

Spectroscopy

INDUSTRIAL TRENDS

Sample Preparation

Evaluation of a Block Digester for Preparing Environmental Samples for Trace Metal Analysis

The quest for a simple way to prepare environmental samples for trace metal analysis at the parts-per-billion and parts-per-trillion levels has become like the elusive quest for the Holy Grail itself (1).

Digestion systems containing robotics or designs that automatically carry samples across a hot plate or through a microwave oven are usually too expensive or too big for the typical environmental laboratory where consideration of price and space are foremost in purchasing decisions.

There has been a need for a simple device that reduces acid digestion contamination and increases productivity. This need appears to be met by the Hot Block system (Environmental Express, Mt. Pleasant, SC), a block digester in which the heating area is composed of graphite and the surrounding box is made of a high-temperature thermoplastic. It has no exposed metallic parts. With a 15 in. × 15 in. footprint, it holds as many as 36 graduated 50-mL polypropylene vessels and has a temperature range of ambient to 180 °C controlled to within 1.5 °C. However, because polypropylene vessels are used, one would not want to increase the temperature much higher than 95 °C, which is the maximum temperature for EPA digestions (2).

The manufacturer claims that the unit's unique design results in

- cost savings due to disposable digestion vessels
- uniform temperature across the block
- minimal radiant heat loss

- reduced metallic contamination
- higher throughput of samples.

This study represents an independent assessment of the block digester, which has been set up in two different environmental laboratories to verify or disprove the manufacturer's claims.

EQUIPMENT

Studies were carried out using the 50-mL, 36-well Hot Block (P/N SC100) equipped with two individual 18-cup trays (P/N SC200) and polypropylene digestion cups (P/N SC 500), which were supplied by Environmental Express. Temperature measurements were made using a total-range digital thermometer (VWR, South Plainfield, NJ) that is traceable to NIST (P/N 61161-277).

The digestors were located in two separate laboratories: Progress Environmental Laboratory, Tampa, Florida, and Environment One Laboratory, Greenville, North Carolina. Identical studies were performed at each site to assess the effect of site location on digestion parameters.

The measuring instrument used by Progress Environmental Laboratory was a Thermo Jarrell Ash (Franklin, MA) 61E Trace ICP equipped with an axial torch. Conditions used for analysis have been reported elsewhere (3). The measuring instrument used by Environment One Laboratory was a Perkin-Elmer (Norwalk, CT) Optima ICP equipped with an axial torch.

EXPERIMENTAL DESIGN

To test the manufacturer's claim of uniform temperature across the heating block, 12 digestion cups filled with 50 mL of deionized water were placed in predetermined wells in the block (Figure 1) and monitored for temperature every 30 min for a total of 2 h as the

target temperature of 95 °C was reached. In addition, the final volume of water remaining in the digestion cups was measured to assess the evaporation after heating. The results from both laboratories are shown in Tables I and II.

To test the manufacturer's claim of reduced contamination due to the unit's non-

metallic construction, 12 digestion cups filled with an acid blank of 5% HCl and 1% HNO₃ were placed in the same wells as depicted in Figure 1. The digester was heated to a target temperature of 95 °C for 2 h, after which the acid blank digests were diluted to 50 mL and analyzed by axial torch ICP for selected elements. Table III shows the results of the acid blank analysis from both laboratories.

Finally, both laboratories used the block unit for routine digestion of water and soil samples. The recovery of predigestion spikes added to both water and soil samples were measured. The recovery percentage from samples digested on different days and from random well sites on the block were assessed to measure the interday reproducibility of metal analyses from digests using the block digester. The data for water digests are reproduced in Table IV; the data for soil digests are given in Table V.

RESULTS AND DISCUSSION

Temperature uniformity. The wells used to monitor the water temperature during heating (Figure 1) were selected to represent the areas where excessive cooling would be most likely to occur (well sites 1, 2, 3, 4, 7, 10, 11, and 12) and the areas where excessive heating would be most likely to occur (well sites 5, 6, 8, and 9).

As shown in Tables I and II, the temperature was extremely uniform where the relative standard deviation of the temperatures across the entire block was generally less than 1%. Hot spots and cool spots, as are usually found on hot plate surfaces, were not observed with the block digester. This finding is backed up by the uniform volume of water remaining in the digestion cups after heating.

The necessity for setting the control temperature differently at the two sites (111 °C vs. 119 °C) was probably due to differences in incoming voltages between the two laboratories and shows the importance of having this control feature incorporated in the unit's design.

Interestingly, the digester took longer to heat to the target temperature at Progress Environmental Laboratory. It was observed dur-

Table I. Temperature data from Environment One Laboratory. The Hot Block control temperature was set at 111 °C.

Hot Block Well. No.	Initial Temp (°C)	30 Min (°C)	60 Min (°C)	90 Min (°C)	120 Min (°C)	Final Volume (mL)
1	24.7	93.7	94.3	92.8	92.2	22
2	24.7	94.2	94.0	93.7	93.2	22
3	24.7	92.3	93.8	93.8	92.9	22.5
4	24.7	94.6	95.7	94.2	92.7	21.5
5	24.7	94.1	94.8	94.2	92.5	22.5
6	24.7	93.9	94.1	93.7	93.5	22
7	24.7	94.1	94.4	94.9	92.5	22
8	24.7	94.3	94.5	93.9	92.4	22
9	24.7	94.4	94.5	94.5	92.6	22
10	24.7	93.3	94.5	94.1	92.9	22.5
11	24.7	94.6	94.9	93.8	93.4	21
12	24.7	93.4	93.3	93.8	93.0	22.5
Average		93.9	94.4	94.0	92.8	
% RSD		0.7	0.6	0.5	0.4	

Table II. Temperature data from Progress Environmental Laboratory. The Hot Block control temperature was set at 119 °C.

Hot Block Well. No.	Initial Temp (°C)	30 Min (°C)	60 Min (°C)	90 Min (°C)	120 Min (°C)	Final Volume (mL)
1	29.0	81.0	95.3	94.7	93.1	18
2	29.0	84.1	95.4	95.1	94.2	19
3	29.0	81.3	95.6	96.1	94.3	18.5
4	29.0	85.6	93.9	96.1	94.5	20
5	29.0	86.2	95.0	95.3	94.0	19.5
6	29.0	87.4	95.8	96.0	94.2	20
7	29.0	86.4	95.1	95.3	92.8	20
8	29.0	87.8	93.5	95.5	94.1	20
9	29.0	90.2	94.8	96.0	92.7	20
10	29.0	90.3	95.1	95.4	93.5	18.5
11	29.0	91.5	92.9	95.9	95.2	19
12	29.0	90.6	92.8	95.1	93.5	19.5
Average		86.9	94.6	95.5	93.8	
%RSD		4.0	1.1	0.5	0.8	

Table III. Preparation blank concentrations. All ICP detection limits are from Progress Environmental Laboratory except Al and Fe, which are from Environment One Laboratory.

Element	Concentration (ppb)
Ag	<1.0
Al	<50
As	<2.4
Ba	<3.0
Be	<1.0
Cd	<1.0
Co	<2.0
Cr	<2.0
Cu	<3.0
Fe	<10
Mn	<3.0
Ni	<2.0
Pb	<1.4
Se	<1.7
Sn	<2.0
V	<1.0
Zn	<1.0

Table IV. Average recoveries of predigestion spike and spike duplicate from soil digests on six separate days using the Hot Block. The spike concentration was at 200 ppb ($n = 12$). Data are from Progress Environmental Laboratory.

Element	Spike Recovery (%)
Ag	95 ± 6
As	97 ± 7
Ba	99 ± 12
Be	98 ± 8
Cd	95 ± 6
Co	99 ± 6
Cr	97 ± 5
Cu	99 ± 9
Mn	100 ± 6
Ni	95 ± 5
Pb	95 ± 8
Se	95 ± 5
V	99 ± 6
Zn	96 ± 12

Table V. Average recoveries of predigestion spike and spike duplicate from water digests on six separate days using the Hot Block. The spike concentration was at 500 or 1,000 ppb ($n = 12$). Data are from Environment One Laboratory.

Element	Spike Recovery (%)
Ag	109 ± 4
Al	96 ± 8
As	101 ± 7
Ba	105 ± 12
Be	99 ± 6
Cd	98 ± 6
Co	96 ± 5
Cr	96 ± 6
Cu	105 ± 4
Fe	93 ± 9
Mn	97 ± 6
Ni	97 ± 6
Pb	97 ± 6
Se	100 ± 5
V	99 ± 4
Zn	100 ± 5

ing the initial setup that the flow of air into the hood at Progress was much higher than that at Environment One and that the room temperature was lower at Progress than at Environment One. We therefore concluded that this higher flow of cooler air contributed to the cooling of the unit and must be taken into consideration when setting it up.

Preparation blanks. Hot plate acid digestion is often beset with a corroded metal hot plate and rings eaten into the metal heating surface caused by acid spilled from beakers. Contamination problems are common with elements such as Al, Cr, Fe, Ni, and Zn when axial torch ICP and ICP-MS instruments are used.

This study confirmed that, because of the digester's graphite and plastic construction, contamination is not an issue. Adding to the advantage of inert construction material is the use of the disposable polypropylene digestion cups with lids. Avoiding the use of glass is highly beneficial in reducing contamination at the parts-per-billion and parts-per-trillion concentration levels.

The digester proved to be very advantageous at Environment One, where acid digestion space was at a premium and corrosion products from a metal hot plate were causing elevated blanks for aluminum and iron. The data for aluminum and iron in Table III come from Environment One and show that, although the blanks for these two elements are still elevated, the levels of aluminum and iron have been reduced significantly since the installation of the unit. The authors expect these levels to drop further as the laboratory environment is further cleansed from previous corrosion products stemming from the metal hot plates.

Spike recoveries. The ultimate test of a digestion system is based on whether one can consistently prepare spiked samples for which the spiked recoveries fall within acceptable limits. Productivity suffers when labs are forced to rerun samples because of contaminated preparation blanks or unacceptable spike recovery levels.

This study was designed to evaluate the in-

terday variation of predigestion spike recoveries from both soils and waters as is required by laboratories that are setting up accuracy control charts. Acceptable recoveries are due not only to uniform heating and inert construction materials but also to the ease of sample handling.

The unique design of the digestion cups used with the Hot Block allows the analyst to dilute the final digest to volume in the digestion cup and to either decant the sample into ICP autosampler cups or to use the digestion cup itself as an autosampler cup. Eliminating the need to transfer the digest from a beaker to a volumetric flask or cylinder, and in many cases avoiding filtration aids in ensuring that spiked digests will consistently fall within acceptable quality control windows thereby reduces the need for reruns.

CONCLUSION

The claims made by the block digester's manufacturer have been verified through independent testing. The Hot Block indeed does seem

to not only reduce labor and glassware costs, but the nonmetallic construction reduces background contamination. The uniform heating of samples results in even sample evaporation.

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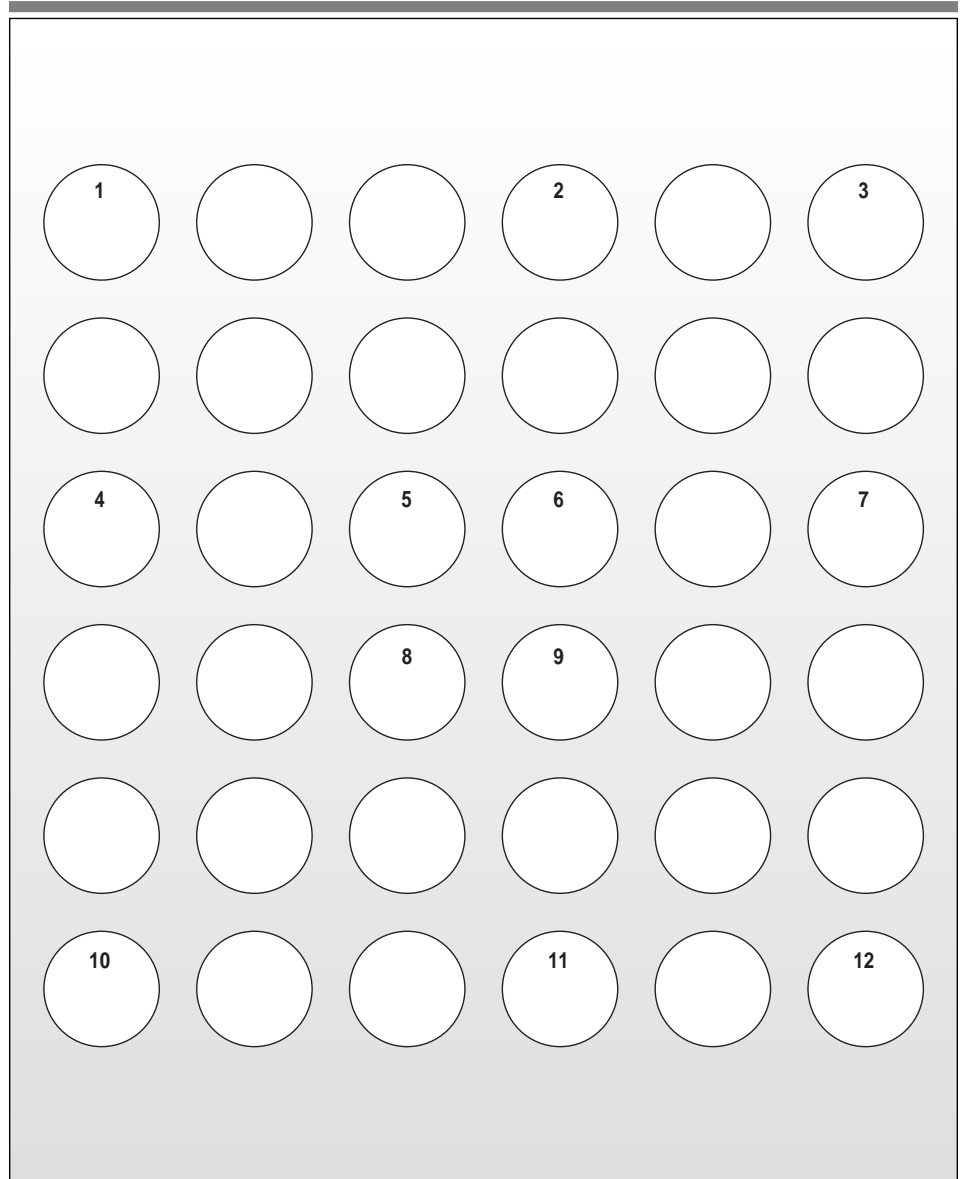


Figure 1. Designation of block digester wells where the temperature of water in digestion cups was measured.