

By Kathy Gagnon Pappas

A comprehensive system for mercury analysis

MERCURY is a ubiquitous element whose harmful effects on plants, animals, and humans are well documented. Consequently, the need to measure mercury levels in a variety of samples is becoming increasingly important. Mercury is being detected in river and lake water and sediment, as well as in fish. The AP/PS200II automated mercury preparation and analysis system (Leeman Labs, Inc., Lowell, MA), shown in *Figure 1*, was used to digest and analyze the material reported in this paper. The AP/PS200II is fully automated, providing the convenience of unattended operation.

The most widely used technique for mercury analysis is cold vapor atomic absorption spectrometry (CVAAS). Dedicated analyzers, such as the PS200II, are commercially available. They require a small sample size, making the dedicated analyzer an economical choice. Dedicated mercury analyzers are also more sensitive than conventional AA spectrometers. The PS200II has an instrument de-

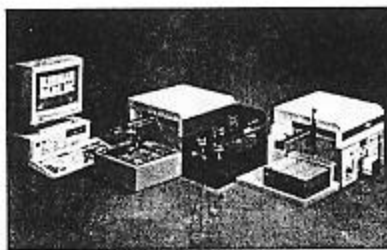


Figure 1 The AP/PS200II automated mercury preparation and analysis system.

tection limit in the single-digit parts-per-trillion level, well below the 0.2 µg/L detection limit stipulated by U.S. EPA methods. This detection limit requirement is continually being lowered and that trend will continue.

For accurate results, samples must be digested to convert all forms of mercury into the mercuric ion (Hg^{+2}). When performed manually, the only approved digestion procedure is very labor intensive. The AP200II system completely automates this process. The mercuric ion is reduced, typically by stannous chloride, to liberate elemental mercury vapor and the absorption is read at 254 nm. Dedicated analyzers incorporate an absorption cell that is long (~30 cm) for improved sensitivity, and narrow (~7 mm) for fast response time.

Stability

While analytical sensitivity is important, instrument stability (or

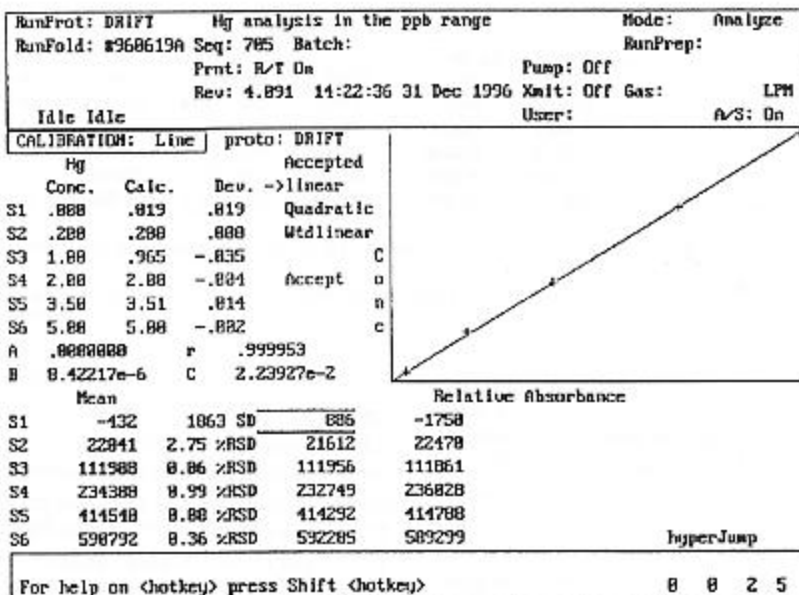


Figure 2 Calibration curve for drift study.

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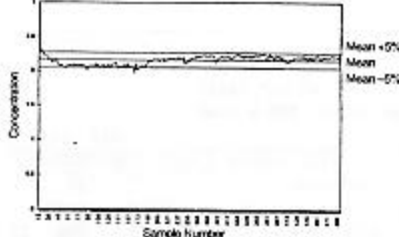


Figure 3 Long-term stability test showing each data point. The PS200II was run continually for over 10 hr.

the ability to obtain near identical measurements from the beginning to the end of the day) is imperative. An unstable instrument requires frequent recalibration, which increases both the analysis time and the consumption of reagents and standards. To demonstrate the stability of the PS200II system, freshly prepared mercuric chloride standards in 1% HCl ranging in concentration from blank to 5 µg/L were used to generate the calibration curve. The accepted calibration curve (Figure 2) had a correlation coefficient of 0.999953, indicating excellent linearity. A 2 µg/L mercuric chloride solution in 1% HCl was run continuously for over 10 hr; each data point is displayed in Figure 3. Evaluating each data point is more revealing than displaying an average of many samples per data point on a chart. When a chart shows an average of many data points, the noise of the individual readings is smoothed out. There was less than ±5% total drift from the mean value of 2.165 µg/L, indicating any check standards run over this period would be well within the typical ±20% criterion used for mercury analysis. The initial drop represents pump tubing break-in (fresh tubing was installed just prior to running samples). The readings enter the ±5% range after approx. 20 min. The standard deviation (SD) of all 486 samples was 0.069. The percent relative standard deviation (%RSD) was 3.18%, indicating very good stability over the 10-hr period.

Table 1

Results from certified water samples digested using the AP/PS200II			
Lot #426	Value found	Certified value	Performance acceptance limits
	3.87 µg/L	3.89 µg/L	2.92–4.86 µg/L
	Value found	Expected value	Replicate summary
Check standard 1	-0.088	-0.043	-0.093, -0.114, -0.079, -0.076, -0.079
Check standard 2	1.92 µg/L	2.03 µg/L	1.98, 2.00, 1.81, 1.88, 1.92

Table 2

Results from certified soil samples digested using the AP/PS200II			
Lot #226	Value found	Certified value	Performance acceptance limits
	1.49 mg/kg	1.68 mg/kg	0.806–2.62 mg/kg
Blank lot #57006	-0.057 mg/kg	<0.10 mg/kg	
	Value found	Expected value	Replicate summary
Check standard 1	-0.072 mg/kg	-0.061 mg/kg	-0.071, -0.073, -0.707, -0.075
Check standard 2	1.02 mg/kg	1.03 mg/kg	1.07, 1.06, 0.976, 0.986

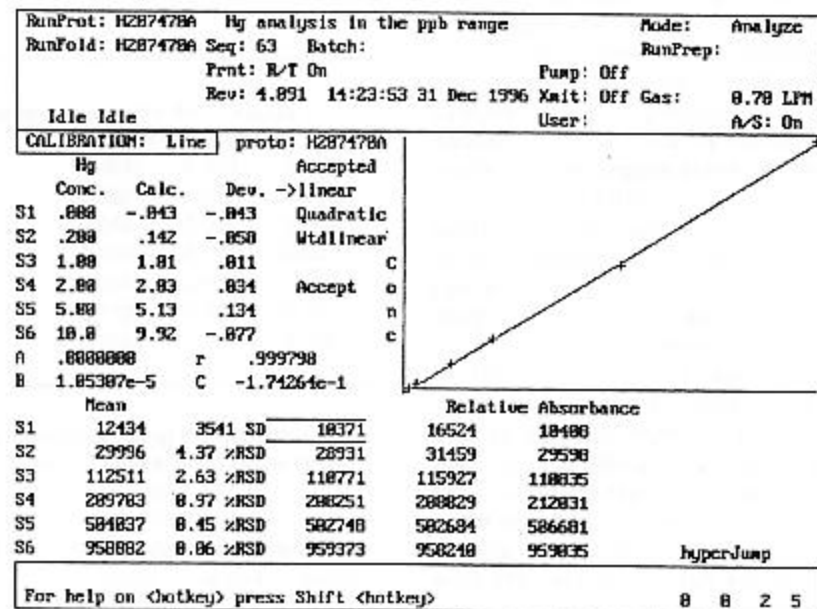


Figure 4 Calibration curve for aqueous samples digested according to U.S. EPA Method 7470A.

Protection

When analyzing mercury samples, especially waste samples, the sample batch may occasionally contain samples with a mercury level well outside the calibration range of the other samples. Mercury vapor adheres to internal surfaces but has a

Table 3

Conditions used to operate the PS200II for fish analysis	
Pump rate	3 mL/min
Gas	0.04 Lpm
Uptake time	45 sec
Integration time	10 sec

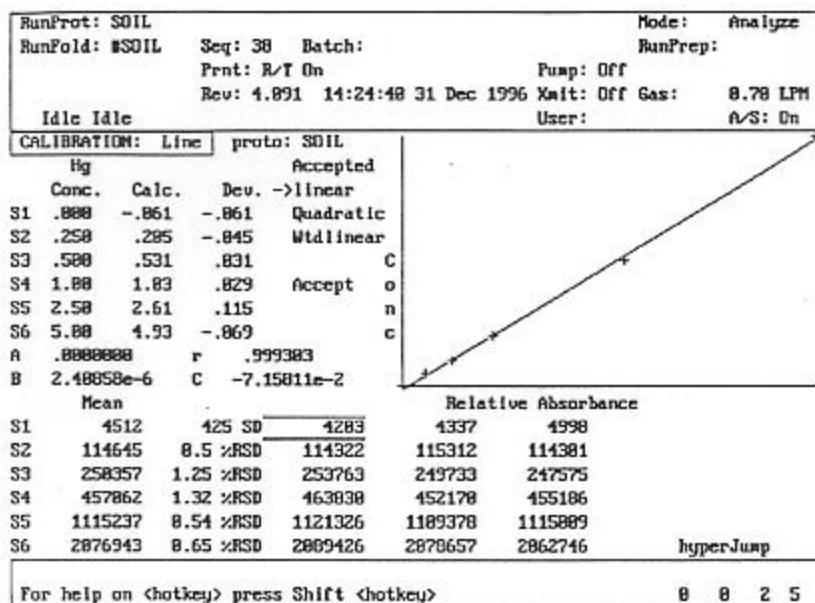


Figure 5 Calibration curve for soil samples digested according to U.S. EPA Method 7471A.

Table 4

Results from fish samples digested using the AP/PS200II					
Sample	Concentration	%RSD	Replicate summary		
Cod	0.060 µg/g	1.04%	0.061	0.060	0.060
Haddock	0.052 µg/g	1.49%	0.052	0.051	0.053
Salmon	0.044 µg/g	1.47%	0.044	0.044	0.045
Scallop	-0.008 µg/g	-8.82%	-0.009	-0.009	-0.007
Shrimp	0.006 µg/g	22.9%	0.004	0.007	0.007
Swordfish	0.722 µg/g	0.492%	0.719	0.726	0.721
Tuna	0.753 µg/g	0.639%	0.758	0.754	0.748

Table 5

Results from certified fish samples digested using the AP/PS200II					
	Value found	Certified value	Performance acceptance limits		
DOLT-2	2.02 µg/g	1.99 µg/g	1.89-2.0 µg/g		
DORM-2	4.83 µg/g	4.64 µg/g	4.38-4.90 µg/g		
	Value found	Expected value	Replicate summary		
Check standard 1	-0.022 µg/g	-0.019	-0.024	-0.024	-0.019
Check standard 2	1.05 µg/g	1.00 µg/g	1.02	1.06	1.06

very slow elution rate; thus, it can take hours to clean a system after exposure to high levels of mercury. The PS200II analyzer is equipped with a high-concentration protection system to prevent contamination of the instrument from an unexpectedly high sample. (When running samples ranging from a blank to 20 ppb, the high-concentration system will

be triggered by a sample of approx. 500 ppb.) The PS software monitors the slope of the uptake, and if the slope is found to be out of range, the high-concentration system is triggered automatically. The sample uptake is halted and the liquid and gaseous areas are flushed to remove the sample and any vapor that may have been generated. This continues

until a stable baseline is once again achieved. This typically requires a couple of minutes for a sample of approx. 1 mg/L. The report indicates that the concentration was out of range and the analysis of subsequent samples continues.

Versatility

Environmental samples

Environmental laboratories analyze water samples for mercury content according to U.S. EPA methods: SW-846 Method 7470A is used for waste samples or Method 254.1 is used for drinking water samples. Most mercury analysis is performed at the parts-per-billion or mg/L level. The AP200II precisely dispenses the required reagents into each sample cup, then mixes, monitors, and heats the samples according to the method selected. Water samples were digested on the AP200II and analyzed for mercury levels. The calibration curve shown in Figure 4 exhibits excellent linearity (0.999798) and reproducibility as evidenced by the %RSD. The curve was accepted and samples were analyzed. The spiked samples showed good correlation to the expected values and the replicates showed good reproducibility. Each sample required approx. 1 min for analysis. The check standards read back within the expected range. The value of 3.87 µg/g for the certified sample, shown in Table 1, agreed with the certified value and was well within the performance acceptance limits (Environmental Resource Associates, Arvada, CO).

Solid waste

Analyzing solid waste requires a more vigorous digestion procedure as described by SW-846 Method 7471A or Method 245.5. Many solid samples contain considerable organic contamination and must be digested thoroughly. The AP200II requires just 0.1 g of

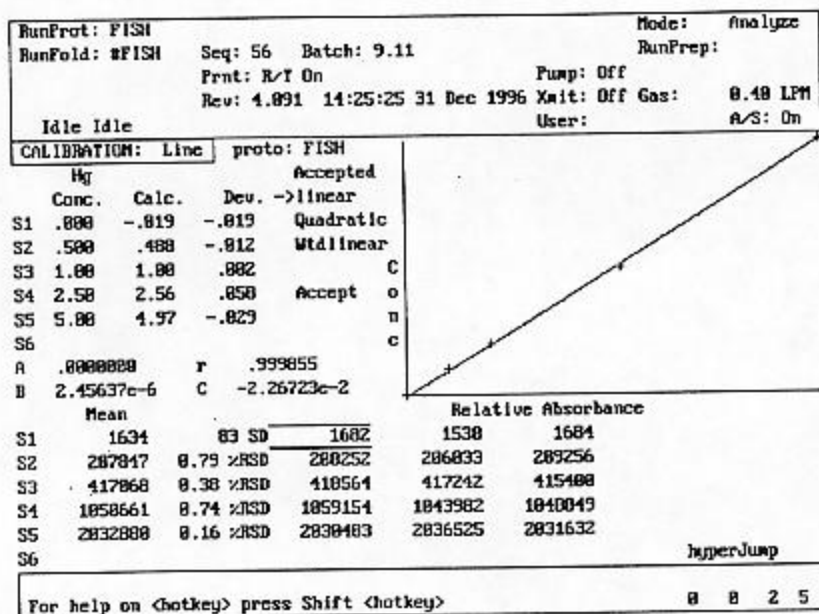


Figure 6 Calibration curve for fish samples digested according to U.S. EPA Method 245.6.

sample. Mercuric chloride standard solutions in 2% HNO₃ ranging in concentration from blank to 5 µg/g were digested and generated the calibration curve shown in Figure 5. An inorganic blank soil and Contract Laboratory Program (CLP) inorganic soil certified samples (Environmental Resource Associates) were digested and the results agreed with the published values (see Table 2). The check standard values were close to expected concentrations with little fluctuation.

Fish tissue

Analyzing fish tissue for mercury content is becoming more popular. The fat content varies considerably depending on the type of fish. The two dogfish (*Squalus acanthias*) certified reference materials (CRMs) analyzed contained approx. 5% fat (dogfish muscle tissue or DORM-2) and 24% fat (dogfish liver tissue or DOLT-2) (National Research Council Canada,

Ottawa, Canada). The digestion procedure must be rigorous enough to extract any mercury compounds from the fat and convert all forms of mercury into the mercuric ion for analysis. A variety of fish samples were digested on the AP200II using the FISH protocol based on U.S. EPA Method 245.6 (Determination of Mercury in Tissues by Cold Vapor Atomic Absorption Spectrometry). The digested solution tends to be frothy but the PS200II accommodates foaming without loss of accuracy. Freshly prepared mercuric chloride standards in 2% HNO₃, ranging in concentration from blank to 5 µg/g, were used to generate the calibration curve shown in Figure 6. The instrument operating conditions, shown in Table 3, were selected for sensitivity and to minimize frothing. The tissue samples of different species varied considerably, as shown in Table 4, from a low value of -0.008 µg/g for scallop to a high of 0.753 µg/g for tuna. Not surprisingly, the swordfish was also high at 0.722

µg/g. Two dogfish CRMs for trace metals, DORM-2 and DOLT-2, as well as the check standards, showed excellent agreement with expected values, as shown in Table 5.

Others

Preliminary work analyzing blood samples on the AP/PS200II system has been done; a full report will be released at a later date.

Productivity

The versatile AP/PS200II system can be used for a wide variety of samples. The preparation unit and analyzer run independently and can operate simultaneously for maximum productivity gain. A fully automated system delivers rapid, reproducible results, including any required QC samples. Run-to-run consistency is enhanced when a process is automated because each sample is handled in exactly the same manner. The AP/PS200II uses proportionally reduced volumes to minimize reagent consumption and waste, which reduces disposal costs. The key is that the specified method volumes are scaled down proportionally to ensure adherence to the methods. Throughput is increased because the AP200II digests up to 88 aqueous samples simultaneously with little setup time.

Conclusion

There are many challenges facing today's laboratory. Laboratories compete fiercely for business and the productivity of each process needs to be closely scrutinized. The AP/PS200II automated mercury preparation and analysis system is a solution to managing the mercury sample load efficiently and economically.