Pyrolytic Graphite Platforms – Guidelines for use with the GTA-95 Graphite Tube Atomizer

Application Note

Atomic Absorption

Author

L. M. Voth

Introduction

This application note provides guidelines for the use of pyrolytic graphite platforms with the Agilent GTA-95 graphite tube atomizer and PSD-95 programmable sample dispenser. Following a preliminary discussion on why and when the analyst should use the graphite platform, procedures for positioning the platform and adjusting the sample dispenser are outlined as well as guidelines for developing effective temperature programs. Practical suggestions for dealing with difficult sample matrices are included to aid methods development. A companion AA at Work, "Pyrolytic Graphite Platforms"[1] is highly recommended to provide further information.

Why and When Should the Pyrolytic Graphite Platform be Used?

The pyrolytic graphite platform provides a highly effective means of reducing vapor phase chemical interferences in many analytical situations that are plagued by matrix-dependent interferences. For further information, a general discussion of matrix interferences and techniques for controlling them is included in AA at Work "Dealing with Matrix Interferences in the Determination of the Priority Pollutant Metals by Furnace AA" [2].

Temperature is a major factor in vapor phase chemical interferences. In pulse type graphite tube atomizers the sample is deposited directly on the furnace wall and is vaporized from the surface of the graphite during a time of rapidly increasing wall temperature. The sample is not heated to the maximum atomization temperature before vaporization occurs. In other words, the analyte vaporizes and can leave the furnace at a temperature much lower than that attained later in the atomization cycle. The vapor temperature lags behind the furnace wall temperature. The cooler vapor temperature increases the probability of interfering reactions. For example, volatile compounds such as monohalides can be formed which remain stable over the vaporization temperature range and can be lost before the temperature is hot enough to decompose them.

Agilent Technologies

L'vov has shown that in these situations such interferences can be effectively reduced by vaporizing samples in a furnace which has already reached a steady-state temperature. The L'vov proposal involves the use of a graphite platform which is inserted into the graphite furnace tube. The sample solution is deposited on the platform instead of the furnace wall, and during atomization the platform temperature lags the furnace wall temperature by several hundred degrees. Under these conditions, the analyte compounds are not vaporized until the gaseous environment in the furnace has approached a higher steady-state temperature.

The vaporization of the sample into a hotter gaseous environment minimizes vapor phase interferences. Use of the platform will also assist in the reduction of background absorption through the increased dissociation of molecular species at the higher gas phase temperature achieved in the furnace prior to analyte vaporization [1,3,4].

Figure 1 illustrates the wall atomization peak for 20 µg/L Pb in 0.2% NaCI. The HP-86 graphics program displays the analyte atomization peak as well as the background absorbance peak. On the GTA-95 VDU the analyte atomization peak is superimposed on a profile of the temperature program. This provides the analyst with valuable information on background absorbance, peak shape and appearance time.

Figure 2 illustrates the atomization peak of the same sample when the graphite platform is used. A significant reduction in background absorbance is indicated by the HP-86 graphics display. The delay in analyte atomization is evident by the temporal shift of the atomization peak shown by both the GTA-95 VDU and the HP-86 graphics display.

In general, the pyrolytic graphite platform will be most useful in reducing chemical interferences for the more volatile elements. Because the platform heats at a slower rate than the graphite tube wall, the absolute sensitivity in peak height will usually be less with the platform. This is particularly true for the less volatile elements such as chromium, aluminium, andvanadium. In fact, the platform atomization of these elements may produce such broad tailing peaks that accurate measurement is difficult and memory from incomplete atomization may occur. Atomization from the graphite tube wall is the most effective means of determining the more refractory elements (where the recommended atomization temperature exceeds 2400 °C). For the more volatile elements, though peak height signals may be somewhat reduced with platform atomization due to the slower heating rate, peak area measurements will often be comparable. Occasionally, there may be determinations where sensitivity improves in both peak height and peak area when the platform is used.

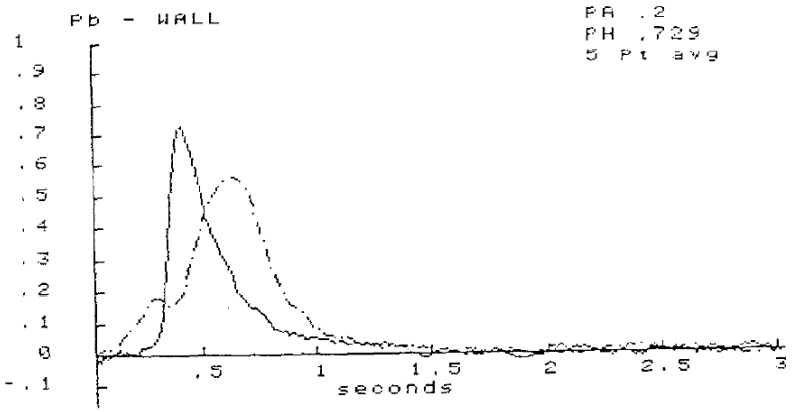
When properly utilized with an effective temperature program, the pyrolytic graphite platform technique along with other techniques for reducing matrix interferences, such as matrix modification, can eliminate the need for time-consuming standard additions. Direct calibration with appropriate standards can often be used to obtain accurate and precise results in difficult sample matrices. The remaining portion of this AA at Work will focus on guidelines for positioning the platform, adjusting the sample dispenser capillary, choosing optimum sample volume, and developing temperature programs. Practical tips and suggestions are included to help the analyst develop effective methods and obtain accurate and precise results with difficult sample matrices.

Platform Installation and Sample Dispenser Adjustment

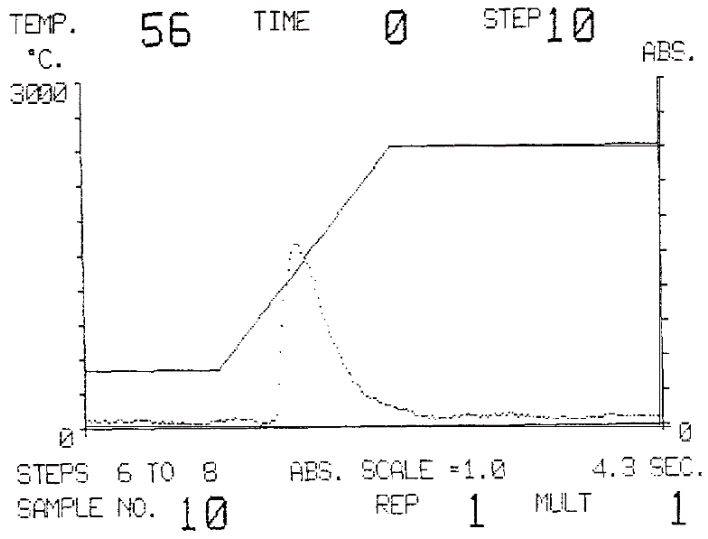
The platform must be aligned with respect to the graphite tube entrance port so that the sampler dispensing capillary is exactly perpendicular to the level surface of the platform during sample deposition. If this is not the case, problems may be encountered with difficult sample matrices. For example, the sample droplet may dispense toward one edge and partially deposit on the tube wall or even underneath the platform. Incorrect sample deposition is illustrated in Figure 3. During the analysis of samples with high surface tension this can cause the platform to shift as the capillary tip leaves the graphite tube, particularly when larger sample volumes are used.

Placement of Platform in Graphite Tube

After inserting the platform in the graphite tube, use plastic tweezer or a disposable micro-pipet tip to slide the platform until the end protuberances "slip" over the ends of the central plateau. A small disposable micro-pipet tip (small enough to fit through the graphite tube entrance port and touch the platform) can then be used to align the platform in relation to the graphite tube entrance port. If the platform is not perpendicular to the pipet inserted through the entrance port, use the pipet tip to tap either side of the platform, moving it slightly to a perpendicular position. When the platform position is satisfactory, place the graphite tube in the furnace workhead, taking care to prevent any jarring that may dislodge the platform. The graphite tube should be positioned in the furnace workhead so that the entrance port is centered. A small flashlight or desk lamp is helpful. Then recheck that the platform is perpendicular to the pipet tip inserted through the entrance port of the graphite tube, using the mirror provided with the GTA-95. Because the mirror is not level when used to view the graphite tube, it is impossible to determine whether the platform is positioned properly, unless you insert the pipet tip



HP-86B Graphics Display



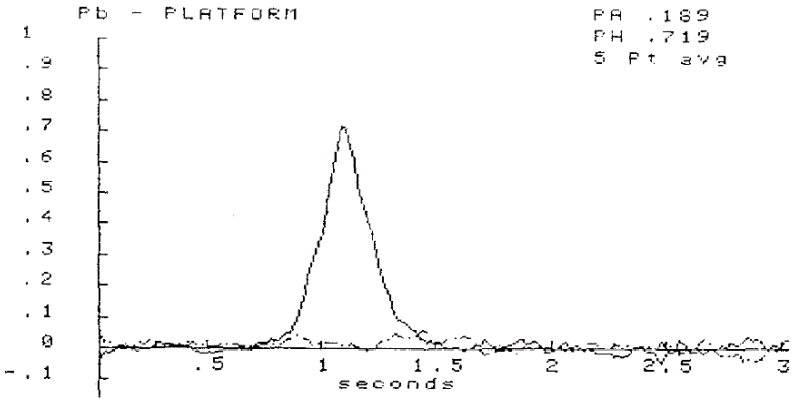
GTA-95 VDU

Figure 1. Wall atomization (20 µg/L Pb; 0.2% NaCl).

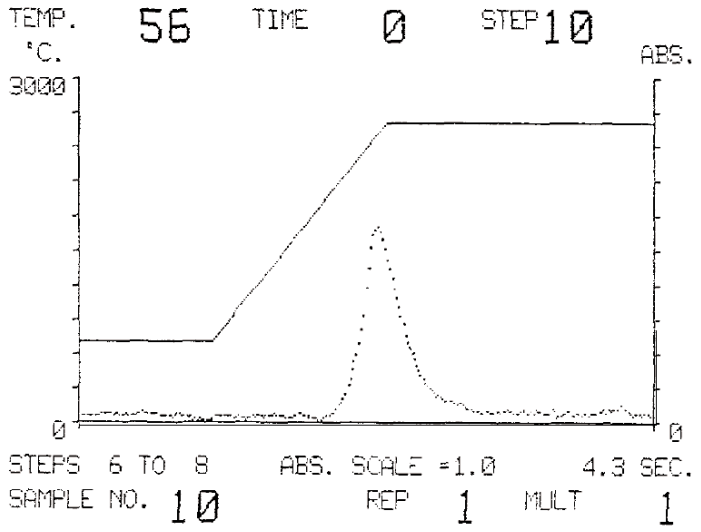
or, alternatively, start the sample dispenser and check that the sampler dispensing capillary is perpendicular to the platform.

Alignment in the AA Light Path

The furnace alignment for maximum light throughput is outlined in the "Operation Manual for the GTA-95 Graphite Tube Atomizer" sections 4.4 and 4.5 [5]. If the graphite tube is properly positioned for wall atomization the only adjustment necessary after the insertion of the platform is a slight lowering to maximize the light throughput above the platform [1]. Reduced height slits may be advantageous for elements at wavelengths above 350 nm.



HP-86B Graphics Display



GTA-95 VDU

Figure 2. Platform atomization (20 µg/L Pb; 0.2% NaCl).

Sample Dispenser Adjustments

The sampler dispensing capillary must be adjusted to a higher position to accommodate the platform. With the first injection following a change from wall atomization to platform atomization, manually catch the sampler arm at the injection port, press the stop key on the furnace and sampler control unit, and adjust the depth of the sampler dispensing capillary to a higher position before the capillary tip hits the platform. (The force of the capillary hitting the platform, particularly at an angle not perpendicular, could shift a carefully positioned platform.) If the sampler capillary is properly adjusted for wall atomization, a depth adjustment should be all that is necessary. In general, adjust the depth of the capillary tip to a position just barely above the surface of the platform. This will

force the sample to "push out" to the ends of the indented platform and will produce the best results for larger sample volumes (20 µL) and for sample matrices of high surface tension. The capillary tip should be straight, its position when in the graphite tube should be exactly perpendicular to the bottom of the tube or the surface of the platform, and the capillary tip should be cut straight across so the droplet dispenses straight down and not towards one side or the other.

Proper sample dispensing is outlined in AA at Work "Practical Operation with the GTA-95 Graphite Tube Atomizer" [6].

Sample Volume Optimization

Carefully choose the sample volume to be dispensed onto the pyrolytic graphite platform to achieve optimum precision. Sample volumes will be more limited than those used for wall atomization. Depending on the physical characteristics of the sample such as high surface tension, sample migration can occur when larger volumes are used, as shown in Figure 3. It is important that none of the sample be deposited on the tube wall. The slower heating rate of the platform requires a higher wall temperature program. Any portion of the sample deposited on the tube wall will boil and spatter causing very poor results. The following guidelines will help to prevent dispensing problems.

- The capillary tip should be clean.
  A good technique for removing dirt and grease from the capillary is as follows: Place the GTA-95 and PSD control unit in single sample mode and program a sample size of 70 µL. Fill the sample cup with acetone. While the sample dispenser is picking up the acetone press the stop key on the control unit. The sampler dispensing capillary will remain in the acetone cup after 70 µL has been pulled back. Allow it to remain in this position 5-10 minutes. Then press the reset button and the sampler will rinse out the acetone into the rinse. Do not inject acetone into the furnace. This can be repeated as many times as necessary. If metal contamination has been a problem, 50:50 HNO_3 can be used with the same procedure. The desired sample deposition is shown in Figure 4. Depending on surface tension, the sample can either form a rounded droplet or spread out as shown. Sample solutions of low surface tension, such as organic solvents and aqueous solutions with high acid concentrations, spread out and "lie low" in the indentation of the platform permitting larger volumes (up to 40 µL) to be deposited correctly on the platform. The addition of some matrix modifiers may have the same effect.
- Use 10–25 µL volumes for best results. (10 µL for very difficult matrices).
- The capillary tip should be barely above the surface of the platform when the sample is dispensed to force the sample to spread evenly over the platform indentation.
- Always add 1% HNO_3 to aqueous standards and samples. This lessens surface tension of aqueous solutions. Larger volumes (20–30 µL) of aqueous solutions without added acid form rounded droplets that can "pull up" and migrate as the capillary tip exits the graphite tube (Figure 3).

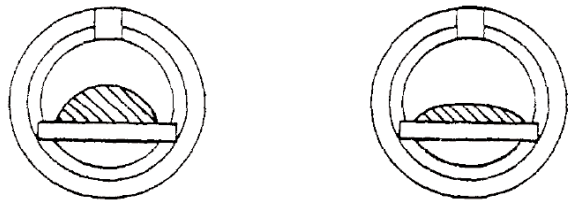


Figure 4. Desired sample deposition.

Platform Temperature Programs

Because the temperature of the platform lags that of the tube wall, the temperature programs used with the pyrolytic graphite platform generally involve higher temperatures than programs for wall atomization. The following guidelines address the dry, ash, atomize, and atomization ramp parameters for platform use.

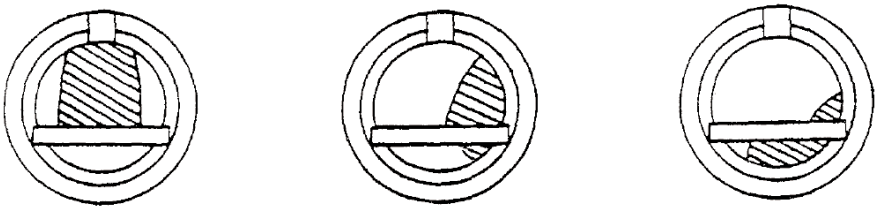


Figure 3. Incorrect sample deposition.

Dry
The platform temperature will be significantly lower than the wall temperature, therefore a much higher temperature program will be required. The following parameters can be taken as a general guideline when using the platform for aqueous samples.

Step no.	Temp (°C)	Time (sec)
1	100	5
2	210	60
3	300	20

Dry parameters for particular samples will vary depending on matrix composition. The last two steps of the platform dry program can change significantly for various matrices. Though the dry times shown here may seem excessive for the sample volumes typically used on the graphite platform (10–25 µL), this can contribute to better precision. Since it is difficult to visually watch the sample dry on the platform using the mirror provided with the GTA-95, longer dry times will prevent poor precision resulting from any boiling or spattering of the sample. With difficult matrices the third step can significantly improve precision, though it may not be required for the analysis of drinking water.

Ash
The appropriate ash temperature will generally be 100–200 °C above that recommended for wall atomization. It will of course also be affected by matrix components and should be carefully investigated as recommended for wall atomization. AA at Work "Practical Operation with the GTA-95 Graphite Tube Atomizer" outlines the procedure for optimizing ash stage parameters [6].

Atomization
Atomization temperatures will either be the same as recommended for wall atomization or slightly higher (100–200 °C) for the more volatile elements. The peak shape can be evaluated either by viewing the HP-86 graphics display or the VDU of the GTA-95. An example of a good platform atomization peak is shown in Figure 2.

Atomization Ramp
The actual heating rate of the platform is lower than that of the tube wall, since the platform is heated predominantly by radiation. Therefore, most elements in a simple aqueous matrix will show a slight loss in sensitivity in peak height measurement compared to wall atomization.

In general, the maximum atomization ramp rate (2000 °C/sec) is used for the platform atomization of all elements. A possible exception would be when a lower ramp rate would give better time separation between the analyte signal and a large background signal and therefore a more accurate absorbance measurement.

Cool Down
The graphite platform will also cool at a slower rate than the tube wall. A cool down step should be included at the end of the temperature program to ensure that the platform is always at the same temperature for each sample injection. This is accomplished by adding a cooldown to 40 °C over 14 seconds followed by a 5–10 second delay at 40 °C.

Signal Measurement – Peak Height or Peak Area?

The reduction of matrix interferences may be most significant in peak area measurements, though both peak height and peak area measurements should be investigated during methods development. Peak height measurements will be larger for most samples and possibly more precise. The accuracy of peak area measurements can be improved by making sure that the read steps closely bracket the peak and do not extend beyond the atomization peak. For example, the inherent flexibility of the GTA-95 allows the temperature program to be modified as shown in the following example:

	Temp (°C)	Time (sec)	Gas flow (L/min)	Read command
End of ash	500	1.0	0.0	*
ramp	2400	0.9	0.0	*
atomize	2400	2.0	0.0	
	2400	2.0	3.0	

Change to:

	Temp (°C)	Time (sec)	Gas flow (L/min)	Read command
End of ash	500	1.0	0.0	*
ramp	2400	0.9	0.0	*
atomize	2400	1.0	0.0	
	2400	1.0	0.0	
	2400	2.0	3.0	

The above temperature programs provide exactly the same heating cycle. The only difference is that in the second program the signal measurement at the atomization temperature is programmed for only 1.0 second rather than 2.0 seconds. This can increase the accuracy of peak area measurements. It is not necessary for peak height measurements.

Summary

Use of the pyrolytic graphite platform is a highly effective means of reducing vapor phase chemical interferences as well as reducing background absorbance. When properly utilized with an effective temperature program, this technique, along with other techniques for reducing matrix interferences such as matrix modification, can eliminate the need for time-consuming standard additions. Standard additions or recovery studies should still be used to confirm that direct calibration is adequate for a particular sample matrix. Operational guidelines for using the graphite platform with the Agilent GTA-95 graphite tube atomizer and programmable sample dispenser have been presented to enable the analyst to obtain accurate and precise results with difficult sample matrices.

Acknowledgement

The author gratefully acknowledges the contribution of Deen Johnson, Varian Instruments, Sugarland, TX.

References

1. P. S. Doidge, "Pyrolytic Graphite Platforms", Varian Instruments at Work No. AA-25, Varian Techtron (Sept. 1982).
2. L. M. Voth, "Dealing with Matrix Interferences in the Determination of the Priority Pollutant Metals by Furnace AA", Varian Instruments at Work No. AA-35, Varian Techtron (Sept. 1983).
3. B. V. L'vov, "Electrothermal Atomization –The Way Toward Absolute Methods of Atomic Absorption Analysis", Spectrochim. Acta., 33B 153 (1978).
4. P. S. Doidge, T. N. McKenzie, "Applications of the Graphite Platform to the Reduction of Interferences in Graphite Furnace Atomic Absorption Spectroscopy", Varian Techtron (1983). (Presented at 1983 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy)
5. "Operation Manual for the GTA-95 Graphite Tube Atomizer", Varian Techtron Publication No. 85-100442-00 (1981).
6. K. G. Brodie, "Practical Operation with the GTA-95 Graphite Tube Atomizer", Varian Instruments at Work No. AA-28, Varian Techtron (March 1983).

For More Information

For more information on our products and services, visit our Web site at www.agilent.com/chem

www.agilent.com/chem

Printed in the USA
November 1, 2010
AA045

Agilent Technologies