



# Evaluation of Three Methods of Matrix Modifier Injection in Graphite Furnace AAS

## Application Note

Atomic Absorption

### Author

Deen Johnson

### Introduction

The determination of metals by graphite furnace atomic absorption spectroscopy (GFAAS) often requires the use of a chemical matrix modifier. The chemical modifier is used to stabilize the analyte or volatilize the bulk of the sample matrix. This reduces the background signal or chemical interference present in the sample. Many chemical modifiers have been proposed for either the stabilization of the analyte and/or volatilization of the sample matrix. Some of these modifiers are discussed in references 1, 2, 3 and 4.

When using a chemical matrix modifier, for GFAAS method development numerous factors must be considered.

- The selection of a suitable modifier, to obtain the desired reaction for changes in the analyte or matrix stability.
- Proper mixing of the modifier with analyte and sample matrix. The mixing can be performed automatically with the use of an autosampler. However, it is often desirable to manually mix the matrix modifier with the sample to ensure proper mixing and to ensure the desired reaction has taken place.
- The minimization of contamination and dilution errors. When working at trace levels (parts per billion), the use of an autosampler can minimize contamination and dilution errors otherwise caused by analyst error.



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With the introduction of the Agilent Graphite Tube Atomizer-95/96 (GTA-95/96) and the Programmable Sample Dispenser-95/96 (PSD-95/96), the analyst typically had two ways to introduce the matrix modifier in the graphite furnace:

1. Injection of the modifier simultaneously with the sample.
2. Pre-injection of the modifier on the furnace and optional drying prior to injection of the sample.

Both methods have been proven successful. The simultaneous injection with the sample is generally used with complex sample matrices.

Many analytical chemists, conducting graphite furnace analyses, have requested a means of pre-injecting the matrix modifier onto the furnace, leaving the modifier wet and then injecting the sample into the modifier. It is thought that this would improve the mixing of the modifier and sample. If they were allowed to sit on the surface together, the desired reaction would take place. The purpose of this investigation was two fold:

1. To develop a suitable automated method (furnace and autosampler parameters) for pre-injecting the chemical modifier and leaving it wet to accept the sample
2. Comparison of this method with:
  - a. Normal simultaneous injection of modifier with sample.
  - b. Pre-injection and drying the modifier followed by injection of the sample.

The criteria used to compare the methods of modifier injection were sensitivity (characteristic mass), accuracy and precision for arsenic, using a nickel matrix modifier.

The three methods of chemical matrix modifier introduction are:

1. Pre-injection, wet deposition
2. Pre-injection, dry deposition
3. Normal injection with sample

## Reagents and Instrumentation

The study used arsenic (As) solutions of 10.0, 25.0 and 50.0 mg/L as test solutions. The arsenic solutions were made in 1% Nitric Acid (HNO<sub>3</sub>). The modifier of choice in this investigation was 50 mg/L nickel (Ni) as nickel nitrate.

The study used two instrument configurations. The first was the Agilent SpectrAA 20ABQ atomic absorption spectrometer equipped with the GTA-96 graphite furnace and PSD-96 autosampler. The second system was the Agilent SpectrAA 400P equipped with the GTA-96 and PSD-96. Both spectrometers were equipped with Deuterium Background Correction (used in the study). Pyrolytically coated, plateau graphite tubes were used. Arsenic hollow cathode lamps were used on both instruments. Both instruments used Ultra High Purity (99.999%) Argon as the inert gas for the analysis.

## Procedure

The instrument parameters were identical for the three matrix modifier introduction methods under investigation (Table 1). The graphite furnace parameters are given in Tables 2, 3 and 4, the autosampler parameters in Tables 5, 6 and 7. The variation in the furnace and autosampler parameters will be discussed further.

Table 1. Instrument Parameters

Instrument mode	Absorbance
Calibration mode	Concentration
Measurement mode	Peak height
Lamp position	1
Lamp current (mA)	12
Slit width (nm)	0.5
Slit height	Normal
Wavelength (nm)	193.7
Sample introduction	Sampler automixing
Time constant (sec)	0.20
Measurement time (sec)	1.0
Replicates	3
Background correction	On

Table 2. Graphite Furnace Parameters

Pre-injection, wet deposition					
Step no.	Temperature °C	Time sec	Gas flow L/min	Gas type	Read command
1	45	5.0	3.0	Normal	No
2	75	5.0	3.0	Normal	No
3	100	100.0	3.0	Normal	No
4	120	10.0	3.0	Normal	No
5	120	3.0	3.0	Normal	No
6	700	5.0	3.0	Normal	No
7	700	10.0	3.0	Normal	No
8	700	1.0	0.0	Normal	No
9	2500	0.9	0.0	Normal	Yes
10	2500	2.0	0.0	Normal	Yes
11	2500	2.0	3.0	Normal	No
12	2800	0.2	3.0	Normal	No
13	2800	2.0	3.0	Normal	No

Table 3. Graphite Furnace Parameters

Pre-injection, dry deposition					
Step no.	Temperature °C	Time sec	Gas flow L/min	Gas type	Read command
1	75	5.0	3.0	Normal	No
2	100	100.0	3.0	Normal	No
3	120	10.0	3.0	Normal	No
4	700	5.0	3.0	Normal	No
5	700	10.0	3.0	Normal	No
6	700	1.0	0.0	Normal	No
7	2500	0.9	0.0	Normal	Yes
8	2500	2.0	0.0	Normal	Yes
9	2500	2.0	3.0	Normal	No
10	2800	0.2	3.0	Normal	No
11	2800	2.0	3.0	Normal	No

Table 4. Graphite Furnace Parameters

Normal injection with sample					
Step no.	Temperature °C	Time sec	Gas flow L/min	Gas type	Read command
1	75	5.0	3.0	Normal	No
2	100	100.0	3.0	Normal	No
3	120	10.0	3.0	Normal	No
4	120	3.0	3.0	Normal	No
5	700	5.0	3.0	Normal	No
6	700	10.0	3.0	Normal	No
7	700	1.0	0.0	Normal	No
8	2500	0.9	0.0	Normal	Yes
9	2500	2.0	0.0	Normal	Yes
10	2500	2.0	3.0	Normal	No
11	2800	0.2	3.0	Normal	No
12	2800	2.0	3.0	Normal	No

Table 5. Autosampler Parameters

	Volume (µL)		
	Solution	Blank	Modifier
Blank	—	20	20
Standard 1	4	16	20
Standard 2	10	10	20
Standard 3	20		20
Sample	20		20
Recalibration rate	10		
Reslope rate	0		
Multiple inject	No		
Hot inject	No		
Pre inject	Yes		
Last dry step	1		

Table 6. Autosampler Parameters

	Volume (µL)		
	Solution	Blank	Modifier
Blank	—	20	20
Standard 1	4	16	20
Standard 2	10	10	20
Standard 3	20		20
Sample	20		20
Recalibration rate	10		
Reslope rate	0		
Multiple inject	No		
Hot inject	No		
Pre inject	Yes		
Last dry step	5		

Table 7. Autosampler Parameters

	Volume (µL)		
	Solution	Blank	Modifier
Blank	—	20	20
Standard 1	4	16	20
Standard 2	10	10	20
Standard 3	20		20
Sample	20		20
Recalibration rate	10		
Reslope rate	0		
Multiple inject	No		
Hot inject	No		
Pre inject	No		

The dry parameters were selected to ensure the proper drying of the sample prior to the ash/char stage. An additional step was included for the wet deposition of the modifier. The pre-injection parameter of 45 °C for 5 seconds was used to facilitate the wet deposition of the nickel modifier. After injection of the arsenic solution, the dry stage was ramped to 100 °C (from 75 °C to 100 °C) in 100 seconds. This ensures a proper dry with the high volume (40 µL) of solution injected into the furnace. The dry deposition of the modifier was performed by deposition and drying through Step 5 (at 700 °C) followed by injection of the arsenic.

An ash/char temperature of 700 °C was used with an atomize temperature of 2500 °C for all three temperature programs. A clean-out step of 2800 °C was programmed to ensure that the graphite tube was cleaned, preventing a build-up of nickel.

The system was calibrated using the automixing capability of the PSD-96. The 50 mg/L As solution was used to automatically prepare the 0.0, 10.0, 25.0 and 50 mg/L As standards by dilution with 1% HNO<sub>3</sub> reagent blank solution. Solutions of 10.0, 25.0 and 50 mg/L As in 1% HNO<sub>3</sub> were prepared manually and placed in the carousel for the determination. The system was programmed to perform a recalibration after every 10 samples.

## Results

The evaluation was conducted for maximum productivity, using the full automation capabilities of the SpectrAA atomic absorption system. It was conducted in this manner to simulate situations and criteria established in many working and contract laboratory facilities. If there were calibration, injection, errors, etc. the editing feature of the software was used to correct the specific error. The editing feature was only used if it could be determined, by the operator, exactly what the cause of the problem was. The editing feature was used only twice in the evaluation; once on a calibration error when the autosampler ran out of nickel modifier and once when the operator noticed the autosampler misinjected.

The statistical results of the evaluation are presented in Table 8 (sensitivity), Table 9 (accuracy) and Table 10 (precision). The results of the statistical analysis will be discussed in turn.

Table 8. Sensitivity (Characteristic Mass)

	Pre-inj wet	Pre-inj dry	Normal w/sample
Mean absorbance	0.261	0.242	0.251
Characteristic mass (pg)	8.4	9.1	8.8

Note: Characteristic mass calculated using 25 µg/L solution  
Published characteristic mass = 10.0 picograms

## Sensitivity

In graphite furnace AA, sensitivity is best expressed as the Characteristic Mass in picograms (pg) which is defined by the following equation:

$$\text{Characteristic Mass} = C \times V \times 0.0044 A$$

where:

C = Concentration of Analyte in Solution (µg/L)

V = Volume of Sample Injected (µL)

A = Absorbance

The data in Table 8 shows that all three methods of injection of the matrix modifier produced Characteristic Mass results better than the published [1] 10.0 pg value for arsenic. The Characteristic Masses were 8.4, 9.1 and 8.8 pg respectively for:

1. Pre-injection, wet deposition
2. Pre-injection, dry deposition
3. Normal injection with the sample

The best results were obtained by pre-injecting the modifier (leaving it wet) followed by injection of the sample. The other two methods exhibit poorer sensitivity (increasing Characteristic Mass) values.

The results indicate that wet deposition (either pre-injection or normal injection) of the matrix modifier exhibits slightly better sensitivity than drying the matrix modifier on the furnace prior to injection of the sample. Wet deposition of the matrix modifier permits good mixing and reaction of the modifier with the analyte in the sample. Dry deposition does not allow the analyte sufficient time to contact the modifier on the furnace or platform surface. If inadequate mixing occurs between the matrix modifier and the analyte, the desired reactions for stabilizing the analyte may take place. Poorer sensitivity and higher Characteristic Mass Values would be expected.

## Accuracy

Accuracy for the three methods of matrix modifier injection is compared in Table 9. All the methods of injection exhibited good accuracy when compared to the actual values of 10.0, 25.0 and 50.0 µg/L As. The composite range of recoveries was between 94.5% and 106.3%.

The pre-injection, wet deposition method of matrix modifier injection produced more accurate results at the highest concentration value. The recoveries ranged from 99.9% to 104.4%. The standard deviations for this method of modifier introduction were better (0.7, 2.2 and 3.3 respectively for the 10.0, 25.0 and 50.0 µg/L As solutions) than the other two methods of modifier injection. Again this could be attributed to better mixing and reaction of the modifier with the analyte in the sample. The mixing of the sample into the modifier may also contribute to the improved accuracy. Even though the recoveries for the pre-injection, dry deposition and normal injection with the sample are slightly poorer, they are still very good. If the limits of ±10% of 100% recovery are considered as good recoveries, all results are well within these limits.

Table 9. Accuracy

<b>Pre-injection, wet deposition</b>			
Concentration (mg/L)	10.0	25.0	50.0
Mean (µg/L)	10.4	25.9	49.9
Standard deviation (µg/L)	0.7	2.2	3.3
% Recovery	104.0	103.7	99.9
<b>Pre-injection, dry deposition</b>			
Concentration (mg/L)	10.0	25.0	50.0
Mean (µg/L)	9.5	24.7	48.8
Standard deviation (µg/L)	2.2	6.9	8.6
% Recovery	94.5	98.8	97.6
<b>Normal injection with sample</b>			
Concentration (µg/L)	10.0	25.0	50.0
Mean (µg/L)	10.6	26.4	52.9
Standard deviation (µg/L)	1.2	3.4	4.3
% Recovery	106.3	105.6	105.4

## Precision

Precision was acceptable for the three methods investigated. In conducting graphite furnace analysis, a Percent Relative Standard Deviation (%RSD) under 10% is generally considered good, under 5% is very good, and under 2% is excellent precision. Precision is generally poorer in graphite furnace analysis than flame atomic absorption.

Precision results (expressed in %RSD) are shown in Table 10. Also calculated in the table is the overall precision for each injection method. The pre-injection, wet deposition method was again the best means of introduction when the precision (3.7% RSD, overall) of the analysis is considered. Normal injection with the sample exhibited the poorest precision (5.7% RSD, overall). This may be indicative of incomplete mixing and reaction time of the modifier with the analyte prior to preceding to the elevated temperatures of the furnace program (this situation may be improved by changing the parameters, such as; modifier volume, injection rate, drying rate).

Table 10. Overall Precision for Each Injection Method (%RSD)

<b>Pre-injection, wet deposition</b>				
Concentration (µg/L)	10.0	25.0	50.0	Overall
Mean (%RSD)	2.7	5.5	2.9	3.7
Standard deviation	± 1.8	± 10.4	± 7.1	± 7.5
<b>Pre-injection, dry deposition</b>				
Concentration (µg/L)	10.0	25.0	50.0	Overall
Mean (%RSD)	5.2	3.7	4.7	4.6
Standard deviation	± 3.1	± 3.8	± 6.4	± 4.7
<b>Normal injection with sample</b>				
Concentration (mg/L)	10.0	25.0	50.0	Overall
Mean (%RSD)	7.8	6.0	3.3	5.7
Standard deviation	± 15.3	± 12.3	± 7.4	± 12.3

## Conclusion

The Agilent SpectrAA Graphite Tube Atomizer systems offer three different methods to introduce the chemical matrix modifier and sample into the graphite furnace:

1. Pre-injection, wet deposition
2. Pre-injection, dry deposition
3. Normal wet injection with the sample

When considering the sensitivity, accuracy and precision of the Se three graphite furnace methods, they are all useful. Under the test conditions (spectrophotometer, graphite furnace and autosampler parameters) established for the evaluation, the pre-injection with wet deposition method was the best for all the evaluation criteria. This method has improved the sensitivity, accuracy and precision for water, wastewater, domestic sewage, and many other environmental samples analyzed in this laboratory.

The SpectrAA systems offer flexibility in developing methods for the graphite furnace. The analyst can use one of three methods to inject the chemical matrix modifier into the graphite furnace and thus improve the sensitivity, accuracy and precision of the analysis accordingly.

## References

- 1 "Analytical Methods for Graphite Tube Atomizers", Varian Techtron Publication No. 85-100848-48 (September 1988).
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