White Paper

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Optimizing GFAAS Ashing and Atomizing Temperatures using Surface Response Methodology

To obtain the best analytical results in Graphite Furnace Atomic Absorption Spectrometry (GFAAS), it is necessary to optimise the furnace temperature program.

Complex samples require optimization of the temperature and time parameters to ensure maximum removal of the sample matrix without loss of analyte.

A temperature program for analysis by graphite furnace contains a minimum of three basic steps: Drying, Ashing and Atomization. Unfortunately, selecting the optimum temperatures of the Ashing and Atomization steps often requires considering many interacting parameters. There are two common ways to optimize the ashing and atomization temperatures, both of which will be discussed in this white paper.

Optimization via “One variable at a time”

Optimizing the temperature program using the ‘one variable at a time’ method involves the following steps:

1. Select an atomization temperature and vary the ashing temperature to produce a series of absorbance readings.
2. Monitor both the background absorbance and the absorbance of the analyte during the ash stage. Select an ashing temperature that corresponds to the highest analyte absorbance signal and the lowest background signal (the red arrow indicates this temperature in Figure 1).
3. Using the selected ashing temperature, vary the atomization temperature and monitor the absorbance signal. Select the atomization temperature that corresponds to the highest analyte absorbance (refer to the red rectangle on the right hand side of Figure 1.

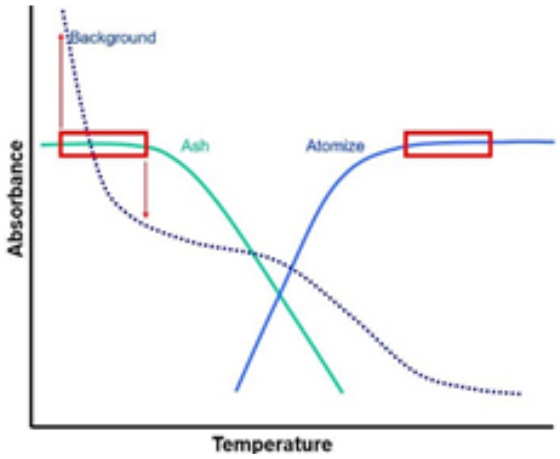

Figure 1. Using the "One variable at a time'' optimization method requires the analyst to run many tests to determine the ashing and atomization temperatures that correspond to the highest analyte absorbance with the lowest background signal (the red rectangles).

The major drawback of the 'One variable at a time' optimization method is that it assumes the two temperatures are independent of each other. This assumption is incorrect as the ashing step determines the chemical form of the analyte prior to atomization and therefore the absorbance during the atomization. This makes the 'One variable at a time' method unsuitable for determining the optimum temperatures for ashing and atomisation, particularly when the sample has a complex matrix.

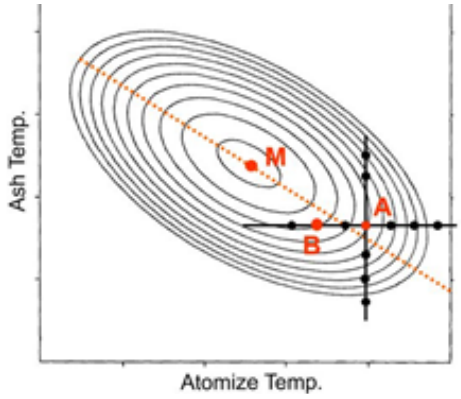

Figure 2. Using the 'one variable at a time' method of optimizing the graphite furnace temperature program often results in the analyst determining optimum temperatures (A & B in this diagram) that are some way off the true optimium (M in this diagram).

Figure 2 illustrates the limitations associated with the "One variable at a time" optimization method. The ashing temperatures are plotted on the Y-axis and atomization temperatures are plotted on the X-axis with the concentric circles representing the absorbance response. As previously explained, the analyst selects a "suitable" atomization temperature and the ashing temperature is varied to give a series of absorbance readings. Point A would be considered to be the optimum ashing temperature.

With the optimum ashing temperature determined, it is then held constant in another series of tests, while the atomization temperature is varied to give a new series of absorbance readings. As a result of plotting these readings on Figure 2, it is then possible to determine that Point B is the optimum atomization temperature.

As shown on Figure 2, the Point B is far removed from the true optimum, indicated on the diagram as point M. To get closer to the true optimum, the optimization process must be repeated several times. Starting at the temperature corresponding to Point B, the ashing temperature must be varied to give a new series of absorbances. The result of this process would be Point C in Figure 3, which corresponds to the new optimum ashing temperature. This iterative process needs to be repeated to get the optimum temperatures closer and closer to the true optimum. Obviously, this process quickly becomes very time consuming.

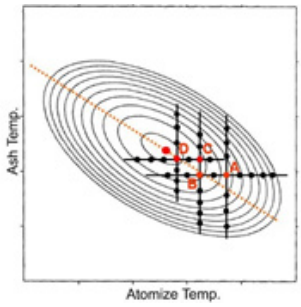

Figure 3. Through an iterative process, the analyst can optimize the ashing and atomization temperatures to get them closer to the optimum, but this is very time consuming.

Optimization via "Surface Response Methodology"

The second method that can be used to optimize the furnace temperature program is surface response methodology. This mathematical method is used to establish a relationship between variables by conducting a series of experiments, with the aim of determining the optimum response.

For graphite furnace AAS, surface response methodology (SRM) can be used to establish the relationship between ashing temperature, atomization temperature and analyte absorbance. Based on the results of only 12 experiments where the ashing and atomization temperatures were varied, Figure 4 shows the use of a second order polynomial equation to graphically represent the relationship between the three variables.

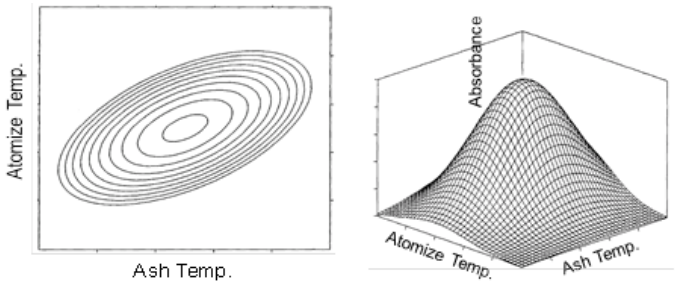

Figure 4. Surface response methodology can be used to determine the ashing and atomization temperatures that yield the best analyte absorbance. The figure on the left includes iso-response lines on a 2 dimensional surface. The 3 dimensional figure on the right includes a Z-axis of absorbance.

Surface response methodology can provide much more than the optimum ash and atomize temperatures. It can also be used to provide information on:

- The robustness of the method and the stability of the vapor phase. This is done by looking at the shape of the 3D plot.
- The best chemical modifier. A response surface study for the analysis of a single element with different modifiers can identify differences in vapor behaviour and therefore vapor phase stability.

Depending on the experiments performed, the response surface plot can take one of four different forms:

- Elliptic – with a single maximum
- Elliptic – with a single minimum
- Parabolic – with a line of maximum or minimum
- Parabolic – with no unique centre

Figure 5 shows the four different forms.

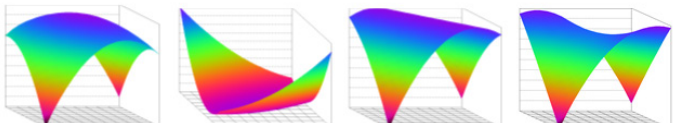

Figure 5. The four different forms of a response surface plot.

When applied to GFAAS, only the elliptical form, with a single maximum, is valid as it includes a single maximum point, corresponding to the coordinates of the optimum ash and atomise temperatures.

Practical example of the surface response methodology

Determining the optimum ashing and atomization temperatures

After referring to the literature for the quantification of lead in water, the following parameters would be selected for the analysis of Pb in a water sample:

- Chemical modifier: phosphate modifier
- Ashing step temperature: between 600 to 800 °C
- Atomization step temperature between 1600 to 1800 °C
- Platform atomization

In this experiment, we opted to vary the ash and atomization temperatures in an increment of 200—250 °C. This increment is likely to produce significant changes in the response for an element.

The temperature parameters used were:

Step	Starting temperature	Temperature increment
Ashing	700 °C	200 °C
Atomization	1600 °C	250 °C

Optimum ash and atomization temperatures are determined automatically by the SRM Wizard, built into the SpectrAA software of the Agilent 240Z atomic Absorption Spectrometer. The mathematical model uses only 12 experiments to determine the optimum ashing and atomization temperatures.

To avoid the introduction of a third variable (the atomization ramp rate) the SRM Wizard includes a feature to "normalize" all experiments by using a cool down step to have the same atomization slope.

In this example, the analysis was done with a standard solution and a real water sample. This provided two sets of data for interpretation.

Once the experiments were completed, the software performed the surface response calculations. If the calculated surface was not elliptical, the software indicated it could not determine the optimum temperature and suggested another series of experiments to run to achieve the desired outcome.

A 3D model of each set of experimental data was created by the software and is shown in Figure 6.

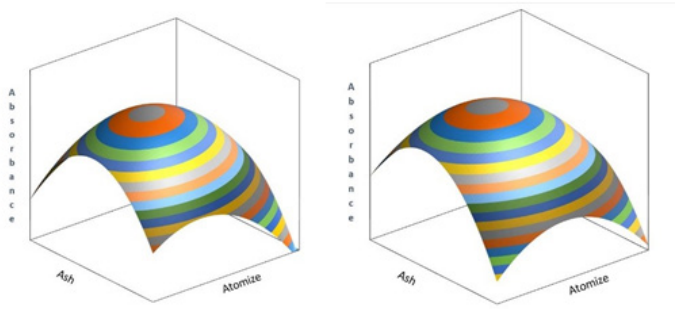

Figure 6. A surface response plot of the data from the standard (left) and the water sample (right).

Acquisition and interpretation of all the experimental data was completed in less than one hour.

The optimum temperatures determined by the surface response method for the standard and the sample were very close to each other, as shown in Table 1. From the results, we can assume that 600 °C is the optimum ashing temperature and 1450 °C is the optimum atomization temperature.

Table 1. The optimum temperatures, as determined by the surface response method.

Step	Optimum temperature for standard (°C)	Optimum temperature for water sample (°C)
Ashing	598	614
Atomization	1435	1476

Evaluation of modifiers

The 3D surface plot, resulting from the surface response experiments, also provides information about the stability of the vapour phase. We can use this to evaluate different modifiers for an element.

For the analysis of cadmium, the two modifiers used most frequently in published papers are:

- a mix of phosphate and magnesium (modifier 1), and
- a mix of palladium with magnesium (modifier 2).

After completing a surface response study for both modifiers, the optimum ashing temperatures (Table 2) are very close for both modifiers. However, there is an almost 300 °C difference in the atomization temperatures determined for the two modifiers.

Referring to the 3D plot of modifier 1 (Figure 7, left), it shows better stability than the plot for modifier 2 (Figure 7, right).

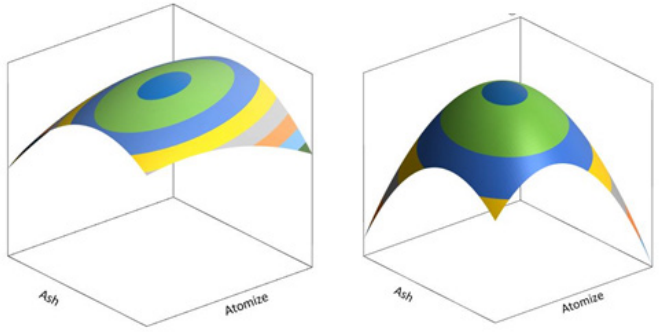

Figure 7. Surface response plots using modifier 1 (left) and modifier 2 (right).

Table 2. The optimum ashing and atomization temperatures, determined for two different modifiers, using the surface response methodology.

Step	Modifier 1	Modifier 2
Ash (°C)	858	844
Atomize (°C)	1587	1861

The variation of absorbance responses is very low across all experiments for modifier 1. The modifier 1 plot also shows a flatter surface response, indicating better vapor phase stability and a lower atomization temperature, which will contribute to an extended lifetime of the graphite tube.

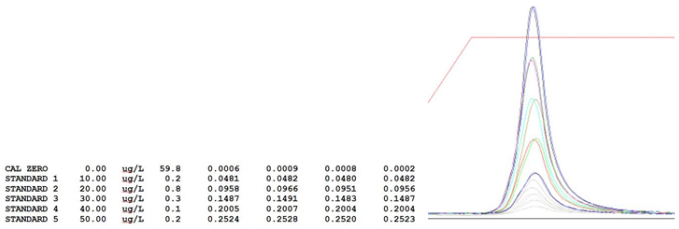

Figure 8. Determination of Al in water using the surface response method shows %RSD below 1% for all standards. The graph on the right is an overlay of the absorbance plots of three replicates of each of the five standards.

The maximum temperatures determined via the surface response method are always in the most stable vapor phase, so an improvement in short term precision (%RSD) can also be expected. Figure 7 illustrates this, with the %RSD of all the analyses of aluminum in water being below 1% RSD.

Conclusion

Response surface methodology mathematically determines the optimum ashing and atomization temperatures for graphite furnace atomic absorption spectrometry. It offers considerable time saving and accuracy advantages over the One variable at a time optimization method. A minimum of experiments is needed and the software can typically determine optimum parameters in less than one hour.

The surface response methodology offers further advantages in the selection of chemical modifiers for use in GFAAS. The 3D shape of the surface response plot provides an indication of the stability of the vapor phase, which is affected by the modifier being used.

The methodology also speeds up optimization procedures for the furnace. It improves the robustness of the method and eliminates the need for an experienced operator.

Another advantage of this methodology is that we can expect excellent %RSD of replicates as the maximum absorbance point is being used for the analysis.

Response surface methodology is part of the SpectrAA software and incorporated into an automated optimization software package (SRM Wizard). SRM can be adopted for use with any Agilent Zeeman or non-Zeeman GFAAS spectrometer, guiding the user through the set up procedure.

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