

AP200 II

Automated
Mercury
Preparation
System

Recovery of Digested Methyl Mercury Chloride using the AP200II

Application Note 1015

Recovery of Digested Methyl Mercury Chloride using the AP200II

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Introduction

Mercury, which is found in a variety of forms, both organic and inorganic, must be digested to produce elemental mercury vapor for analysis via Cold Vapor Atomic Absorption Spectroscopy (CVAAS). Potassium permanganate oxidizes many forms of mercury compounds, but some of the organic mercurial compounds may be only partially oxidized. EPA Methods requires the addition of potassium persulfate to the digestion to assure that 100% of the organic mercurial compounds are oxidized to mercuric ions. If they are not fully oxidized, these volatile organic materials may be lost during the heating step of the digestion. This study was designed to evaluate the recovery of methyl mercury chloride digested using the Leeman Labs AP200II Automated Mercury Preparation System.

Instrument and Method

In this experiment, mercuric chloride solutions in 0.15% HNO₃ and methyl mercury chloride solutions in 0.15% HNO₃ were digested according to EPA SW-846 Method 7470A using the AP200II Automated Mercury Preparation System. The concentration scheme used for both mercuric chloride and methyl mercury chloride was blank, 0.1 ppb, 0.5 ppb, 1.0 ppb, and 5.0 ppb. The mercuric chloride solutions were run as standards. Two certified samples, Priority Pollutants Trace Metals (lot number 3408) and Potable Trace Metals (lot number 426), were also included. All samples were run in triplicate with one exception; only two blanks were run after the last methyl mercury sample before the Priority Pollutant certified samples. A check standard of 1.0 ppb concentration was run every 10 samples. The COP (Complete Oxidation Probe) was calibrated immediately before the digestion. The COP probe checked the color of the cups for the persistence of the characteristic purple potassium

permanganate color. None of the samples required an additional aliquot of potassium permanganate. The samples were analyzed on the Leeman Labs PS200II Mercury Analyzer using 10% SnCl₂ in 0.5N H₂SO₄ as the reductant. A fresh drying tube of magnesium perchlorate was attached before the standards were run. Normal operating conditions were used (see Table 1).

Results and Discussions

The calibration curve using the mercuric chloride standards is shown in Figure 1. A linear fit was used and the correlation coefficient of 0.999981 indicated excellent linearity. The methyl mercury chloride samples consistently produced recoveries greater than 90% (see Figure 2). The mercuric chloride samples had an average recovery rate of 101% (see Figure 3). Both of the certified samples had recoveries of over 100% (see Figure 4). Check standards were run every 10 samples. The check standards both showed excellent reproducibility. Check standard 2 was a 1.0 ppb mercuric chloride solution, and check standard 3 was 1.0 ppb methyl mercury chloride (see Figure 5).

A second rack containing mercuric chloride and methyl mercury chloride samples as described above was also digested, however, the vapor barrier was replaced during the heating step

Table 1
Operating Conditions for
the PS200II

Gas Flow	0.30 LPM
Pump Rate	5 mL/min
Integration Time	10 sec
Uptake Time	10 sec
Rinse Time	50 sec

with weighted plastic caps. When the heating step was completed the caps were removed and the vapor barrier was replaced. The methyl mercury samples showed recoveries equivalent to the mercuric chloride samples (see Figure 6).

Conclusion

This study shows that samples containing volatile organic mercurial compounds were digested and analyzed without significant loss of mercury. The digestion procedure adequately

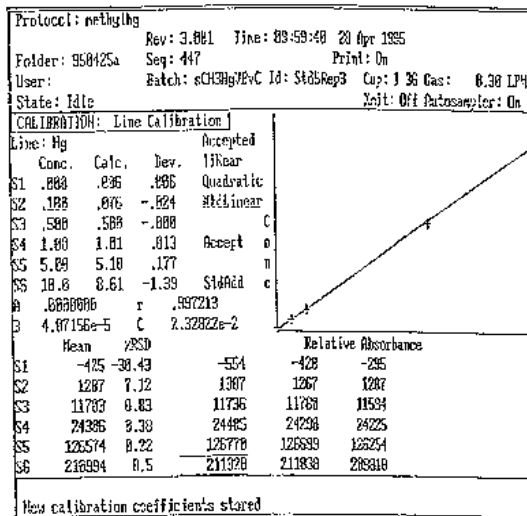


Figure 1. Calibration Curve using mercuric chloride standards

Line	Conc.	Units	SD/RSD	1	2	3	4	5
*** Sample ID: 0.0 Replicate Summary, Seq. 467 to 471								
Hg	.017	ppb	.017	-.001	.033	.020		
*** Sample ID: 0.1 MethHg Replicate Summary, Seq. 472 to 474								
Hg	.114	ppb	.007	.120	.116	.106		
*** Sample ID: 0.5 MethHg Replicate Summary, Seq. 475 to 477								
Hg	.463	ppb	.008	.472	.457	.461		
*** Sample ID: 1.0 MethHg Replicate Summary, Seq. 478 to 480								
Hg	.914	ppb	.007	.907	.921	.915		
*** Sample ID: 10 MethHg Replicate Summary, Seq. 486 to 488								
Hg	9.24	ppb	.043	9.19	9.28	9.24		
*** Sample ID: 5.0 MethHg Replicate Summary, Seq. 483 to 485								
Hg	4.53	ppb	.125	4.47	4.44	4.67		

Methyl Mercury Chloride Recovery	
Concentration	%Recovery
0.1 ppb	114%
0.5 ppb	92.6%
1.0 ppb	91.4%
5.0 ppb	90.6%
97.15% Average	

Figure 2. The Methyl Mercury Chloride Samples consistently produced recoveries greater than 90%

Line	Conc.	Units	SD/RSD	1	2	3	4	5
*** Sample ID: 0.0 Replicate Summary, Seq. 447 to 449								
Hg	.025	ppb	.003	.027	.026	.021		
*** Sample ID: 0.10 HgCl2 Replicate Summary, Seq. 450 to 452								
Hg	.094	ppb	.002	.093	.093	.097		
*** Sample ID: 0.50 HgCl2 Replicate Summary, Seq. 453 to 455								
Hg	.530	ppb	.015	.547	.519	.524		
*** Sample ID: 1.0 HgCl2 Replicate Summary, Seq. 456 to 460								
Hg	.997	ppb	.028	1.01	1.01	.964		
*** Sample ID: 10.0 HgCl2 Replicate Summary, Seq. 464 to 466								
Hg	10.4	ppb	.368	9.99	10.7	10.5		
*** Sample ID: 5.0 HgCl2 Replicate Summary, Seq. 461 to 463								
Hg	5.14	ppb	.108	5.03	5.24	5.15		

Mercuric Chloride Recovery	
Concentration	%Recovery
0.1 ppb	94%
0.5 ppb	106%
1.0 ppb	99.7%
5.0 ppb	103%
100.68% Average	

Figure 3. The Mercuric Chloride Samples had an average recovery rate of 101%.

14:26:00 28 Apr 1995 Folder: 950425a Page 1
Protocol: methylhg

Line	Conc.	Units	SD/RSD	1	2	3	4	5
*** Sample ID: 0.0				Replicate Summary, Seq. 489 to 490				
Hg	.169	ppb	.224	.010	.327			
*** Sample ID: Metal#3408				Replicate Summary, Seq. 496 to 498				
Hg	7.03	ppb	.112	6.94	6.98	7.15		
*** Sample ID: Trace#426				Replicate Summary, Seq. 491 to 495				
Hg	3.91	ppb	.082	3.94	3.82	3.97		

Figure 4. Both certified samples had recoveries of over 100%.

breaks down mercury complexes into mercuric ions for analysis by Cold Vapor Atomic Absorption. The vapor barrier used by the AP200II Automated Mercury Digestion System allowed possible interfering volatile materials such as chlorine gas to outgas without losing undigested mercury containing materials. The difference in the recovery data from the capped cups when compared to those covered exclusively with the vapor barrier was consistent with the slight evaporation present with the vapor barrier.

Certified Samples

Priority Pollutant Trace Metals #3408

Concentration % Recovery
 Certified Value 6.66 ppb 106%
 Performance Acceptance Limits 4.66 - 8.66 ppb
 Digested Sample 7.03 ppb (from above)

Potable Trace Metals #426

Concentration % Recovery
 Certified Value 3.89 ppb 101%
 Performance Acceptance Limits 2.92 - 4.86 ppb
 Digested Sample 3.91 ppb (from above)

14:21:59 28 Apr 1995 Folder: 950425a Page 2
Protocol: methylhg

Line	Conc.	Units	SD/RSD	1	2	3	4	5
*** Sample ID: Ck2				Replicate Summary, Seq. 457 to 551				
Hg	1.08	ppb	.035	1.14	1.11	1.10	1.07	1.08
				1.06	1.09	1.05	1.03	
*** Sample ID: Ck3				Replicate Summary, Seq. 458 to 552				
Hg	1.12	ppb	.025	1.17	1.13	1.13	1.12	1.11
				1.11	1.11	1.10	1.09	

Figure 5. Both check standards showed excellent reproducibility.

**Vapor Barrier vs. Capped Cups
Mercury Chloride**

Concentration	Vapor Barrier	Capped	Difference	%
0.1 ppb	0.094 ppb	0.080 ppb	0.014	14.9
0.5 ppb	0.530 ppb	0.470 ppb	0.060	11.3
1.0 ppb	0.997 ppb	0.990 ppb	0.007	0.70
5.0 ppb	5.14 ppb	4.97 ppb	0.17	3.3
Check Standard	1.14 ppb	1.07 ppb	0.07	6.14
1.0 ppb				Average 7.27%

**Vapor Barrier vs. Capped Cups
Methyl Mercury Chloride**

Concentration	Vapor Barrier	Capped	Difference	%
0.1 ppb	0.114 ppb	0.109 ppb	0.005	4.39
0.5 ppb	0.463 ppb	0.421 ppb	0.042	9.07
1.0 ppb	0.914 ppb	0.846 ppb	0.068	7.44
5.0 ppb	4.53 ppb	4.33 ppb	0.20	4.42
Check Standard	1.13 ppb	1.10 ppb	0.03	2.65
1.0 ppb				Average 5.59%

Figure 6. The Methyl Mercury Samples showed recoveries equivalent to the mercuric chloride samples.