Technical Overview

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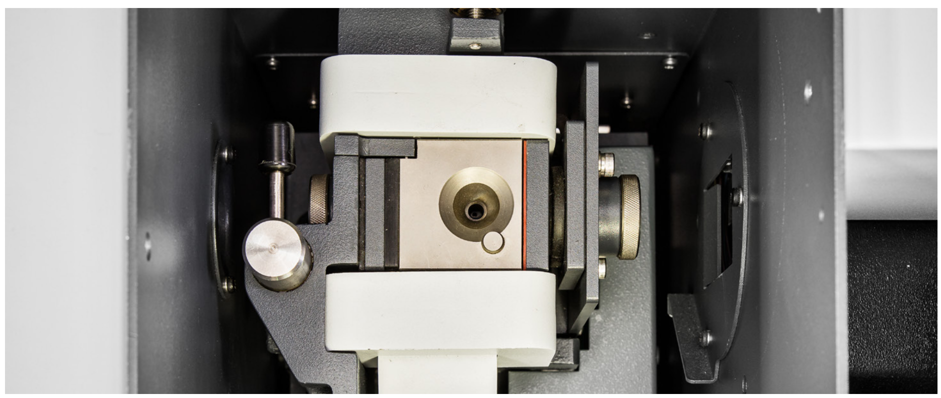
The Role of Chemical Modifiers in Graphite Furnace Atomic Absorption Spectrometry



Introduction

Chemical modifiers are used in graphite furnace atomic absorption spectrometry (GFAAS) to change the thermochemical behavior of both the analyte and the sample matrix. Modifiers allow the analyst to control various parameters of the analysis, from the precision and accuracy through to reducing interferences.

The Benefits of Chemical Modifiers in GFAAS

Chemical modifiers can aid analysis by changing the behavior of the analyte element, including:

1. Stabilizing volatile analytes at higher temperatures. This allows a higher pre-treatment temperature to be used, which can eliminate some, if not all, interferences.
2. Increasing the volatility of the analyte during atomization. This allows a lower atomization temperature to be used, which can help to atomize the analyte before the sample matrix. This can reduce background signal during atomization.
3. Increasing the analyte signal. Mixtures of palladium nitrate-magnesium nitrate (Pd-Mg) are often used for this effect. This improves the signal-to-noise ratio of the measurement, improving the precision and accuracy of the analytical result.

The modifier can also act on the sample matrix, increasing the volatility of interfering contaminants in the matrix. Interfering species can then be volatilized during the ash stage. For example, NH_4NO_3 is used as a chemical modifier to remove chloride salts from a sample matrix by volatilization:

$$NaCl + NH_4NO_3 \rightarrow NH_4Cl \uparrow + NaNO_3$$

In this case, NH_4Cl is removed during the ashing step and the residual $NaNO_3$ does not interfere with the analyte signal during the atomization.

By using the right modifier or mix of modifiers, we can simplify an analytical method, through:

- Allowing direct injection of a sample, removing the need for dilution,
- Avoiding the use of standard additions,
- Improving the lifetime of an atomizer,
- Better long-term stability.

This can improve accuracy, precision, sensitivity, and quantification limits.

Drawbacks of Chemical Modifiers

In some cases, injecting a large volume of a chemical modifier into an atomizer can cause negative effects: high background signal, corrosion of the graphite tube, sensitivity reduction, or contamination if the chemical modifier is not high-purity. Using too much modifier or the wrong type can also increase costs. To reduce these impacts, the chemical type and concentration of modifier should be optimized.

As an example, Figure 1 shows the effect of $Mg(NO_3)_2$ used as modifier on the chromium absorption signal. The modifier enhances the signal, making the peak narrower and higher. This improves the accuracy and precision of the analytical result.

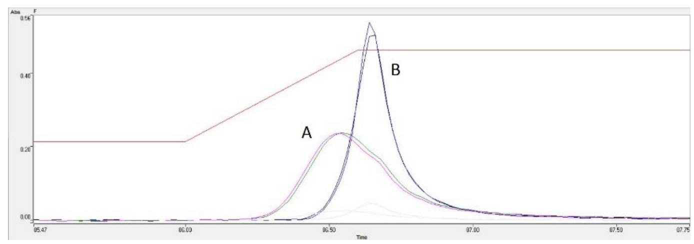


Figure 1. The effect of $Mg(NO_3)_2$ as a modifier on Chromium analysis. The peak A is Cr without modifier and peak B is Cr with the modifier.

Palladium Nitrate-Magnesium Nitrate: A Universal Modifier?

It has been demonstrated that a mixture of Pd-Mg has equivalent performance to previously recommended individual modifiers for a lot of elements. However, this mixture has limitations. It does not perform equally for all elements or matrices and generally requires higher atomization temperatures, resulting in higher characteristic masses, m_0. Please refer to the Agilent whitepaper "Characteristic Mass in Graphite Furnace AAS", publication number 5991-9286EN, for advice and guidance on checking the performances of GFAAS.

The Table 1 highlights the fact that Pd-Mg can be used for a range of elements, but alternative modifiers are recommended for the best performance for specific elements.

Selecting a Chemical Modifier

The action of chemical modifiers is very complex in samples with matrices other than pure water. Table 1 lists most of the typical modifiers used in GFAAS.

When selecting and evaluating a chemical modifier, it is crucial to understand the importance of ash and atomize temperatures in graphite furnace atomic absorption spectrometry. Please refer to the Agilent whitepaper "Optimizing GFAAS Ashing and Atomizing Temperatures using Surface Response Methodology", publication number 5991-9156EN, for advice and guidance on optimizing these temperatures. The publication "Analytical Methods for Graphite Tube Atomizers - User's Guide", Agilent publication number 8510084800 also includes useful information for the analyst.

Table 1. Typical chemical modifiers used for elemental analysis by GFAAS.

Element	Modifiers						
Ag	Pd+Mg	Ascorbic acid	Pd	$NH_4H_2PO_4$			
Al	Pd+Mg	NH_4NO_3	Ca+NH_4NO_3	$(NH_4)_2Cr_2O_7$	Mg		
As	Pd+Mg	Ni+Mg	Cu	Ni	Mg	Pd	Ir+Mg
Au	Pd+Mg	Pd	$Ni(NO_3)_2$				
Be	Pd+Mg	Cu	Ni	Pd	La+Mg		
Bi	Pd+Mg	Cu	Ni	Pd			
B	$Ba(OH)_2$	$La(NO_3)_3$					
Cd	Pd+Mg	PO_4+Mg	PO_4	Pd+Hydroxylamine HCl	Pd+Ascorbic acid		
Co	Pd+Mg	Mg	Pd				
Cr	Pd+Mg	Mg	Pd				
Cu	Pd+Mg	Pd					
Fe	Pd+Mg	Mg					
Hg	Pd	$(NH_4)_2S$					
Mg	NH_4NO_3						
Mn	Pd+Mg	Mg					
Mo	Mg	Pd					
Ni	Pd+Mg	Mg	PO_4				
Pb	Pd+Mg	PO_4+ Mg	PO_4	Pd+Hydroxylamine HCl	Mg	Pd	EDTA Oxalate
Sb	Pd+Mg	Ni	Mg	Pd	Ni+Mg	Ir+Mg	
Se	Pd+Mg	Ni	Cu	Pd	Ni+Mg	Ir+Mg	Rh
Si	Pd+Mg	Pd					
Sn	Pd+Mg	PO_4+Mg	Pd	Di-ammonium citrate			
Te	Pd+Mg	Ni					
Tl	Pd+Mg	Ni	Pd	H_2SO_4			
V	Mg	Ni					
Zn	Mg						

Table 2. Agilent offers a comprehensive range of modifiers for GFAAS. They can be ordered from agilent.com.

Description	Concentration	Matrix	Part No.
Modifiers (solutions ready to use)			
Palladium nitrate, magnesium nitrate	750 µg/mL $Pd(NO_3)_2$, 500 µg/mL $Mg(NO_3)_2$, 250 mL	2 % HNO_3	5190-8340
Palladium nitrate, magnesium nitrate	1,000 µg/mL $Pd(NO_3)_2$, 600 µg/mL $Mg(NO_3)_2$, 250 mL	2 % HNO_3	5190-8341
Ammonium phosphate, magnesium nitrate	10 mg/mL $NH_4H_2PO_4$, 600 µg/mL $Mg(NO_3)_2$, 250 mL	2 % HNO_3	5190-8342
Palladium nitrate, magnesium nitrate	750 µg/mL $Pd(NO_3)_2$, 500 µg/mL $Mg(NO_3)_2$, 250 mL	2 % HNO_3	5190-8340
Modifiers			
Palladium nitrate	0.1 % $Pd(NO_3)_2$, 100 mL	5 % HNO_3	5190-8335
Palladium nitrate	1 % $Pd(NO_3)_2$, 100 mL	10 % HNO_3	5190-8336
Ammonium phosphate	10 % $NH_4H_2PO_4$, 100 mL	2 % HNO_3	5190-8337
Magnesium nitrate	1 % $Mg(NO_3)_2$, 100 mL	2 % HNO_3	5190-8338
Nickel nitrate	1 % $Ni(NO_3)_2$, 100 mL	2 % HNO_3	5190-8339

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This information is subject to change without notice.

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