Dealing with Matrix Interferences in the Determination of the Priority Pollutant Metals by Furnace AA

Application Note

Atomic Absorption

Authors

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Introduction

Atomic absorption methods are recommended for the determination of the priority pollutant metals, being relatively simple, rapid, and applicable to various types of water and waste samples from drinking water to industrial sludges. Often the concentration levels which must be determined to meet regulatory requirements are extremely low. Therefore, furnace atomic absorption methods are EPA approved. Though furnace methods are characterized by excellent analytical sensitivity, in some analytical situations they can be subject to interferences. The purpose of this AA at Work is to briefly describe the nature of matrix interferences and to discuss effective techniques to minimize or eliminate them. By using one or a combination of techniques, a skilful analyst can develop furnace methods to accurately determine the priority pollutant metals in a variety of sample matrices.

In some respects, the interferences encountered in furnace AA can be compared to those found in flame AA, but their nature and extent are changed by differences in sample introduction and atomimation mechanisms. Therefore, correcting or compensating for interferences in furnace AA requires a different approach than for flame AA. Spectral interferences are relatively rare for both techniques due to the specificity of the AA technique. Physical interferences are more pronounced for flame AA since sample viscosity and surface tension play a role in sample nebulization, therefore affecting analyte atom production. Because a specific volume is delivered to the furnace, viscosity and surface tension factors have less effect on atom preduction, but can influence the precision with which the required volume is injected into the furnace. Also, surface tension and viscosity will affect sample spreading and this can influence analytical response. Solutions of low surface tension, such as organic solvents and more concentrated acid solutions will spread more than the equivalent volume of an aqueous sample. These effects are more pronounced with higher injection volumes. Therefore, it is important that the physical properties of the standard match those of the sample. If solutions of low surface

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tension must be analyzed, for example high acid concentrations from digestion procedures, these effects can be minimized by smaller volumes and careful selection of dry parameters [1]. The most significant interferences in furnace AA are non-specific (background) absorption and chemical interferences, the severity of which can sometimes leave the analyst baffled.

Background Absorption

Background absorption is a false signal due to either molecular absorption and/or light scattering. Background absorption is far more severe in furnace AA than flame AA. The vaporization of the total sample volume and long residence time in the furnace establish the superior sensitivity of the furnace technique but also greatly increase the background absorption encountered. Also, the furnace typically does not always decompose molecular components as thoroughly, leading to increased molecular absorption. Light scattering occurs when high concentrations of salt scatter some of the source radiation out of the instrument light path. Both types of background interferences are particularly pronounced in the lower wavelengths (below 250 nm). If the absorbance signal due to either molecular or light scattering overlaps the resonance line of the analyte element, it increases the apparent absorbance signal. If not corrected for, large positive errors can occur. Accurate simultaneous background correction is used to correct for background absorption. The need for background correction can be determined by comparing the non-corrected and the corrected absorbance signal, by using computer graphics, or using a background only measurement mode if available.

In some analytical situations, such as the determination of a volatile element in a complex matrix at a low wavelength, the background signal may be so massive as to preclude accurate instrumental correction. The anomalous signal obtained may be seen graphically with the use of computer graphics or the AA instrument may indicate photometric overrange. The accuracy of the background correction will depend in part on the magnitude of the analytical signal and background signal, the spectral band width, and the extent of temporal overlay [1]. The furnace method developed should efficiently remove the background-producing matrix components prior to the atomization of the analyte element. Not only will this allow for more accurate background correction, but the removal of bulk matrix components prior to atomization will reduce chemical interferences during atomization.

Background absorption can be reduced by selecting a temperature program whose ash and atomize steps are optimized to effectively separate the background signal and the analyte

peak signal. The ash temperatures should be carefully optimized to remove bulk matrix components and enhance the analyte peak. The maximum ash temperature can be determined by increasing the ash temperature and measuring the background corrected absorbance peak. Reduction of the analyte peak will indicate an excessive ash temperature. Separation of the background signal and analyte signal may sometimes be improved by controlled temperature ramping between the ash and atomize temperatures if volatilization occurs at somewhat different temperatures. But in cases where volatility of the matrix components and the analyte are similar, time separation may be difficult and matrix components cannot be removed prior to atomization of the analyte element [2].

Matrix Modification to Reduce Background Absorption

The situation can be improved by changing the volatility of either the interfering species, making it more volatile, or the analyte element, making it less volatile. This means of chemically altering the volatilities of either the analyte element or matrix constituents defines the technique of matrix modification. A well-documented matrix modification technique is the addition of NH_4NO_3 to samples containing high concentrations of NaCl. The formation of NH_4Cl, having a higher volatility, allows for the removal of the major matrix component prior to atomization. An example of reducing the volatility of the analyte element is the addition of Ni in the determination of As. The formation of the less volatile nickel arsenide allows for the more efficient removal of matrix components without loss of analyte prior to atomization.

The graphic display of the atomization peak is a useful aid in diagnosing interference problems. Until recently, due to the speed of transient furnace signals and the relatively slow response of recorders, only a limited amount of information could be obtained. But with the recent application of computer graphics, the ability to graphically display atomization peaks in real time became a valuable aid in developing methods for dealing with matrix interferences. Because the development of a furnace method involves optimization of the temperature program and possible use of matrix modification to enhance the atomization signal and minimize background, this simultaneous display of separate analyte and background signals can be particularly useful. Figure 1 demonstrates the use of computer graphics in the determination of Cu in seawater. The addition of 10% NH_4NO_3 not only reduces background absorption but enhances the analyte signal by reducing chemical interferences from the salt matrix.
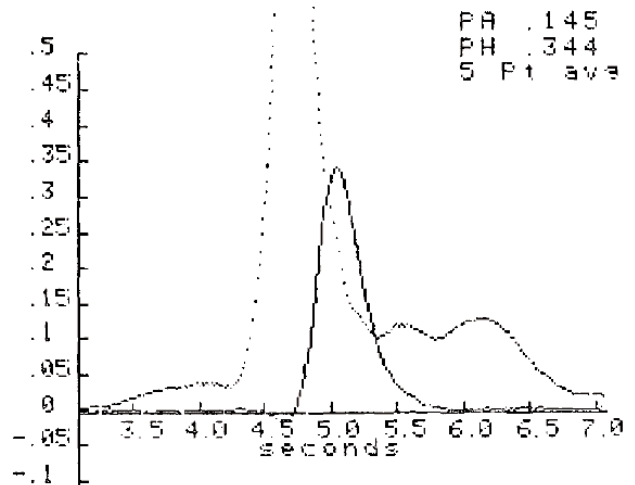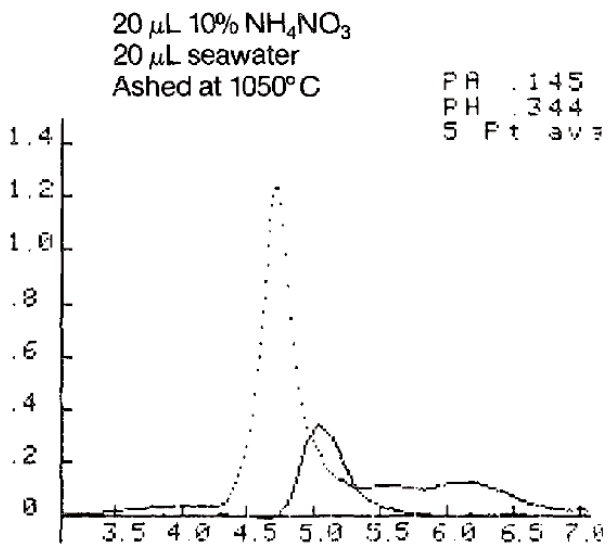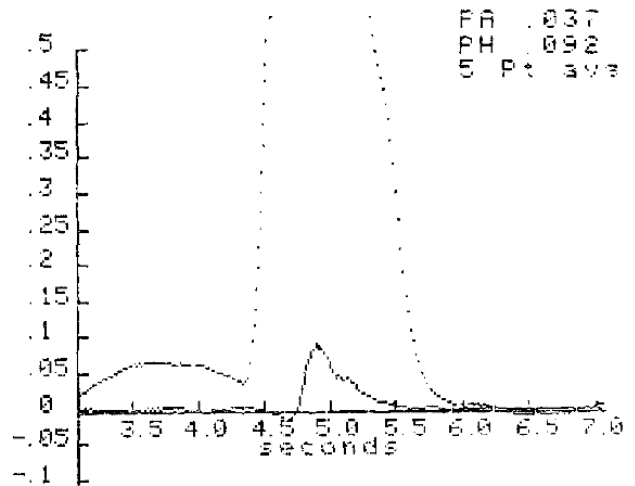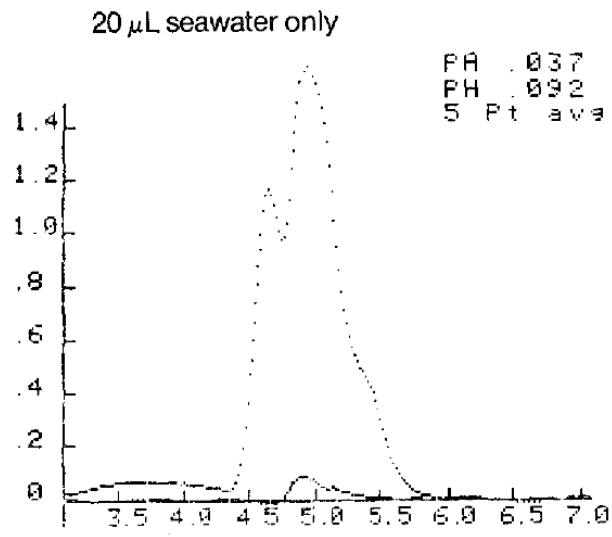
Figure 1.   GTA-95, Cu in seawater, chemical modifier.

Chemical Interferences

Ideally, the matrix should not significantly change the appearance time or the shape of the analyte peak with respect to a simple aqueous solution. But, the atomization peaks for volatile elements in complex matrices can show shifts in appearance time and multiple peak maxima as well as signal suppression or enhancement. These phenomena indicate that chemical interferences are occurring. This has prompted numerous studies to determine atomization mechanisms and the effects of matrix components. The application of computer graphics has provided a means of studying the shape of atomization peaks.

The mechanisms of interferences in complex matrices are not well understood but various models have been used to describe a number of simple matrix interferences. Though it is beyond the scope of this paper to present the various theories of atomization mechanisms, it would be helpful to summarize some of the reactions that take place in the graphite furnace.

One cannot think of atomization as a simple vaporization of the element but as a complex set of interacting reactions that can at one point or another involve the analyte, matrix constituents, the graphite surface, and gases either produced during atomization or entrained in the inert gas. A simple model of the mechanism of atom production is summarized in the following equations:

Thermal Reduction

$$MX_{(s)} \longrightarrow M_{(g)} + X_{(g)}$$

Oxide Reduction

$$MO_{(s)} + C_{(s)} \longrightarrow CO_{(g)} + M_{(g)}$$
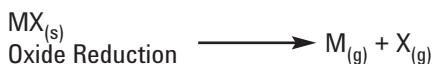
The first is the simple thermal reduction of the analyte salt and the second is an oxide reduction involving the graphite surface. Though these reductions might be adequate to explain the atomization mechanisms of a single analyte in dilute nitric acid, they cannot be extrapolated to analysis of real samples with complex matrices. Chemical interferences in the graphite furnace can be broadly classified as two types, vapor phase interferences and condensed phase interferences. Table 1 illustrates some of the various reactions that contribute to chemical interferences. Though the complex nature of chemical interferences can make them unpredictable, there are means of either reducing interferences or compensating for them and obtaining accurate results. These include matrix modification, use of a graphite platform, and the method of standard additions.

Table 1 [3,4,5,6].

Vapor Phase Interferences	Comments
Lack of dissociation of analyte containing compound during atomization Recombination of the analyte atom with a matrix interferent or the formation of a molecular compound	Usually causes suppression that cannot be corrected for by switching to peak area measurement
Changes in rate of analyte removal	Vapor phase kinetic effects

Condensed Phase Interferences (or solute phase)	
Volatile compound is lost in the dry or ash before atomization temperature is reached	
Incomplete atomization due to refractory compound formation	Such as stable carbides
Occlusion of the analyte in the interfering matrix Co-volatilization of the analyte with a more volatile matrix components	Sometimes referred to as physical interferences
*Changes in rate of analyte supply	Changes in solute phase reaction kinetics
Presence of analyte in forms of different volatilities	Volatilization of less stable form shifts peak appearance time and can result in enhancement or multiple peak maxima

Matrix Modification to Reduce Chemical Interferences

Matrix modification was discussed earlier as a means of changing the volatility of either the analyte or a major matrix constituent. A matrix modifier can also be used to alter the chemical environment to improve analyte atomization efficiency. Some of the interferences in Table 1 can be minimized by such means as increasing the nitric acid concentration, the addition of an alternate acid such as sulphuric or phosphoric, adding hydrogen to the inert gas (CRA-90 only), air ashing, or adding various inorganic and organic salts. Table 2 lists some of the matrix modifiers that have been used to reduce furnace interferences in the determination of the priority pollutants. As discussed earlier, computer graphics are very useful in evaluating the effects of matrix modification, showing changes in peak shape and shifts in peak appearance times due to volatility changes. The following suggestions are presented to help the analyst develop furnace methods that minimize chemical interferences [1].

Table 2. *Matrix Modifiers for the Determination of the Priority Pollutants [1].*

Analyte	Modifier	Comments	Reference
As, Se	Ni (minimum of 20X excess)	Forms more stable nickel arsenide and nickel selenide permitting higher ash temperatures	7,8
Pb, Zn, Cd	H_3PO_4 (1000X excess)	Formation of a less volatile phosphate which atomizes at a higher temperature	9,10
Pb, Cd	$NH_4H_2PO_4$	Allows use of higher ash temperatures	11
Pb	EDTA, citrate, oxalate (0.5-1% w/v)	Stabilizes lead at a lower atomization temperature than that of a nitrate or	12
Tl	H_2SO_4 (1-2% v/v)	In chloride matrices, prevents loss due to formation of volatile compounds	13
NaCl Matrices	ammonium nitrate ammonium oxalate [NH_4NO_3, $(NH_4COO)_2$]	Removal of NaCl prior to atomization of analyte element, reducing interferences and minimizing non-specific absorption	14

1. Many analysis problems due to interferences arise when the analyte element and the matrix components volatilize at similar temperatures.

2. An appropriate matrix modifier added to both the standards and sample could eliminate the sensitivity differences due to matrix interferences.

3. The study of a chemical handbook such as the "CRC", Handbook of Chemistry and Physics provides useful information as to which compounds of the analyte element have higher melting and boiling points. Information from chemical textbooks on decomposition temperatures and intermediate compounds can also be useful. If a more stable compound exists, the matrix modifier added to the sample should provide the appropriate anion or element to produce the more stable compound either in solution or during the ash step of the temperature program.

4. To minimize trial-and-error, when a difficult analysis is encountered the analyst should search available manufacturer's literature and various analytical chemistry journals for information applicable to his particular analysis.

Pyrolytic Graphite Platforms

Another means of effectively reducing chemical interferences is by the use of a graphite platform placed inside the carbon tube from which the sample is volatilized. 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 atomize temperature before vaporization occurs. In other words, the analyte

vaporizes and can leave the furnace at a temperature much lower than that obtained later in the atomization cycle, due to the time lag between the temperature reached by the furnace wall and the vapor temperature. The cooler vapor temperatures increase the probability of interfering reactions. For example, volatile compounds (such as monohalides) can be formed which remain stable over the temperature range where vaporization occurs and can be lost before the furnace temperature 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.

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 and gaseous environment has approached a steady-state temperature, therefore, minimizing vapor phase interferences [15,16,17].

Standard Additions Calibration

If interferences cannot be eliminated by the previously mentioned methods, the standard additions method of calibration can be used to effectively compensate for any sample interferences (other than background absorption) provided a working signal is obtained in the sample matrix. In this method, aliquots of increasing analyte concentration are added to equal volumes of the sample. A sample of zero addition is also prepared and all final volumes are equalized. The absorbances are determined and plotted on the vertical axis of a graph and the concentrations of the analyte additions are plotted on the horizontal axis. The resulting line is extrapolated to intercept the abscissa on the left. The point of interception determines the concentration of analyte in the sample. An example of a three-point standard additions calibration is shown in Figure 2. For the best results additions of approximately 50, 100, and 150% of the expected analyte concentration should be used.

A three-point standard additions calibration is recommended to check for the existence of interferences. If the analyte is not detected in the sample, spikes of known concentrations should be added to check for interferences, and spike recoveries of less than 90% or more than 110% of the added amount would indicate a significant matrix interference. If the regular calibration and standard addition curves are parallel (their calibration slopes are equal), significant interferences do not exist and a regular calibration can be used. When matrix interferences are encountered, standard additions is an
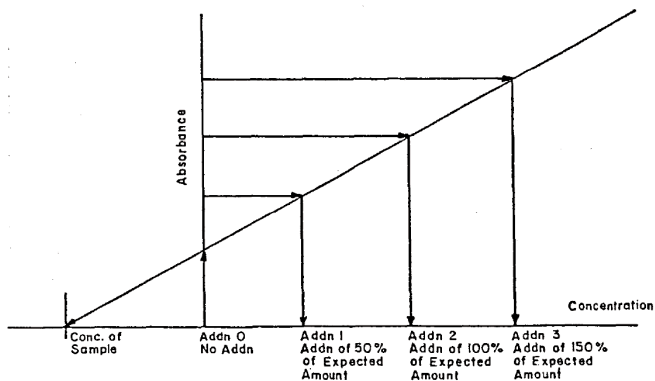
Figure 2.   Standard addition plot.

effective means of compensating for them, provided that the linear portion of the calibration curve is used and background absorption is corrected for by accurate background correction.

Ideally, it is preferable to develop furnace methods that do not require standard additions because of the increased sample handling required. Instruments such as the Agilent GTA-95 graphite furnace can be programmed to automatically prepare standard addition calibration and automatically add measured volumes of matrix modifier solution, greatly minimizing sample handling and the possibility of sample contamination. But if large numbers of samples are to be analyzed, a considerable amount of time can be saved by direct calibration methods. Therefore, the time and effort spent developing an effective analytical method including the use of proper temperature pro-grams and the possible use of matrix modifiers and/or graphite platforms can result in considerable time savings for routine analyses. Graphite furnace methods for the determination of the priority pollutant metals can be successfully automated for large number of samples.

In conclusion, though graphite furnace methods are at times subject to matrix interferences, the skilled analyst with a gen-eral understanding of their nature can anticipate those inter-ferences and apply techniques to eliminate or minimize them. Careful methods development including appropriate selection and optimization of temperature programs and use of matrix modifiers and/or the graphite platform will allow him to obtain accurate analytical results by direct calibration for many analyses. With these analytical tools and the method of standard additions, the analyst should be able to accurately analyze the variety of samples presented for determination of the priority pollutant metals.

References

1. "Analytical Methods for Graphite Tube Atomizers", Varian Techtron Publication No. 85-100447-00 (Jan. 1982).

2. K. G. Brodie, "Practical Operation with the GTA-95 Graphite Tube Atomizer", Varian Instruments at Work, No. AA-28 (March 1983).

3. J. P. Matousek, "Interferences in Electrothermal Atomic Absorption Spectrometry, Their Elimination and Control", Prog. Anal. At. Spectrosc., 4,247 (1981).

4. J. A., Krasowski, T. R. Copeland, "Matrix Interferences in Furnace Atomic Absorption Spectrometry", Anal. Chem., 51 (11), 1843 (1979).

5. E. J. Czobik, J. R. Matousek, "Interference Effects in Furnace Atomic Absorption Spectrometry", Anal. Chem., 51 (1), 3 (1978).

6. L. R. Hageman, J. A. Nichols, P. Viswanadham, R. Woodriff, "Comparative Interference Study for Atomic Absorption Lead Determinations using a Constant Temperature vs. a Pulsed-Type Atomizer", Anal. Chem., 51 (9), 1406 (1979).

7. K. G. Brodie, "Determining Arsenic and Selenium by AAS", Amer. Lab., 9 (3), 73 (1977).

8. R. Ediger, "Atomic Absorption Analysis with the Graphite Furnace using Matrix Modification", At. Absorp. Newsl., 14, 127 (1975).

9. E. J. Czobik, J. P. Matousek, "Effect of Anions on Atomization Temperatures in Furnace Atomic Absorption", Talanta, 24,573 (1977).

10. K. G. Brodie, J. P. Matousek, "Determination bf Cadmium in Air by Non-Flame Atomic Absorption Spectrometry", Anal. Chim. Acta, 200,69 (1974).

11. E. J. Hinderberger, M. L. Kaiser, S. R. Koirtyohann, "Furnace Atomic Absorption Analysis of Biological Samples using the L'vov Platform and Matrix Modification", At. Spectrosc., 2, 1 (1981).

12. T .N. McKenzie, M. W. Routh, "A Mechanistic Approach toward Matrix Modification in Electrothermal Atomic Absorption Spectrophotometry", Varian Techtron (1981). (Presented at 1981 Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy).

13. C. W. Fuller, "The Effect of Acids on the Determination of Thallium by Atomic Absorption Spectrometry with a Graphite Furnace", Anal. Chim. Acta, 81,199 (1976).

14. T .N. McKenzie, P. S. Doidge, M. W. Routh, D. E. Shrader, "The Reduction of Chemical Interferences in High Salt Matrices using Chemical Modification in Graphite Furnace AAS", Varian Techtron (1982). (Presented at 1982 Federation of Analytical Chemistry and Spectroscopy Societies Meeting).

15. P. S. Doidge, "Pyrolytic Graphite Platforms", Varian Instruments at Work, No. AA-25, Varian Techtron (Sept. 1982).

16. B. V. L'vov, "Electrothermal Atomization — The Way Toward Absolute Methods of Atomic Absorption Analysis", Spectrochim. Acta., 33B, 153 (1978).

17. P. S. Doidge, T. N. McKenzie, "Application 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).

18. US EPA, Methods for Chemical Analysis of Water and Wastes, EPA-600/4-79-020 (1979).

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