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Inductively Coupled Plasma-Mass Spectrometry: Arsenic, Beryllium, Lead, Mercury, Osmium, and Thallium in Aqueous Media

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RESEARCH AND TECHNOLOGY DIRECTORATE

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The findings in this report are not to be construed as an official Department of the Army position unless so designated by other authorizing documents.

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Members of the Forensic Analytical Center (FAC) at the U.S. Army Combat Capabilities Development Command Chemical Biological Center (DEVCOM CBC) (Aberdeen Proving Ground, MD) were requested to analyze samples that were suspected of containing arsenic, beryllium, lead, mercury, osmium, and/or thallium using inductively-coupled plasma mass spectrometry (ICP-MS). The capability to process samples for specific elemental components allows for scientists to further analyze the samples for specific chemical warfare materials.

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PREFACE

The work described in this report was started in November 2019 and completed in January 2020.

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INDUCTIVELY-COUPLED PLASMA MASS SPECTROMETRY: ARSENIC, BERYLLIUM, LEAD, MERCURY, OSMIUM, AND THALLIUM IN AQUEOUS MEDIA

1. INTRODUCTION

Members of the Forensic Analytical Center (FAC) at the U.S. Army Combat Capabilities Development Command Chemical Biological Center (DEVCOM CBC; Aberdeen Proving Ground, MD) developed an analytical method for investigating samples using inductively-coupled plasma mass spectrometry (ICP-MS). Specifically, the aqueous samples were analyzed for arsenic (As) beryliium (Be), lead (Pb), mercury (Hg), osmium (Os), and thallium (Tl). ICP-MS is capable of detecting elements from subpart-per-trillion to percent-level concentrations. This capability to process samples for specific elemental components allows scientists to do further sample testing, if needed, to screen for additional possible suspect chemical warfare agents.

2. BACKGROUND

A central mission of the DEVCOM CBC FAC is to develop and validate quantitative and qualitative analytical methods, with a focus on chemical agents. Forensic capabilities were originally developed at the Research, Development and Engineering Command Chemical and Biological (RDECOM C&B) Center to support U.S. obligations under the Chemical Weapons Convention, whereby the United States was required to procure sampling and analysis expertise to verify treaty compliance. As required for treaty compliance, the DEVCOM CBC EC/B FAC is accredited to the ISO/IEC 17025 standard that refers to laboratory operations and quality control.[1] To demonstrate its high standards in chemical and biological agent detection and analysis, the DEVCOM CBC EC/B FAC maintains elite status in international proficiency testing sponsored by the Organisation for the Prohibition of Chemical Weapons (The Hague, Netherlands).

People are exposed to metal every day, but some metals can be toxic in higher quantities. Metal poisoning can cause many severe symptoms, including death. Poisoning via metals can be discreet and occur unbeknownst to the person consuming the metals, which is why crime enforcement officers screen for metals in the body in the event of a suspicious death.

The Agilent 7900 ICP-MS system (Agilent Technologies; Santa Clara, CA) has an argon plasma and Ultra High Matrix Introduction accessory that operates at more than 100 times the traditional matrix limit for ICP-MS technology.[2] The samples are routinely prepared using 3% nitric acid. Because dichloromethane (DCM) is used for sample extraction when the sample is a solid material, a small amount of the solvent ends up in the 3% nitric acid solution. This requires the same solvent concentration to be used in the calibration standards that are used for the corresponding sample.

3. MATERIALS AND METHODS

3.1 Materials

Laboratory-grade chemicals from any supplier are appropriate for this procedure. The following chemicals were used:

- liquid argon (dewar);
- helium (tank);
- hydrogen (tank);
- 18 MΩ of double-distilled water that was free of metals;
- concentrated HNO_3 of a minimum trace-metal grade or grade that was suitable for the intended detection level; and
- tuning solution of 1 ppm Ce, Co, Li, Tl, and Y.

The following common laboratory equipment and supplies were used:

- analytical balance with readability of 0.001 mg;
- disposable plastic droppers;
- polypropylene (PP) bottles;
- PP graduated cylinders or equivalent;
- PP Falcon tubes of 15 and 50 mL or equivalent;
- pipetters and disposable tips covering the range of 10 µL to 10 mL;
- waste container and
- laboratory cleaning wipes.

The following specialized equipment and supplies were used:

- 7900 Series ICP-MS system (part no. G8403A; Agilent Technologies);
- ICP-MS MassHunter workstation (part no. G7215C with #003; Agilent Technologies);
- Cetac ASX-500 auto sampler (part no. G3286A; Cetac Technologies; Omaha, NE);
- 1000 µg/mL As in 2% HNO_3 (Chemical Abstracts Service (CAS) no. 7440-38-2; part no. CGAS1; Inorganic Ventures; Christiansburg, VA); and
- 1000 µg/mL Pb in 0.5% HNO_3 (CAS no. 7439-92-1; part no. CGPB1; Inorganic Ventures).
- 100 µg/mL Be in 3% HNO_3 (CAS no. 7440-41-7; part no. MSBE-100PPM; Inorganic Ventures).
- 1000 µg/mL Hg in 5% HNO_3 (CAS no. 7439-97-6; part no. CGHG1; Inorganic Ventures).
- 1000 µg/mL Os in 15% HCl (CAS no. osmium tetraoxide 20816-12-0; part no. CGOS1; Inorganic Ventures).
- 1000 µg/mL Tl in 1% HNO_3 (CAS no. thallium nitrate 7440-28-0; part no. CGTL1; Inorganic Ventures).

3.2 Methods

3.2.1 Preparation of the Matrix Solution

All stock solutions and the dilutions from those stock solutions must be remade every three months unless a stability study is performed that shows a longer storage time is acceptable. All solutions must be stored at ambient temperatures.

Solutions were prepared as follows:

- a PP, 1 L volumetric flask or high-density polyethylene (HDPE) bottle was approximately half filled with water;
- 30 mL of concentrated nitric acid was added;
- the mixture was swirled; and
- the final volume or weight was adjusted to 1 L (volumetric flask) or 1000 g (HDPE bottle) by adding water, respectively, for a 3% solution.

3.2.2 Preparation of Stock Standard Solutions

The standard solutions (Table 1) were made in 15 mL PP tubes. Dilutions of the standard solutions were prepared by pipetting the solvent of diluted nitric acid into a tube and then pipetting the standard solution. For the samples that required DCM, 100 µL of the solvent per every 5 mL of solution was added to each sample tube as the last step. Note that the solvent must match the acid composition and concentration that was used for the sample preparation. Ideally, the standards and samples will have the same percentages of acids in them. This allows for the same amount of sample to be introduced from the nebulizer to the detector thereby minimizing matrix effects.

The indicated amount of stock solution was added to the tube with a volumetric pipet. The remaining volume of solvent (3% HNO_3) was pipetted to generate a total volume of 10 mL. One hundred microliters of the solvent was added to 5 mL of each sample to that required DCM as the last step before analysis was performed. The samples were vortexed vigorously after the DCM was added before they were placed on the autosampler.

Table 1. Nominal Concentrations of Elemental Calibration Standards

Solution Name	Final Concentration	Amount Added to 15 mL PP Tube
Level 1 (10 mL)	10 ppm	0.100 mL of each As, Pb, Hg, Os, Tl 1 mL Be 8.5 mL 3% HNO_3
Level 2 (10 mL)*	100 ppb	0.1 mL level 1, 9.9 mL 3% HNO_3
Level 3 (10 mL)	50 ppb	5 mL of level 2 5 mL 3% HNO_3
Level 4 (10 mL)	25 ppb	2.5 mL of level 2 7.5 mL 3% HNO_3
Level 5 (10 mL)	10 ppb	1 mL level 2, 9 mL 3% HNO_3
Level 6 (10 mL)	5 ppb	1 mL level 3, 9 mL 3% HNO_3
Level 7 (10 mL)	1 ppb	1 mL of level 5, 9 mL 3% HNO_3

*Make two of these.

3.2.3 Quality Assurance Samples

For the method blank, a sample of appropriate solvent (from the same lot) was processed through the entire sample preparation procedure with each batch of samples. The method blank was then analyzed with the samples.

For the reagent blank, a sample of 3% HNO_3 was run after each continuing calibration verification sample to ensure that no carryover occurred.

3.2.4 Sample Analysis

To prepare the instrument for analysis, necessary performance verification was completed in accordance with WI-091-ICP-MS-7900.[3] Fresh 3% HNO_3 solutions, which served as rinses were added to the 15 mL PP tubes, and a set was required between each sample. Tubing was changed as necessary. The calibration curve samples, unknown samples, and rinse samples were loaded into the auto sampler, and the sequence was run.

4. RESULTS AND DISCUSSION

4.1 Calibration Curves

Qualitative analyses of the analytes in the solutions were determined by the presence of a signal for the most abundant isotope of a given element. Interferences of major isotopes were minimized by running the collision reaction cell in no-gas (no. 1), helium gas (no. 2), and hydrogen gas (no. 3) modes. In this instance, the ions were analyzed under helium mode. Quantitative analysis of analytes in solution was performed by generating at least a five-point calibration curve and forcing the intercept through zero. Equation 1 was used to convert the signal into a concentration using the slope and intercept of the calibration curve:

$$Y = \frac{(A/S) - B}{M} \quad (1)$$

where Y is the measured concentration , A is the signal of the analyte, S is the signal of the standard, B is the y intercept, and M is the slope of the calibration curve.

The measured concentration was converted to a final concentration by multiplying by a dilution factor as shown:

$$C_f = C_M \times (V_f / V_s) \quad (2)$$

where C_f is the final concentration, C_M is the measured concentration, V_f is the final volume of the solution analyzed, and V_s is the volume of the sample.

The concentrations used in this study were optimized to produce linear regression fits for the calibration curves ranging from 1 to 100 ppb for each isotope (Table 2).

Table 2. Concentration Range for Each Analyte

Analyte		Concentration Range (ppb)
No.	**Isotope**	
1	^{75}As	1–100
2	^{9}Be	
3	^{202}Hg	
4	^{208}Pb	
5	^{205}Tl	
6	^{189}Os	

4.2 Relative Percent Differences

The precision of the analysis of the samples is determined by calculating the relative percent difference between the measured and expected concentrations:

$$\left(\frac{C_M - C_E}{\text{Average } (C_M + C_E)}\right) \times 100\% \quad (3)$$

where C_M is the concentration measured by the instrument, and C_E is the expected concentration.

Each ion had a minimum of five valid points in the calibration curve.

4.3 Method Detection Limits (MDLs)

An MDL was performed as described in Chapter 1 of Test Method 6020A, Rev. 1.[4] Five replicate solutions with all of the analytes were prepared by spiking the matrix with the analyte at a concentration equal to three to five times the estimated MDL. The solutions were analyzed in random order. Each element was spiked at 0.001 ppm. The MDL was determined by multiplying the appropriate one-sided 99% *t* statistic (2.82 for ten measurements) by the standard deviation (SD) of the replicate measurements:

$$\text{MDL} = 2.82 \times \text{SD} \quad (4)$$

The MDLs for the analytes are listed in Tables 3 and 4.

Table 3. ICP-MS MDL Data (in Nitric Acid Only)

Replicate	Recovered Concentration of Analyte (ppb)*					
	Be	**As**	**Hg**	**Os**	**Tl**	**Pb**
1	1.13	1.19	1.18	1.07	0.98	1.05
2	1.29	1.10	1.18	1.04	0.95	1.01
3	0.98	1.22	1.24	1.10	0.99	1.05
4	1.16	1.26	1.25	1.07	1.00	1.05
5	1.04	1.16	1.21	1.06	0.97	1.04
6	1.44	1.29	1.35	1.20	1.11	1.17
7	0.89	0.97	0.99	0.84	0.76	0.83
8	1.05	1.12	1.18	1.04	0.97	1.02
9	0.76	1.02	1.13	0.97	0.89	0.96
10	0.98	1.05	1.16	0.98	0.93	0.98
MDL:	0.55	0.30	0.26	0.27	0.25	0.24
Standard Deviation:	0.19	0.11	0.09	0.09	0.09	0.09

*All analytes were at a spiked concentration of 1 ppb.

Table 4. ICP-MS MDL Data (in Nitric Acid with DCM)

Replicate	Recovered Concentration of Analyte (ppb)*					
	Be	**As**	**Hg**	**Os**	**Tl**	**Pb**
1	0.84	1.29	1.19	1.04	0.13	1.18
2	1.08	2.54	1.18	1.23	0.35	3.06
3	0.73	2.92	1.21	1.38	1.03	1.18
4	1.23	2.40	2.50	1.13	0.77	0.97
5	0.84	1.47	2.86	1.06	0.48	0.58
6	0.92	1.34	1.32	1.05	0.94	1.07
7	0.95	2.36	1.21	0.95	1.03	1.17
8	1.15	2.13	0.93	0.89	1.03	1.12
9	0.32	1.26	1.65	0.87	0.58	0.64
10	0.34	1.29	1.51	0.77	0.60	0.70
MDL:	0.87	1.79	1.77	0.51	0.90	1.99
Standard Deviation:	0.31	0.63	0.63	0.18	0.32	0.70

*All analytes were at a spiked concentration of 1 ppb.

4.3.1 Precision and Accuracy (P&A) Study

Three solutions at each calibration level were prepared and analyzed in random order. This procedure was repeated on a second day to prepare a separate batch of standards at each level for a total of six analyses at each calibration level. Concentrations of the tested calibration levels are listed in Tables 5 and 6.

Table 5. Concentration of Analyte in 3% Nitric Acid Calibration Solution Used for P&A Levels

Level	Concentration (ppb)		
	Target	Day 1	Day 2
As			
1	1	1.34	1.05
2	5	5.77	5.57
3	10	11.35	10.54
4	25	23.97	26.43
5	50	47.37	53.64
6	100	101.40	97.74
Be			
1	1	0.98	1.32
2	5	5.41	5.30
3	10	11.67	10.92
4	25	24.29	26.40
5	50	46.93	53.11
6	100	101.52	97.98
Pb			
1	1	1.05	1.10
2	5	4.66	4.68
3	10	9.21	9.32
4	25	22.73	24.73
5	50	49.56	46.62
6	100	100.88	101.84
Hg			
1	1	0.83	1.15
2	5	4.44	5.77
3	10	9.66	10.83
4	25	25.19	27.51
5	50	46.10	56.50
6	100	101.97	96.00
Os			
1	1	1.12	0.89
2	5	5.50	4.98
3	10	10.49	9.76
4	25	24.62	21.76
5	50	51.90	47.80
6	100	99.57	101.94
Tl			
1	1	0.97	0.94
2	5	4.60	4.70
3	10	9.21	9.17
4	25	22.86	24.28
5	50	50.47	46.23
6	100	100.40	102.16

Table 6. Concentration of Analyte in 3% Nitric Acid with DCM Calibration Solution Used for P&A Levels

Level	Concentration (ppb)		
	Target	Day 1	Day 2
As			
1	1	2.25	0.88
2	5	7.70	3.89
3	10	9.51	7.69
4	50	49.52	41.78
5	100	101.55	103.95
Be			
1	1	1.35	0.81
2	5	7.34	3.81
3	10	9.19	8.06
4	50	52.00	41.16
5	100	98.86	104.19
Pb			
1	1	1.09	1.21
2	5	4.80	4.92
3	10	9.56	9.67
4	50	50.77	49.00
5	100	99.67	100.93
Hg			
1	1	1.59	1.25
2	5	3.29	4.68
3	10	4.65	10.61
4	50	52.24	51.44
5	100	102.25	99.63
Os			
1	1	1.00	0.98
2	5	4.92	4.90
3	10	10.02	9.97
4	50	50.60	49.35
5	100	99.70	100.45
Tl			
1	1	0.94	1.12
2	5	4.64	4.81
3	10	9.48	9.41
4	50	51.16	47.04
5	100	99.49	101.94

The relative standard deviation (RSD) of the three solutions at each calibration level was calculated using eq 5:

$$\text{RSD} = \left(\frac{\text{SD of replicates}}{\text{average result}}\right) \quad (5)$$

Percent recoveries were ≥90% for the six elements (Tables 7–18).

Table 7. ICP-MS Data for the Be in Nitric Acid P&A Study. “Helium” Mode

	Recovered Concentration (ppb)					
Level	**1**	**2**	**3**	**4**	**5**	**6**
Spiked Conc. (ppb)	**1**	**5**	**10**	**25**	**50**	**100**
Replicate 1	1.01	5.38	11.20	25.97	52.83	102.90
Replicate 2	1.11	5.67	12.25	27.42	56.71	108.30
Replicate 3	1.01	5.43	11.80	29.16	54.54	116.90
Replicate 4	0.86	6.04	9.56	27.89	63.28	106.20
Replicate 5	1.07	5.27	11.31	23.85	53.49	118.00
Replicate 6	1.30	5.46	12.17	30.15	55.43	115.40
Mean Value:	1.06	5.54	11.38	27.41	56.05	111.28
Mean % Recovery:	150.23	126.70	123.29	107.03	105.38	105.73
Standard Deviation:	0.15	0.28	0.99	2.26	3.80	6.30
%RSD:	13.69	5.01	8.69	8.25	6.78	5.66

Table 8. ICP-MS Data for the Be in Nitric Acid with DCM P&A Study. “He” Mode

	Recovered Concentration (ppb)				
Level	**1**	**2**	**3**	**4**	**5**
Spiked Conc. (ppb)	**1**	**5**	**10**	**50**	**100**
Replicate 1	0.53	2.72	4.98	27.15	88.60
Replicate 2	0.01	2.34	0.01	27.66	76.38
Replicate 3	0.47	5.97	6.17	58.68	66.76
Replicate 4	0.88	3.41	7.37	39.25	83.54
Replicate 5	0.71	3.37	7.56	36.72	76.76
Replicate 6	0.52	3.67	6.32	36.89	73.86
Mean Value:	0.52	3.58	5.40	37.73	77.65
Mean % Recovery:	52.02	71.54	54.03	75.45	77.65
Standard Deviation:	0.29	1.27	2.80	11.46	7.62
%RSD:	56.28	35.49	51.83	30.37	9.81

Table 9. ICP-MS Data for the As in Nitric Acid P&A Study. “He” Mode

	Recovered Concentration (ppb)				
Level	**1**	**2**	**3**	**4**	**5**
Spiked Conc. (ppb)	**1**	**5**	**10**	**50**	**100**
Replicate 1	1.52	6.05	29.79	58.59	112.30
Replicate 2	1.34	6.15	25.46	60.11	113.20
Replicate 3	1.46	6.35	29.55	57.43	114.00
Replicate 4	1.37	5.85	20.84	58.68	125.20
Replicate 5	1.27	5.46	20.75	54.26	116.90
Replicate 6	1.30	5.57	21.56	54.18	116.00
Mean Value:	1.38	5.90	11.97	57.21	116.27
Mean % Recovery:	137.77	118.09	119.72	114.42	116.27
Standard Deviation:	0.10	0.34	0.48	2.47	4.70
%RSD:	7.01	5.83	4.02	4.31	4.04

Table 10. ICP-MS Data for the As in Nitric Acid with DCM P&A Study. “He” Mode

	Recovered Concentration (ppb)				
Level	**1**	**2**	**3**	**4**	**5**
Spiked Conc. (ppb)	**1**	**5**	**10**	**50**	**100**
Replicate 1	0.55	3.75	8.69	38.68	87.85
Replicate 2	0.54	2.70	9.55	38.21	62.65
Replicate 3	0.03	0.03	4.46	0.03	23.84
Replicate 4	0.98	4.56	8.65	41.90	83.50
Replicate 5	0.87	4.37	8.04	39.37	74.31
Replicate 6	0.80	3.59	8.47	34.64	64.33
Mean Value:	0.63	3.17	7.98	32.14	66.08
Mean % Recovery:	62.62	63.31	79.77	64.28	66.08
Standard Deviation:	0.34	1.67	1.79	15.90	23.00
%RSD:	54.60	52.81	22.45	49.49	34.80

Table 11. ICP-MS Data for the Hg in Nitric Acid P&A Study. “He” Mode

	Recovered Concentration (ppb)					
Level	**1**	**2**	**3**	**4**	**5**	**6**
Spiked Conc. (ppb)	**1**	**5**	**10**	**25**	**50**	**100**
Replicate 1	1.39	5.16	11.87	24.83	78.26	137.70
Replicate 2	1.20	6.37	12.06	29.38	59.78	156.10
Replicate 3	1.26	6.75	12.00	59.54	61.97	147.40
Replicate 4	1.56	6.07	12.18	28.64	58.91	153.70
Replicate 5	1.46	6.35	10.87	31.00	62.18	371.20
Replicate 6	1.54	6.60	10.59	30.24	71.65	150.00
Mean Value:	1.40	6.22	11.60	33.94	65.46	186.02
Mean % Recovery:	140.02	124.36	115.95	135.75	130.92	186.02
Standard Deviation:	0.15	0.57	0.68	12.72	7.75	90.95
%RSD:	10.57	9.15	5.89	37.49	11.84	48.89

Table 12. ICP-MS Data for the Hg in Nitric Acid with DCM P&A Study. “He” Mode

	Recovered Concentration (ppb)				
Level	**1**	**2**	**3**	**4**	**5**
Spiked Conc. (ppb)	**1**	**5**	**10**	**50**	**100**
Replicate 1	3.27	2.48	3.92	43.63	210.90
Replicate 2	2.16	3.31	4.36	26.19	91.00
Replicate 3	0.64	13.09	1.01	11.04	7.68
Replicate 4	4.79	5.68	10.80	137.00	381.10
Replicate 5	3.60	4.73	19.62	108.90	371.40
Replicate 6	7.23	20.10	16.16	88.12	241.30
Mean Value:	3.62	8.23	9.31	69.15	217.23
Mean % Recovery:	361.57	164.65	93.12	138.29	217.23
Standard Deviation:	2.26	6.94	7.46	49.83	149.06
%RSD:	62.50	84.24	80.07	72.07	68.62

Table 13. ICP-MS Data for the Os in Nitric Acid P&A Study. “He” Mode

	Recovered Concentration (ppb)					
Level	**1**	**2**	**3**	**4**	**5**	**6**
Spiked Conc. (ppb)	**1**	**5**	**10**	**25**	**50**	**100**
Replicate 1	1.40	5.11	10.50	27.05	52.66	105.60
Replicate 2	1.09	5.13	10.39	25.77	52.61	89.07
Replicate 3	1.06	5.13	10.46	25.36	51.01	94.78
Replicate 4	0.94	6.08	12.64	29.64	55.68	121.70
Replicate 5	1.23	6.02	12.46	30.57	58.85	119.30
Replicate 6	0.52	0.35	12.67	31.04	60.64	118.10
Mean Value:	1.04	4.64	11.52	28.24	55.24	108.09
Mean % Recovery:	104.12	92.72	115.20	112.95	110.48	108.09
Standard Deviation:	0.30	2.15	1.17	2.49	3.84	13.83
%RSD:	28.66	46.31	10.20	8.82	6.96	12.79

Table 14. ICP-MS Data for the Os in Nitric Acid with DCM P&A Study. "He" mode

	Recovered Concentration (ppb)				
Level	**1**	**2**	**3**	**4**	**5**
Spiked Conc. (ppb)	**1**	**5**	**10**	**50**	**100**
Replicate 1	1.13	5.70	11.58	61.39	118.70
Replicate 2	1.52	5.65	14.02	58.97	117.50
Replicate 3	0.70	5.72	4.40	42.14	113.40
Replicate 4	1.35	6.13	8.86	62.02	126.90
Replicate 5	1.19	6.59	6.60	34.65	129.10
Replicate 6	0.82	3.23	12.70	39.60	107.50
Mean Value:	1.12	5.50	9.69	49.80	118.85
Mean % Recovery:	111.98	110.04	96.91	99.59	118.85
Standard Deviation:	0.31	1.17	3.73	12.33	8.13
%RSD:	27.74	21.25	38.52	24.76	6.84

Table 15. ICP-MS Data for the Tl in Nitric Acid P&A Study. "He" Mode

	Recovered Concentration (ppb)					
Level	**1**	**2**	**3**	**4**	**5**	**6**
Spiked Conc. (ppb)	**1**	**5**	**10**	**25**	**50**	**100**
Replicate 1	1.32	6.85	13.91	34.71	74.74	148.50
Replicate 2	1.44	6.97	13.48	37.01	74.71	144.20
Replicate 3	1.35	7.12	13.77	35.02	76.30	145.70
Replicate 4	1.42	7.58	14.16	33.59	70.07	155.60
Replicate 5	1.49	7.57	15.27	41.00	74.56	145.30
Replicate 6	1.55	7.92	14.97	32.44	74.47	153.40
Mean Value:	1.43	7.33	14.26	35.63	74.14	148.78
Mean % Recovery:	142.98	146.68	142.60	142.51	148.28	148.78
Standard Deviation:	0.08	0.42	0.71	3.04	2.11	4.70
%RSD:	5.86	5.67	4.96	8.54	2.84	3.16

Table 16. ICP-MS Data for the Tl in Nitric Acid with DCM P&A Study. "He" Mode

	Recovered Concentration (ppb)				
Level	**1**	**2**	**3**	**4**	**5**
Spiked Conc. (ppb)	**1**	**5**	**10**	**50**	**100**
Replicate 1	1.18	6.01	13.03	67.91	125.60
Replicate 2	1.12	4.25	13.94	61.19	123.60
Replicate 3	0.64	2.94	12.29	57.59	70.20
Replicate 4	1.63	6.64	16.45	84.96	180.40
Replicate 5	0.95	8.30	11.86	86.48	176.90
Replicate 6	0.79	5.81	17.26	54.46	165.10
Mean Value:	1.05	5.66	14.14	68.77	140.30
Mean % Recovery:	105.13	113.16	141.38	137.53	140.30
Standard Deviation:	0.35	1.87	2.23	13.88	42.36
%RSD:	33.13	33.05	15.80	20.19	30.19

Table 17. ICP-MS Data for the Pb in Nitric Acid P&A Study. "He" Mode

	Recovered Concentration (ppb)					
Level	**1**	**2**	**3**	**4**	**5**	**6**
Spiked Conc. (ppb)	**1**	**5**	**10**	**25**	**50**	**100**
Replicate 1	1.14	6.03	10.26	29.30	67.49	116.40
Replicate 2	1.22	4.74	9.44	26.06	55.14	111.90
Replicate 3	1.17	5.41	10.93	25.45	58.76	128.50
Replicate 4	0.91	4.71	8.37	24.29	48.13	97.64
Replicate 5	1.10	5.10	10.59	22.74	50.72	94.29
Replicate 6	1.03	5.07	9.19	22.66	46.14	95.05
Mean Value:	1.09	5.18	9.80	25.08	54.40	107.30
Mean % Recovery:	109.28	103.52	97.95	100.33	108.79	107.30
Standard Deviation:	0.11	0.49	0.97	2.48	7.90	13.90
%RSD:	10.15	9.49	9.87	9.90	14.52	12.95

Table 18. ICP-MS Data for the Pb in Nitric Acid with DCM P&A Study. "He" Mode

	Recovered Concentration (ppb)				
Level	**1**	**2**	**3**	**4**	**5**
Spiked Conc. (ppb)	**1**	**5**	**10**	**50**	**100**
Replicate 1	1.65	4.35	7.59	49.60	95.37
Replicate 2	0.94	4.46	5.06	51.08	90.18
Replicate 3	0.74	5.15	4.66	40.20	87.43
Replicate 4	1.41	5.98	9.15	52.67	94.53
Replicate 5	1.43	4.24	8.26	46.45	95.28
Replicate 6	1.19	2.63	6.92	48.27	97.11
Mean Value:	1.23	4.47	6.94	48.05	93.32
Mean % Recovery:	122.68	89.41	69.41	96.09	93.32
Standard Deviation:	0.34	1.12	1.78	4.41	3.70
%RSD:	27.68	24.95	25.61	9.18	3.96

4.3.2 Measurement of Uncertainty (MU)

The measurement uncertainty for the three solutions at each calibration level was determined in accordance with DEVCOM CBC EC/B FAC work instruction WI-098.3 The major sources contributing to the MU were errors from the calibration curve and process repeatability. These sources were measured during the method validation and then combined to determine the overall uncertainty at 95% confidence (Table 19). Mercury has a high level of uncertainty; therefore, it will only be used in a qualitative measure, not a quantitative measure like the other ions.

Table 19. MU

Analyte	Concentration (ppb)	Uncertainty (%)
Be in 3% nitric acid	1	413
	*5	84
	10	50
	25	31
	50	23
	100	19
Be in 3% nitric acid with DCM	1	903
	5	193
	10	117
	*50	62
	100	23
As in 3% nitric acid	1	420
	*5	87
	10	45
	50	17
	100	15
As in 3% nitric acid with DCM	1	851
	5	191
	*10	98
	50	84
	100	60
Hg in 3% nitric acid	1	690
	5	142
	*10	73
	25	146
	50	47
	100	257

Table 19. MU (Continued)

Analyte	Concentration (ppb)	Uncertainty (%)
Hg in 3% nitric acid with DCM	1	779
	5	372
	10	199
	50	256
	100	383
Os in 3% nitric acid with DCM	1	503
	5	157
	*10	60
	25	35
	50	25
	100	39
Os in 3% nitric acid with DCM	1	120
	*5	63
	10	96
	50	63
	100	21
Tl in 3% nitric acid with DCM	1	430
	*5	90
	10	48
	25	39
	50	15
	100	14
Tl in 3% nitric acid with DCM	1	410
	5	125
	*10	70
	50	72
	100	109
Pb in 3% nitric acid with DCM	1	398
	*5	85
	10	49
	25	33
	50	45
	100	39
Pb in 3% nitric acid with DCM	1	634
	5	140
	*10	79
	50	31
	100	12

*PQL identified through P&A and MU.

5. CONCLUSIONS

ICP-MS is a viable method for qualitative and quantitative analysis of two analytes in aqueous solutions. Calibration curves were valid for a minimum of five points for all analytes. MDLs were calculated for each element. Measurements of uncertainty were also calculated for each metal at each calibration level in each sample matrix.

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ACRONYMS AND ABBREVIATIONS

CAS	Chemical Abstracts Service
CBC	Chemical Biological Center
DCM	dichloromethane
DEVCOM	U.S. Army Combat Capabilities Development Command
ECBC	U.S. Army Edgewood Chemical Biological Center
FAC	Forensic Analytical Center
HDPE	high-density polyethylene
HNO_3	nitric acid
ICP-MS	inductively coupled plasma mass spectrometry
IEC	International Electrotechnical Commission
ISO	International Organization for Standardization
MDL	method detection limit
MU	measurement of uncertainty
P&A	precision and accuracy
PP	polypropylene
RDECOM C&B	Research, Development and Engineering Command
RSD	relative standard deviation
SD	standard deviation

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