

Automating the digestion and determination of mercury in a variety of environmental sample matrices

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In the last 40 years, mercury pollution has caused numerous deaths and thousands of hospitalizations globally. The first widely publicized occurrence was in Minimata, Japan, where thousands of people were poisoned from eating fish contaminated with methyl mercury. Other episodes occurred in Japan (Ni-gata), Iraq, Pakistan, Guatemala, and Brazil. The estimated annual contribution by man to the total mercury burden is as high as 75%.

For decades, cold vapor atomic absorption spectroscopy (CVAAS) has provided a sensitive and relatively interference-free approach to mercury determination in a wide variety of samples. Today's CVAAS systems are more productive than earlier models and are capable of low nanogram-per-liter detection limits but have continued to require significant operator attention during sample preparation and subsequent analysis.

Although this work describes the automation of both sample digestion and analysis, these steps employ independent instrumentation, permitting the automation of either separately.

Experimental

Instrumentation: Sample preparation

In this work, all sample digestions were performed using the Hydra Prep automated digestion system (Leeman Labs, Inc., Hudson, NH). The Hydra Prep consists of a temperature-controlled water bath, an automated reagent dispensing system providing up to six independent reagents, an autosampler with capacity for 13 standards and up to



Figure 1 Hydra Prep system.

88 samples, and a computer datastation preprogrammed for numerous matrices (Figure 1). Table 1 contains the digestion parameters and reagents used in two of the preprogrammed procedures (waters and solids).

Because of the extremely corrosive nature of the mineral acids and oxidizers used in the digestion process, care must be taken in the design of the dispensing mechanism. In the case of the Hy-

dra Prep system, reagents are dispensed by pressurizing the bottles and opening inert valves for precisely timed intervals. This design avoids the use of mechanical pumps whose components cannot stand up to the digestion chemicals. A schematic of the system appears in Figure 2.

In the digestion procedure for water, reagents 1-4 are automatically dispensed into all standards and samples. Next, the bath is automatically filled and heated to 95 °C. A thermostat located in the bath continuously monitors temperature and controls the heater during the 2-hr heating phase. Following the heating step, the bath fluid is exchanged to cool the digestion solutions. Reagent 5 (NaCl:[NH₂OH]₂·H₂SO₄) is dispensed to all standards and samples. After a 15-min reaction pe-

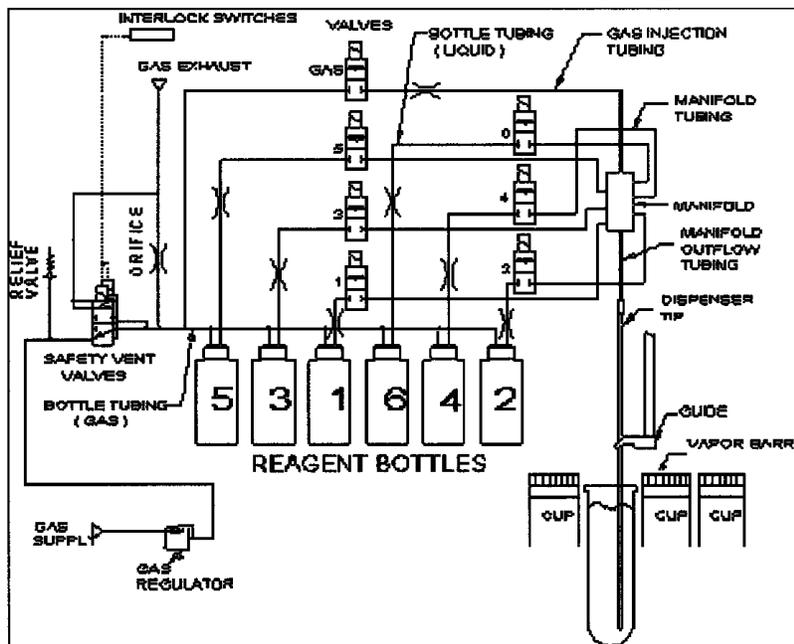


Figure 2 System schematic.

Table 1

Parameters	Automated preparation	
	Waters (7470)	Soils (7471)
Heater setting	95 °C	95 °C
Standard size	12 mL*	5 mL
Sample size	4 mL	0.1 g
Sample matrix	0.2% HCl:0.2% HNO ₃	
Reagents		
1	0.2 mL H ₂ SO ₄ (conc.)	2.25 mL Aqua Regia (conc.)**
2	0.1 mL HNO ₃ (conc.)	2.5 mL distilled water
3	1.2 mL KMnO ₄ (5%)	6.75 mL KMnO ₄ (5%)
4	0.32 mL K ₂ S ₂ O ₈ (5%)	3.6 mL NaCl:NH ₂ OH (12%:12%)
5	1.333 mL NaCl:(NH ₂ OH) ₂ :H ₂ SO ₄	4.5 mL distilled water
6	1.000 mL distilled water	4.5 mL distilled water

*All standard reagents are added at three times the sample reagent volumes to provide enough solution for recalibration should it be desired.

**Aqua Regia is 3:1 HCl:HNO₃.



Figure 3 Hydra AA system.

Table 2

Protocol	Analysis protocols	GE3
Pump rate		3 mL/min
Gas flow		0.5 L/min
Gas type		Argon
Rinse		60 sec
Uptake		15 sec
Replicates		3
Integration		10 sec

riod, all standards and samples are remixed and sparged, completing the digestion procedure.

In the digestion procedure for soils, reagent 1 is dispensed to standards, and reagents 1 and 2 are dispensed to all samples. Reagent 2 is distilled water and is used as makeup volume for samples since standard tubes had 5 mL of (standard) solution added. The bath is filled and heated to 95 °C for 2 min. The bath is drained and refilled with cool water. After a 5-min cooling period, reagents 3, 5, and 6 are added to all tubes. The bath is then heated to 95 °C for 30 min. Following this step, valves automatically empty the bath and refill it with

is a makeup volume. The addition of reagent 2 in two installments equals the volume of solution placed in the standard cups.

Instrumentation: Sample analysis

After digestion, the samples were transferred to the Hydra AA system for analysis (Leeman Labs Inc.) (Figure 3). This system consists of an autosampler, CVAAS spectrometer, and computer datastation running WinHg software. The WinHg operating software is Microsoft (Redmond, WA) Windows™ 95, 98, 2000, or NT compatible. For this analysis, the default operating conditions appearing in Table 2 were employed.

The Hydra AA is a third-generation standalone mercury an-

cool water. After a 5-min cooling period, reagent 4 is dispensed into the standard cups, and 4 and 2 dispensed into sample cups. Reagent 2

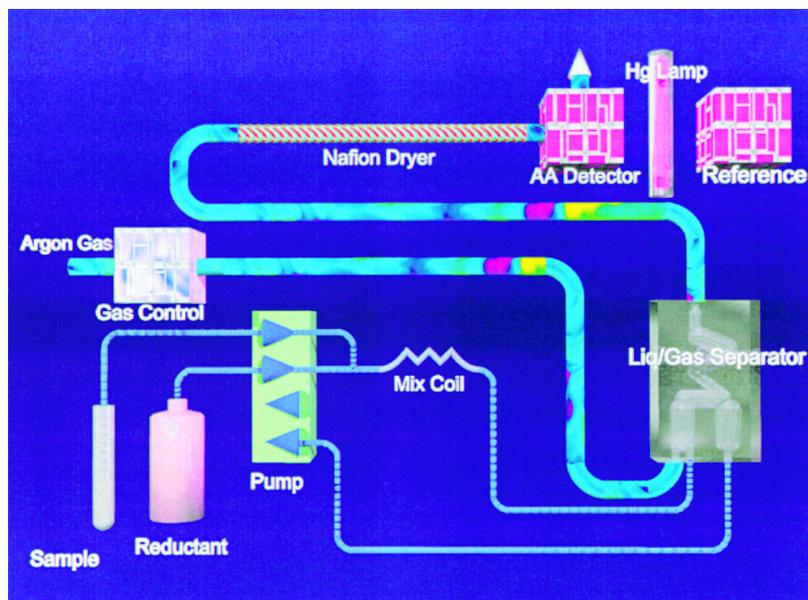


Figure 4 Hydra AA schematic.

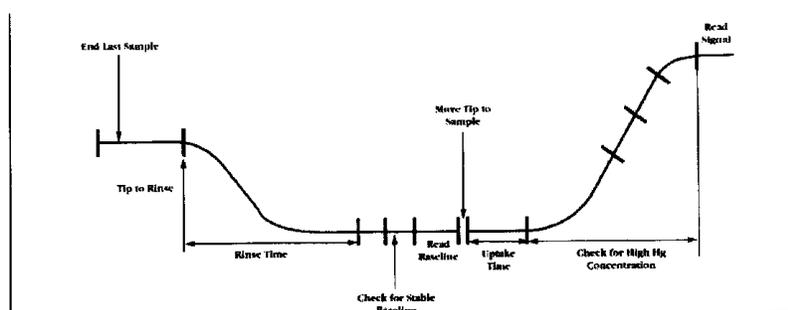


Figure 5 Hydra AA sample cycle.

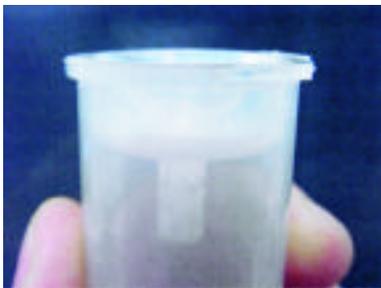


Figure 6 Fifty-milliliter vapor barrier cap.

Table 3

	Preparation precision	
	7470	Fishx
n	20	10
Reagent wt (avg.)	3.6 g	30.19 g
SD	0.082 g	0.12 g

alyzer capable of achieving instrument detection limits approaching 1 ng/L. Although equipped with a 30-cm-long absorption cell for very high sensitivity, the system can accommodate sample concentrations ranging from low-ppt to high-ppb levels by adjusting parameters such as pump and gas flow rates. Its gas/liquid separator provides favorable sample throughput together with exceptional spike recoveries even for poorly digested samples. This is accomplished by combining a low-volume/high-turbulence liquid well that efficiently releases dissolved Hg^0 from the liquid stream with a serpentine gas path designed to handle foaming samples. Condensation of moisture in the absorption cell, a common problem in early CVAAS designs, is eliminated by an in-line Nafion™ dryer (Perma Pure Inc., Toms River, NJ). This dryer is a tube made of a copolymer of Teflon® (DuPont, Wilmington, DE) and an organosulfonic acid. Gas passing through the tube loses moisture to the polymer membrane and in turn the membrane loses moisture to the surrounding ambient air. Unlike conventional chemical drying tubes, the Nafion dryer continually refreshes itself and does not lose efficiency with moisture contact. To minimize sample carryover, the spectrometer's autosampler is equipped with a con-

tinuous flowthrough rinse. Figure 4 shows a schematic diagram of the Hydra AA system.

The instrument software automates the analysis cycle, wherein each sample cycle (shown in Figure 5) consists of rinse, baseline check, overrange check, and measurement periods. Samples whose mercury content is significantly above

the calibrated concentration range cannot be analyzed but in some cases can contaminate the instrument and cause errors in subsequent determinations if left unaddressed. The high-concentration protection feature of the Hydra AA continuously monitors the emerging signal for each new sample. When the rate of signal increase

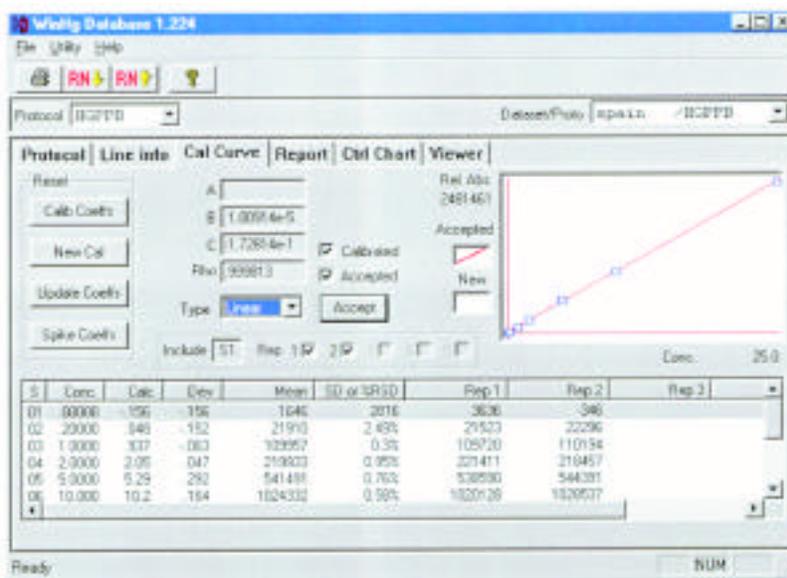


Figure 7 Calibration display window.

Table 4

Sample	Replicates (ppb)	Sample precision		Sample average (ppb)	Sample %RSD	Known value (ppb)*
		Aliquot average (ppb)	Aliquot %RSD			
1a	12.1, 13.1, 13.1	12.7	4.7			
1b	13.4, 13.3, 13.1	13.3	1.3	13.1	2.2	12.5
1c	13.4, 13.2, 13.1	13.2	1.1			
2a	62.1, 61.5, 62.3	62.0	0.7			
2b	62.8, 62.4, 59.8	61.7	2.7	61.8	0.3	60
2c	61.5, 62.3, 61.3	61.7	0.9			
3a	21.5, 21.3, 20.5	21.1	2.6			
3b	21.5, 21.4, 21.0	21.3	1.1	21.2	0.5	20
3c	21.2, 21.1, 21.0	21.1	0.4			
4a	63.3, 63.4, 61.9	62.9	1.3			
4b	61.0, 60.2, 59.1	60.1	1.6	61.4	2.3	60
4c	61.9, 61.9, 59.4	61.1	2.4			
5a	78.9, 76.7, 75.2	76.9	2.4			
5b	78.2, 77.2, 75.9	77.1	1.5	77.0	0.1	75
5c	77.9, 78.2, 74.6	76.9	2.6			
6a	8.6, 8.0, 9.1	8.6	6.1			
6b	8.7, 8.5, 8.4	8.5	1.6	8.6	0.8	8
6c	8.5, 9.0, 8.5	8.7	3.5			
7a	20.8, 20.9, 20.8	20.8	0.2			
7b	21.0, 20.6, 20.6	20.7	1.1	20.7	0.9	20
7c	20.6, 20.5, 20.3	20.5	0.8			

*Known values were supplied by an independent laboratory but not certified.

Table 5

SRM catalog number	Matrix	Standard Reference Materials			Certified value (ppb)	Deviation from certified value (ppb)	%Rec.
		Result (ppb)	Mean (ppb)	SD (ppb)			
ERA 514 ^a	Wastewater	1.206					
ERA514		1.166					
ERA514		1.187	1.186	0.020	1.22	0.03	97.2
ERA514 ^b	Wastewater	10.19					
ERA514		10.03					
ERA514		10.19	10.14	0.09	10.8	0.7	93.9
SRM 1641d	Water	1.360					
SRM 1641d		1.344					
SRM 1641d		1.334	1.346	0.013	1.48	0.13	90.9
ERAPPS-46 ^c	Soil	1689					
ERA PPS-46		1692					
ERA PPS-46		1646	1676	26	1680	4	99.7
SRM 2704	River sediment	1364					
SRM 2704		1386					
SRM 2704		1405	1390	21	1470	80	94.2

^aLot number A9989.^bLot number A99101.^cLot number 228.

Table 6

IDL readings (ppt)*	SD (ppt)	Detection limits			SD (ppt)	MDL (ppt)
		IDL (ppt)	MDL readings (ppt)**	MDL (ppt)		
11.8	0.995	2.98	2.48	8.07	24.2	
10.9			-4.26			
8.6			-14.0			
10.5			-11.9			
10.2			3.59			
10.5			-12.9			
9.7			-13.0			
			-9.96			
			1.63			
			6.03			

*Replicate readings of acid blanks.

**Separate fortified blanks (10 ppt) carried through digestion process.

exceeds the protection value, the sample probe immediately moves to rinse and the argon flow increases to purge the vapor path. The detector monitors the signal as the mercury is removed from the system and analysis resumes after a stable baseline is reestablished.

Results and discussion

Automated digestion procedures require not only accurate dispensing but also minimal solvent evaporation to ensure accurate results. In the case of the Hydra Prep, evaporation is controlled using the vapor barrier caps shown in *Figure 6*. To test the system's ability to con-

trol both reagent dispensing and evaporation, sample cups were weighed before the start of digestion protocols and again after completion (reagent additions, heating cycles, and cooling cycles). *Table 3* shows precision of approx. 0.1 g for the two digestion protocols (fishx and 7470) evaluated in this work.

Calibration employed a linear fit of five standards (including blank) to a maximum concentration of 20 ppb. The resultant correlation was better than 0.9999. The calibration display appears in *Figure 7*.

The results for triplicate aliquots of several water samples digested on the Hydra Prep using protocol 7470 appear in *Table 4*. Three

aliquots of each sample were carried through the digestion procedure (e.g., 1a, 1b, and 1c). Following the digestion, each aliquot was then measured in triplicate. Within-aliquot and within-sample precision is comparable.

To confirm the accuracy of both the automated preparation and the analysis, several Standard Reference Materials (SRMs) were prepared with the Hydra Prep and subsequently analyzed on the Hydra AA. New polypropylene standard and sample cups were used. *Table 5* shows an average recovery (accuracy) of approx. 94%.

While instrument detection limits (IDLs) for the Hydra AA spectrometer approach 1 ng/L (ppt), the method detection limit (MDL), which includes sample handling and digestion, is higher. Without extraordinary care in sampling handling (neither cleanroom environment nor sample cup precleaning), method detection limits remain in the low nanogram-per-liter range as shown in *Table 6*. The method detection limits suffer because some of the Method 245.1 reagents, notably nitric acid and potassium permanganate, can be contaminated with significant levels of mercury. Also worth noting is that the digestion reagents effectively produce a 7.6/4.0 dilution in standards and samples. (The water digestion protocol starts with 4.0 mL sample and adds a total of 3.6 mL of reagents.)

Conclusion

Cold vapor atomic absorption spectrometry is capable of determining mercury in a wide variety of matrices with well-established accuracy. The Hydra Prep automated digestion system in combination with the Hydra AA spectrometer provide a fully automated alternative for the modern analytical laboratory where laboratory staff is not available for extended digestion protocols.

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