AAS
APPLICATION NOTES

Mercury determination at ultra-trace concentration using
GBC AAS and MC3000 Mercury Concentrator

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Introduction

The high toxicity of mercury (Hg), particularly in the form of methyl mercury (MeHg), and its propensity to accumulate in the food chain, have caused major concerns for environmental monitoring authorities world-wide. The chemical transport and transformation processes for mercury have mainly been studied in the aquatic environment. Recent studies have also concentrated on atmospheric and terrestrial systems and their interactions. Chemical changes in the environment, particularly pH, may cause mobilisation of mercury in forms that are readily available to water systems.[1] Although mercury occurs widely at low concentration in the environment it is extremely toxic for living organisms.[1,2]

The measurement of total mercury, including, of course, MeHg, is widely performed using the cold vapour atomic absorption technique. This is recognised as the preferred technique due to its high sensitivity and low detection limits. The continuous flow mercury generation apparatus coupled to an atomic absorption spectrophotometer has been able to achieve detection limit and characteristic concentration values of 0.05 and 0.3 µg Hg/L respectively.[3,4,5] An analytical system that is able to improve sensitivity by an order of magnitude or better is required to comply with current environmental legislation for mercury pollution. The combination of atomic absorption with a suitable mercury-concentration accessory attached to the vapour generation apparatus achieves this goal and is suitable for automated routine measurement.

Concentration of mercury vapour can be achieved by entrapment onto a gold ribbon to form a gold-mercury amalgam.[2] After a suitable collection time, the mercury is vapourised from the solid gold surface by a controlled heating process for a specified time. The atomic mercury vapour is then transferred to a quartz cell for atomic absorption measurement. The process produces a transient mercury signal that is proportional to the collection time. The combination of hardware with suitable data collection software allows for the total automation of sample presentation, mercury collection and signal measurement.

This report describes the application of the GBC MC3000 Mercury Concentrator[6] for the analysis of mercury at sub-parts-per-billion levels (less than 1 µg/L) in urine and water quality control materials using United States Environmental Protection Authority method 7470A for liquid waste.[7] A soil sample was also analysed using the Authority's method 7471A for solid or semi-solid waste.[8]

Experimental

Instrumentation

A GBC atomic absorption spectrophotometer equipped with the unique Hyper-Pulse background correction system in conjunction with the GBC HG3000 continuous-flow automatic hydride generator and the GBC MC3000 Mercury Concentrator can be used to perform the analyses.[3,6] A mercury hollow cathode lamp was used throughout.

GBC AAS software controls the complete system—spectrophotometer, MC3000 and auto-sample loader. After simple method development, applications may be stored for future use. All data accumulated during runs is stored automatically on the computer hard disk. Real-time colour graphics of simultaneous signal absorbance and background traces allow the operator to optimise analytical parameters. The operating parameters for mercury are given in Table 1 and the software parameters for the MC3000 Control are displayed in Figure 3.

Instrument Parameters	
Element	Hg
Lamp Current	3 mA
Wavelength	253.7 nm
Slit Width	0.5 nm
Slit Height	Normal
Instrument Mode	Background Correction On
Measurement Mode	Peak Height

Table 1: Operating parameters for mercury

Reagent preparation

Chemicals used throughout were analytical reagent grade. Both sulphuric and nitric acids were high purity Aristar grade. High purity hydrochloric acid was Normatom 37% w/v.

Deionised water
Type 1 ultra-pure water was produced using a reverse osmosis, mixed bed deionising unit.

Aqua regia
Three volumes of concentrated HCl were added to one volume of concentrated HNO_3. This was prepared fresh just prior to use.

Sulphuric acid
Concentrated acid.

Sulphuric acid, 0.5 N
14 mL of concentrated sulphuric acid was diluted to 1.0 litre with deionised, reverse osmosis water.

Potassium persulphate, 5% solution (w/v)
Five grams of potassium persulphate was diluted to 100 mL with deionised, reverse osmosis water.

Sodium chloride-hydroxylamine sulphate solution
Twelve grams of both sodium chloride and hydroxylamine sulphate were dissolved in deionised, reverse osmosis water and diluted to 100 mL. Hydroxylamine hydrochloride may be used in place of hydroxylamine sulphate.

Potassium permanganate, mercury-free, 5% solution (w/v)
Five grams of potassium permanganate was dissolved in 100 mL of deionised, reverse osmosis water.

Stannous chloride reductant
This reagent refers to the 10% $SnCl_2$ in 20% HCl, which is used in the reductant channel. Fifty grams of Analytical Reagent grade tin chloride dihydrate was weighed into a 200 mL beaker. 100 mL of Analytical Reagent grade concentrated hydrochloric acid (37%) was added and heated until the solution was clear. The solution was then allowed to cool. This solution was quantitatively transferred to a 500 mL standard flask and made to volume with deionised, reverse osmosis water.

> **NOTE:**
> **The HG3000 acid reagent bottle was filled with 500 mL of deionised, reverse osmosis water.**

Mercury standards preparation

Stock mercury standard, 10 mg/L

1 mL of a 1000 mg/L stock mercury standard was pipetted into a 100 mL standard flask. 5 mL of concentrated (70%) nitric acid was added to stabilise the mercury and it was made up to volume with deionised, reverse osmosis water. This solution was prepared freshly each week.

First intermediate mercury standard, 100 mg/L

1 mL of the 10 mg/L mercury standard was pipetted into a 100 mL standard flask. 5 mL of concentrated (70%) nitric acid was added to stabilise the mercury solution and it was made to volume with deionised, reverse osmosis water. This standard and those following were prepared freshly each day.

Second intermediate mercury standard, 25 mg/L

25 mL of the 100 mg/L mercury standard was pipetted into a 100 mL standard flask and made to volume with deionised, reverse osmosis water.

Analytical mercury standards

A range of analytical standards were prepared by pipetting 1, 2, 5, 10, and 20 mL of the 25 µg/L mercury standard into separate 100 mL standard flasks. Each flask was made up to 100 mL with deionised, reverse osmosis water, giving standards of concentration 0.25, 0.5, 1.25, 2.50 and 5.00 µg/L.

Procedure—method 7470A

Sample preparation: A sample or standard solution aliquot of 100 mL, containing less than 1.0 g of mercury, was added to a 300 mL flask. 5 mL of H_2SO_4 and 2.4 mL of concentrated HNO_3 were added, mixing after each addition. 15 mL of potassium permanganate solution was added to each sample bottle. (Sewage samples may require additional permanganate. Ensure that equal amounts of permanganate are added to standards and blanks.) The sample was shaken and additional portions of potassium permanganate solution were added, as necessary, until the purple color persisted for at least 15 minutes. 8 mL of potassium persulphate was added and each bottle was heated for 2 hours in a water bath maintained at 95°C. The sample was cooled and 6 mL of sodium chloride-hydroxylamine sulphate added to reduce the excess permanganate.

Procedure—method 7471A

Sample preparation: Triplicate 0.2 g portions of the untreated sample were weighed or 0.2 mL of a standard solution was placed in the bottom of a flask. 5 mL of deionised reverse osmosis water and aqua regia were added. The flask was heated for 2 minutes in a water bath at 95°C then cooled, and 50 mL of water and 15 mL of potassium permanganate solution were added to each sample flask. The solutions were mixed thoroughly and placed in a water bath for 30 minutes at 95°C. The samples were cooled and 6 mL of sodium chloride-hydroxylamine sulphate was added to reduce the excess permanganate.

Cleaning of apparatus

All containers and glassware were soaked in 10% detergent solution for three days followed by rinsing with deionised water. Apparatus was then soaked in a 10% nitric acid solution for three days before rinsing again in deionised water and air drying.

Calibrated displacement pipettes were used along with pre-cleaned (as above) plastic tips for all sample and standard preparation. Containers that are to be used for storing solutions of low mercury concentration (below 1 µg/mL) should not have been in previous contact with strong metal solutions. In general it is important to set aside all containers that are to be used for ultra-trace metal analysis.

Sample preparation

A natural matrix certified (USEPA) reference material, Sewage Sludge Amended Soil Lot Number J050, was prepared according to the instructions and analysed for mercury according to method 7471A for solid or semi-solid waste.

A water sample, APG Setpoint Laboratory Standard, Lot Number 9645-9647, also certified by the USEPA, was prepared according to the instructions. The sample was then diluted 100 times and analysed using method 7470A for mercury in liquid waste.

A third sample, Seronorm human urine Lot Numbers 009024 and 108 (Nycomed Pharma, Norway), was also prepared accordingly. It was diluted 100 times and analysed using Method 7470A.

MC3000 principle of operation

Mercury vapour, which has been generated by reduction of the various forms of mercury from the sample via the HG3000, is trapped by the amalgamation process onto a solid gold ribbon substrate (rather than a thin layer coating of gold as used by other systems). This allows concentration of the mercury over a specified time. This time is set within the software, and is the most important analytical parameter for the analysis.

A patented magnetic induction heating system is used to directly heat the gold ribbon trap rapidly to release mercury vapour so it can be transported into the optical cell by a stream of argon for the absorption measurement. Figure 1 shows a schematic representation of the induction heating coil enveloping the glass chamber that contains the gold ribbon substrate. The direction of the mercury vapour flow is indicated.[6]
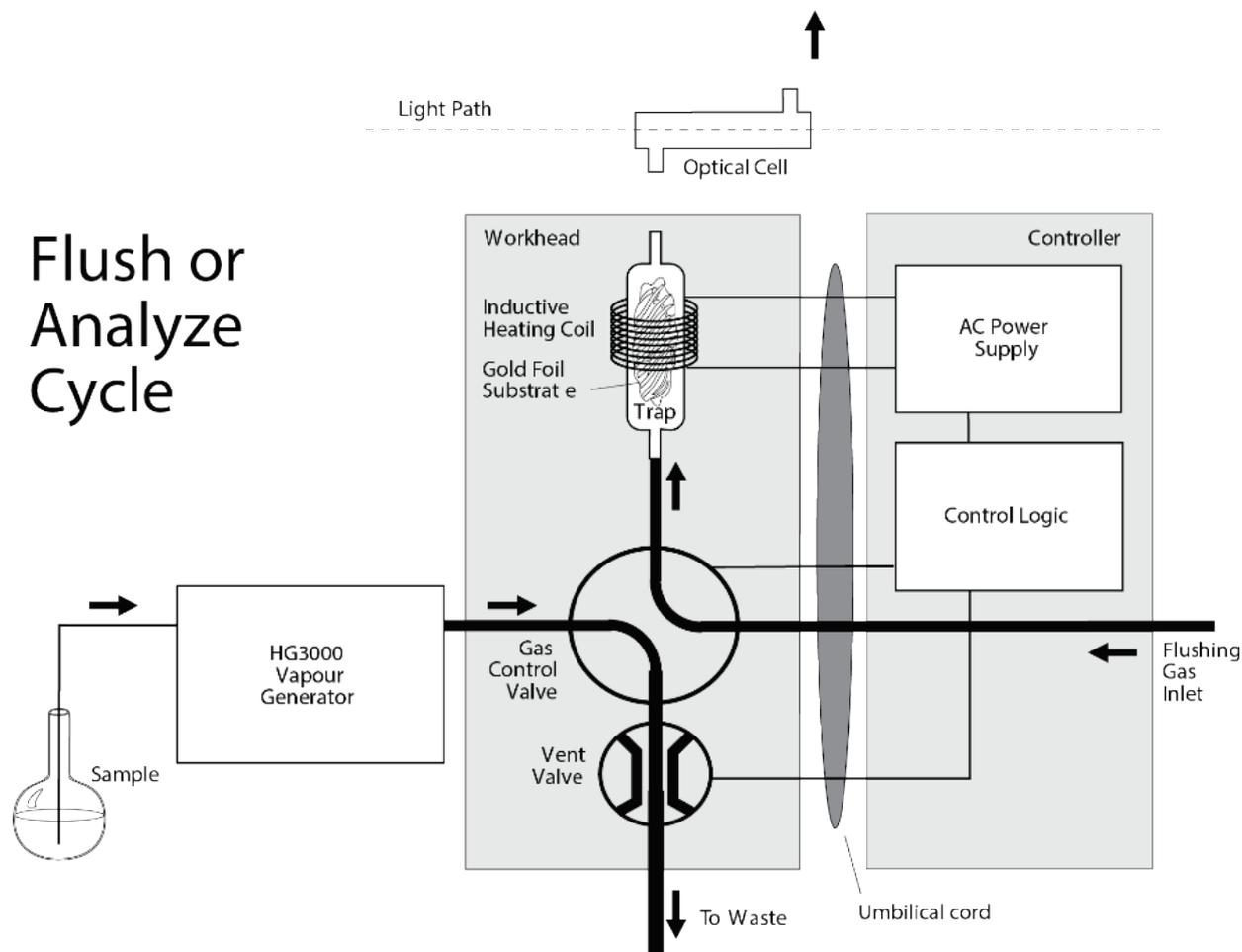

Figure 1: Mercury concentrator schematic

Figure 2: Detail of the MC3000 showing the inductively heated trap and the optical cell

Results and discussion

The MC3000 is completely automated for ultra-trace mercury analysis. This is achieved by the complete software control available through the "MC Control" software interface page. The functions of the software parameters shown in Figure 3 are described here:

1. "Delay Time" is the time for a sample to be taken up from the sample vessel and produce a mercury vapour.

2. "HG3000 Flush Time" is the time that allows the mercury vapour concentration to reach a maximum level for the specific sample prior to the loading of the mercury vapour onto the gold trap.

3. "Sample Load Time" is the period for which mercury vapour is passed through the gold trap to allow amalgamation to occur.

4. "MC Clean Required" programs the software to automatically pulse the patented inductive heating system between sample determinations, to clean the gold trap and eliminate any possible sample carry-over or contamination from one sample to the next.
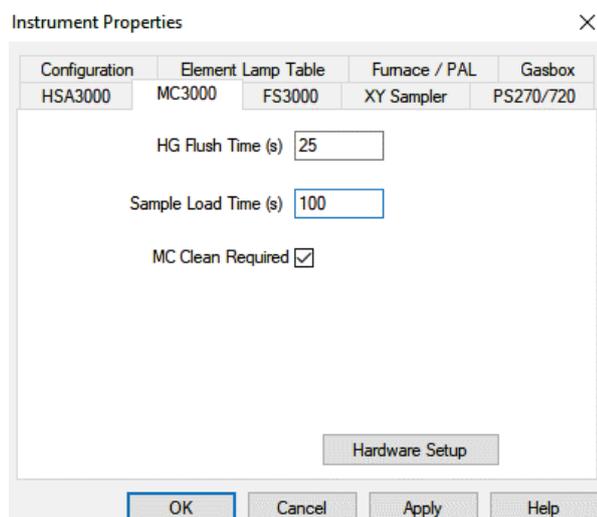

Figure 3: Control page for the MC3000

For the measurement of sub-parts-per-billion (µg/L) levels of mercury, several analytical problems present themselves. The contamination of so-called "clean" reagents with mercury is a major problem and may cause the analytical blank to have a level of mercury sufficient to introduce errors in the sample measurement. Contamination levels greater than 0.05 µg/L may often be encountered. It seems from this example that the advantages of being able to measure at such low levels could be overshadowed by factors beyond control of the analyst, and careful consideration should be given to the selection of suitable reagents.

The detection limit and characteristic concentration values (Table 2) compare very favourably with analysis of mercury by the standard continuous flow cold-vapour technique.

Analytical Results		
	Standard Mercury Analysis[1]	**MC3000[2]**
Detection Limit (ng/L)	50	4
Characteristic Concentration (ng/L)	300	5

1.   Analysis using sodium borohydride reductant for cold vapour generation.

2.   EPA method using stannous chloride reductant with 300 second sample load time.

Both sets of results were obtained using a GBC HG3000 automatic hydride generator

Table 2: Comparison of detection limit (2σ) and characteristic concentration for standard mercury analysis using the HG3000 alone, and in conjunction with the MC3000 mercury concentrator

Improvements in characteristic concentration may be obtained if the collection time is increased, if appropriate. The dramatic improvement in both parameters has occurred due to the use of patented inductive heating of the gold foil substrate. Rapid heating of the gold is achieved by computer control. The "MC Clean" step is responsible for preventing sample carry-over and contamination. The design of the measurement cell is also important, and allows the achievement of lower signal noise and a dramatic improvement in sensitivity.

The urine quality control material "Seronorm" was chosen as a representative sample for monitoring mercury toxicity in humans. Urine is usually considered to be the best body fluid to monitor exposure to mercury especially for the industrial worker. The results for the two samples compared very favourably with the recommended results (Table 3).

Sample	Certified	Measured
#009024	48	46.5 2.1
#108	51	48 6.8

For each sample n=4.

Mean 1 standard deviation.

EPA method 7470A (mercury in liquid waste).

Table 3: Analytical results for urine samples, Seronorm urine #009024 and #108. Results are in µg/L

The monitoring of environmental waters for mercury at ultra-trace levels will allow a greater understanding of how mercury behaves and accumulates in the environment. An APG water sample was chosen for measurement to determine how accurately water could be measured. The mean result for this sample compared very favourably with the certified value and also showed very good precision for the replicates (Table 4).

Certified	Measured	95% Confidence Interval
1.74	1.76 0.4	1.14–2.25

Six aliquots of this sample were digested (n=6).

RSD = 2.1%.

Mean 1 standard deviation.

EPA method 7074A (mercury in liquid waste).

Table 4: Analytical results for the APG Set Point Water sample, lot number 9645–9647. Six aliquots were digested and prepared according to the instructions. Units are µg/L

The contamination of land and soils with mercury has in the past been manifestly ignored. Now, however, great concern has been raised due to studies undertaken to monitor mercury levels in waters that run into underground water systems, lakes and streams. The Natural Matrix certified reference sample is "sewage sludge, amended soil" that was used as a quality control sample. It was prepared and analysed according to the method 7471A. The result was well within the 95% confidence interval for this sample (Table 5).

Certified	Measured	95% Confidence Interval
3.23	3.65	1.37–5.09

EPA method 7471A (mercury in solid or semi-solid waste).

Table 5: Analytical result for the Natural Matrix Certified Reference Material Sewage Sludge Amended Soil, lot number JO50. Units in µg/L

Figure 4 is a typical calibration plot for mercury ranging from 0.25 to 5.00 µg/L. The plot is almost linear over its entire range.
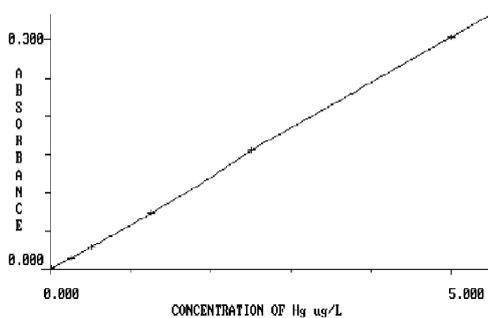

Figure 4: A representative calibration plot for mercury from 0.25–5 µg/L

Figure 5 shows 13 consecutive traces of mercury at 200 ng/L to illustrate the shape of the signal peaks and the excellent precision of the technique.
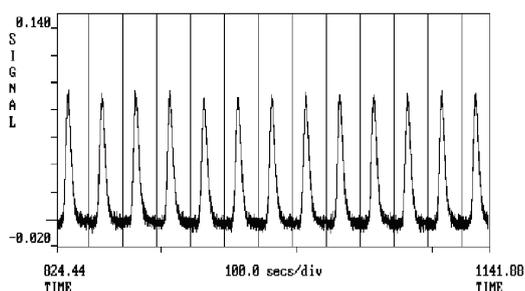

Figure 5: Typical graphics traces illustrating 13 consecutive traces of mercury at 200 ng/L using a 100 second sample load time, with typical relative standard deviations of <0.5%

Conclusion

The MC3000 mercury concentrator is a totally computer controlled accessory for automatic mercury cold vapour analysis. It achieves several advantages over current technology in that it offers:

1. Complete software control.

2. Fast inductive heating technology, allowing a higher temperature to be attained, and ensuring accurate signal detection using peak height or area.

3. Higher sensitivity.

4. Improved speed of analysis.

5. Reduced delay time between samples, no sample carry-over or memory effect, due to automatic cleaning of the solid gold substrate.

6. Optimum timing for automated sample measurement.

All these benefits allow the analyst to have total confidence to run samples unattended, thus increasing productivity. The characteristic concentration is improved by a factor of 60, and the detection limit improved by a factor of 12, allowing mercury measurement at ultra-trace levels. These analytical parameters not only comply with but exceed the requirements of the USEPA and other environmental bodies worldwide.

References

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8. USEPA Test Methods for Evaluating Solid Waste. Physical/Chemical Methods, SW-846, 3rd Edition. Method 7471A. Mercury in Solid or Semi-solid Waste. Revision 1, November 1992.