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Comparison of SW-846 Method 3051 and SW-846 Method 7471A for the Preparation of Solid Waste Samples for Mercury Determination

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ACRONYMS AND INITIALISMS

ANL	Argonne National Laboratory
CVAA	Cold Vapor Atomic Absorption
GFAA	Graphite Furnace Atomic Absorption
ICP-AES	Inductively Coupled Plasma Atomic Emission Spectrum
ICP-MS	Inductively Coupled Plasma Mass Spectrometry
ORNL	Oak Ridge National Laboratory
QAPjP	Quality Assurance Project Plan
RMAL	Radioactive Materials Analytical Laboratory
SRM	Standard Reference Material
TRU	Transuranic
TWCP	Transuranic Waste Characterization Program
WIPP	Waste Isolation Pilot Plant

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ABSTRACT

This report describes experimental studies to evaluate the use of EPA SW-846 method 3051 for the preparation and dissolution of solid samples for mercury analysis. The study showed that the method is effective in the dissolution of four sample types without significant loss of mercury. Based on the results of this study, method 3051 was used for analysis of high radioactive waste samples to obtain results for a number of RCRA regulated metals without the need to utilize a separate sample preparation method (EPA SW-846 method 7471A) specific only for mercury.

INTRODUCTION

The Radioactive Materials Analytical Laboratory (RMAL) located at Oak Ridge National Laboratory (ORNL) is participating in the characterization of transuranic waste targeted for the national Waste Isolation Pilot Plant (WIPP) in Carlsbad, New Mexico. The waste streams contain high concentrations of alpha emitting radionuclides and therefore all raw sample handling and preparations require alpha containment (radiochemical hoods, gloveboxes, or hotcells). To reduce the risk from sample exposure and increase sample throughput, it was be beneficial to prepare for all metal analysis (ICP-AES, ICP-MS, GFAA, and CVAA) in a single digestion with a minimal amount of sample handling. SW846 method 3051 (Microwave Assisted Acid Digestion of Sediments, Sludges, Soils, and Oils) is ideal for this situation. The use of this preparation method would allow for a single fast and efficient digestion for all metals targeted by the WIPP program.

The recent update (Update II) to SW-846 includes an approved method 3051 for the preparation of samples for metals analysis for techniques such as ICP-AES, ICP-MS, and GFAA, but does not include mercury analysis by CVAA. Also, SW-846 method 7471A (Mercury in Solid or Semisolid Waste (Manual Cold-Vapor Technique) does not allow for alternative preparation methods. As part of the WIPP Transuranic Waste Characterization Program the RMAL investigated in collaboration with the Analytical Chemistry Laboratory, located at Argonne National Laboratory, the feasibility of microwave digestion for mercury determination by cold vapor atomic absorption.

For this study four standard reference materials (SRM) were used to cover the range of matrices and mercury levels that most likely would be encountered during the sampling and characterization program. The laboratories independently prepared each SRM in batches of five and analyzed the digestates using method 7471A. For the microwave preparations each SRM batch was digested using three different microwave ovens (one pressure controlled, one temperature controlled, and one high pressure oven that was temperature controlled) using the pressure/temperature profiles specified in method 3051. A conventional water bath preparation as specified in method 7471A was also included.

This report presents the results of this study and examines how each method compared to the acceptance criteria established in the WIPP TWCP Quality Assurance Plan.

1. EXPERIMENTAL

1.1 MICROWAVE OVENS

Oak Ridge National Laboratory performed microwave digestions using a CEM MDS 81 microwave oven with pressure control and a Milestone MEGA 1200 microwave with internal temperature control. Argonne National Laboratory used a CEM MDS 2100 microwave oven with temperature and pressure control.

The CEM MDS 81 is a 600 watt unit employing lined digestion vessels. The liners are made of PFA teflon® and the vessel body made of Ultem® polyetherimide. These vessels can operate with internal pressures up to 190 psi. The Milestone oven is a 1000 watt unit employing TFM™ vessels with HTC liners capable of handling digestion pressures up to 1500 psi. The CEM MDS 2100 is a 1000 watt unit employing heavy duty vessels constructed of liners made of TFM™, sleeves of PFA teflon®, fiber glass and Ultem®, and bodies of polypropylene. These vessels have operating pressures of 600 psi.

1.2 MERCURY ANALYZERS

Oak Ridge National Laboratory performed all mercury analysis on a Thermo Jarrell Ash QS-1 cold vapor mercury analyzer. Argonne National Laboratory performed all mercury analysis on a Leeman Labs PS 200 cold vapor mercury analyzer. Both analyzers employ flow injection and a 5% stannous chloride solution to reduce the mercury. The mercury vapor produced is dried and then carried to an absorption cell. The analytical wavelength used was 253.7 nm.

1.3 REFERENCE MATERIALS

The WIPP samples consist mainly of inorganic or organic radioactive contaminated sludges that have been mixed in cement. No reference material with a certified level of mercury that matched the WIPP sample matrices was available, however, if mercury was recovered in the more difficult standards covering a wide range of silicate concentrations (> 50 % in SRM 2704, > 60% in SRM 1633a/b, and about 20 % in the sewage sludge) and mercury levels, this would demonstrate the ability to recover the mercury in the WIPP samples. Some of the wastes contain oil, so an oil reference material was also used in the validation process. The standards selected were:

- NIST Buffalo River Sediment (SRM 2704)
- NIST Coal Fly Ash (SRM 1633a/b)
- Environmental Resource Associates Sewage Sludge (WW-26 lot#2612)
- Conostan 100 ppm mercury in oil (lot#13015)

1.4 METHODS

For the sample preparations following method 3051 protocol, standards were digested in batches of five using 0.5 g sample sizes (0.25g for the oil) with one blank. The blank not only served as a check for cross-contamination but also rounded each batch to six and served to obtain the recommended energy balance specified in method 3051. The microwave oven without internal temperature monitoring (CEM MDS 81) was operated at the recommended power level of 574 watts for ten minutes for each digestion batch. The microwaves with internal temperature monitoring (Milestone MEGA 1200 and CEM MDS 2100), the units were programmed to raise the internal temperature to 175 ^{o}C in 5.5 mins and hold it at 175 ^{o}C for the remainder of the ten minute digestion in accordance with the method. All digestions were diluted to a known volumes with reagent grade water. Sediment not dissolved by the procedure was allowed to settle prior to analysis.

Sample preparations following method 7471A protocol, reference materials were also digested in batches of five with one blank. The sample portions used were 0.2 g as specified in the method.

Prior to analysis, a 5 % potassium permangante solution was added to all microwave digestate aliquots drop-wise until there was a persistent purple tint. This addition ensures that the mercury in solution is stabilized and would not be lost during analysis. Past experience has shown that if the potassium permangante solution is not added to the microwave digestions until a persistent purple tint develops then mercury could be lost resulting in poor recoveries.

2. RESULTS AND DISCUSSION

Each of the four SRM's used for this study were digested in batches of five using three different microwave ovens and one conventional water bath preparation. Two of the microwave ovens were located at the Radioactive Materials Analytical Laboratory at Oak Ridge National Laboratory while the third microwave and all waterbath preparations were performed by the Analytical Chemistry Laboratory at Argonne National Laboratory. Therefore each standard underwent four independent sample preparations with five replicates per preparation for a total of 20 replicates being analyzed for mercury. Each microwave oven was operated by an independent chemist and all waterbath preparations were performed by a single laboratory technician.

The results of each batch are listed in the following tables. These results are listed by SRM showing the preparation location, preparation method, and microwave unit (if appropriate). Each replicate result is shown including the grand average for the batch. Each sample replicate was analyzed over three integrations. The "Experimental Value" is the average of the three integrations corrected for all dilutions. The "Standard Deviation" is the standard deviation of the three integrations and is also corrected for any dilutions performed on the replicate. The "Percent Recovery of Certified Value" is calculated as the experimental value divided by the certified value multiplied by one hundred. The TWCP acceptance criteria for mercury recovery is set at 80% - 120% per the Quality Assurance Program Plan (QAPP). The certified value for each reference material is given below the tables along with the cold vapor analyzer used for the analysis.

Buffalo River Sediment Results (SRM 2704)

Oak Ridge National Laboratory

Table 2.1

Method 3051 temperature controlled digestion

Milestone MEGA 1200 microwave

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	1.54	0.005	105%
2	1.80	0.001	122%
3	1.52	0.005	104%
4	1.68	0.004	114%
5	1.52	0.002	104%
Average	**1.61**	**0.121**	**110%**
Blank	0.00	0.000	

- Certified Value (mg/Kg): 1.47 +/- 0.07
- Digestions analyzed with a TJA QS-1 mercury analyzer

Table 2.2

Method 3051 pressure controlled digestion

using a CEM MDS 81 microwave

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	1.42	0.002	96%
2	1.45	0.002	99%
3	1.45	0.001	99%
4	1.43	0.002	97%
5	1.54	0.001	105%
Average	**1.46**	**0.050**	**99%**
Blank	0.00	0.000	

- Certified Value (mg/Kg): 1.47 +/- 0.07
- Digestions analyzed with a TJA QS-1 mercury analyzer

Argonne National Laboratory

Table 2.3

Method 3051 temp/press controlled digestion

CEM MDS 2100 microwave

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	1.44	0.124	98%
2	1.49	0.082	101%
3	1.47	0.100	100%
4	1.48	0.113	101%
5	1.49	0.116	101%
Average	**1.47**	**0.022**	**100%**
Blank	0.00	0.007	

- Certified Value (mg/Kg): 1.47 +/- 0.07
- Digestions analyzed with a Leeman Labs PS 200 mercury analyzer

Table 2.4

Method 7471 water bath digestion

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	1.37	0.030	93%
2	1.41	0.012	96%
3	1.44	0.057	98%
4	1.43	0.061	97%
5	1.45	0.060	99%
Average	**1.42**	**0.032**	**97%**
Blank	-0.01	0.016	

- Certified Value (mg/Kg): 1.47 +/- 0.07
- Digestions analyzed with a Leeman Labs PS 200 mercury analyzer

Coal Fly Ash Results (SRM 1633a/b)

Oak Ridge National Laboratory

Table 2.5

Method 3051 temperature controlled digestion

Milestone MEGA 1200 microwave

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	0.157	0.0001	111%
2	0.154	0.0002	109%
3	0.169	0.0002	120%
4	0.152	0.0001	108%
5	0.153	0.0000	108%
Average	**0.157**	**0.0071**	**111%**
Blank	0.012	0.0002	

- Certified Value (mg/Kg): 0.141 +/- 0.019
- Digestions analyzed with a TJA QS-1 mercury analyzer

Table 2.6

Method 3051 pressure controlled digestion

using a CEM MDS 81 microwave

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	0.132	0.000	94%
2	0.138	0.000	98%
3	0.135	0.000	96%
4	0.134	0.001	95%
5	0.152	0.000	107%
Average	**0.138**	**0.008**	**98%**
Blank	0.008	0.000	

- Certified Value (mg/Kg): 0.141 +\- 0.019
- Digestions analyzed with a TJA QS-1 mercury analyzer

Argonne National Laboratory

Table 2.7

Method 3051 temp/press controlled digestion

CEM MDS 2100 microwave

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	0.174	0.0017	109%
2	0.175	0.0015	110%
3	0.173	0.0030	108%
4	0.171	0.0006	107%
5	0.173	0.0025	108%
Average	**0.173**	**0.0015**	**108%**
Blank	0.000	0.0010	

- Certified Value (mg/Kg): 0.16 +\- 0.01
- Digestions analyzed with a Leeman Labs PS 200 mercury analyzer

Table 2.8

Method 7471 water bath digestion

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	0.150	0.006	94%
2	0.151	0.013	95%
3	0.150	0.010	94%
4	0.151	0.010	95%
5	0.152	0.014	95%
Average	**0.151**	**0.001**	**94%**
Blank	-0.01	0.016	

- Certified Value (mg/Kg): 0.16 +\- 0.01
- Digestions analyzed with a Leeman Labs PS 200 mercury analyzer

Sewage Sludge Results (WWS-26)

(Purchased from Environmental Resource Associates (Lot # 2612))

Oak Ridge National Laboratory

Table 2.9

Method 3051 temperature controlled digestion

Milestone MEGA 1200 microwave

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	75.3	0.24	107%
2	72.7	0.02	104%
3	75.0	0.11	107%
4	76.5	0.11	109%
5	75.9	0.06	108%
Average	**75.1**	**1.44**	**107%**
Blank	0.00	0.000	

- Certified Value (mg/Kg): 70.2
- Advisory Range: 44.9 - 100
- Digestions analyzed with a TJA QS-1 mercury analyzer

Table 2.10

Method 3051 pressure controlled digestion

using a CEM MDS 81 microwave

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	81.1	0.12	116%
2	81.0	0.03	115%
3	81.3	0.00	116%
4	82.7	0.08	118%
5	85.6	0.10	122%
Average	**82.3**	**1.93**	**117%**
Blank	0.00	0.001	

- Certified Value (mg/Kg): 70.2
- Advisory Range: 44.9 - 100
- Digestions analyzed with a TJA QS-1 mercury analyzer

Argonne National Laboratory

Table 2.11

Method 3051 temp/press controlled digestion

CEM MDS 2100 microwave

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	54.3	4.49	77%
2	74.5	4.56	106%
3	73.7	3.63	105%
4	73.6	4.04	105%
5	74.2	2.98	106%
Average	**70.1**	**8.82**	**100%**
Blank	0.01	0.011	

- Certified Value (mg/Kg): 70.2
- Advisory Range: 44.9 - 100
- Digestions analyzed with a Leeman Labs PS 200 mercury analyzer

Table 2.12

Method 7471 water bath digestion

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	69.6	5.77	99%
2	67.7	2.52	96%
3	69.8	3.58	99%
4	73.6	5.37	105%
5	72.1	4.67	103%
Average	**70.6**	**2.32**	**101%**
Blank	-0.01	0.016	

- Certified Value (mg/Kg): 70.2
- Advisory Range: 44.9 - 100
- Digestions analyzed with a Leeman Labs PS 200 mercury analyzer

Mercury in Oil Results

(Purchased from Conostan (Lot # 13015))

Oak Ridge National Laboratory

Table 2.13

Method 3051 temperature controlled digestion

Milestone MEGA 1200 microwave

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	108.2	0.26	108%
2	104.3	0.22	104%
3	105.5	0.06	106%
4	105.4	0.33	105%
5	106.4	0.17	106%
Average	**106.0**	**1.48**	**106%**
Blank	0.00	0.000	

- Certified Value (mg/Kg): 100 +\- 10
- Digestions analyzed with a TJA QS-1 mercury analyzer

Table 2.14

Method 3051 pressure controlled digestion

using a CEM MDS 81 microwave

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	113.0	0.15	113%
2	100.3	0.09	100%
3	114.8	0.17	115%
4	115.8	0.00	116%
5	108.0	0.10	108%
Average	**110.4**	**6.38**	**110%**
Blank	0.00	0.000	

- Certified Value (mg/Kg): 100 +\- 10
- Digestions analyzed with a TJA QS-1 mercury analyzer

Argonne National Laboratory

Table 2.15

Method 3051 temp/press controlled digestion

CEM MDS 2100 microwave

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	98.9	8.03	99%
2	99.0	7.80	99%
3	97.8	8.04	98%
4	97.2	6.79	97%
5	101.0	8.79	101%
Average	**98.8**	**1.45**	**99%**
Blank	0.04	0.031	

- Certified Value (mg/Kg): 100 +\- 10
- Digestions analyzed with a Leeman Labs PS 200 mercury analyzer

Table 2.16

Method 7471 water bath digestion

Replicate Number	Experimental Value (mg/Kg)	Standard Deviation	Percent Recovery of Certified Value
1	98.0	6.98	98%
2	95.9	5.26	96%
3	94.9	6.17	95%
4	95.6	5.84	96%
5	94.2	5.90	94%
Average	**95.7**	**1.42**	**96%**
Blank	-0.01	0.032	

- Certified Value (mg/Kg): 100 +\- 10
- Digestions analyzed with a Leeman Labs PS 200 mercury analyzer

Mercury concentration was determined on a total of eighty digestions. Of these, sixty were prepared in accordance with the protocol established in method 3051 and twenty were prepared in accordance with method 7471A protocol. Of those eighty digestions only three did not meet the TWCP acceptance criteria of 80% - 120% recovery. The three outliers consisted of one Buffalo River Sediment microwave digestion with 122% of the certified value, one Sewage Sludge microwave digestion with 122 % of the certified value, and one Sewage Sludge microwave digestion with 77 % of the certified value. All of the outliers were samples prepared and analyzed at ORNL. It is believed that these outliers were due to problems experienced with the Thermo Jarrell Ash QS-1 mercury analyzer and not with the preparation method. This instrument was recently purchased and drifting of the baseline was a noted problem during the initial setup and test period of the unit.

This validation study has shown method 3051 to be a viable method for the preparation of solid samples for mercury determination by cold-vapor. Method 3051 is ideally suited for the preparation of radioactive waste samples. Not only can all metals be prepared with a single quick and efficient digestion using this method, but also most radiochemistry analysis can be pulled from the same preparation aliquot.

The majority of a high level radioactive laboratory technician's exposure results from having to handle raw sample during the it's preparation. Method 3051 allows for a small sample size and does away with having to perform multiple preparations and having to handle a highly radioactive waste more times than necessary. All these factors result in less personnel exposure.

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