Automated Cold Vapor Determination of Mercury: EPA Stannous Chloride Methodology

Application Note

Atomic Absorption

Authors

Peter Dominski

Douglas E. Shrader

Introduction

The determination of Hg by cold-vapor atomic absorption was first proposed by Poluektov et. al. [1] in 1963. In this method mercuric ions in an acidic solution are reduced to ground state mercury atoms by a reducing agent such as stannous chloride. The mercury atoms are then swept by an inert gas stream into a quartz absorption cell placed in the optical path of an atomic absorption instrument. In the past this produced a transient atomic absorption signal with which the analyst attempted to obtain good accuracy and precision.

An automated continuous-flow vapor generation accessory was introduced by Agilent in March 1984 [2]. This accessory, the VGA–76, gives the analyst a choice of methodology for mercury determinations. He may use the EPA Approved Methodology [3] with stannous chloride as the reducing agent, or a new technique suggested by Rooney [4] using an alternative reducing agent, sodium borohydride, which lends itself well to multi-element hydride analysis.

The VGA–76 provides the analyst with the convenience of an automated system in addition to the superior accuracy and precision associated with a continuous-flow system providing steady-state atomic absorption signals.

When used in conjunction with Agilent's Programmable Sample Changer (PSC–55), the VGA–76 is capable of analyzing 40 samples per hour for mercury using the EPA Approved Methodology with precisions of 1% or better at the 2–3 µg/L Hg level.

A study was undertaken to determine the optimum parameters for obtaining maximum sensitivity and precision using the VGA–76 with EPA methodology. Parameters studied included acid concentration, acid type, stannous chloride concentration, and mercuric ion state.

Characteristic concentration and detection limit were determined. The EPA digest matrix was analyzed to identify any potential interference.

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Instrumentation

Spectrometer	Agilent AA–975
Sample presentation	Agilent PSC–55
Source lamp	Agilent Hg Hollow Cathode Lamp
Integration period	5 seconds
Delay time	90 seconds
Cold vapor generator	VGA–76

The VGA–76 is a continuous flow cold-vapor atomic absorption system (Figure 1) employing a peristaltic pump to deliver the sample plus two reagents. These solutions are mixed with inert gas in a reaction coil and then passed to a gas-liquid separator where the liquid phase is removed. The ground state mercury atoms are swept into a quartz flow-thru cell placed in the optical path of an atomic absorption spectrophotometer where a steady state signal is produced.

Parameters

The first variable to be examined was the effect of stannous chloride concentration on the production of the mercury vapor. A 10 µg/L Hg solution was prepared and the $SnCl_2$ concentration was varied from 0 to 30% (wt/vol). All $SnCl_2$ solutions were made up in 20% HCI (vol/vol) for reasons of solubility and stability.

Figure 2 graphically demonstrates the increase in sensitivity with increasing $SnCl_2$ concentration. Although 30% SnCI showed the highest response, the increase over 25% $SnCl_2$ was very slight. The 30% $SnCl_2$ was significantly more difficult to keep in solution, so 25% $SnCl_2$ was used for the remainder of our study.

The next topic examined was the effect of sample HCI concentrations on sensitivity for a 10 µg/L mercury standard. Hydrochloric acid was chosen as the sample matrix because of its known stabilization effect on mercury solutions. Figure 3 shows the dramatic effect of acid concentration on sensitivity with 20% and 25% $SnCl_2$. The largest response was obtained for acid concentrations between 5 and 7.5% HCI (vol/vol).

Preliminary work with 30% $SnCl_2$ produced a maximum sensitivity at 5% HCI, indicating no clear shift to improved sensitivities with higher HCI concentration as the $SNCl_2$ concentration increases. For this reason 5% was chosen as the optimum sample HCI concentration for the remainder of this study.

The uptake rate of standards/samples is approximately 8 mL/minute and is determined by the inner diameter of the sample channel peristaltic pump tubing (0.081 in). The two remaining pump channels (Figure 1) each have an inner diameter of 0.030 in. and produce an uptake rate of approximately 1mL/minute. The solutions pumped through these two channels also contribute to total sample acidity, and the effect of the acid content of these solutions was examined.

One channel contains the reducing agent stannous chloride at a fixed HCI concentration of 20%. The second is used to increase the acid concentration if necessary. Best results were obtained if this channel pumped distilled water. Any HCI in this channel degraded the sensitivity. Therefore, the final HCI concentration of solutions in the system after mixing falls within our optimum range of 5 to 7.5% (ca. 6.0% HCI).

Detection Limit and Characteristic Concentration

A detection limit study was undertaken in order to determine the minimum detectable quantity of Hg distinguishable above the noise level using the EPA approved stannous chloride methodology. The detection limit is a statistically derived number based on ten standard readings interspersed with eleven blank readings. The standard deviation of these readings is found and the following formula applied:

D.K. = $(2\times6\times c)/\overline{X}$
σ = standard deviation
C = concentration of standard
$\bar{x}$ = average absorbance of standard

Three separate detection limits were calculated based on two automated runs involving the VGA–76 and an automatic sampler (PSC–55) and one manual run using the VGA–76 only, The average detection limit found was approximately 0.05 µg/L or 50 parts per trillion.

The characteristic concentration (or sensitivity) using the VGA–76 for Hg was determined using the slope of the calibration curve seen in Figure 4. The average characteristic concentration shown is 0.22 µg/L. This is approximately twice as sensitive as older transient signal techniques and precisions observed are five times better.

Figure 5 shows chart recorder tracings for the mercury calibration curve shown in Figure 4. The Hg concentrations range from 0 to 5 µg/L. A 10 × scale expansion factor was applied to improve readability.

Stability and Acid Matrix

Although hydrochloric acid was thought to be the acid of choice for Hg determinations, several different acids and acid matrices were tested and their characteristic concentrations

compared for a 5 µg/L Hg solution. Table 1 lists these characteristic concentrations and stability over a 24 hour period. The 5% HCl – 5% HNO_3 matrix gave the best sensitivity and 5% HNO_3 the poorest, being approximately 10% less sensitive. The stability of the Hg standard is affected by acid type. The need for stabilization of Hg solutions with $K_2Cr_2O_7$ has been reported, but in this study 0.01% $K_2Cr_2O_7$ caused a 5% sensitivity loss after 24 hours. The EPA digest matrix shows good sensitivity and stability.

Table 1. Absorbance Versus Acid Type. 5 µg/L Hg

	Acid matrix	Abs.	Sensitivity loss after 24 hours
1.	5% HCl – 5% HNO_3	1.095	zero
2.	3.7% H_2SO_4–1.8% HNO_3– 0.5% $KMnO_4$	1.078	zero
3.	5% HCl–5% HNO_3– 0.01% K_2Cr2O_7	1.063	5%
4.	5% HCl	1.057	zero
5.	5% HNO_3– 0.01% $K_2Cr_2O_7$	1.029	5%
6.	5% HNO_3	0.953	15%

Calibration Curves

The ability to extend the calibration range for Hg is important when analyzing samples with widely different mercury concentrations. Figure 4 illustrates a narrow, low concentration range (0–5 µg/L) for Hg. In Figure 6, the versatility of this automated cold vapor technique can be seen with the concentration range extended to 100 µg/L Hg. The precision of the method is shown here as RSD (Relative Standard Deviation) and is 0.2% or better throughout the calibration range. Excellent accuracy is also shown as samples 1 thru 11 were standards containing 0, 1, 2, 3, 4, 5, 10, 25, 50, and 100 µg/L Hg respectively. This printout was taken directly from the data station of the AA–975 atomic absorption spectrophotometer and contains all the raw data from the analysis.

EPA Digestion Procedure

In order to establish the complete validity of the VGA–76 automated stannous chloride methodology, nine EPA reference samples containing mercury in both the inorganic and organic forms were analyzed. The analysis was first attempted without prior digestion to convert all of the Hg to the inorganic form. This procedure resulted in values that were significantly lower than the 'true' certified values. These same samples along with 5 standards and a blank were then subjected to the EPA mercury digestion procedure [3] and analyzed with VGA–76. Optimum reagent concentrations previously determined were used:

- Reductant – 25% $SnCl_2$ in 20% HCl
- "ACID" Bottle – D.I. water
- Sample – The solution reported here contained H_2SO_4, HNO_3, $KMnO_4$, potassium persulphate, sodium chloride, and hydroxylamine hydrochloride as specified in the EPA digestion scheme

The digestion was performed using sealed Nalgene bottles and a drying oven. Table 2 shows the stability of the method. Three standard curves obtained during an afternoon are compared. The reproducibility and stability were excellent.

Table 2. VGA – 76 Mercury Calibrations from EPA Digestions

Standard	Run #1 (3:30 PM)	Run #2 (4:30 PM)	Run #3 (6:30 PM)	Avg. Abs.
2.5 ug/L	0.041	0.040	0.041	0.041
5 ug/L	0.080	0.078	0.079	0.079
20 ug/L	0.301	0.299	0.299	0.300
40 ug/L	0.576	0.573	0.573	0.574
80 ug/L	1.079	1.074	1.074	1.076

Notes: EPA digestion for Hg produces a dilution of standards and samples from 100 ml to 136.5 ml. thus, actual Hg concentrations are 1.83 µg/L, 3.66 µg/L.
Characteristic concentration = 0.2 µg/L
Detection limit = 0.05 µg/L from previous work.
Reductant was $SnCl_2$

Table 3 gives the results from two separate automated runs and compares them with the "true" certified values. Agreement is excellent and well within the ± 2 σ limits provided by the EPA. (Raw data from Run #2 is shown in Figure 7.)

Table 3. VGA – 76 Mercury Calibrations from EPA Digestions

EPA standard	Run #1 (4:30 PM)	Run #2 (6:30 PM)	Avg. value	"True" value	± 2σ limits
Hg 1	0.437	0.487	0.46	0.42	NA
Hg 2	2.437	2.439	2.44	2.40	NA
Hg 3	7.291	7.277	7.28	7.0	NA
WS 2	1.875	1.890	1.88	1.8	1.4–2.2
WS 13	1.500	1.524	1.51	1.4	1.0–1.7
TM 1	0.750	0.731	0.74	0.7	0.3–1.1
TM 2	8.947	8.928	8.94	8.7	5.9–11.1
EP 1	49.68	50.07	49.9	50	NA
EP 2	32.62	32.33	32.5	30	NA

Second dilution (1–10) was done to reduce the "true" value from 300 to 30 µg/L.
NA = not available. Reductant was $SnCl_2$

The precision from the two runs for each of the nine EPA samples averaged 1.40%. If the two samples with Hg content of less than 1 µg/L are disregarded, the average precision was 0.46%.

Conclusion

This paper has described the analytical performance of a new vapor generation accessory (VGA–76) for mercury determinations using the EPA approved Stannous Chloride Methodology. A previous paper [2] described the use of this automated vapor generation technique for the sequential multi-element determination of the hydride forming elements As, Se, Sb, Bi, Te and Sn and also cold vapor Hg using sodium borohydride as the reducing agent.

This work has shown the applicability of the EPA Approved Methodology to the VGA–76 as well as the comparability of the stannous chloride and sodium borohydride techniques. The Hg detection limits are identical at 0.05 µg/L and the Hg characteristic concentrations are comparable at 0.22 µg/L for the stannous chloride technique and 0.30 µg/L for the sodium borohydride technique.

The precisions obtained from this continuous flow system far surpass those from previous methodology and are typically better than 1% at the 2–3 µg/L level. The accuracies obtained on Hg determinations using EPA methodology (digestion and reagents) are excellent.

References

1. N. S. Puluektov et al., Zh. Anal, Khim, 18, 33 (1963).
2. Varian AA at Work No. 38, "An Automated Vapor Generation Accessory for Atomic Absorption Analysis", March 1984.
3. US EPA, Publication No. EPA–600/4–79–020, "Methods for Chemical Analysis of Water & Wastes", (1979), Method 245.1.
4. R. C. Rooney, Analyst, 101, 678 (1976).

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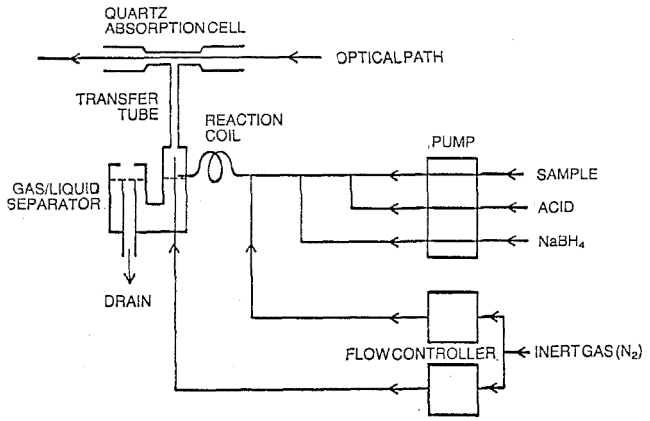


Figure 1. VGA-76 Schematic.

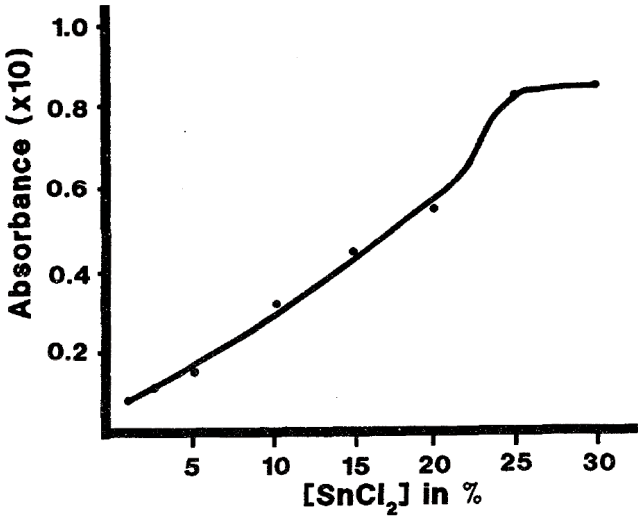


Figure 2. Absorbance versus [$SnCl_2$] 10 ug/L Hg.

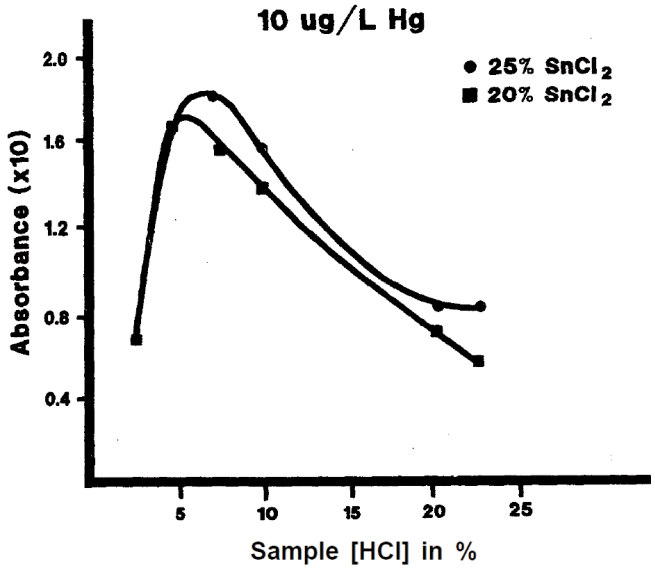


Figure 3. Absorbance versus sample [HCl].

OPERATOR: PETER DOMINSKI
DATE : 2-23-84
BATCH : MERCURY BY VGA-76/SnCl

AUTO-PROGRAM 18 Hg by VGA-76/SnCl

SOLUTION	CONC PPb	RSD	MEAN ABS	ABSORBANCE READINGS				
BLANK	0.000	4.2%	0.024	0.025	0.023	0.023	0.027	0.025
STANDARD 1	1.000	2.0%	0.196	0.194	0.201	0.195	0.201	0.191
STANDARD 2	2.000	0.5%	0.386	0.386	0.385	0.383	0.390	0.386
STANDARD 3	3.000	0.8%	0.597	0.602	0.590	0.603	0.593	0.598
STANDARD 4	4.000	0.8%	0.785	0.786	0.787	0.795	0.783	0.778
STANDARD 5	5.000	0.6%	0.987	0.985	0.978	0.993	0.995	0.986

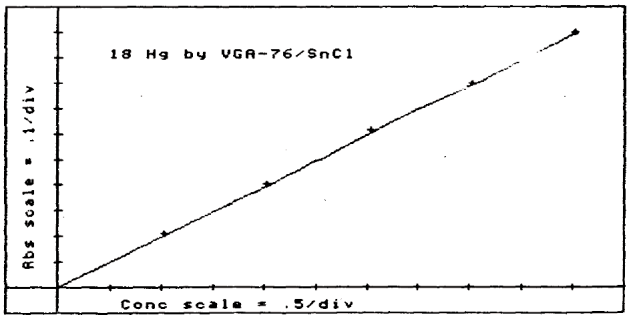


Figure 4.

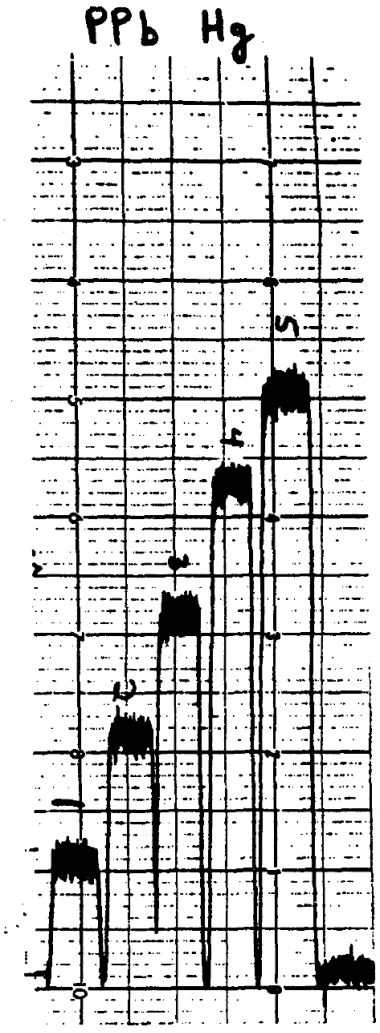
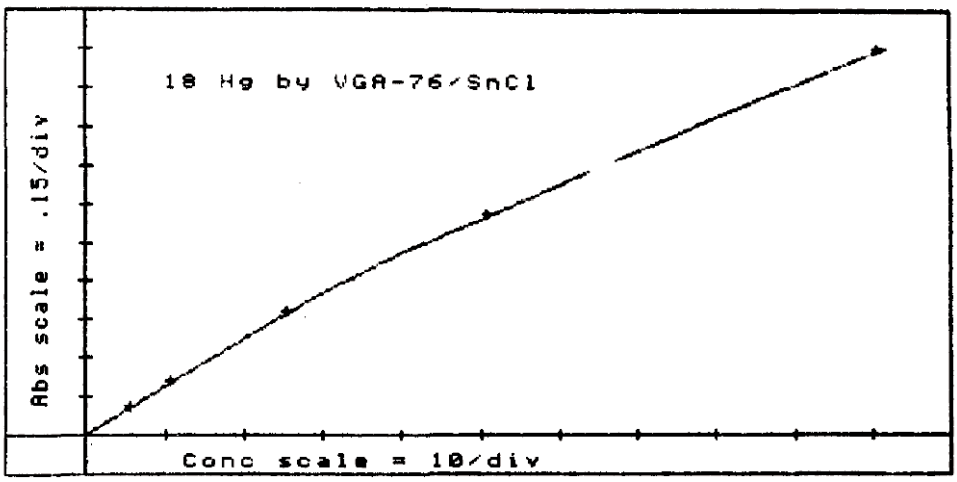


Figure 5.

OPERATOR: PETER DOMINSKI
DATE: 2-23-84
BATCH: MERCURY BY VGA-76/SnCl

AUTO-PROGRAM 18 Hg by USA-76/SnCl

SOLUTION	CONC PPb	RSD	MEAN ABS	ABSORBANCE READINGS				
BLANK	0.000	0.0%	0.004	0.004	0.004	0.004	0.004	0.004
STANDARD 1	5.000	0.0%	0.094	0.094	0.094	0.095	0.095	0.095
STANDARD 2	10.00	0.0%	0.187	0.187	0.188	0.188	0.187	0.188
STANDARD 3	25.00	0.0%	0.463	0.462	0.463	0.464	0.463	0.463
STANDARD 4	50.00	0.0%	0.839	0.839	0.839	0.839	0.840	0.838
STANDARD 5	100.0	0.1%	1.480	1.479	1.482	1.481	1.480	1.481



SAMPLE	1	0.053	0.0%	0.001	0.002	0.001	0.001	0.001	0.001
SAMPLE	3	0.957	0.0%	0.018	0.018	0.019	0.019	0.019	0.018
SAMPLE	4	2.021	0.0%	0.038	0.038	0.038	0.038	0.038	0.038
SAMPLE	5	2.978	0.0%	0.056	0.057	0.057	0.056	0.056	0.057
SAMPLE	6	4.042	0.0%	0.076	0.076	0.076	0.077	0.076	0.076
SAMPLE	7	4.946	1.1%	0.093	0.094	0.094	0.094	0.093	
SAMPLE	8	9.946	0.0%	0.186	0.186	0.185	0.187	0.186	0.187
SAMPLE	9	24.50	0.2%	0.454	0.455	0.455	0.455	0.454	0.455
SAMPLE	10	49.60	0.1%	0.834	0.834	0.834	0.834	0.836	0.833
SAMPLE	11	99.50	0.1%	1.474	1.475	1.475	1.474	1.474	1.472

Figure 6.

O P E R A T O R : DOUG SHRADER
D A T E : FEBRUARY 24, 1984
B A T C H : MERCURY BY VGA-76/SnCl

AUTO-PROGRAM 18 Hg by VGA-76/SnCl

SOLUTION	CONC PPb	RSD	MEAN ABS	ABSORBANCE READINGS				
BLANK	0.000	0.0%	0.004	0.004	0.004	0.004	0.004	0.004
STANDARD 1	2.500	2.4%	0.041	0.042	0.042	0.041	0.042	0.042
STANDARD 2	5.000	0.0%	0.079	0.079	0.080	0.080	0.080	0.079
STANDARD 3	20.00	0.0%	0.299	0.299	0.299	0.299	0.300	0.300
STANDARD 4	40.00	0.0%	0.573	0.574	0.574	0.574	0.573	0.573
STANDARD 5	80.00	0.1%	1.074	1.074	1.074	1.076	1.075	1.074
BLANK	0.000	0.0%	0.000	0.001	0.000	0.000	0.000	0.000
Hg 1	0.487	0.0%	0.008	0.008	0.009	0.008	0.009	0.008
Hg 2	2.439	0.0%	0.040	0.040	0.040	0.041	0.040	0.040
Hg 3	7.277	0.0%	0.114	0.114	0.115	0.115	0.114	0.114
WS 2	1.890	0.0%	0.031	0.032	0.031	0.031	0.032	0.031
WS 13	1.524	0.0%	0.025	0.025	0.025	0.025	0.025	0.025
TM 1	0.731	0.0%	0.012	0.012	0.012	0.013	0.013	0.013
TM 2	8.928	0.0%	0.139	0.139	0.140	0.139	0.140	0.140
EP 1	50.07	0.0%	0.704	0.704	0.705	0.704	0.704	0.704
EP 2	32.33	0.0%	0.469	0.469	0.469	0.470	0.469	0.469
BLANK	0.060	0.0%	0.001	0.001	0.001	0.001	0.001	0.002
5 PPb STD.	5.000	0.0%	0.079	0.079	0.079	0.079	0.079	0.079

Figure 7.

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