DETERMINATION OF LOW LEVEL MERCURY BY COLD VAPOR GENERATION

AND

ATOMIC ABSORPTION SPECTROSCOPY

A. D. King

QUALITY ASSURANCE DEPARTMENT

ANALYTICAL LABORATORIES

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Rockwell International
Atomics International Division
Rockwell Hanford Operations
Richland, Washington 99352

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ABSTRACT

A procedure for determining mercury in liquid samples by cold vapor flameless atomic absorption spectroscopy was developed. The optimum parameter values were determined and mercury standard storage conditions investigated. The effect and tolerance levels of twenty-seven ions, including those ions common to Tank Farm Operations and the Synthetic Wastes, were measured. Standard deviation for the procedure is less than 1%. The procedure can be used to determine mercury at the part per billion level in any liquid sample, a thousand-fold increase in sensitivity over current flame techniques.

INTRODUCTION

Mercury analyses are periodically required by the 242-S Evaporator and Tank Farm Operations. The mercury must be kept at low levels in all solutions going to the receiving tanks as mercury is highly toxic and can complex with nitrogen to form explosive compounds. The samples from these customers are viscous and caustic, containing high concentrations of salts and other dissolved solids. The present Atomic Absorption System (AAS) cannot obtain the required detection limits. Viscosity makes the sample hard to nebulize and the dissolved solids plug the burner head and nebulizer, reducing cell size and sample aspiration rate. These problems result in poor sensitivity and lack of reproducibility. The difficulty in atomizing mercury by flame methods coupled with the sensitivity problems led to the development and utilization of a flameless analytical procedure.

The procedure developed is based on cold vapor flameless atomic absorption spectroscopy, the principle of which was first used by Hatch and Ott.¹ Literature describes many instrumental variations designed to improve the sensitivity and reproducibility in research determination.^{2,3,4} However, for routine applications a sensitive yet simple method is needed. One which can be run by any individual quickly and with reproducible results, thus the development of this flameless mercury analysis procedure.

SUMMARY AND CONSLUSIONS

A highly sensitive procedure for determining mercury by cold vapor flameless atomic absorption spectroscopy was developed. The mercury standards have concentrations ranging from .05 to .07 μg mercury in 50 ml solutions (.001 - .015 $\mu\text{g}/\text{ml}$). Lower standard concentrations can be used if scale expanding modes are employed. The amount of mercury in the customer sample is determined by comparing the sample absorbance to a calibration curve made from the absorbances of the mercury standards. The curve is linear to .75 μg mercury in 50 ml solutions with bending of the curve becoming pronounced at the 1.0 μg mercury per 50 ml solution level. The standard deviation for all samples and calibration standards used in the development of the procedure is less than $\pm 1\%$.

Twenty-seven ions were tested in the procedure for interfering effects. (Table II) No interferences were found for those ions common to the customer samples. However, severe interferences were recorded for Ag(I) and Cu(II) especially in basic solutions. The interfering effects of these ions can be reduced by using an acidic medium and eliminating the Cl^- from the reducing solution.⁵ Temperature changes reportedly cause differences in peak height resulting from changes in the rate of mercury evolution from the solution.⁶ However, the small amount of heat, which would be generated by the radioactivity of the samples after the many dilutions are made was found to have no effect on the procedure. The precision, sensitivity, lack of interferences, and ease of operation in this procedure make it applicable to all routine and non-routine samples which might require mercury analysis.

EXPERIMENTAL

Reagents:

Nitric Acid, 1% Ultra-Tech Nitric acid (w/v) in deionized demineralized water ("Q" water). Used for all sample and standard dilutions.

20%SnCl₂ solution, 40 grams AR Grade SnCl₂ is added to 200 ml concentrated Hydrochloric acid. The solution is boiled gently to dissolution in a covered beaker. One piece AR granulated tin is added and the solution is allowed to cool. The solution will stay at 20% as long as the tin metal is present. (Used as the reducing agent.)

Mercury Standards, 2.7200 grams AR Grade HgCl₂ is dissolved in 20 ml of concentrated Ultra-Tech Nitric acid. The resulting solution is diluted to 200 ml with "Q" water. Store in a dark glass container prerinsed with the concentrated acid solution. This makes a 10,000 ppm stock solution.

A stock standard of 10 ppm is prepared by diluting the above solution 1:1000 into a 5% HNO₃ and .05%Cr₂O₇⁻² matrix. This oxidizing matrix keeps the mercury from plating on the container walls and changing the standard concentration.

Working standards of .05 µg in 50 ml up to .75 in 50 ml are prepared daily by appropriate dilution of the 10 ppm standard with the 1% nitric acid solution.

All mercury standards should be stored in dark glass containers prerinsed with concentrated nitric acid and the matrix in which it will be stored.

EXPERIMENTAL (Contd)

General Procedure:

Optimize the instrumental parameters. Prepare the sample as follows. The sample is pipeted into a glass cylinder, diluted to 50 ml with the 1% nitric acid solution, and a glass stirring bar is added. The cylinder is placed on top of the magnetic stirrer with the stopper containing the long bubbling tube placed loosely atop the vessel. A known amount of the SnCl_2 solution is added to the solution in the cylinder and the stopper is quickly tightened. The magnetic stirrer is turned on to a constant value.

After 60 seconds the chart recorder is turned on to give a baseline. At 90 seconds after the stirring began, the stirrer is shut off and the air supply at the module is turned on. A peak will be recorded within a few seconds. As the peak descends from its maximum, lift the pen and turn off the chart recorder. Remove the stopper and wipe the bubbler dry with the air still flowing. Place the stopper into a dry cylinder until the pen returns to baseline (a few seconds). Turn off the air supply.

The method is calibrated by repeating the procedure using the prepared mercury standard solutions. This will give a calibration curve with which the unknown sample absorbances can be compared and their concentrations determined. Instrument operating parameters are listed in Table I.

EXPERIMENTAL (contd)

Apparatus:

Glass flat-bottom, 40 x 200 mm cylinders, 1/2" glass stirring bars and a Mag-Mix magnetic stirring motor were used throughout the experiments. A Techtron AA5 Atomic Absorption Spectrophotometer with a Jarrell Ash .5 meter Ebert monochromator was used for all determinations. The flame head of the burner - nebulizer system is replaced by a thin metal frame which holds a 20 cm glass cell with optical quality quartz windows. The air support system is rerouted from the nebulizer through the reaction vessel into the absorption cell. A gas washing bottle with strong oxidizing agents inside is connected to the cell exhaust to trap the mercury which will flow from the cell. (See Figure 1). Hollow Cathode Lamps (HCL) were run at 3mA to provide the light source. The slit width was 100 microns for all data. A Hewlett Packard chart recorder was used with the absorbance mode of the AA5 to measure the absorbance peaks at the 253.6 nm wavelength of mercury.

Figure 1

RESULTS & DISCUSSION

Variables:

To understand the influences of different parameters on the data, the process involved in the analysis must be understood. When the reductant (SnCl_2) solution is added and the stirring begun, the mercury ions are reduced to neutral mercury atoms which diffuse from the solution. These atoms are taken by the carrier gas into the absorption cell where their absorbance is measured and recorded. Variables examined were:

1. Length of stirring
2. Rate of stirring
3. Flow rate of the carrier gas
4. Use of drying tubes
5. Volume of standard and samples
6. Volume of reductant used
7. Concentration and amount of acid used

Stir Time:

To study the effect of differing stir times, solutions of .5 μg Hg in 50 mls of 5% HNO_3 were prepared. The volume of reductant and the flow rate were held constant at 300 μl and 4 units (on modular control flowmeter of the AA5) respectively. Each solution was run through the procedure using a fixed stirring rate at ambient temperatures. The result (See Figure 2) shows a short stirring time gives low flat peaks gradually rising as the bubbling in the cell continues. Increasing the stir time shows a sharpening of the peak with a gradual increase in the overall peak height. After

RESULTS & DISCUSSION (contd)

a 60 second stirring time, the peaks level off and remain steady. The peak using the 90 seconds stir time is five times that of the non-stirring peak due to the increase in mercury vapor phase from the equilibrium reaction. A 90 second stir time was selected to be used with this procedure.

Figure 2 Stir Rate:Figure 3

Differing stir rates had much the same effect as varying the stirring times. This is expected as both have a direct effect on the equilibrium of the solution. Solutions of $.5 \mu\text{g Hg}$ in $50 \text{ ml } 5\% \text{ HNO}_3$ were prepared. The volume of reductant and flow rate were kept as before, $300 \mu\text{l}$ and 4 units respectively. A stirring time of 90 seconds at ambient temperatures was employed. The slow stirring rates gave broad peaks which heightened with time as the bubbling proceeded. The peaks sharpen and peak height increases to a maximum at approximately 4 on the magnetic stirrer. (See Figure 3). The peak height stays constant to 6 motor units where the stirring bar begins to flutter and ceases its actual stirring motion. A stirring rate of 5 on the

RESULTS & DISCUSSION (Contd)

Mag-Mix^R stirrer was found to work well with the 90 second stir time.

Flow Rate:

The optimum flow rate was obtained by running the .5 μg Hg in 50 ml 5% HNO_3 solutions through the procedure holding the other variables constant. At low flow rates, the peaks are very low and broad. As the flow rate is increased, the peaks begin to sharpen and the absorbance of the sample increase. Maximum peak height occurs in a range of 3 to 7 units on the flow-rate in the instrument console. (See Figure 4). Flow rates above this cause water droplets to be blown about the reaction vessel and into the absorption cell.

Figure 4

^RRegistered trademark of GCA Precision Scientific

RESULTS & DISCUSSION (Contd)

The readings obtained using these higher flow rates are erratic and unpredictable. A flow rate of 4 units on the instrument flowrater was chosen for the final procedure. After checking the flow rate, the stirring times and rates were redone at other flow rates. The findings from these experiments are as previously mentioned.

Use of Drying Tubes:

When peak areas are employed for calibration a problem is presented. The entire signal peak takes many minutes to complete, baseline to baseline, when no drying system is used. This is due to air saturated with water vapor entering the cell, condensing on the cell walls and end windows. As the bubbling continues, the solution cools clearing the water vapor from the cell.

Various methods were compared for peak height and shape, as well as time of baseline to baseline recorder trace. Separate drying tubes utilizing magnesium perchlorate, and calcium sulfate were used. Both substantially reduced the time of recorder trace but tended to broaden peaks over the non-dried system. After using these drying tubes for several standards, memory effects were noticed which increased with each determination. Use of magnesium perchlorate drying tubes could be used for a set of unknowns, up to ~20 determinations.

RESULTS & DISCUSSION (Contd)

A system of using "dry" air to mix with the saturated air was also tried. (See Figure 5). The air flow going to the reaction vessel is split into a primary flow of ~80% going into the reaction vessel and a secondary flow which bypasses the reaction vessel.

The split air flow is recombined before the absorption cell. This allows unsaturated air to enter the absorption cell which keeps the water vapor condensation to a minimum. This method was found to give excellent peak shape with little or no broadening over the unmoderated system. However, slightly lower peak heights were observed. Recorder trace time is minimal. This is the suggested method for the procedure if peak areas are to be the determining factor.

A third method, which can be used with the procedure, is only for determinations using peak height.

The standard (or sample) is placed in reactor vessel and the reductant added. Solution is stirred and air flow started. The recorder trace reaches a maximum in a few seconds, as soon as the maximum point on the

RESULTS & DISCUSSION (Contd)

recorder trace is observed, the stopper with the bubbling tube is removed from the reaction vessel and placed in an empty dry cylinder. The air pushes the mercury plug from the absorption cell and the trace returns almost immediately to baseline. The next standard is then run through the procedure. This is the method currently used.

Volume of Solution:

To check the effect of the solution volume, solutions were made up using .5 g Hg to 30, 40, 50, 60, 70, 80, 90 and 100 ml solutions of 5% HNO_3 . All other variables were held constant. Flow rate was set at 4 with a stirring rate of 5 units on the stirrer for 90 seconds. The temperature was ambient. The peak height and shape were nearly identical in all cases. Volumes less than 30 ml gave erratic results as the bubbler tube came out of the solution and blew water droplets into the cell. (See Figure 6.) Smaller volumes may be used if smaller reaction vessels or longer bubbling tubes are employed. Using the 40 x 200 mm cylinder, 50 ml was found to be a convenient volume.

Figure 6

RESULTS & DISSCUSSION (Contd)

Volume of Reductant:

Solutions of . 75 μg Hg in 50 ml of 5% HNO_3 were prepared to run through the procedure. The stir time, stir rate, and flow rate were kept at their predetermined levels. The solutions are then put through the procedure using differing volumes of the SnCl_2 solution. Volumes of 50, 100, 200, 300, 400, 800, 900, and 1500 μl were used. The 50 and 100 μl reductant volumes show low results, probably due to incomplete reduction of the mercury in the sample. The other volumes through the 600 μl volume show identical peak heights ($\pm .015$ units). The 1500 μl volume showed a slight decrease in peak height (See Figure 7).

Concentration and Amount of Acid:

The effects of different concentrations of acid were found accidentally. The results of the previous section were the clue. Next, while measuring aliquots of stock solutions to make up ten standards, extra nitric acid was introduced into one sample standard. These particular standards were diluted with water and ran through the procedure. The solution with the extra acid gave a lower peak than the others. A study was done to find the concentration at which the solutions would record a maximum absorbance. The result is a curve (See Figure 8) which shows the optimum acid concentration to be approximately 1% for the diluent.

RESULTS & DISCUSSION (Contd)

Figure 7 Figure 8

This concentration will be used with the procedure as the samples run come sporadically and new standards are prepared as samples arrive. If mercury samples are run continuously, it would be advantageous to make the low level mercury standards in the $\text{HNO}_3 - \text{K}_2\text{Cr}_2\text{O}_7$ matrix which can be kept for a week or longer.

Mercury Storage:

The problems of mercury loss or contamination at the ppb level are critical. The standards deteriorate rapidly in aqueous media. An acidic oxidizing matrix is essential for keeping the mercury levels constant for reasonable periods of time (Table III). A 1% HNO_3 matrix was found to be adequate for storing the low level mercury standards for up to 4 hours without noticable loss. For longer periods of storage, the $\text{HNO}_3 - \text{K}_2\text{Cr}_2\text{O}_7$ preservative suggested by Feldman⁷ is superior. This oxidizing matrix gave stable standards at the 1 to 10 ppb level for one week periods.

RESULTS & DISCUSSION (Contd)

The higher standards have been kept for two month periods with no concentration change.

Interfering Ions:

Varying amounts of possible interfering ions (See Table II) were added in making up .5 μg Hg in 50 ml standard solutions. A peak absorbance was recorded for each ion alone and in combinations common to customer samples. A deviation of greater than 10% in the peak absorbance was considered interfering. No interferences were found for the differing matrices or ions of customer samples. However, severe interferences were recorded with $\text{Ag}_{(\text{I})}$ and $\text{Cu}_{(\text{II})}$. These interferences may be reduced by elimination of the Cl^- ions from the reducing solution⁵

Precision and Accuracy:

The precision for the procedure is consistently high with accurate responses over the entire linear range. Typical results for a .75 μg Hg spike in a 50 ml solution is $99.9 \pm .8\%$ based on 30 analyses.

The standard deviation for all calibration standards is a .7%. The calculated precision of a single observation at the 95% confidence level is 1.6%.

APPLICATIONS

The procedure is applicable to all samples which require mercury analysis. The present system allows only cold samples to be run. However, hot routine samples could be run with this procedure if the AA unit were connected to a hood such that all sample handling could be done in the hood. The procedure as written applies to the determination of inorganic mercury only. If a separate answer for organic mercury is needed, or if organic mercury is suspected as being present, do the following:

- (1) Use the directed air drying system. Then use peak height or peak area.
- (2) For total mercury use 10% NaBH_4 solution rather than the 20% SnCl_2 solution.
- (3) For separate inorganic-organic mercury determinations:
 - (a) Run sample through procedure as written, this will give amount of inorganic mercury.
 - (b) Use same sample as (a) and run through procedure again using the 10% NaBH_4 solution. This will give amount of organic mercury present.
 - (c) The total mercury concentration can then be found by addition of the answers from (a) and (b).

Work is being done to set-up a permanent mercury system to do hot and cold samples. This system will use a DU spectrophotometer in place of an AA unit. The permanent system with minor alterations will also be able to analyze any element which has a volatile compound easily formed. (e.g. As, Se, Te, as their hydrides.)

TABLE I
INSTRUMENT OPERATING PARAMETERS

Stir Time	90 Seconds	Lamp Current 3mA
Stir Rate	5 Units (Mag-Mix)	Slit width 100 μ Damping A
Flow Rate	4 Units	Wavelength 253.6 nm
Reductant Volume	300 μ l	Recorder Range 10 mV
Temperature	Ambient	Absorbance (Log) mode
Acid Concentration	~1% HNO ₃	

TABLE II
INTERFERENCE STUDY

Interfering Ion	Concentration of Interfering Ion Molarity [mg/50 ml]		%Recovery of .75 µg of Hg	Comments
Ag	.001	(5.4)	¹ 69.7, ² 88.9 ³ 94.3	¹ Basic Medium Cl ⁻ present
Al	.005	(6.75)	99.4	² Acid Medium Cl ⁻ present
	1.0	(1350)	95.7	³ Acid medium No Cl ⁻ present
BA	.005	34.4	97.8	⁴ This for all matrices exclud- ing Ag & Cu
CA	.011	22.2	100.2	
CD	.001	5.5	99.6	
CR	.005	12.9	99.7	
	.0025	6.5	100.1	
Co	.001	2.95	99.5	
Cs	.338	2240	100.4	
	.1317	876	99.9	
Cu	.001	3	¹ 72.4, ² 91.1 ³ 96.6	
Fe	.0025	7	100.2	
	.0015	4.2	101.0	
K	.001	2	99.6	
	.019	37	98.7	
	.027	52	98.4	
Mg	.05	61	100.3	
Mn	.01	27.5	100.7	
	.1	11.5	101.4	
Na	.008	8	100.1	
	.015	17	100.0	
	>3	>3450	97.8	
	>10	>11,500	94.2	
Ni	.005	15	100.5	
	.0015	6.3	100.3	
Pb	.001	10.5	99.8	
Rb	.019	80	97.9	
	.0014	6.3	101.2	
Sr	.093	406	100.4	
Zn	.001	3.3	102.3	
Zr	.002	9.2	99.3	
NO ₂	1.0		100.2	
NO ₃	2.8		97.3	
Cl ⁻	.01		⁴ 93.3	
F	.001		99.6	
PO ₄	.01		99.7	
CO ₃	3.0		102.4	
OH	3.0		97.6	

TABLE III³
PERCENT LOSS OF MERCURY OVER 24 HOURS

	<u>Polyethylene</u> <u>H₂O</u>		<u>Polyethylene</u> <u>HNO₃</u>		<u>Glass 1% HNO₃</u> <u>+ .002% KMnO₄</u>	<u>Glass 6% HNO₃</u> <u>+ .006% KMnO₄</u>
	Closed/Open		Closed/Open		Closed	Closed
Blank					16	29
.01 ppb					6	29
1 ppb	80	90	60	80	10	28
10 ppb	28	28	20	20	1	12

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APPENDIX

Procedure for Determining Hg in Aqueous Solutions Using a Varian AA-5 Atomic Absorption Spectrophotometer.

1. Turn on the power to the Lamp and Indicator Modules.
2. Place the mercury hollow cathode lamp in the lamp turret and adjust current to 3 mA.
3. Set the monochromator to 235.6 nm and a slit width of 100 μ m.
4. Peak the wavelength in the transmission mode.
5. Use the coarse and fine gain to give 100 percent transmission.
6. Switch to the absorbance mode.
7. Adjust the fine gain to give 0 absorbance.
8. Adjust the strip chart recorder baseline to 0.
9. Remove the burner head and replace with the metal absorption cell holder.
10. Place the absorption cell in the holder.
11. Adjust the frame height and position to give minimum absorbance.
12. Change the support air line from the nebulizer to the reaction vessel.
13. Adjust the air flow rate to 4 on the meter in the gas control module.
14. Prepare standards of 0.05, 0.1, 0.2, 0.35, 0.5, 0.75, 1.0, and 3.0 g of Hg in 50 ml of one percent HNO_3 . These are prepared in the cylinders used as reaction vessels.
15. Add a glass covered stir bar.
16. Pipet 500 μ l of 20 percent SnCl_2 solution into the first cylinder and stopper immediately with the stopper containing the bubbling tube.

APPENDIX (Contd)

17. Set this on a magnetic stirrer and begin stirring. Stir for 90 seconds, then turn off the stirrer and turn on the chart recorder and the air flow.
18. After the peak maximum has been observed, stop the recorder and remove the stopper from the reaction tube.
19. Clean the bubbling tube and place in a dry cylinder and allow it to purge the system until the absorbance returns to 0.
20. Repeat for all standards and samples.

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