The Determination of Mercury by Cold Vapor Atomic Absorption

Application Note

Atomic Absorption

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Introduction

Mercury contamination of the environment and its toxic effects have been known for centuries. The novel "Alice in Wonderland" refers to "mad hatters" who were hat makers gone "mad" due to exposure to mercury used in cleaning felt hats. In 1810, a British man-of-war salvaged 130 tons of mercury from a Spanish wreck off Cadiz. Parchment bags had been used to confine the mercury within wooden barrels, but owing to the sodden condition of the bags after salvage and the prevailing heat, mercury vapor very quickly diffused throughout the man-of-war. Almost everyone on board soon showed signs of mercury poisoning, several members of the crew died, and the ship's livestock was wiped out [1].

Since then we have learned to handle and transport mercury itself with more caution, but disposal of industrial wastes containing mercury has often been less than responsible. Over the last two decades, a growing concern about increasing mercury concentrations in wateways and lakes has resulted in extensive surveys and large scale monitoring. This resulted in fishing bans in areas where mercury levels as high as 7 ppm had been recorded. During this same time, studies on the determination of mercury were carried out.

Because of the relatively poor sensitivity for mercury provided by traditional flame atomic absorption, alternative atomization techniques for the AA determination of mercury have been developed. Furnace methods for mercury are not recommended due to the extreme volatility of mercury, which has a significant vapor pressure even at room temperature. The cold vapor atomic absorption technique for mercury has received the greatest attention.

The cold vapor principle was first proposed by Poluektov and co-workers in 1963 [2]. However the most popular method is that usually credited to Hatch and Ott published in 1968([3]. In this method, an acidified solution containing mercury is reacted with stannous chloride in a vessel external to the AA instrument. Ground state mercury atoms are produced which subsequently are transported by an air or

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inert gas flow to an absorption cell installed in the AA instrument. This method provides sensitivities approximately four orders of magnitude better than flame AA.

The US EPA has set a limit for mercury in drinking water of 2 µg/L or 2 ppb. The cold vapor technique is the only EPA approved method for determining mercury at this level [4].

The Cold Vapor Techinque

The processes occurring in the mercury cold vapor technique are simple but they can be affected by numerous factors. Ionic mercury in acidic solution will be reduced by stannous ions producing ground state atomic mercury. After equilibration the mercury vapor is swept from the reaction vessel with air, nitrogen or argon. In most instances the atomic mercury is swept through an absorption cell placed in the optical path of the AA instrument, atomic absorption takes place, and a transient signal is recorded. Alternatively, a closed system can be used, producing a somewhat lower "steady-state" signal.

Results obtained can be affected by the type and concentration of acids employed, the actual form of mercury in the sample, and other reagents or matrix components of the sample. In order for the reaction to proceed efficiently, samples containing organically bound mercury must be subjected to an acid digestion producing ionic mercury in solution. Various digestion schemes have been reported. Among them are potassium permanganate and perchloric acid [5], nitric acid [1], and sulphuric acid and sodium hydroxide [6]. The EPA recommends a rather extensive digestion scheme for waters and wastes which will be outlined later.

A study was performed to determine optimum acid concentrations and types, sample preparations, and reagents to provide the best sensitivity, precision, and freedom from interference using the Agilent Model 65 Vapor Generation Accessory. A mercury hollow cathode lamp was used as the light source.

The Agilent Model 65 Vapor Generation Accessory

The Agilent Model 65 accessory is used not only for the mercury cold vapor technique but also for the determination of metallic hydride-forming elements. It includes a reaction vessel, a built-in magnetic stirrer to ensure rapid reactions, and a push-button drain system for convenient removal of samples after analysis. A septum is incorporated to permit injection of reagent solutions and a pellet dispenser allows solid sodium borohydride to be used for hydride generation

techniques. A quartz absorption cell attached to a standard air-acetylene burner is used for the determination of mercury by the cold vapor technique. It can also be heated with an air-acetylene flame to decompose volatile hydrides.

For mercury, samples or standards are placed in the reaction vessel (normally 20 mL), 1–2 mL of 20% by weight $SnCl_2$ in concentrated HCl is added with pipette or syringe, the vessel is closed, then the solution is mixed by the built-in magnetic stirrer. After a reaction/equilibration time of 1.5 to 2 minutes, the inert gas or air is turned on, sweeping the atomic mercury out of the reaction vessel and into the open-ended quartz tube aligned in the optical path of the AA instrument. A transient atomic absorption peak is produced.

Results

The first topic explored was the effect of acid type on the evolution of mercury vapor and the resultant signal. Table 1 shows results obtained for 5 µg/L mercury in different acid matrices. Acid concentrations were 10% by volume. H_3PO_4 and H_2SO_4, by themselves produce low signals especially when allowed to stand for several hours. If HCl is added to either of these acid solutions the problem does not occur. HNO_3 and HCl give approximately equivalent results. Several papers have discussed the use of a mixture of $SnCl_2$, and $CdCl_2$ or $Cd(NO_3)_2$ as the reducing agent [6,7]. Responses for the Sn/Cd mixture were equivalent to those using $SnCl_2$ alone.

Table 1.   Acid Type Effects-Hg

Acid		Peak ht. absorbance	Peak area absorbance
HCL		.110	.246
H_3PO_4	Fresh	.106	.219
	Old	.020	.043
HCL + H_3PO_4		.121	.286
H_2SO_4	Fresh	.088	.196
	Old	.029	.066
HCL+ H_2SO_4		.124	.278
MNO_3	$SnCl_2$ in conc HCL	.120	.274
	$SnCl_2$ in 10% HCL	.116	.249
	$SnCl_2$ = $Cd(No_3)_2$	.114	.258

The effect of acid concentration was then studied. Figure 1 shows representative mercury peaks for varying HCl concentrations. Above 20% by volume HCl, sensitivity and precision are both degraded. Likewise, higher concentrations of HNO_3 degraded sensitivity and precision (Figure 2). The best results for either acid are obtained in the 10–20% by volume range.

HCL

Concentration	Peak Ht Absorbance	Peak Area Absorbance
5%	.149	.339
20%	.145	.339
40%	.112	.260

Figure 1.   Acid concentration effects - Hg.

HNO₃

Concentration	Peak Ht Absorbance	Peak Area Absorbance
5%	.119	.274
20%	.134	.307
40%	.110	.254

Figure 2.   Acid concentration effects - Hg.

Equilibration time for the mercury reduction reaction was investigated. As shown in Figure 3, the mercury signal increased quite rapidly up to 1.5 minutes, then increases very slowly with longer stirring times.
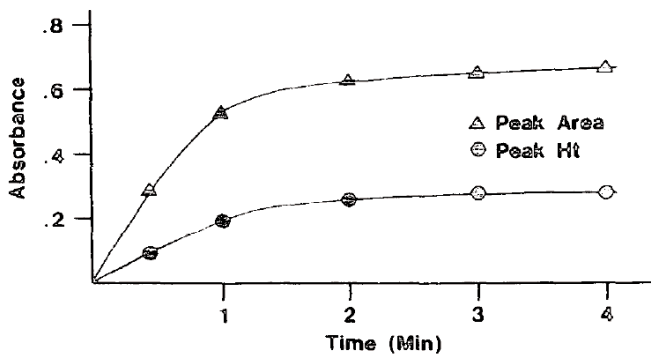
Figure 3.   Equilibration time versus absorbance.

Therefore, 1.5 to 2 minutes is recommended. Since the reaction does not go to completion but is rather an equilibrium situation between mercury in the vapor and liquid phases [8], stirring time should be the same for all standards and samples. Temperature of standards and samples must also be the same.

The effect of sample volume on absorbance is shown in Figure 4. The mercury signal increases with sample volume up to 20 mL, then increases at a somewhat slower rate not proportional to volume. Normally 20 mL sample volumes are recommended, but smaller or larger volumes (up to 30 mL) can be accommodated. Volumes of standards and samples must be equal.
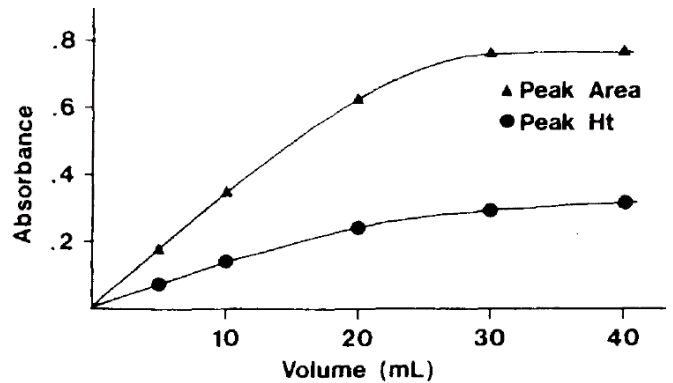

Figure 4.   Sample volumn versus absorbance.

With the recommended sample volume (20 mL), equilibration time of 2 minutes, 10% HCl acid matrix, and 2 mL of 20% $SnCl_2$, in concentrated HCl, the standard peaks in Figure 5 were produced. The reaction vessel was rinsed with distilled water between samples to ensure no residual $SnCl_2$ or mercury was carried over to the next sample. These standards were the basis for the calibration curves shown in Figure 6. Either peak height or peak area measurements may be used for calibration and analysis of samples.
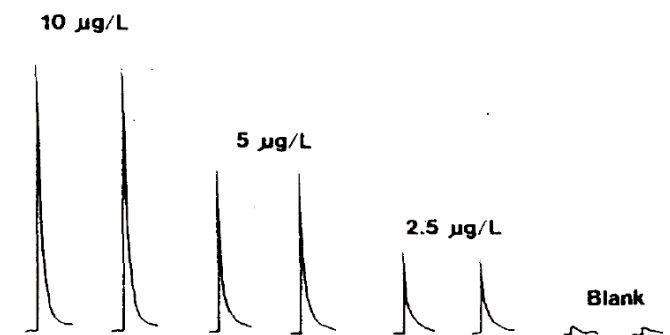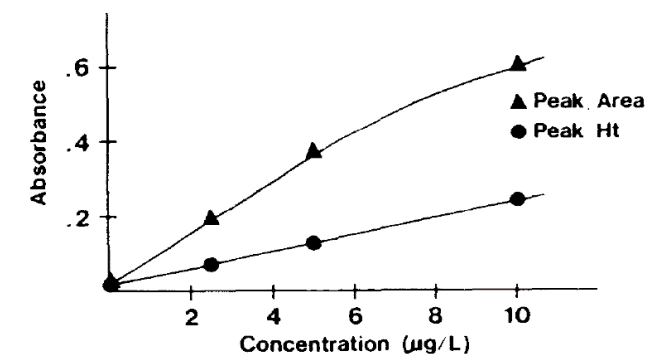

Figure 5.   Hg standards (20mL).

Figure 6.   Hg standard curve.

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Because of the extremely quiet baseline (characteristic of the cold vapor technique) scale expansion can be used to aid in reading very low concentrations of mercury. A scale expansion of 10X produces a peak of almost 0.5 absorbance when a sample containing the EPA maximum drinking water level of 2 µg/L Hg is analyzed (Figure 7).
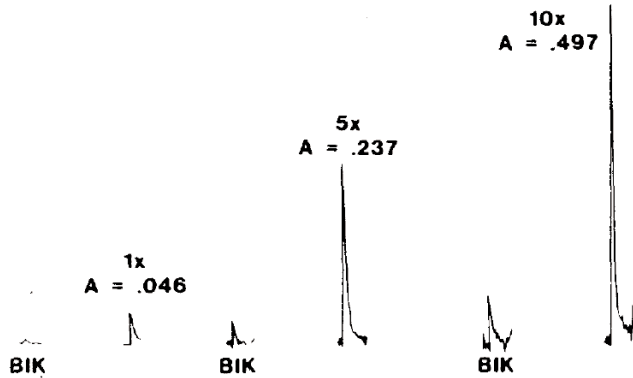

Figure 7.   2µg/L Hg, 20 mL expanded scale.

As stated earlier, organically bound mercury is not efficiently reduced in the normal cold vapor technique. Figure 8 shows that the very toxic methyl mercury compound gives low results (poor recoveries) if it remains in the organic form. In HCl, slightly more than 10% is recovered when compared to inorganic mercury. In HNO_3, no response was obtained. Similar results were obtained even after allowing the acidified standards to stand overnight.

	HCl	HNO₃	Inorganic Hg
Peak Area	.045	−.005	.363
Peak Ht	.014	−.002	.121

10% HCl   10% HNO₃

Figure 8.   Organo, Hg response.

The digestion procedure recommended by the EPA to allow determination of organically bound mercury is outlined in Table 2 [4]. The digestion is quite involved and requires several reagents. Due to the extremely low levels of mercury to be determined, one must guard against potential contamination from reagents and glassware. Following addition of the sodium chloride-hydroxylamine hydrochloride reagent, samples should be mixed (swirled) thoroughly, and allowed to stand for at least 30 seconds before analysis. Otherwise, low results are obtained.

Table 2. EPA Digestion Scheme for Hg

1.   100 mL of sample
2.   Add 5 mL of conc H_2SO_4 and 2.5 mL of conc HNO_3
3.   Add 15 mL of 5% potassium permanganate
4.   Shake and add additional potassium permanganate until purple color persists
5.   Add 8 mL of potassium persulfate
6.   Heat for 2 hours at 95 °C
7.   Cool and add 6 mL of sodium chloride-hydroxylamine sulfate (or hydrochloride)
8   Analyze

Standards subjected to the EPA digestion scheme were used to produce the Hg standard curves shown in Figure 9. There is slight upward curvature perhaps indicating the loss of small amounts of mercury, this loss becoming negligible at higher concentrations (5 µg/L Hg and above). For best accuracy, standards should be subjected to the digestion procedure whenever samples are digested.
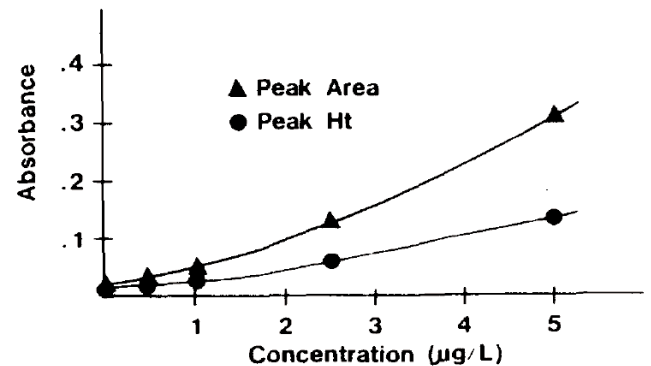

Figure 9.   Hg standard curve after EPA digestion.

In order to confirm the applicability of the EPA digestion procedure for Hg in various forms, three samples were subjected to the digestion. Table 3 presents the results obtained for the three digested samples, each containing known concentrations of Hg. The ERA* WasteWatR standard was found to contain 0.8 µg/L Hg. This falls within the target range of 0.8–1.4 µg/L Hg for the standard. The methyl mercury sample, which previously gave a recovery of slightly over 10%, produces an acceptable 92% recovery after digestion. The third sample, mercury in the presence of KI, gave a poor recovery for Hg. Iodine has been reported to interfere with the mercury reaction and, as shown, the EPA digestion procedure does not overcome this problem.

Table 3.   Hg Recoveries After EPA Digestion

Sample	Concentration found	True value
ERA*	0.8 μ/L	1.1 μ/L
MeHgCl	2.3 μ/L	2.5 μ/L
Hg standard plus 100 ppm Ki	0.6 μ/L	2.5 μ/L

*Enviromental Resource Assoc. WasteWatR

Conclusion

Mercury may be determined at the low μg/L and sub-μg/L concentration range accurately and precisely using the Model 65 Vapor Generation Accessory. Acid concentration of standards and samples should be 10–20% by volume HCl or HNO_3 for best results. Organically bound mercury can be adequately recovered only following acid digestion of the sample. In order to obtain accurate results, sample preparation and analysis procedures should be exactly the same for both standards and samples.

References

1. R. Stux and E. Rothery, "A Simple Procedure for Determining Mercury at ppb Levels", Technical Topics, Varian Techtron, January (1971).

2. N. S. Poluektov, R. A. Vikun, and Y. V. Zelyukova, Zh.Anal.Khim., 18,33 (1963).

3. W. R. Hatch and W. L. Ott, Anal. Chem., 40, 2085 (1968).

4. US EPA, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (1979).

5. R. Seeger, At. Absorption Newslett., 15, 45 (1976).

6. N. Velghe, A. Campe, and A. Claeys, At. Absorption Newslett., 17, 139 (1978).

7. U. Ebbestad, N. Gundersen, and T. Torgrimsen, At. Absorption Newslett., 14, 142 (1975).

8. S. R. Koirtyohann and M. Khalil, Anal. Chem., 48, 136 (1976).

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