

Graphite furnace AAS

Fully automated and easier-to-use systems designed for increased productivity continue to emerge.

Britt E. Erickson

When axial inductively coupled plasma atomic emission spectrometry (ICP-AES) hit the market in the early 1990s, some manufacturers of graphite furnace atomic absorption spectrometry (GFAAS) systems feared it was time to start looking for a new job. But despite increased pressure from ICP and other competing techniques, GFAAS continues to hold a place in the elemental analysis market.

"Graphite furnace sales took a big hit about eight years ago," recalls David Pfeil of TJA Solutions. This was due to the declining environmental testing market and the introduction of axial ICP-AES, which was touted as being sensitive enough to detect low levels of elements traditionally analyzed by GFAAS, such as lead, thallium, arsenic, and selenium. "ICP can do all 23 metals targeted by EPA's Contract Laboratory Program, including the four traditionally done by graphite furnace, faster than four graphite furnaces can do four elements," says Pfeil. For routine environmental testing labs, ICP-AES became an attractive alternative to GFAAS. From 1993 to 1997, AA sales in North America dropped significantly, says Bob Clifford of Shimadzu. ICP prices dropped, and in response, AA prices dropped. Today, a low-end ICP-AES system costs about



Table 1. Summary of selected GFAAS systems.

Model	AI 1200	Avanta UltraZ	Avanta Σ (with GF3000)	SIMAA 6000	AAnalyst 800
Manufacturer	Aurora Instruments 1001 East Pender St. Vancouver, B.C., Canada V6A 1W2 800-883-2918	GBC Scientific Equipment 3930 Ventura Dr. Arlington Heights, IL 60004 800-445-1902	GBC Scientific Equipment 3930 Ventura Dr. Arlington Heights, IL 60004 800-445-1902	PerkinElmer Instruments 761 Main Ave. Norwalk, CT 06859 800-762-4000	PerkinElmer Instruments 761 Main Ave. Norwalk, CT 06859 800-762-4000
URL	www.aurora-instr.com	www.gbcsoci.com	www.gbcsoci.com	www.perkinelmer.com	www.perkinelmer.com
Background correction	Deuterium and Self-Reversal	Zeeman	Deuterium	Longitudinal Zeeman	Deuterium and longitudinal Zeeman
Flame capability	Yes	No	Yes	No	Yes
Autosampler capacity	180 test tubes or 4 x 96 microplates	150	40	80	146
Number of source lamps	5	8	8	4 (HCLs or EDLs)	8 (up to 4 EDLs)
Furnace tube design	Transverse	Transverse	Longitudinal	Transverse	Transverse
Detector	PMT	PMT	PMT	Solid-state (photodiode)	Solid-state (photodiode)
Options	Single/double beam switching capability; flame/furnace switching capability; built-in high-intensity HCLs; continuous-flow vapor generation	High-intensity Super Lamps; CCD imaging capability inside graphite tube	Hydride generation; mercury concentrator; high solids analyzer; automatic dilution system; high-intensity Super Lamps; CCD imaging capability inside graphite tube	Ultrasonic slurry sampler; automated flow injection (FI) cold vapor mercury and hydride generation; FI-GFAAS coupling kit	AutoPrep 50 Dilution System; flow injection (FI) cold vapor mercury and hydride generation; FI-GFAAS coupling kit; ultrasonic slurry sampler
Special features	Small footprint (68 x 55 x 37 cm, including power supply); transverse heating with high heating rate (3800 K/s); automatic sample dilution; universal autosampler for use with all atomizers; two temperature probes for low-/high-temperature control; automatic lamp alignment	Ultra-fast magnetic field modulation; variable magnetic field strength; self-aligning graphite tubes; automatic lamp selection and alignment; automatic dilution; automatic addition of matrix modifiers; low maintenance; compact size	Fully automated, including automatic burner rotation for flame, automatic dilution, and automatic addition of matrix modifiers; Asymmetric Modulation for improved S/N; fast ULTRA-PULSE background correction	Simultaneous analysis of up to six elements; automatic generation of reference solutions; automatic dilution	Automatic flame/furnace switching; solid-state furnace heating; uniform heating rate (190–250 V); automatic dilution; automatic injection into pre-heated tube; advanced data handling; automatic tube resistance compensation

EDL = electrodeless discharge lamp

\$50,000, which overlaps with the upper end of the GFAAS range (\$35,000–60,000).

The AA market began to rebound when analysts realized that the increase in sensitivity gained by axial ICP came at the cost of increased interferences, says Glen Carnrick of PerkinElmer Instruments. “Graphite furnace sales have actually started to pick up again. They haven’t come back to what they were, but they now remain quite steady,” he says. As for competition with ICPMS, “there will be pressure if the manufacturer can figure out how to make an ICPMS that performs well for about

\$90,000,” Carnrick adds. But for now, ICPMS still remains in a class of its own, with conventional quadrupole systems starting at about \$150,000 (*Anal. Chem.* **1999**, *71*, 811 A–815 A).

In contrast to flame AAS, which has had little improvement in detection limits and performance over the past 10–15 years, GFAAS continues to improve even to this day, albeit slower now that it is a mature market, says Carnrick. To find out just what improvements have been made recently, *Analytical Chemistry* surveyed several GFAAS manufacturers. Although not comprehensive, a summary of selected

commercially available GFAAS systems in North America is given in Table 1. The GFAAS market in Asia and Europe encompasses manufacturers not included in this review.

New developments

When *Analytical Chemistry* last reviewed the GFAAS market (*Anal. Chem.* **1995**, *67*, 51 A–55 A), solid-state detectors or charge transfer devices (CTDs) did not even get a mention. Today, they have found more than one use in GFAAS. PerkinElmer’s high-end AAnalyst 600, 700, 800 systems all use solid-state detectors. “As

Table 1. Summary of selected GFAAS systems (continued).

Model	AA-6800 Series	SOLAAR M Series	SPECTRAA 220Z/880Z	SPECTRAA Series
Manufacturer	Shimadzu Scientific Instruments 7102 Riverwood Dr. Columbia, MD 21046 800-477-1227	TJA Solutions 27 Forge Pkwy. Franklin, MA 02038 800-229-4087	Varian, Inc. 2700 Mitchell Dr. Walnut Creek, CA 94598 800-926-3000	Varian, Inc. 2700 Mitchell Dr. Walnut Creek, CA 94598 800-926-3000
URL	www.shimadzu.com	www.tjasolutions.com	www.varianinc.com	www.varianinc.com
Background correction	Deuterium and Self-Reversal	Deuterium and Zeeman	Zeeman	Deuterium
Flame capability	Yes	Yes	No	Yes
Autosampler capacity	68	60	50	50
Number of source lamps	8	6	4 (220Z), 8 (880Z)	2 (50/55), 4 (110/220), or 8 (880)
Furnace tube design	Longitudinal	Longitudinal	Longitudinal	Longitudinal
Detector	PMT	PMT	PMT	PMT
Options	Vapor mercury and hydride generation	Continuous-flow vapor system; segmented flow injection vapor system; heated hydride cell; in-line diluter; CCD imaging capability inside graphite tube	High-intensity UltrAA lamps; continuous-flow vapor generation; unattended hydride and cold-vapor mercury analysis; off-line sample preparation; validation packages	High-intensity UltrAA lamps; continuous-flow vapor generation; unattended hydride and cold-vapor mercury analysis; off-line sample preparation; validation packages
Special features	Automatic flame/furnace switching via keyboard; same autosampler for flame and furnace; automatic dilution of off-scale samples (up to 300 times); auto-addition of matrix modifiers; multipoint calibration curve from single standard	Fully automated optimization steps; two atomizer compartments (one for furnace autosampler and one for flame autosampler); small footprint; automated validation package with full quality control software and audit trail reporting	Multitasking software automatically stores method, sequence parameters, sample labels, and data; low thermal mass graphite tubes for improved S/N; peak area algorithm minimizes effects of noise; same features as SPECTRAA Series	Automatic dilution of over-range samples; calibration from a single standard; remote servicing and support; 14 EPA-compliant and 10 user-defined QC tests; same features as Zeeman systems

in ICP, AAS is moving to that area,” says Carnrick. “We recognized the advantages of solid-state detectors years ago, in terms of increased quantum efficiency. The higher the quantum efficiency, the more light throughput, the better the detection limit. That’s the name of the game in graphite furnace,” he says.

But the same issues that apply to ICP-AES (*Anal. Chem.* **1998**, *70*, 211 A–215 A) with regard to CTDs, also apply to GFAAS. Photomultiplier tubes (PMTs) are generally more sensitive and linear than CTDs, and not all manufacturers are convinced that the speed, flexibility, and multiplex advantage of solid-state detectors are worth the compromise.

GFAAS typically involves a minimum

of four stages—drying (to remove water), pyrolysis (to remove matrix interferences), atomization (to vaporize the metal analyte), and cleaning (to remove leftover residue). Traditionally, a simple mirror assembly is used to look inside the graphite furnace tube during the various stages to aid in method development. Some manufacturers now offer GFAAS systems equipped with a CCD camera, which continuously records images of the events taking place inside the tube.

“We show a live picture of what is going on inside the furnace at all times,” says Sally Dowling of GBC Scientific. “The real benefit is that you can watch how the sample dries and how the gases evolve during pyrolysis,” says TJA Solutions’ Pfeil. “If

the sample gets too hot and boils, it will splatter and end up outside the cuvette, resulting in a loss of signal,” he says. The CCD images provide a way to confirm that all of the sample stayed in the tube.

The depth of the sample probe is also critical in GFAAS, particularly when using an autosampler, says Pfeil. “If the probe isn’t all the way at the bottom of the tube, a drop can hang on the tip,” he says. “With electronic sample viewing, you can look into the furnace tube and see exactly where the needle is with respect to the graphite tube. You can see how it is depositing your sample and whether the droplet is even. When the needle comes out, you can tell whether the droplet stuck to the needle or whether it stayed

product review

where you want it in the furnace,” adds Dowling.

Because GFAAS is a mature technique, there haven't been major technological advances in the past five years. Most improvements have centered

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around making GFAAS systems easier and faster to use. Features such as automated flame-to-furnace switching, self-aligning graphite furnace tubes, computer-coded source lamps (automatic wavelength and slit selection), automatic sample dilution, and automatic standard preparation are now available. Today, nearly every aspect of GFAAS has been touched by automation.

The users

Environmental testing has traditionally been one of the biggest applications of GFAAS. Several EPA methods still require the use of GFAAS. Although steps have been taken toward a more flexible, performance-based measurement system, which would allow the use of alternative techniques such as ICPMS, few environmental testing laboratories have actually migrated in that direction. And even in laboratories that are big enough to afford an ICPMS system, “You're still going to find at least one graphite furnace system to back up results of other techniques,” says Doug Shrader of Varian, Inc. GFAAS is still widely used in industrial areas, such as catalysts and mining. State agricultural labs also use GFAAS for determining metals, such as selenium and arsenic, in soil samples.

“One of the big markets for graphite furnace in the past 10 years has

been blood lead analysis,” says Carnrick. It is not uncommon for a state laboratory to have 6–10 graphite furnace systems dedicated to blood lead analysis, he says. “Blood lead is a major problem. It is still one of the

most important environmental health problems we have to deal with.

Many states have mandatory laws for screening children for lead exposure,” says Patrick Parsons of the New York State Department of

Health's Lead Poisoning Laboratory. In contrast to EPA's approved standard methods for environmental laboratories, the National Committee for Clinical Laboratory Standards (NCCLS) has its own set of recommended methods for clinical laboratories. According to Parsons, who chairs the lead subcommittee for NCCLS, the GFAAS method for blood lead is so well established and validated that a consensus method has been proposed by NCCLS. To have a consensus method, the major GFAAS manufacturers had to agree on it, which is quite an accomplishment, he says. An alternative method proposed by the subcommittee for lead analysis is anodic stripping voltammetry, although future revisions could include ICPMS and newly emerging portable methods for blood lead. “Graphite furnace

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AA spectrometry is currently attractive because of its reasonable cost and because it can be automated,” adds Parsons.

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