

Measuring Ultra-Trace Levels of Mercury

Application Note

Atomic Absorption

Author

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Introduction

Liquid mercury metal has a wide range of uses. While some major applications such as the manufacture of sodium hydroxide and chlorine, and the refining of gold are gradually being replaced by other techniques, mercury is still found in certain types of battery cells and in dental amalgam fillings. Inevitably, some of it is released into the environment. Mercury is an extremely toxic metal so ultra-trace levels in drinking water, for example, must be routinely monitored.

Detection limits of 0.1 $\mu\text{g Hg/L}$ had, until recently, met most regulations around the world. Many countries now specify that levels as low as 0.05 $\mu\text{g Hg/L}$ (ppt levels) must be measured. To do this an instrument must have a detection limit of 0.01 $\mu\text{g Hg/L}$ or lower. Atomic absorption spectrometry (AAS), with its excellent sensitivity is normally a logical choice for trace metal analysis, however the standard AAS technique cannot achieve this level of detection for mercury.

A new accessory (the MCA-90 Mercury Concentration Accessory) allows measurement of mercury at the parts per trillion levels.

Signal Enhancement

Mercury readily forms an amalgam with gold. A gold collecting surface is inserted into the mercury vapor flow produced by the Vapor Generation Accessory (VGA-76). Mercury is collected on this surface which is then heated to drive off the trapped mercury. This mercury trapping and release process greatly enhances the signal for the determination of mercury.



Agilent Technologies

Practical Implementation

The MCA-90 is a microprocessor based accessory for the SpectrAA instrument series, which fully controls the mercury signal enhancement process. The MCA-90 is quickly and easily fitted to the VGA-76 and can be used with either manual sampling or the PSC-56 Programmable Sample Changer.

The Mercury Amalgamation Trap (MAT) is a thin layer of gold, plated onto a fine noble metal mesh. It has a large surface area - to trap mercury efficiently, and is thin - so that mercury is released with no memory effects. Mechanical strength allows repeated handling for removal of surface contamination which can hinder collection. The MAT is fitted into a quartz tube. A high temperature heating element is wrapped around the outside of the quartz tube. The element is heated electrically and causes indirect heating of the MAT.

A Rapid Isolation Valve (RIV) is used to stop mercury vapor flow to the MAT between samples to minimize carryover.

The MAT, heater and RIV are built into a single workhead unit, which can be quickly installed and removed from the VGA-76. The workhead circuit board is plastic dipped and the MAT contacts are gold-plated to minimize corrosion effects.

The MCA-90 unit has four stages:

- Ready
- MCA delay
- Collect
- Heat

On power up, the MCA-90 workhead goes through a “heat stage”. This feature keeps the collector clean and helps the MCA-90 recover from a power fail situation.

The MCA-90 is in “ready stage” until it detects a start signal. This start signal can come from either the SpectrAA IDB (Intercommunication Data Bus) in automatic operation, or from the keypad in manual operation. This is shown in the timing diagram in Figure 1. The MCA-90 then goes through a defined operation cycle of drain, collect and heat.

“MCA delay time” is a delay time to allow the reaction coil to fill with sample solution.

The RIV then switches solution to the gas-liquid separator at the start of the “collect stage”. Mercury vapor generated by the VGA-76 is then passed over the MAT for a programmed period. This is the “collect time”.

After the collect stage, the RIV switches solution to waste thus isolating the MAT. The MAT is then heated long enough (about 30–40 s) to drive off all the mercury.

The MCA delay and collect times are factory pre-set, although they can be altered to suit individual installations.

In the case of collect time, an operator must be able to change this easily. In manual operation this is done by entering the collect time in seconds, using the keypad on the front of the control unit.

Mercury Concentration Accessory
Timing diagram (Automatic mode)

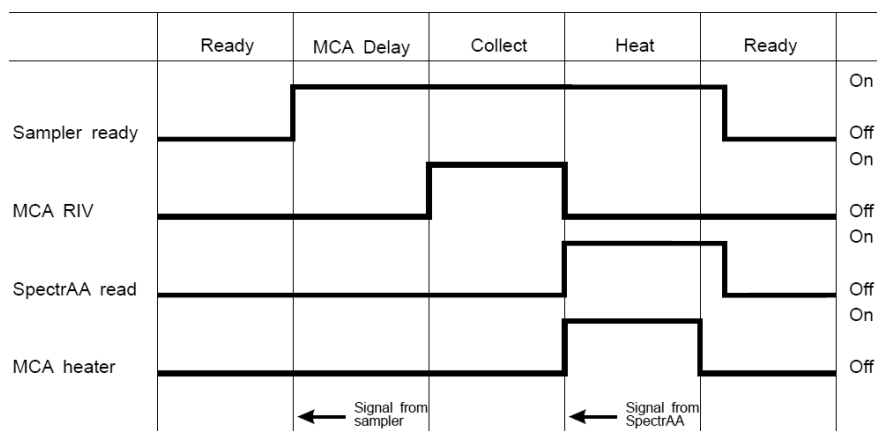


Figure 1. System timing diagram of the MCA-90.

In automatic operation, the delay time on the SpectrAA Instrument Parameters page controls collect time. This is set by applying the formula:

$$\text{SpectrAA delay time} = \text{Collect time} + \text{MCA delay time}$$

Collect times up to 999 s are possible (using the latest version of flame software which is also supplied with the MCA-90). In practice an upper limit of 600 s is recommended.

MCA Delay Time

When developing an MCA-90 method it is essential to ensure the selected MCA delay time is appropriate for the sampling technique used. As the first solution is sampled, observe the solution flow through the VGA-76. The mercury vapor generated must reach a stable flow through the gas liquid separator before the Rapid Isolation Valve switches to the MAT, that is, before the MCA delay time has elapsed.

If the RIV switches to the MAT before the vapor flow is stabilized, poor reproducibility will be observed. The MCA delay time should therefore be extended.

Table 1 gives the recommended instrument parameters for optimum results. For manual operation, the sampler is not used and the delay time must be set to zero.

Instrumentation and Reagents

A SpectrAA-400P atomic absorption spectrometer was used with IBM PS/2 Model 30/286 computer as controller; a PSC-56 Programmable Sample Changer; a VGA-76 configured as a cold vapor generator; an MCA-90 Mercury Concentration Accessory; and an Agilent mercury hollow cathode lamp.

All reagents were analytical grade or better. Water was distilled and deionized. The reductant was 10 g tin(II) chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) in 100 mL of 20% v/v HCl. Samples were stabilized with 1% v/v nitric acid/ 0.01% w/v potassium dichromate.

Note: The very low levels of mercury measured here are very difficult to stabilize. Carefully cleaned glassware and plasticware is essential and should not be used for any other purpose.

Only one reagent channel on the VGA-76 was used. Uptake rate was 1 mL/min. Sample uptake rate was 7 mL/min.

Table 1. Recommended Instrument Parameters for Optimum MCA-90 Operation

Program 01: Hg MCA/PSC/auto coll_n	
Instrument mode	Absorbance
Calibration mode	Concentration
Measurement mode	Peak height
Sample introduction	Auto normal (automatic operation) Manual (manual operation) (Drain time + Collect time) (automatic operation) 0 (manual operation)
Delay time (sec)	40.0
Measurement time (sec)	1
Replicates	1
Rinse rate	(Every sample in automatic operation)
Rinse time (sec)	20.0 (Provides cool-down period in automatic operation)
MCA-90 parameters	
MCA delay time (sec)	25 (Time to fill reaction coil)
Heat time (sec)	40
Collect time (sec)	(Set by Delay Time in automatic operation)

Results and Discussion

Conditioning the System

Conditioning of the MCA-90 and VGA-76 system is necessary to achieve reproducible results. The conditioning process prepares the active sites of all parts of the system (tubing, connectors, the MAT and the quartz absorption cell) for receiving and releasing mercury. When using the MCA-90, low level (for example, parts per trillion) standards of often employed. If the system is conditioned with these low level solutions, the conditioning process will be lengthy.

To quickly condition the active sites, use a higher level standard, for example, 20 parts per billion (20 $\mu\text{g/L}$) with a 60 second collect. The signal will stabilize within 10 replicates. This process should be followed by further conditioning using a standard which is more representative of the levels you wish to determine. A standard solution from the middle of the calibration range would be suitable. Again this signal should be stable within 10 replicates.

After this process the system is ready for use.

Note: Reconditioning the system may be necessary whenever any component of the system (tubing, connectors, quartz absorption cell, gas-liquid separator or MAT) is cleaned and/or replaced or if the system is left unused.

Figure 2 shows both the sensitivity of the MCA-90 and the ubiquitous nature of mercury. Nitric acid (1% v/v) was spiked with 20 ng Hg/L. The signal graphics traces for the spiked solution (SSR) clearly show higher peaks compared with the unspiked solution (SR). From the difference in heights it was calculated that there was about 25 ng Hg/L in the 1% nitric acid (or about 2.5 µg Hg/L in the concentrated acid).

One supplier quotes its distilled nitric acid as 99.999%. Even this would contain about 10 ppm of unspecified impurities. Therefore the acid used in this study is actually quite low in mercury contamination and highlights the problem of reagent contamination.

Laboratories undertaking these ultra-low determinations must monitor levels of mercury contamination in all reagents used for the determinations. Purification of acids using a sub-boiling still, for example, may be required.

It is mandatory to reserve carefully cleaned glassware and plasticware exclusively for trace mercury studies. The minimum cleaning recommended is soaking in nitric acid (200 mL/L) solution for 30 minutes at room temperature. This should be followed by a minimum of three water washes using deionized distilled water, or until acid free. If this is not sufficient, then soaking first in sodium EDTA (20% w/v) solution for one hour may be necessary.

Figure 3 illustrates the signal graphics traces of the calibration standards (100, 200 and 300 ng Hg/L) used to obtain the calibration graph in Figure 4. Collect time for the standards and samples was 180 s.

Melbourne (Australia) drinking water was used for a recovery study. The solutions made up were: stabilized drinking water (SR), stabilized drinking water spiked with 200 ng Hg/L (SSR) and 200 ng Hg/L standard (SA). Local health authorities recommend a maximum level of 1 µg/L of mercury in drinking water [1].

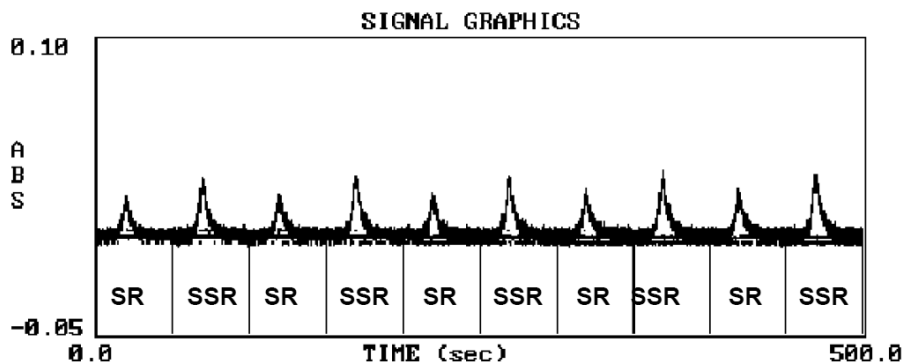


Figure 2. Peaks of 300 s collect time for 1% v/v HNO₃(SR) and 1% v/v HNO₃ (SSR) spiked with 20 ng Hg/L; 5 replicates.

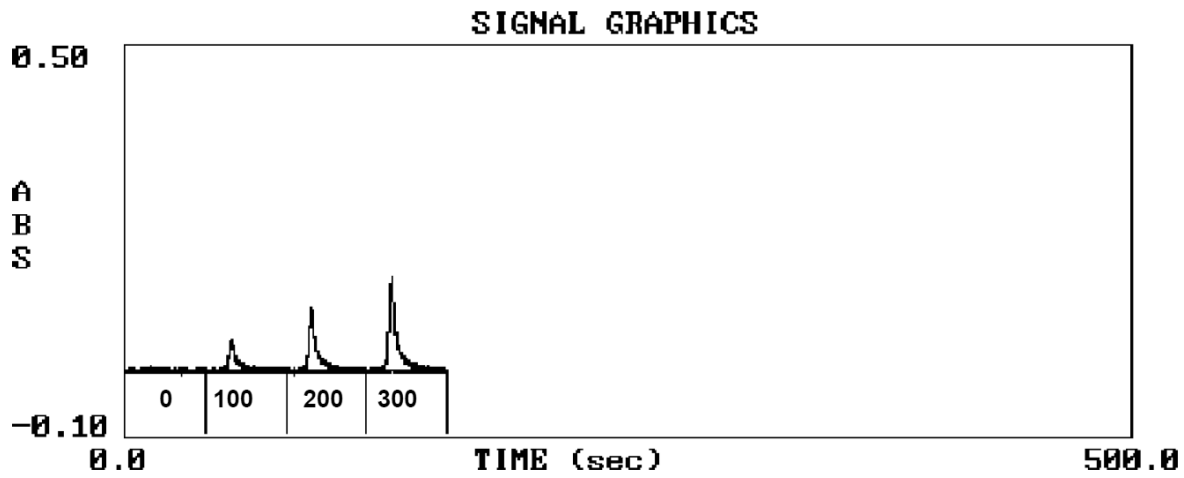


Figure 3. Peaks for blank, 100, 200 and 300 ng Hg/L. 180 s collect time.

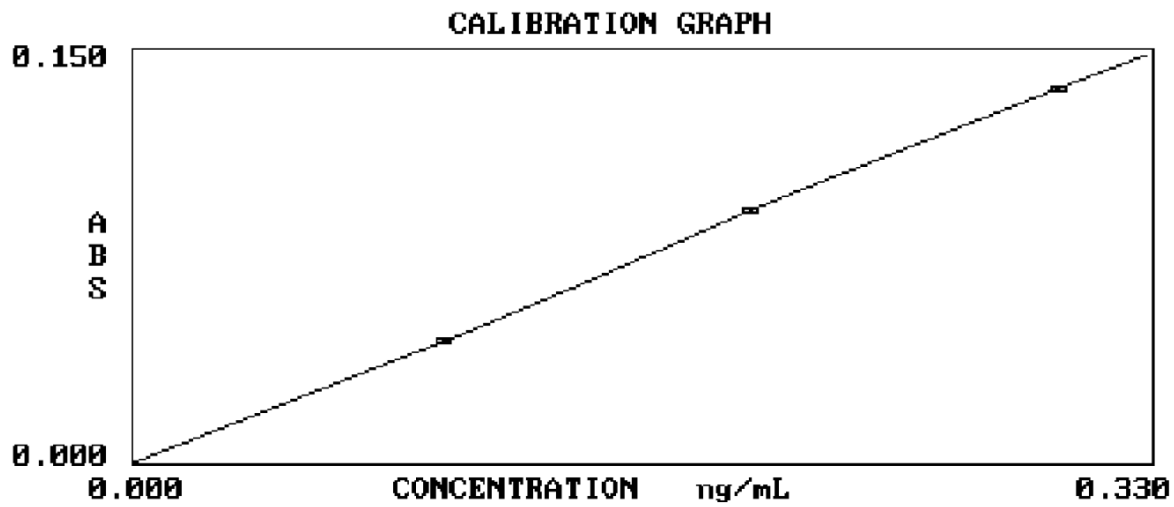


Figure 4. Calibration graph of results in Figure 3.

Figure 5 shows the signal graphics traces of these solutions repeated four times. (Refer to Table 2.) For ten spiked samples, the recoveries were $89 \pm 2\%$, well within US EPA requirements. The average result was 39 ± 2 ng Hg/L for the water sample. A lower spike level may be advisable for such drinking water samples, with an associated improvement in recovery expected.

Greater sensitivity can be obtained by using longer collect times. The enhancement is directly proportional to collect time. Figure 6 shows the signals as a $1 \mu\text{g Hg/L}$ solution collected for 600 s. Peak heights are about 1 absorbance unit and the RSD for 9 replicates less than 5%.

Measurement Mode

In general, the peak height measurement mode produces more reproducible results than the peak area mode. This is because the MCA-90 produces a relatively narrow transient signal within a wide read window. In the peak area mode the integrated signal is calculated right across the measurement window. Small variations in the peak therefore produce less significant changes in the integrated signal than when the peak height mode is used. The peak height mode is therefore recommended for all MCA-90 applications.

Table 2. Results of a Recovery Study for Drinking Water Agilent SpectraAA 300/400 System Report

Sample	Conc (ng/mL)	Mean ABS	Recovery %
Operator		Jonathan Moffett	
Date		21 February 1991	
Batch		910221...recovery studies..01	
Program 26		Hg MCA/PSC/180s/CONC/1r	
Blank	0.000	0.008	
Standard 1	0.100	0.044	
Standard 2	0.200	0.092	
Standard 3	0.300	0.137	
SR 01	0.039	0.017	87.1
SSR 01	0.215	0.099	
SA 01	0.202	0.093	
SR 02	0.037	0.016	93.2
SSR 02	0.229	0.105	
SA 02	0.206	0.095	
SR 03	0.041	0.018	85.9
SSR 03	0.218	0.100	
SA 03	0.206	0.095	
SR 04	0.037	0.016	82.5
SSR 04	0.193	0.088	
SA 04	0.189	0.087	
SR 05	0.039	0.017	89.7
SSR 05	0.221	0.101	
SA 05	0.203	0.094	
SR 06	0.043	0.019	89.5
SSR 06	0.222	0.102	
SA 06	0.200	0.092	
SR 07	0.039	0.017	87.5
SSR 07	0.214	0.099	
SA 07	0.200	0.092	
SR 08	0.039	0.017	88.0
SSR 08	0.215	0.099	
SA 08	0.200	0.092	
Average			87.9

SR = Tap water result
 SSR = Spiked tap water result
 SA = Spike added (0.2 ppb)

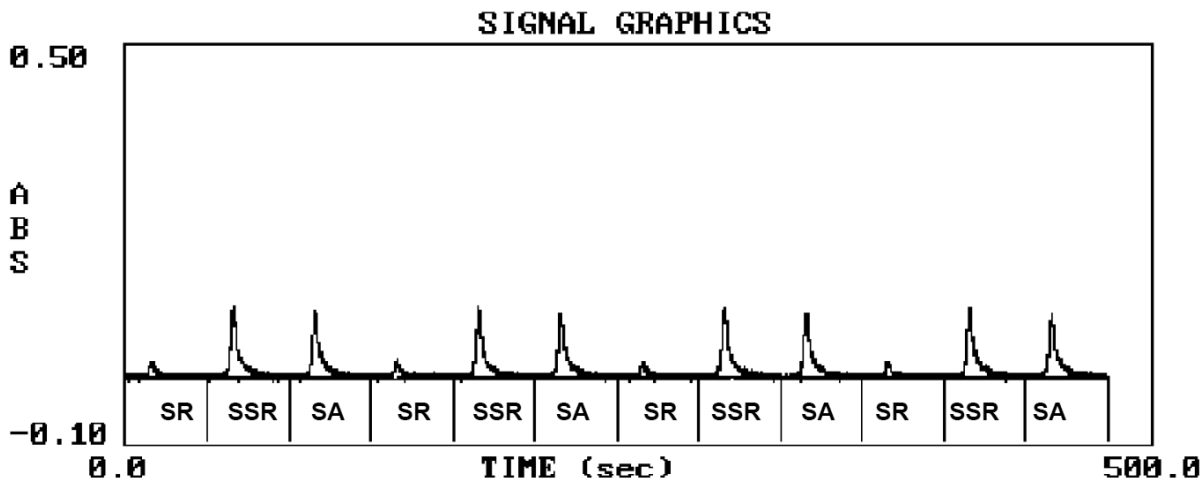


Figure 5. Peaks for drinking water (SR), spiked drinking water (SSR) and spike added (SA). SA is 200 ng Hg/L. 180 s collect time.

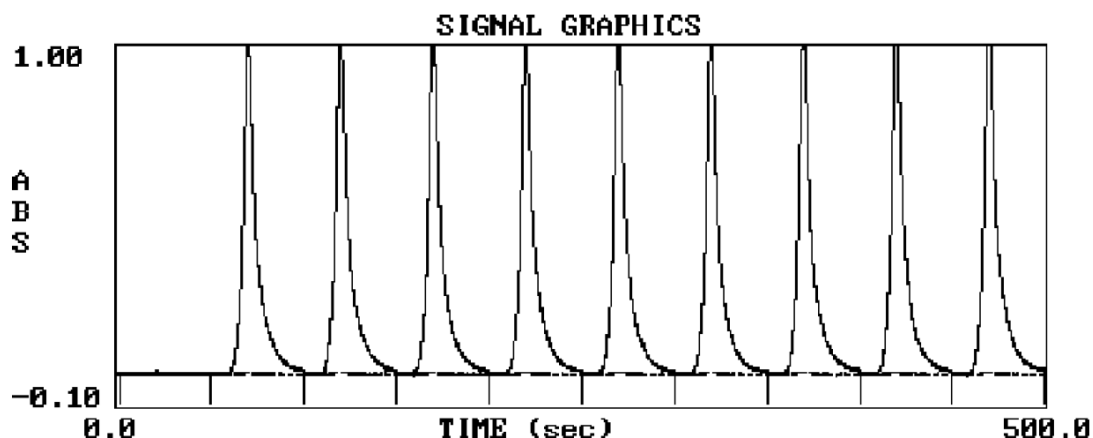


Figure 6. Peaks of 1 µg Hg/L collected for 600 s. %RSD < 5.

Practical Hints

- If the signal starts to deteriorate after extended operation, then the MAT may require cleaning. The MAT can be removed from the heater and boiled in 1% nitric acid for one to two hours. Rinse thoroughly with deionized distilled water. Blot dry with a clean tissue and replace in the heater. (Use talc-free plastic gloves or plastic tweezers to handle the MAT.) The heater must be installed in the workhead and the tubing from the gas-liquid separator re-connected. Check that the inert gas supply to the VGA-76 is turned on. This ensures a gas-stream flows over the MAT before any heating occurs. (Note that heating the MAT in air adversely affects the MAT collection surface.) Press the "Heat" key (number 3) on the MCA-90 keypad. This will dry the MAT. After the heater cools, the tubing to the absorption cell may be re-connected and the workhead closed up. For best results, the inert gas-stream should be allowed to flow over the MAT all the time.
- Sufficient heating time must be programmed into the MCA-90 to clean the MAT surface between samples. A heat time of about 40 s is recommended.
- Mercury standards for ppb and sub-ppb levels of mercury must be prepared daily. These may be prepared from a 1 mg Hg/L standard which in turn should be prepared weekly.
- All mercury solutions should be stabilized. This is usually done by adding 2 mL/L of 20% (w/v) K₂Cr₂O₇ solution (prepared in 1 + 1 nitric acid). This is only effective if the storage containers have been carefully cleaned as described previously [2].
- Sodium borohydride reductant is not recommended.
- It is suggested that a recovery study be conducted to quantify the effect of any interferences which may be present in a sample.
- Rigorous attention to cleanliness and minimization of contamination is mandatory.
- To assist with rapid drainage of solution from the GLS of the VGA, the drain tube should not be bent or obstructed. If the drain tube is kinked, solution can build up in the tube creating back pressure which hinders drainage of the GLS.
- Some samples can produce foaming in the GLS of the VGA-76. This foaming may spill over from the GLS to the MAT. If this occurs the surface of the MAT may be permanently damaged. To avoid foaming all samples must be digested as completely as possible. When testing for foaming disconnect the black tubing from the GLS to the MCA workhead, to avoid damage to the MAT. If foaming still occurs, add 100 ppm of Dow Corning Antifoam B to suppress foaming. The antifoam is most easily added as a small drop to 200 millilitres of sample with gently mixing.

Antifoam B has a limited shelf life and cannot be stored diluted. Use fresh Antifoam B and ensure the product you obtain is within its "Use By Date". Remember that the Antifoam B should be added to your Blank to check for mercury contamination.

Conclusion

The MCA-90 is a dedicated accessory for the determination of ultra-trace levels of mercury. Such measurements are complicated by solution stability and reagent contamination. The MCA-90 controls the variable factors which affect the sensitivity of the analytical procedure to provide a detection limit of 0.01 µg Hg/L or less. This meets legislative requirements for most countries. Laboratories must stringently monitor mercury levels in reagents and minimize contamination caused by handling.

References

1. "Desirable Quality for Drinking Water in Australia". Department of Health, NHMRC, 1980.
2. "Standard methods for the examination of water and wastewater", 16th Edition. American Public Health Association. Washington, 1985, p143.

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