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# Comparison of Sludge Digestion Methods for High Organic Hanford Tank 241-C-204

M. J. Lindberg  
W. J. Deutsch

December 2006

Prepared for CH2M HILL Hanford Group, Inc. and  
the U.S. Department of Energy  
under Contract DE-AC05-76RL01830



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Richland, Washington 99352

## Summary

This report presents the results of an investigation into methods for digesting sludge from tank 241-C-204 at the Hanford Site in south-central Washington State. Researchers at Pacific Northwest National Laboratory performed this study, which was funded by CH2M HILL Hanford Group, Inc., as part of the U. S. Department of Energy's (DOE's) program for tank closure.

The objective of this study was to compare the recovery of uranium, neptunium, and plutonium using three digestion methods: EPA Method 3052, EPA Method 3050B, and alkaline fusion. Results show that EPA Method 3052, microwave assisted acid digestion, is the most efficient digestion method with higher recoveries for both uranium and plutonium. This may also be the case for neptunium; however, the analytical results are uncertain for this element.

The microwave digestion method has the added benefits of being quicker and producing less waste, which lowers the overall cost per sample. Further testing with samples from other tanks will confirm that microwave assisted digestion is a viable method of digesting Hanford tank sludges (including those with a high organic content) for chemical analysis.

## Contents

Summary .....	iii
1.0 Introduction .....	1
2.0 Method and Materials .....	1
2.1 EPA Method 3052 - Microwave Assisted Acid Digestion .....	1
2.2 Alkaline Fusion Digestion .....	2
2.3 EPA Method 3050B - Acid Digestion .....	2
2.4 Radioanalytical Analysis .....	3
3.0 Results of Laboratory Investigation .....	4
4.0 Conclusions .....	5
5.0 References .....	5

## Figures

1 Filter Paper Showing Particulates Removed from Method 3050B Digestate .....	3
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## Tables

1 Moisture Contents and Percent Solids of C-204 (Jar 19650) Sludge Sample .....	4
2 Sludge Concentrations for the Three Digestion Methods .....	4

## 1.0 Introduction

The current accepted methods for digestion of Hanford tank sludges for chemical/radiochemical analyses have been alkaline fusion and a modified U. S. Environmental Protection Agency (EPA) SW-846 Method 3050B acid digestion (EPA 1996a). In some cases, these methods have not been successful in completely dissolving the tank sludge sample, resulting in a measurement that does not reflect the total concentration of elements in the sludge. In an effort to achieve complete digestion of the sludge and more accurate measurements of the total elemental content of the sludge, EPA SW-846 Method 3052 (microwave assisted acid digestion, EPA 1996b) was tested. This report compares the recoveries/analyses of uranium, neptunium and plutonium for the three different digestion methods on a sludge sample from tank 241-C-204. This sludge material was chosen for testing because of its high organic content and the potential for low recoveries using the current digestion methods. The total organic content of the pre-retrieval sludge is reported in the Tank Waste Information System (TWINS) as 104,000 µg-C/g-sludge (10.4 wt%). Comparison of these test results can assist in verifying past sample results and determine the most effective digestion method for future analyses.

## 2.0 Method and Materials

Sample S03T001815 (Jar #19650) of pre-retrieval sludge from tank 241-C-204 was homogenized by stirring the material with a spatula. Subsamples of the homogenized sludge were digested in duplicate by each of the three methods described in detail in Sections 2.1 through 2.3. Each sample digestate was analyzed in duplicate for uranium, neptunium, and plutonium. It was noted during sample digestion that, not only was the microwave assisted method (Section 2.1) more effective in dissolving the sample, it was also considerably quicker and resulted in less waste generation. The average amount of time for digesting a set of samples by the microwave method was about two hours. This compares to a minimum of 7 hours for the alkaline fusion and the modified 3050B methods. Also, due to the reduced usage of glassware, there was an overall reduction in the amount of waste generated. Digestion and analytical methods are described in detail in this section.

### 2.1 EPA Method 3052 - Microwave Assisted Acid Digestion

EPA Method 3052 (EPA 1996b) is designed to digest siliceous and organically based matrices. It is designed for total decomposition analysis of oil contaminated soils, sediments, and sludges, as well as other matrices. The method allows for flexibility in the choice of acid and reagent combinations. The acids and reagents used for these tests are described in the following paragraph.

Approximately 300 mg of the tank waste sludge was placed in a 100-mL Teflon microwave digestion vessel. Following this, 10 mL water, 5 mL of a 16 M nitric acid (HNO<sub>3</sub>) solution, 2 mL of a 12 M hydrochloric acid (HCl) solution, and 1 mL of a 29 M hydrofluoric acid (HF) solution were added, and the vessel was sealed and placed in a CEM<sup>1</sup> MARS5™ microwave assisted digestion system. The

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<sup>1</sup> CEM Corporation, 3100 Smith Farm Road, Matthews, NC 28104.

temperature of the samples was increased to 180°C in 5.5 minutes, then held at this temperature for 9.5 minutes. The sample was then allowed to cool, transferred to a 50-mL centrifuge tube containing 0.45 g of powdered boric acid and brought to a final volume of 30 mL. The digestate was shaken by hand to dissolve the boric acid. Boric acid reacts with residual HF in the digestate to form a boron complex, preventing the residual HF from etching the sample introduction glassware in the inductively coupled plasma mass spectrometer analytical system. Samples were filtered through a 0.45- $\mu$ m pore-size syringe filter prior to analysis. There were no visible solids in the digestate prior to filtration.

## **2.2 Alkaline Fusion Digestion**

Approximately 300 mg of the tank waste sludge material was mixed with 10 mL of a 20% KOH and 2% KNO<sub>3</sub> solution as a fluxing agent in a nickel crucible. The crucible was placed on a 95°C hot plate and the solution was allowed to evaporate to dryness. Once dried, the crucible was transferred to a muffle furnace preheated to 550°C. After 60 minutes, the crucible was removed from the furnace and allowed to cool. The fused solid was then dissolved in double deionized (DDI) water. The resulting solution was transferred to a 100 mL volumetric flask to which 1 mL of 1.0 M hydroxylamine HCl was added. Ten mL of an 8 M HNO<sub>3</sub> solution was added to the crucible to try to dissolve any remaining residual solid. The acid wash solution was also added to the volumetric flask. The crucible was then triple-rinsed with DDI water, and these solutions were also added to the volumetric flask. The resulting solution was diluted to the total volume of the volumetric flask with DDI water. Prior to chemical analysis, the final 100-mL solution was passed through a Whatman 41 filter with final filtration through a 0.45- $\mu$ m pore-size syringe filter to remove the insoluble particles remaining after digestion. Because of the difficulty in removing solids from the filter media, an estimate of the quantity of particulates is not available.

## **2.3 EPA Method 3050B - Acid Digestion**

EPA Method 3050B (EPA 1996a) is a very strong acid digestion method designed to dissolve almost all elements in sediments, soils, and sludges that could become “environmentally available.” It is not a total digestion technique for most samples because most of the silicate minerals are not soluble in the acids used in this method.

For this test, approximately 300 mg of the sample was placed in a 50 mL Griffin beaker. Five milliliters of an 8 M HNO<sub>3</sub> solution was added to the beaker; the beaker was then covered with a watch glass, and the unit was heated to 95°C. Successive additions of concentrated HNO<sub>3</sub> and heating were performed until no reaction with the sample was noted. The sample was then allowed to digest for two hours at 95°C. The sample was removed and allowed to cool. After cooling, 1.5 mL of 30% H<sub>2</sub>O<sub>2</sub> was added to the sample and the temperature was increased to 95°C. Successive additions of H<sub>2</sub>O<sub>2</sub> and heating were performed until no further reaction was noticed. The sample was allowed to digest for 2 hours at 95°C. After cooling, the solution was filtered through a Whatman 41 filter to remove the insoluble particles and brought to a final volume of 50 mL with DDI water. Samples were filtered through a 0.45- $\mu$ m pore-size syringe filter prior to analysis. Figure 1 shows the particulates on the filter paper. The limited quantity of the insoluble fractions remaining after digestion and the inability to remove this material from the filter media precluded their characterization.



**Figure 1.** Filter Paper Showing Particulates Removed from Method 3050B Digestate

## 2.4 Radioanalytical Analysis

Uranium, neptunium, and plutonium analyses were performed using an inductively coupled plasma mass spectrometer (ICP-MS) as described in an internal PNNL procedure.<sup>1</sup> This method is similar to EPA Method 6020 (EPA 1994). Due to the high concentrations of uranium in the sample digestates, high-purity calibration standards were prepared in uranium solutions to match the matrix of the samples. These standards were used to generate calibration curves and to verify continuing calibration during the analysis.

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<sup>1</sup> Geiszler KN. 2005. *Inductively Coupled Plasma Mass Spectrometric (ICP-MS) Analysis*. PNNL-AGG-415, Rev. 1, unpublished PNNL Technical Procedure, Pacific Northwest National Laboratory, Richland, Washington.



### 3.0 Results of Laboratory Investigation

This section contains the analytical results for the three digestion methods tested in this study. Table 1 provides the moisture contents and percent solids of the tested samples. All concentration values reported in Table 2 are calculated on a dry sludge weight basis. If concentrations were calculated on a wet weight basis they would be lower than the dry weight basis by an average of 28%.

**Table 1.** Moisture Contents and Percent Solids of C-204 (Jar 19650) Sludge Sample

Sample Number	Moisture Content <sup>(a)</sup>	Percent Solids <sup>(b)</sup>
Jar 19650 (204)	28.7%	71.3%
Jar 19650 (204) Dup <sup>(c)</sup>	27.1%	72.9%
(a) Moisture Content = [(wet wt- dry wt)/wet wt]		
(b) Percent Solids = (dry wt/wet wt)		
(c) Dup = Duplicate sample.		

**Table 2.** Sludge Concentrations for the Three Digestion Methods

Digestion Methods/Sample Numbers	Sludge Concentrations (dry weight basis)					
	<sup>238</sup> U	<sup>238</sup> U	<sup>237</sup> Np	<sup>237</sup> Np	<sup>239</sup> Pu	<sup>239</sup> Pu
	µg/g	nCi/g	µg/g	nCi/g	µg/g	nCi/g
3052 Microwave Acid Digestion						
Jar 19650 (C-204) REP 1	9.30E+04	3.16E+01	(2.13E-01)	(1.51E-01)	9.28E-01	5.75E+01
Jar 19650 (C-204) REP 2	9.31E+04	3.16E+01	(2.16E-01)	(1.53E-01)	1.14E+00	7.06E+01
Jar 19650 (C-204) Dup REP 1	9.04E+04	3.07E+01	(1.95E-01)	(1.38E-01)	8.62E-01	5.34E+01
Jar 19650 (C-204) Dup REP 2	9.07E+04	3.08E+01	(1.89E-01)	(1.34E-01)	7.27E-01	4.51E+01
3050B Acid Digestion						
Jar 19650 (C-204) REP 1	2.75E+04	9.34E+00	<4.07E-01	<2.89E-01	<4.07E-01	<2.52E+01
Jar 19650 (C-204) REP 2	2.76E+04	9.37E+00	<4.07E-01	<2.89E-01	<4.07E-01	<2.52E+01
Jar 19650 (C-204) Dup REP 1	3.55E+04	1.21E+01	<3.98E-01	<2.82E-01	<3.98E-01	<2.47E+01
Jar 19650 (C-204) Dup REP 2	3.61E+04	1.23E+01	<3.98E-01	<2.82E-01	<3.98E-01	<2.47E+01
Alkaline Fusion Digestion						
Jar 19650 (C-204) REP 1	7.22E+04	2.45E+01	<9.51E-01	<6.76E-01	<9.51E-01	<5.90E+01
Jar 19650 (C-204) REP 2	7.77E+04	2.64E+01	<9.51E-01	<6.76E-01	<9.51E-01	<5.90E+01
Jar 19650 (C-204) Dup REP 1	7.53E+04	2.56E+01	(1.71E-01)	(1.22E-01)	(2.32E-01)	(1.44E+01)
Jar 19650 (C-204) Dup REP 2	7.42E+04	2.52E+01	(1.94E-01)	(1.38E-01)	(2.93E-01)	(1.81E+01)
Dup = Duplicate REP = Replicate						

Concentrations listed in parentheses in Table 1 are defined as less than the estimated quantitation limit (EQL) but greater than a zero instrument signal. These values are reported for informational purposes only. They may reflect actual concentrations that are real, but have larger associated uncertainties than values above the EQL, or may reflect values that were calculated from the instrument's background signal and are not representative of actual sludge composition. The EQL of an element is determined by

analyzing a suite of continuing calibration verification (CCV) standards at the beginning and end of each analytical run. The lowest CCV standard that is within  $\pm 10\%$  of its certified value is multiplied by the dilution factor for the sample to determine the EQL for the element for the particular analytical run. The EQL may vary with each analysis depending on sample matrix, the total dilution performed on each sample, and instrument performance.

Concentrations listed as less-than (<) values in the table refer to instrument measurements that are less than zero. In these instances, the reported analyte concentration is assigned a value of “<EQL” using the EQL value appropriate for that particular analyte and set of analytical conditions.

Uranium was detected in all three of the digestion methods, with the highest concentrations measured in the microwave assisted digestions at an average of 91,800  $\mu\text{g/g}$ . The second highest concentrations were measured in the alkaline fusion digestions with an average of 74,800  $\mu\text{g/g}$ , and the lowest values were measured in the 3050B extractions with an average of 31,600  $\mu\text{g/g}$ . The relative percent difference (RPD) for uranium analyses ranged from 0.1% to 0.3 % for microwave assisted digestion, 0.4% to 1.7% for 3050B digestion and 1.5% to 7.3% for the alkaline fusion digestion. The RPD for this measurement are within the 10% expected accuracy for an analytical method. Plutonium was only measured above the EQL in the microwave assisted digestion samples, with an average of 0.914  $\mu\text{g/g}$  (56.7 nCi/g). There were no quantitative concentrations measured for neptunium above the EQL in any of the digestates; however, the microwave assisted digestion method provided a qualitative average concentration of 0.203  $\mu\text{g/g}$ .

## 4.0 Conclusions

Based on the limited testing of sludge samples from tank C-204, it appears that microwave assisted digestion is a more efficient digestion method with higher recoveries for uranium and plutonium. This may also be the case for neptunium; however, the analytical results are uncertain for this element. Unlike the other digestion methods, which both showed visible solids post-digestion, there were no visible solids in the microwave assisted digestate. The microwave digestion method also has the added benefits of being quicker and producing less waste, which lowers the overall cost per sample. Further testing with samples from other tanks will confirm that microwave assisted digestion is a viable method of digesting Hanford tank sludges (including those with a high organic content) for chemical analysis.

## 5.0 References

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