Evaluation of the Mercury Concentration Accessory for US EPA Methodology

Application Note

Atomic Absorption

Author

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Introduction

The Agilent Mercury Concentration Accessory (MCA-90) was designed to allow the determination of mercury at ultra-low levels. Mercury is a toxic metal and increasingly, legislation around the world is requiring environmental monitoring at the sub-ppb levels. For example, European regulations require measurements to be made at 0.05 µg/L (or 50 parts per trillion (ppt)). The Agilent VGA-76 Vapor Generation Accessory is capable of routine detection limits of 0.1 µg/L by atomic absorption spectroscopy. With the addition of the MCA-90, detection limits an order of magnitude lower (0.01 µg/L) are easily attainable.

Mercury readily forms an amalgam with gold. A gold collecting surface is inserted into the mercury vapor flow produced by the cold vapor technique. After a suitable collection time, the gold surface is electrically heated and the adsorbed mercury released. The MCA-90 uses this mercury amalgamation and release process to provide enhanced mercury signals. The signals can then be measured by atomic absorption spectroscopy. The degree of enhancement is proportional to the collection time. For improved sensitivity, longer collection times are used.

The MCA-90 is a microprocessor based accessory for the SpectrAA series which fully controls the mercury enhancement process. The microprocessor control module coordinates the timing of events in the mercury enhancement process. Three parameters must be set by the operator using the numerical keypad of the MCA-90.

- The MCA delay (or flush) time, which allows time for the VGA-76 to pump the analytical solutions through the tubing up to the Rapid Isolation Valve (RIV). At the end of the MCA delay time, the RIV is switched allowing solution to flow into the gas-liquid separator.
- The collect time, which determines the extent of signal enhancement. During the collect time, mercury vapor separated by the VGA-76 is trapped on the gold surface of the Mercury Amalgamation Trap (MAT), for the programmed period. At the end of the collect time the RIV is switched once again, diverting all soutions to waste and terminating the amalgamation process.
- The heat time, which heats the MAT to release the adsorbed mercury and generated atomic vapor for measurement.

The design and operation of the MCA-90 have been previously described in Agilent AA-at-Work No. 104 [1].

The determination of mercury by the cold vapor technique requires a digestion to convert organically bound mercury to inorganic mercury. For that purpose the US EPA has established a specific digestion procedure for environmental samples. This EPA digestion method was used to prepare several water samples and certified standards for mercury determination by the MCA-90. The results of this study are reported in this AA-at-Work. Practical information on the operation of the MCA-90 is also included.

Experimental

Methodology

An Agilent SpectrAA-400 Atomic Absorption Spectrometer was utilized to measure the mercury signals. A blank, five standards, three water samples and two reference standards (EPA Trace Metals - AA Quality Control Sample Lot TMA 989, and ERA* Priority PollutionTTM/CLP Quality Control Standard) were digested according to the EPA mercury digestion procedure [2]. This procedure is outlined in Table 1. The digestion was performed using sealed 250-mL Nalgene PMP bottles and a Precision TM Model 25 Shaking Water Bath. The blank, standards, and samples were then analyzed with the MCA-90.

The reductant channel of the VGA-76 contained 10% $SnCl_2$ (wt/vol) in 20% HCl. The "acid" channel contained 1% hydroxylamine HCl. Refer to Figure 1. This channel may contain D.I. water or can be removed to create a two channel system.

The MCA-90 was operated in the manual mode. The following MCA-90 parameters were programmed.

MCA delay (flush) time	35 seconds
Collect time	40 seconds
Heat time	45 seconds

SpectrAA-400 instrument parameters are listed in Table 2.

Although background correction was utilized in this study, it is generally not needed for this type of analysis.

Table 1. EPA Digestion Scheme for Hg

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

The sample is now ready for analysis.

Table 2. Instrument Parameters

Instrument mode	Absorbance
Calibration mode	Concentration
Measurement mode	Peak height
Lamp position	4
Lamp current (ma)	4
Slit width (nm)	0.5
Slit height	Normal
Wavelength (nm)	253.7
Flame	Air only
Sample introduction	Manual
Delay time (sec)	0
Time constant (sec)	0.05
Measurement time (sec)	30.0
Replicates	1
Background correction	On

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*Environmental Resource Associates, Arvada, Colorado

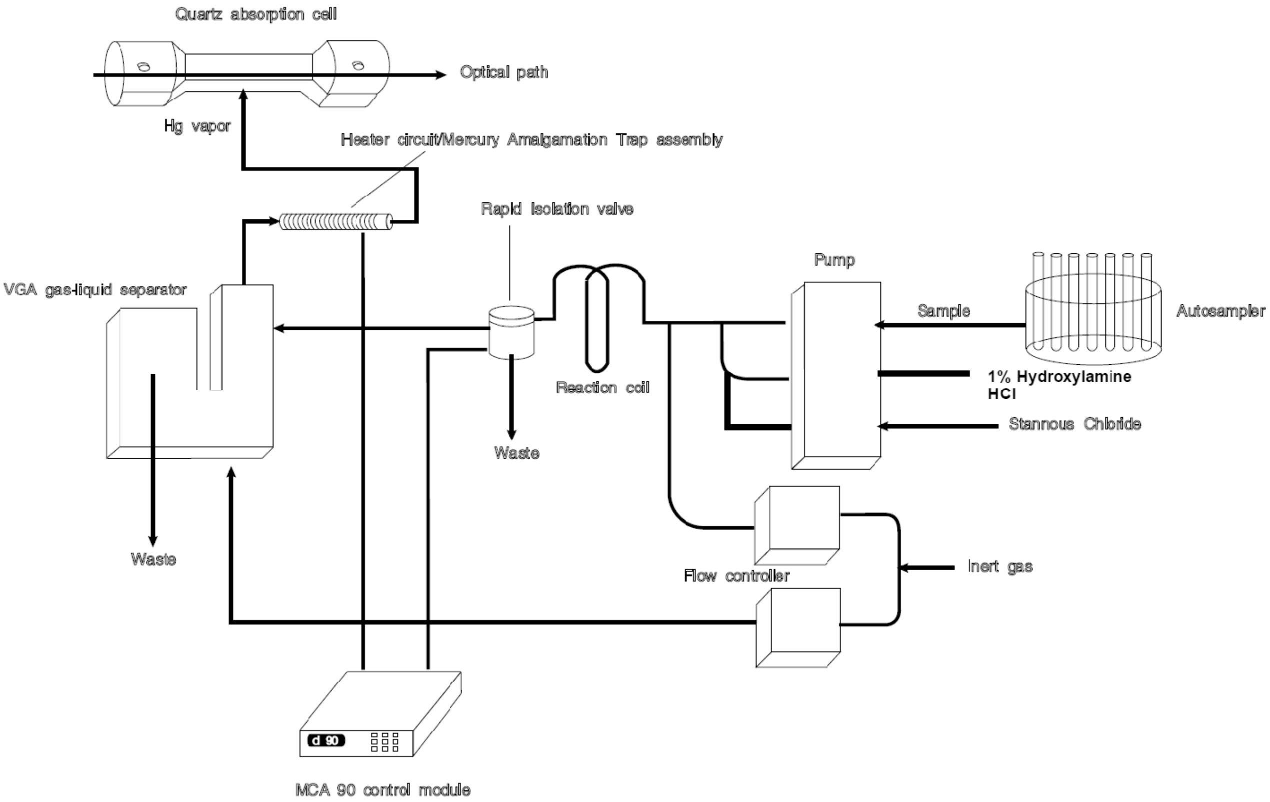

Figure 1. A schematic diagram, showing the key components of the MCA-90 with the VGA-76.

Results

Standards of 0.25, 0.50, 1.00, 2.50, and 5.00 µg/L Hg were used. The calibration graph obtained is shown in Figure 2.

The reagents required for the EPA digestion diluted the 100 mL samples to 136.5 mL. However, because the standards were treated in exactly the same manner, a dilution factor correction was not required. A relatively short collection time of 40 seconds was used. The detection limit was estimated at 20 ppt with this method. The original sample was diluted by the addition of EPA required reagents and there was a slight loss in sensitivity due to the higher acid concentration. Lower detection limits would be achievable with longer collect times.

Sample		Conc (ppb)	Mean Abs
Blank		0.00	0.007
Standard	1	0.25	0.028
Standard	2	0.50	0.053
Standard	3	1.00	0.111
Standard	4	2.50	0.267
Standard	5	5.00	0.554

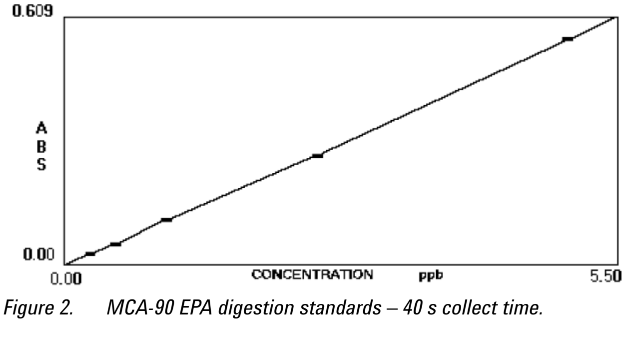

Figure 2. MCA-90 EPA digestion standards – 40 s collect time.

A stability study of the digested standards (EPA method) was also performed. A second set of standards was taken through the EPA digestion procedure. The standard absorbances were measured 3 times over a 4 hour period. The results of this study are listed in Table 3. As these results indicate, stability was excellent. Following the EPA digestion procedure, the standards will remain stable for at least several hours.

Table 3. EPA Digestion Standard Stability –40 s Collect Time

Standard µg/L	Absorbance Run #1	Run #2	Run #3	$\bar{x}$
0.25	0.019	0.023	0.021	0.021
0.50	0.045	0.046	0.047	0.046
1.00	0.102	0.108	0.102	0.104
2.50	0.247	0.256	0.258	0.254
5.00	0.531	0.538	0.536	0.535

The mercury results from the digestion method applied to the reference standards are listed in Table 4. The EPA Trace Metal Standard was digested twice and analyzed with separate sets of digested standards. The results agree with the "true" value and are well within the ± 2σ limit. The concentration found in the ERA-CLP standard also shows good agreement with the certified value and is well within the advisory range. This range is similar to the 95% confidence interval (± 2σ), determined by US EPA interlaboratory performance evaluation programs.

Three water samples were also digested and analyzed. These samples had been previously analyzed with the VGA-76 vapor generation accessory. A comparison of results is shown in Table 5. The detection limit with the VGA-76 is approximately 0.1 µg/L. With a 40 second collect time the detection limit of the MCA-90 is 10 times lower at 0.01 µg/L. With the dilution by the reagents in the EPA digestion, the expected detection limit would be approximately 0.02 µg/L with this method.

Table 4: Hg Results from EPA Digestions

Sample	Results µg/L	"True" value µg/L	$\bar{x} \pm 2\sigma$ µg/L
EPA trace metal Std lot TMA 989	1.86 2.05	2.02	1.46–2.58

Sample	Results µg/L	Certified value µg/L	Advisory range µg/L
ERA CLP std Inorganics	3.17	3.32	2.5–4.2

Table 5. Hg Results from EPA Digestions

Sample	MCA-90 results* µg/L	VGA-76 results µg/L
#1	< 0.02	N.D
#2	0.35	~0.4
#3	< 0.02	N.D

*40 sec collect time

N.D. = Not detected

A lower detection limit is possible with longer collection times. There was excellent agreement between the two results on sample 2.

Practical Operation of the MCA-90

The sensitivity attainable with the MCA-90 is directly proportional to the collection time. Longer collection times require larger sample volumes. The collect time should be chosen to meet analytical requirements. A guideline for choosing collect time and calibration range is shown in Table 6. The approximate sample volume needed for a single measurement is also listed.

In the manual mode of operation, sample consumption can be minimized and analysis time reduced by removing the VGA sample capillary from the sample at the beginning of the heat time. The heat time can also be used to begin the sample flush or drain off the next sample. This can also significantly increase sample throughput.

A very low level mercury determination is illustrated in Figure 3. With a 10 minute collect time, a solution containing 5 ppt Hg produced a very reproducible signal. Detection limits in the low part-per-trillion level are attainable with the MCA-90. Although contamination was not significant in this study, reagent contamination can become significant in part-per-trillion mercury determinations.

Table 6. Collect Time Versus Analytical Sensitivity

Collect time (s)	40	180	360
Standard range (ppb)	0.2–5.0	0.05–1.00	0.02–0.50
Sensitivity (ppt)	20	5	~2
Detection limit (ppt)	10	2–3	~1
Sample volume (mL)	16	35	60*

*Concentration required to give 0.0044 abs after sensitivity (ppt)

For reproducible results , it is essential that the VGA-76 and MCA-90 are conditioned prior to an analytical run. This is especially important when any VGA-76 tubing is replaced or when a new MAT is utilized. Conditioning can be performed by alternating a blank and high level standard solution until a stable signal is obtained. Alternately, one or two initial calibrations can be carried out prior to an actual analytical run. A conditioning procedure is described in detail in Section 5.8 of the MCA-90 operation manual [3].

There is a small amount of carryover between samples (< 1.0%). To minimize errors due to carry-over, it is recommended that a reagent blank be run after the highest standard and following samples of high mercury concentrations. One “blank run” is generally sufficient to remove residual mercury.

The condition of the MAT directly impacts sensitivity and precision. Only the inert gas containing mercury is passed over the MAT. Analytical solutions containing acids and stannous chloride should never contact the MAT. A “back up” of these solutions onto the MAT will severely damage it. To prevent this, VGA-76 gas flows should be set as recommended by Agilent. Gas flow calibration should only be necessary when the VGA-76 is being serviced, or to enable foreign matter that may have entered through the gas lines, to be cleared. The gas flow to the gas liquid separator should be 45 ± 5 mL/min and the gas flow to the reaction coil should be 45 ± 5 mL/min [4]. Prior to operation, the gas liquid separator should also be checked to ensure proper drainage.

When analyzing samples which foam, the use of an anti-foaming agent (for example, Dow Corning Antifoam B) can minimize or eliminate this problem [1].

Strongly oxidizing solutions and sample contaminants can reduce the efficiency of the MAT. Indications of this include degraded sensitivity and poor precision. Periodic cleaning of the MAT is required for efficient and reproducible operation of the MCA-90. The recommended cleaning procedure is outlined in section 6.1 of the MCA-90 operation manual [3]. The effect of strongly oxidizing solutions may be minimized by the addition of hydroxylamine HCl through the “acid” channel of the VGA-76, as used in this study.

Measurement mode	**Readings**			$\bar{x}$	**%RSD**
Peak height (abs)	0.014	0.014	0.014	0.014	0.1
Peak area (abs/sec)	0.097	0.103	0.097	0.099	3.5

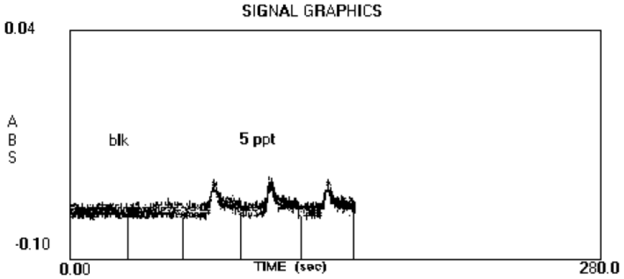

Figure 3. 5 ppt Hg – 10 minute collect time.

Conclusion

The MCA-90 allows the determination of mercury at sub-ppb levels. Detection limits of 0.01 µg/L are readily attainable. The sensitivity is directly proportional to the collection time. The collection time is influenced by analytical requirements such as the sample size and existing reagent contamination levels. In this study a collect time of 40 seconds was sufficient to obtain the necessary sensitivity. Several certified standards and water samples were prepared using the US EPA digestion method for mercury determination in environmental samples. The digested reference standards and three water samples were analyzed for mercury and excellent results were obtained. Stability studies showed that the digested standards were stable for at least several hours. This work has shown that the VGA-76/MCA-90 can be successfully used with US EPA approved methodology for the determination of mercury at ultra-trace (parts per trillion) levels.

References

1. Varian AA at Work No. 104, December 1991.
2. “Methods for Chemical Analysis of Water & Wastes”, U.S. E.P.A., Publication No. EPA-600/4-79-020, 1979, Method 245.1.
3. MCA-90 Operation Manual (Publication No. 85-100973-00), Varian Australia Pty Ltd, Mulgrave, Victoria, Australia.
4. VGA-76 Service Manual (Publication No. 85-100568-06), Varian Australia Pty Ltd, Mulgrave, Victoria, Australia.

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