listed in Table 1. Mercury in extracts was determined by inductively coupled plasma mass spectrometry (ICP-MS) and by anodic stripping voltammetry (ASV). The results of analyzing this mixture according to the speciation scheme shown in Figure 1 are given in Table 2. The results indicate that, at high mercury concentrations in sand, the speciation procedure quantitatively separates mercury compounds into the predicted classes.

Table 2. Extraction and Speciation of Mercury in Sand.

Mercury Species (Compound)	Mercury Added (mg/kg)	Mercury Found (mg/kg)	Mercury Recovery
Organic (CH_3HgCl)	399	395	99 %
Water-Soluble (HgCl_2)	369	413	112 %
Acid-Soluble (HgO)	463	403	87 %
HNO_3 -Soluble (Hg)	500	520	104 %
HNO_3/HCl -Soluble (HgS)	431	414	96 %

Extraction of Hg Species at Low Concentration.

Mercury-free sand (-325 mesh) was fortified with a single mercury compound at a concentration of 10 mg/kg Hg. The fortified sand was then analyzed in octuplicate with complete speciation according to the procedure in Figure 1. The procedure was repeated for a

Table 3. Specificity of the Sequential Extraction Procedure at Low Hg Concentration.

Mercury Compound Class (Representative Compound)	Concentration ($\mu\text{g/L}$) in Extract				
	Organic	Water-Soluble	Acid-Soluble	HNO_3 -Soluble	HNO_3/HCl -Soluble
Organic (CH_3HgCl)	1012	0.3	<0.3	<0.3	<0.3
Water-Soluble (HgCl_2)	0.5	914	4.2	0.3	<0.3
Acid-Soluble (HgO)	<0.3	740	26.1	<0.3	3.1
HNO_3 -Soluble (Zn amalgam)	<0.3	<0.1	0.6	1015	2.6
HNO_3/HCl -Soluble (HgS)	<0.3	0.2	0.5	<0.3	1074

Table 4. Recovery and Repeatability for Model Compounds Determined by Sequential Extraction Procedure at Low Hg Concentration.

Mercury Compound Class (Representative Compound)	Mercury Recovery in Appropriate Extract (%)	Relative Standard Deviation (%; n=8)
Organic (CH_3HgCl)	101	2
Water-Soluble (HgCl_2)	99	2
Acid-Soluble (HgO)	4	134
HNO_3 -Soluble (Zn amalgam)	102	4
HNO_3/HCl -Soluble (HgS)	100	2

Extraction of Hg Species from Contaminated Soils.

The sequential extraction procedure has been applied to a variety of soils from mercury-contaminated industrial and mining sites. The results, shown in Table 5, indicate that the speciation procedure can be utilized for a wide variety of environmental soil samples. Although the "true" concentration of each mercury species in these soils is not known, the indicated values are reasonable considering the history of the mercury contamination.

Table 5. Extraction and Speciation of Hg in Soil Samples.

Sample Source	Mercury Species and Concentration, mg/kg				
	Organic	Water-Soluble	Acid-Soluble	HNO_3 -Soluble	HNO_3/HCl -Soluble
19th-century gold mining streambed	<1	<1	6	292	2826
Mercury switch disposal site (tropical soil)	5	<1	8	181	34
Industrial spill site streambed (proximal)	<0.002	10.3	216	1070	1740
Industrial spill site streambed (distal)	<0.004	4.98	120	173	179
Cinnabar refinery and storage site	<0.012	0.18	1370	13500	1130
Cinnabar mine	0.0	0.3	54.4	103	541

representative compound of each mercury compound class. Ideal method performance would have yielded 1000 $\mu\text{g/L}$ Hg in the extractant for the appropriate compound class and no Hg in any other extractant. The results of this test are given in Tables 3 and 4.

Except in the case of HgO , Table 3 demonstrates that each representative compound was extracted almost exclusively into the solvent for its compound class. The concentrations found in the other solvents were generally near or below the instrumental detection limits (i.e., 0.3 $\mu\text{g/L}$ for all but water-soluble Hg, which has a detection limit of 0.1 $\mu\text{g/L}$). Table 4 shows the percentage of each Hg compound extracted into the solvent for its compound class, as well as the reproducibility of that recovery. At the low HgO concentration used in this experiment, very low recovery of Hg in the acid-soluble extractant was observed. It can be seen from Table 3 that 96% of the HgO was dissolved in the extractant for water-soluble compounds. At the higher concentrations used in the Table 2 experiments, most of the HgO dissolved in the extractant for acid-soluble mercury compounds. This is consistent with the slight solubility of HgO in water. Because the compound classes distinguished by this procedure are operationally defined, not compound-specific, this crossover of HgO between the acid-soluble and water-soluble extracts is not considered a limitation of the method. Also, from an exposure perspective, it is irrelevant what causes the water-solubility of Hg.