Pyrolytic Graphite Platforms

Application Note

Atomic Absorption

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Introduction

In practical graphite tube atomizers, the sample is deposited directly on the furnace wall, and the analyte is vaporlzed while the wall temperature is increasing as a consequence of the high-current pulse passing through the tube. This procedure is characterized by excellent analytical sensitivity, simple operation. and the ability to automate the complete analytical program. In some analytical situations, however, the procedure is subject to severe vapor-phase interferences which cannot be controlled by simple manipulation of furnace parameters. Such interferences are encountered when volatile compounds of the analyte are formed which remain stable over the temperature range at which atomization occurs. In this circumstance, these analyte compounds (mono-halides for example) can be lost before the furnace is hot enough to decompose them.

L’vov has shown that in these situations such interferences can be effectively reduced by vaporizing solutions in a furnace which has already reached a steady-state temperature [1]. 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 by several hundred degrees. Under these conditions, the analyte compounds are not vaporized until the furnace wall has approached a steady-state temperature.

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Description and Installation

The platform designed for use with the Agilent GTA-95 is shown in Figure 1. The platform is machined from solid pyrolytic graphite and the dimensions are such as to allow the platform to be positioned in the furnace tube with the light beam passing above the platform as shown in Figure 2. The end protuberances enable the platform to be located with respect to the elevated central ('plateau') section of the furnace tube while the indentation in the upper surface prevents spillage of the sample over the platform edges. In addition, only the four end proturberances make contact with the tube wall and this minimizes thermal conduction from the tube.

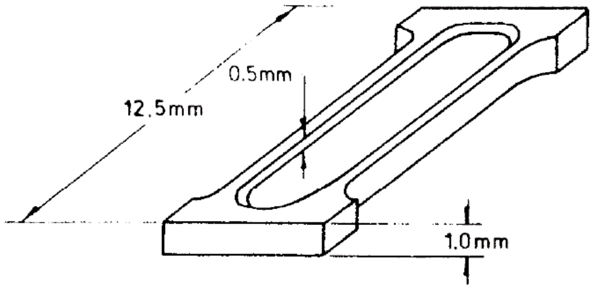


Figure 1. Pyrolytic graphite platform for use with Agilent GTA-95 graphite tube atomizer. (All dimensions are mm).

The platform should be inserted into the furnace tube by using plastic tweezers to slide the platform until the end protuberances 'slip' over the ends of the central plateau. The platform is then aligned with respect to the sample entrance port, as shown in Figure 2. This may be achieved using a disposable micropipette tip to rotate the platform in the tube. The tube may then be replaced in the workhead and the GTA-95 tube clean facility used to remove contamination introduced during the handling process.

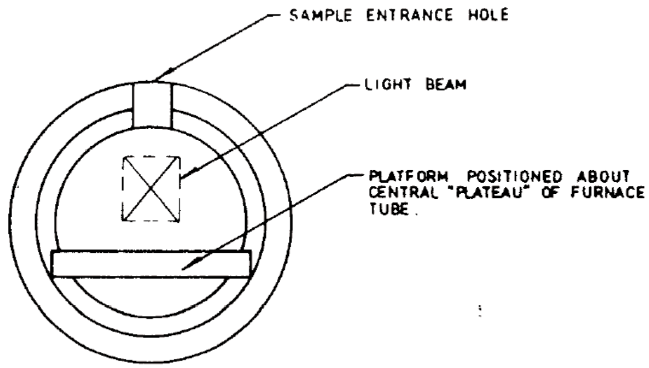


Figure 2. End-on view of platform inside graphite tube.

The height of the furnace with respect to the light path is more critical when the platform is used. The furnace should be aligned for maximum light throughout before the platform is inserted into the tube (see Operation Manual for GTA-95 Graphite Tube Atomizer sections 4.4 and 4.5). After insertion of the platform the furnace may be lowered slightly to further maximize the amount of light passing over the platform. The attenuation of the light beam by the platform should not be more than about 0.02 Absorbance.

General

The platform lags the tube wall in temperature and as a result, the temperature program used with the platform will be different to that used when the sample is vaporized from the tube wall. Generally, the programmed tube temperatures will be higher for most steps of the temperature program when the platform is used.

During the dry stage, heating of the platform by radiation will be negligible and the platform temperature will be significantly lower than the wall temperature, even at steady-state conditions. Therefore, a much higher programmed temperature will be required during the dry stage with the platform. For example, if the dry times are comparable, a dry temperature of 160 °C–170 °C may be required for the platform compared to 90 °C for drying on the wall.

Similarly, the programmed temperature for sample ashing or charring will be one or two hundred degrees higher than for ashing on the wall.

During atomization, the platform heats at a slower rate than the wall and for many elements this characteristic will result in a loss in absolute sensitivity with peak height measurement. This will apply particularly to less volatile elements such as chromium. The platform will generally be more useful in reducing interferences for the more volatile elements. This is because the delay of the time corresponding to the peak of the absorbance signal (and therefore the difference in wall temperature at the peak maxima for signals with wall and platform atomization) increases with increasing volatility of the element, as shown by L'Vov [1]. Also the peak area signals for atomization from the platform and from the wall will be comparable for many elements, while the advantages of the platform in the reduction of matrix interferences are realised to the greatest extent when peak area measurements are used.

With aqueous samples, the maximum volume capacity of the platform is less than that of the tube. With dilute samples, volumes of 10 to 20 µL will generally give the best precision although volumes of 40 µL may be used with no spillage over the platform edges. In the case of organic solvents, the platform may allow the use of greater sample volumes than can be used with the tube. This is probably due to the effectiveness of the indentation in the platform in preventing the spreading of low surface tension solvents.

Reduction of Interferences with Inorganic Matrices

The determination of lead in halide matrices often involves interferences which occur as a result of the vapor phase formation of lead monohalides [1,2].

The effect of the platform in reducing the interference of sodium chloride on lead can be seen in Figures 3 and 4, which show peak absorbance and peak area signals for lead as a function of sodium chloride concentration with both platform and wall atomization. The standard solution, containing 1.0 x 10^{-9}g as Pb, was delivered to the furnace using a PSD-95 programmable sample dispenser. Varying volumes of sodium chloride solution and blank were added to give a total sample volume of 20 µL.

Figure 3 indicates that the peak height signals for atomization from both wall and platform are considerably affected with increasing concentration of sodium chloride. The smallest interference was found with platform atomization and peak area measurement (Figure 4).

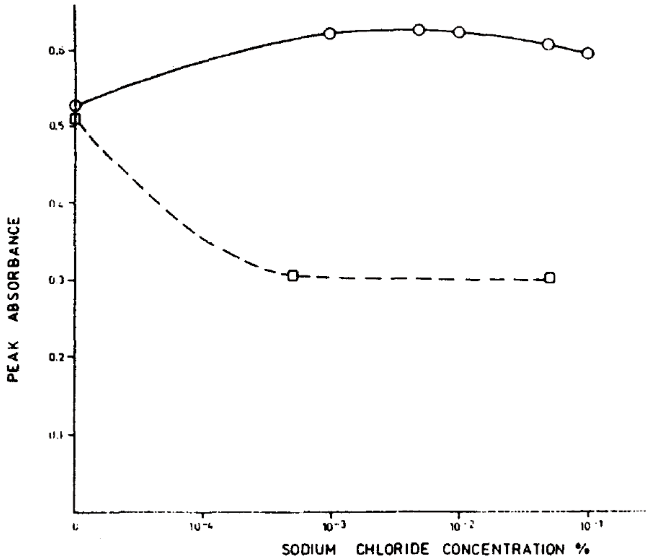


Figure 3. Peak absorbance for lead as a function of sodium chloride concentration.
☐ *Atomization from tube wall*
○ *Atomization from platform*
Sample volume 20 µL
Heating rate 2000 °C per second

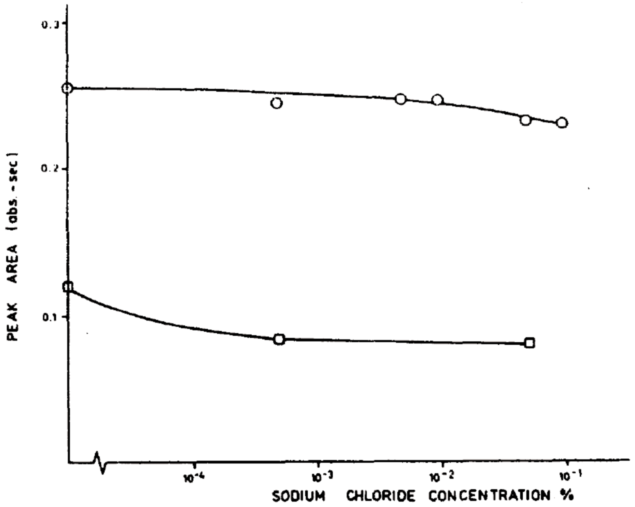


Figure 4. Peak area for lead as a function of sodium chloride concentration
☐ *Atomization from tube wall.*
○ *Atomization from platform*
Sample volume 20 µL
Heating rate 2000 °C per second

The choice of atomization temperature may affect the extent of interference, as can be seen from Figure 5 where the peak area response for lead is shown for atomization temperatures of 1800 °C and 2100 °C. The higher atomization temperature is more effective in this case and this is probably related to the greater efficiency with which the interfering species are decomposed in the higher temperature environment.

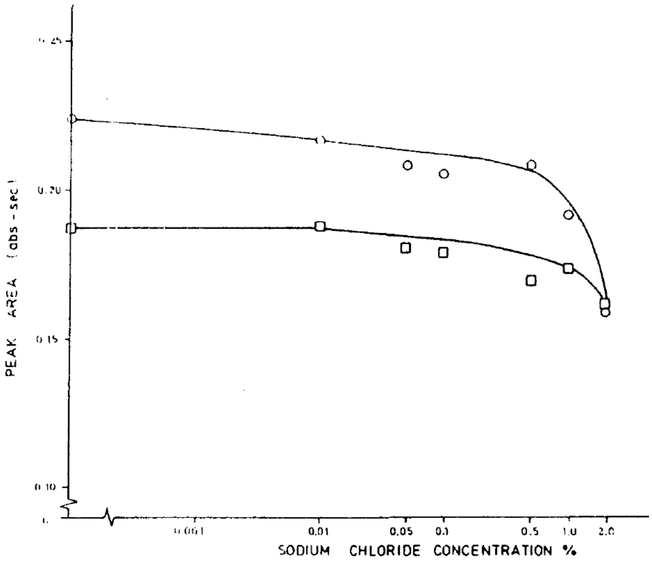
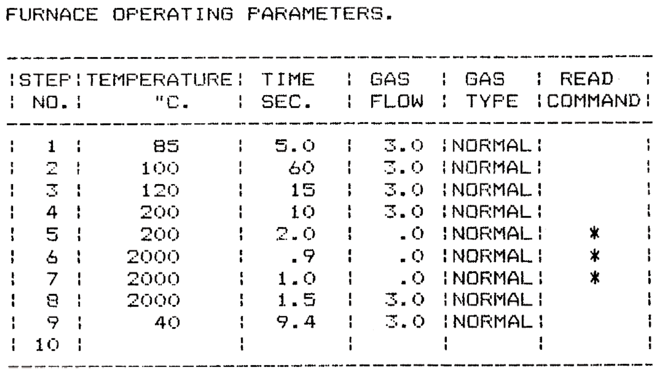


Figure 5. Peak area for lead with atomization from the platform at steady-state temperature.
☐ *1800 °C*
○ *2100 °C*

The furnace operating parameters are shown in Figure 6 for sampling from the wall and in Figure 7 for platform sampling. The higher temperatures in the dry steps (1–4) with sampling from the platform should be noted. The atomization temperatures for lead are comparable with platform and wall atomization, although a longer atomization time was required with the platform due to the later and broader peaks generated when the analyte vaporizes from the platform. During atomization, maximum heating rate of the wall (2000 °Cs^{-1}) was used with the platform since the object is to heat the tube to steady-state temperature before the analyte has substantially vaporized from the platform. The cool-down step was required to allow the platform to cool sufficiently before delivery of the next sample to the furnace. An atomization temperature higher than 2000 °C may require the addition of an extra step in the program of 5 or 10 seconds to allow the platform to cool sufficiently.



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FURNACE OPERATING PARAMETERS.

--------------------------------------------------------
|STEP|TEMPERATURE| TIME  | GAS  | GAS  | READ  |
| NO.|    "C.    | SEC.  | FLOW | TYPE |COMMAND|
--------------------------------------------------------
|  1 |     85    |  5.0  |  3.0 |NORMAL|       |
|  2 |    100    |   60  |  3.0 |NORMAL|       |
|  3 |    120    |   15  |  3.0 |NORMAL|       |
|  4 |    200    |   10  |  3.0 |NORMAL|       |
|  5 |    200    |  2.0  |   .0 |NORMAL|   *   |
|  6 |   2000    |   .9  |   .0 |NORMAL|   *   |
|  7 |   2000    |  1.0  |   .0 |NORMAL|   *   |
|  8 |   2000    |  1.5  |  3.0 |NORMAL|       |
|  9 |     40    |  9.4  |  3.0 |NORMAL|       |
| 10 |           |       |      |      |       |
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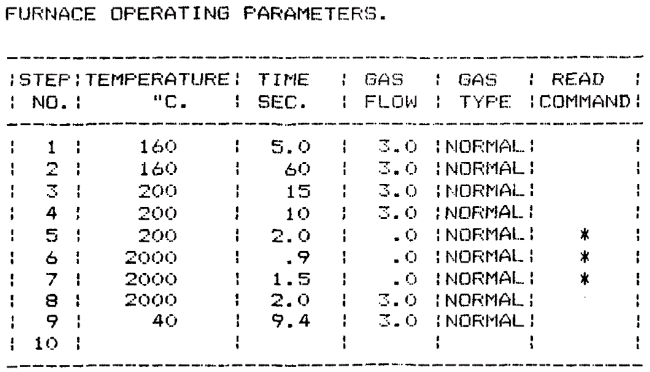
Figure 6. Furnace operating parameters for the determination of lead in sodium chloride solutions. Atomization from the tube wall.



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FURNACE OPERATING PARAMETERS.

--------------------------------------------------------
|STEP|TEMPERATURE| TIME  | GAS  | GAS  | READ  |
| NO.|    "C.    | SEC.  | FLOW | TYPE |COMMAND|
--------------------------------------------------------
|  1 |    160    |  5.0  |  3.0 |NORMAL|       |
|  2 |    160    |   60  |  3.0 |NORMAL|       |
|  3 |    200    |   15  |  3.0 |NORMAL|       |
|  4 |    200    |   10  |  3.0 |NORMAL|       |
|  5 |    200    |  2.0  |   .0 |NORMAL|   *   |
|  6 |   2000    |   .9  |   .0 |NORMAL|   *   |
|  7 |   2000    |  1.5  |   .0 |NORMAL|   *   |
|  8 |   2000    |  2.0  |  3.0 |NORMAL|       |
|  9 |     40    |  9.4  |  3.0 |NORMAL|       |
| 10 |           |       |      |      |       |
--------------------------------------------------------
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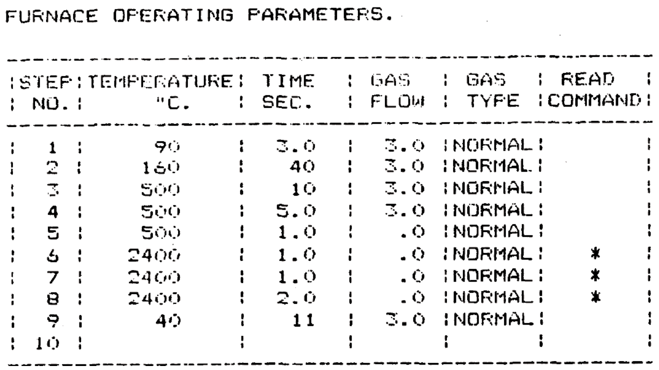
Figure 7. Furnace operating parameters for the determination of lead in sodium chloride solutions. Atomization from the platform.

Determination of Organic Matrices

Vaporization of the sample from the graphite platform may also give advantages over vaporization from the wall in the analysis of organic matrices. The determination of lead in engine oil illustrates certain advantages that may be obtained when the platform is used.

Figure 8 shows the furnace operating parameters used with the graphite platform for engine oil samples diluted 100-fold with DIBK. The program used with sampling from the tube wall was the same except that the temperature for the ash steps (3 to 5) was 300 °C rather than 500 °C since lead was lost at an ash temperature of 350 °C.



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FURNACE OPERATING PARAMETERS.

--------------------------------------------------------
|STEP|TEMPERATURE| TIME  | GAS  | GAS  | READ  |
| NO.|    "C.    | SEC.  | FLOW | TYPE |COMMAND|
--------------------------------------------------------
|  1 |     90    |  3.0  |  3.0 |NORMAL|       |
|  2 |    160    |   40  |  3.0 |NORMAL|       |
|  3 |    500    |   10  |  3.0 |NORMAL|       |
|  4 |    500    |  5.0  |  3.0 |NORMAL|       |
|  5 |    500    |  1.0  |   .0 |NORMAL|       |
|  6 |   2400    |  1.0  |   .0 |NORMAL|   *   |
|  7 |   2400    |  1.0  |   .0 |NORMAL|   *   |
|  8 |   2400    |  2.0  |   .0 |NORMAL|   *   |
|  9 |     40    |   11  |  3.0 |NORMAL|       |
| 10 |           |       |      |      |       |
--------------------------------------------------------
```

Figure 8. Furnace operating parameters for the determination of lead in engine oil samples diluted 100-fold with DIBK. Atomization from the platform.

Figures 9 and 10 show the signals for lead as well as the non-specific absorption due to the organic matrix (broken trace); 5 µL sample volumes were used in each case with the same lead concentration. The most significant feature of the two traces is the elimination of the non-specific absorption when the sample is vaporized from the platform. This is presumably due to more efficient decomposition of the matrix at the higher temperatures experienced by the sample when vaporized from the platform. When the platform was used, there was no detectable non-specific absorption with sample volumes up to 30 µL. The second feature of Figures 9 and 10 is the enhancement of the lead signal when atomization occurs from the platform. This may be due to more efficient atomization of molecular compounds formed by lead in the presence of the organic matrix.

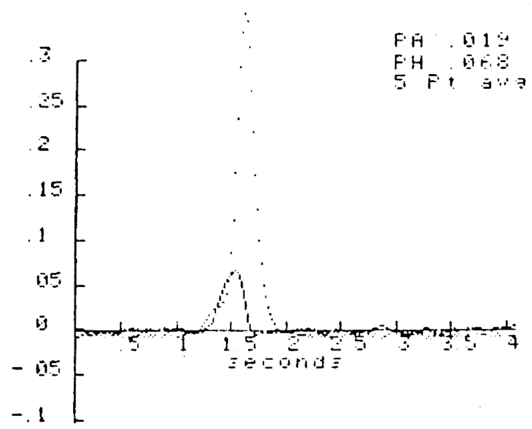

Figure 9. —— *Absorbance signals for lead*
•••• *Background*
Atomization from the tube wall.
Sample volume 5 µL

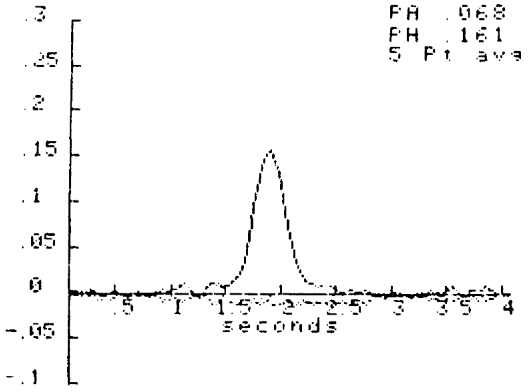

Figure 10. —— *Absorbance signals for lead*
•••• *Background*
Atomization from the platform.
Sample volume 5 µL

Summary

The platform technique is advantageous where volatile compounds of the analyte are formed which are stable over the range at which atomization from the wall occurs. With such elements and matrices, the extent of chemical interferences is generally reduced.

Atomization from the platform will generally give greater separation in time between the analyte and background absorption peaks and will often result in a significant decrease in the maximum background absorption. The nature of the matrix and the behaviour of the background absorption as a function of the temperature of the gas phase will determine the extent of the reduction in background absorption.

With platform atomization, the results with measurement of the peak area will often be superior to those for peak height measurement since the peak area at constant atomization temperature is independent of the rate at which atoms are formed, provided that the atomization efficiency is unaltered. The two modes of signal measurement should be compared to determine the better approach.

References

1. B. V. L'vov, "Electrothermal atomization – the way toward absolute methods of atomic absorption analysis", Spectrochim. Acta **33B**, 153 (1978).
2. E. J. Czobik and J. P. Matousek, "Interference Effects in Furnace Atomic Absorption Spectrometry", Anal. Chem. **50**, 2 (1978).

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