

Elemental Analysis Manual

for Food and Related Products

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3.6.1 Graphite Furnace Atomic Absorption Spectrometer

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This section provides information to assist the analyst on assuring analytical instrumentation is performing properly.

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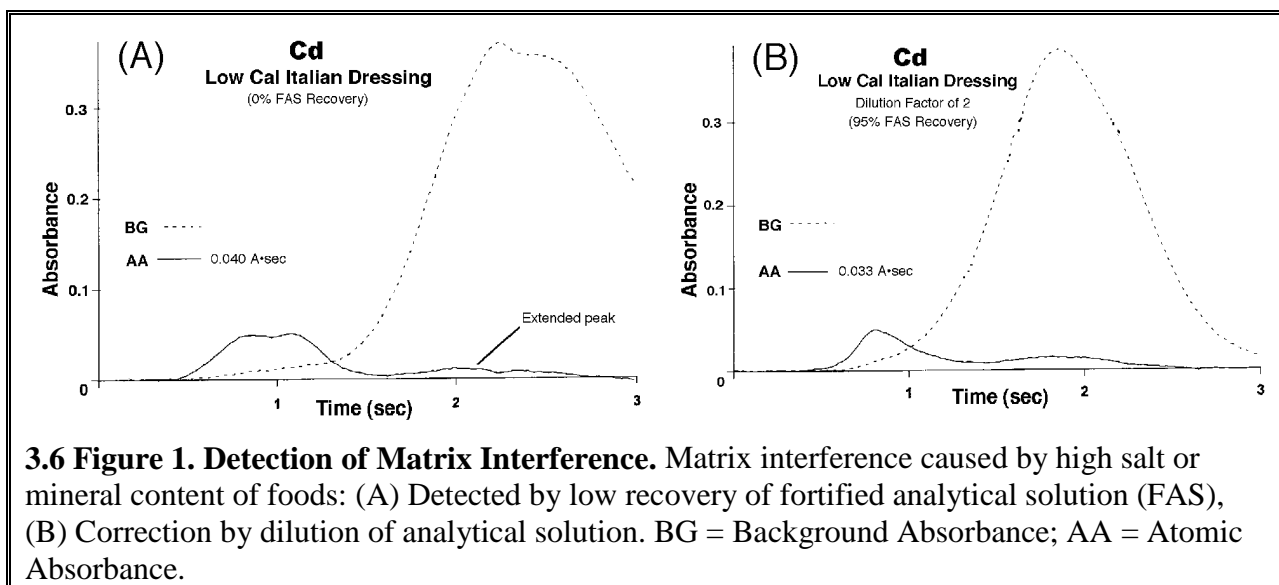
GLOSSARY

3.6.1.1. Interferences

Several types of interferences are associated with graphite furnace atomic absorption spectrometry (GF-AAS) and can be classified into three major divisions: spectral, matrix and memory. An instrument with the capability to graphically display absorbance versus time is required to evaluate interferences.

Spectral interference is the result of absorption of light by an element or molecule that is not the analyte of interest or from black body radiation. Spectral interference caused by another element is rare with GF-AAS because of the narrow atomic line widths emitted by source lamps and the narrow absorption profiles.

Molecular species, however, can produce broadband absorption profiles. The use of matrix modifiers, optimized furnace temperature programs and Zeeman effect background correction can help minimize the effect of this nonspecific absorption. Black body emission from the hot graphite tube can also produce spectral interference. Not using atomization temperatures higher than what is necessary to volatilize the analyte and maintaining proper furnace alignment can minimize this type of interference.



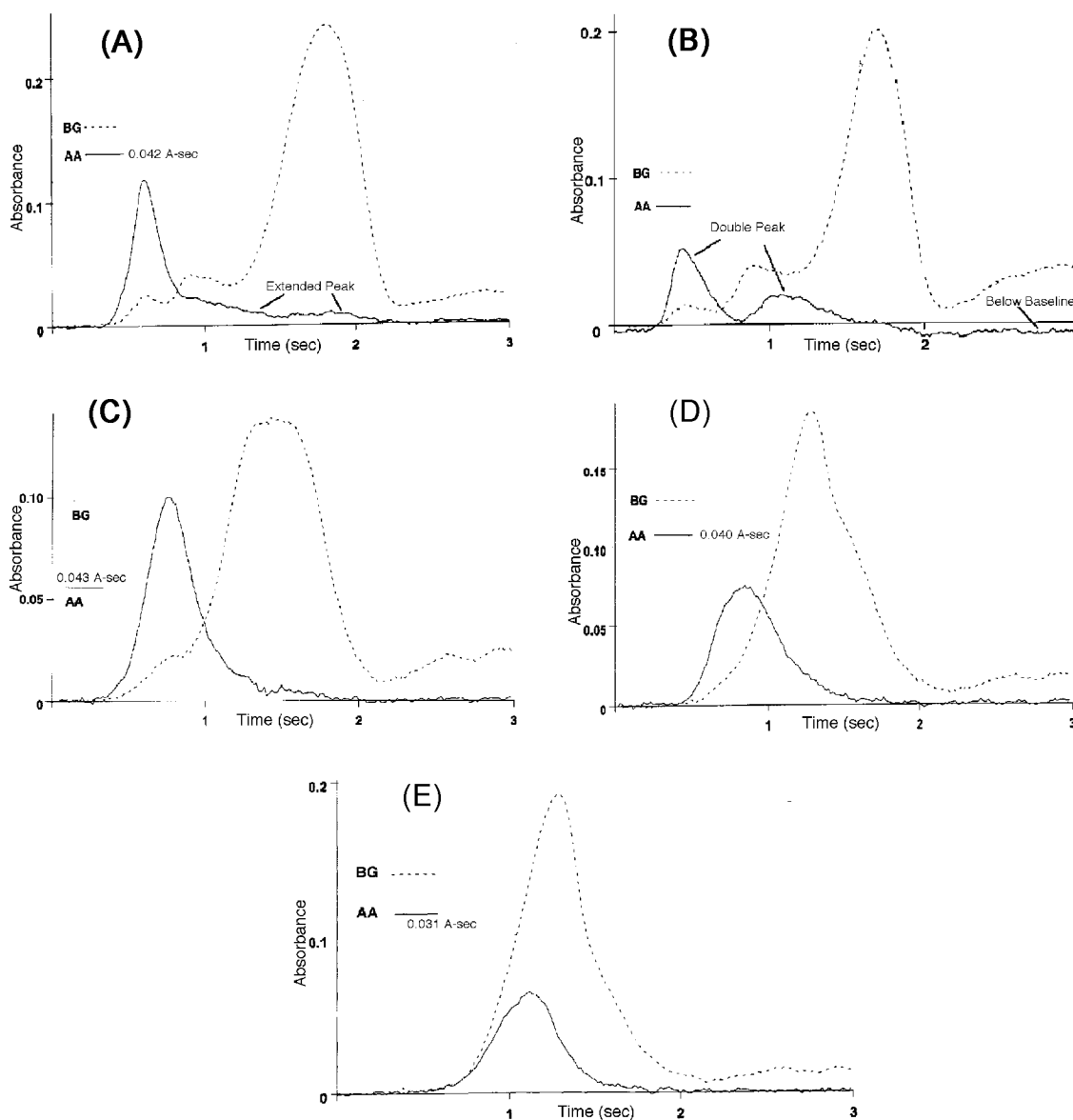
Matrix interferences are caused by matrix components in the analytical portion that inhibit formation of free analyte atoms during the furnace program's atomization step. Components in the matrix may also contribute to pre-atomization volatilization of analyte. The use of platform atomization (instead of tube wall) provides for a more constant temperature environment for volatilization of analyte atoms. This environment is more conducive to the formation of free analyte atoms and helps to minimize matrix interference. The use of 5% hydrogen in the argon gas during the dry and char steps reduces interference from high levels of chloride¹. Matrix interference is still a challenge to overcome with many foods even with these aids for reducing interferences. High salt and high mineral content foods are a particular analytical challenge for the GF-AAS technique (3.6 Figure 1). Some examples of these foods are condiments (mustard, ketchup etc.), pickles, cheese and processed meats. Matrix interference can be detected by poor fortification recovery of the FAP and FAS quality control analyses. If the fortification recovery is outside the acceptable range, then a matrix effect should be suspected and the analytical solution must be diluted and re-analyzed or analyzed by method of standard additions. See 3.6 Figure 2.

In addition to low fortification recovery, an irregular peak profile (sec. 3.6.1.2) might also indicate matrix interference. Analysts should examine analyte peaks for each sample and compare with the standard solution peaks (3.6 Figure 3A). Irregularities to recognize include excessively broadened peaks (low peak height to peak area ratio) (3.6 Figure 3B), doubled or multiple analyte peaks (3.6 Figures 2B and 3C) or a peak's appearance time shifted from expected (3.6 Figures 4A and 4B). For example, American cheese usually exhibits low fortification recovery due to the presence of relatively high levels of salt and other minerals (*i.e.*, phosphate) which hinder the rapid atomization of both cadmium and lead resulting in a very broad peak profile (3.6 Figures 4C and 4D). The peak height to peak area ratio will typically be as much as 40-60% lower than the ratio for the standard solutions. A 0.8 g analytical portion of American cheese will typically result in a 75% percent recovery of lead for the FAS. The slope of the standard addition curve will be approximately 75% of the slope of a check solution that has a matrix of just nitric acid.

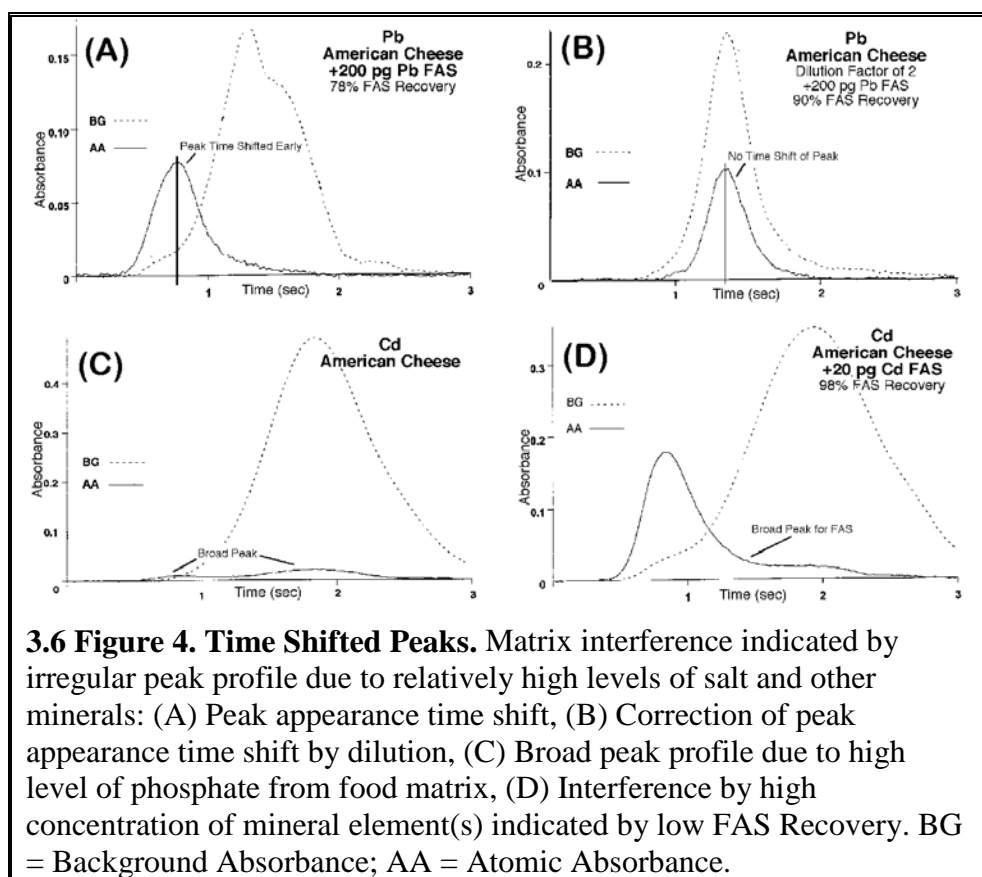
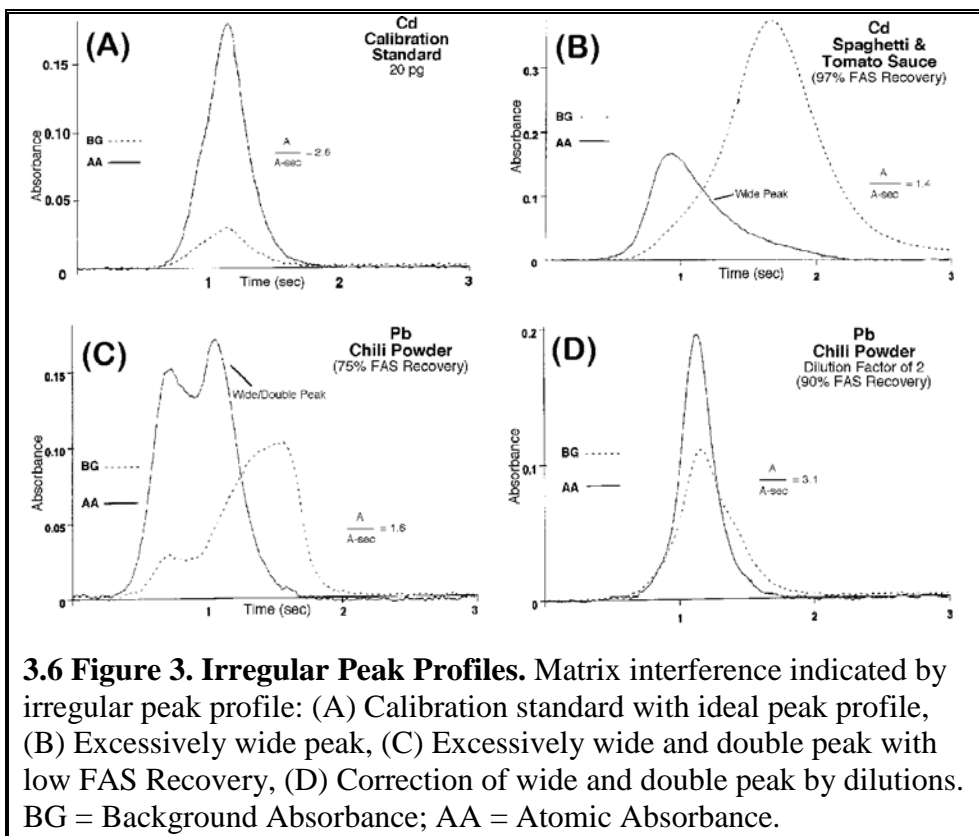
Since furnace programs are usually optimized using a standard solution (no matrix effect), the read step might need to be lengthened to include the entire broadened analyte peak obtained from the food. Ensure that analyte peak tails return to the baseline before the end of the integration/read step (3.6 Figures 5A and 5B). A standard solution peak might return to base line after 2-3 sec whereas some food samples might require 3-4 sec.

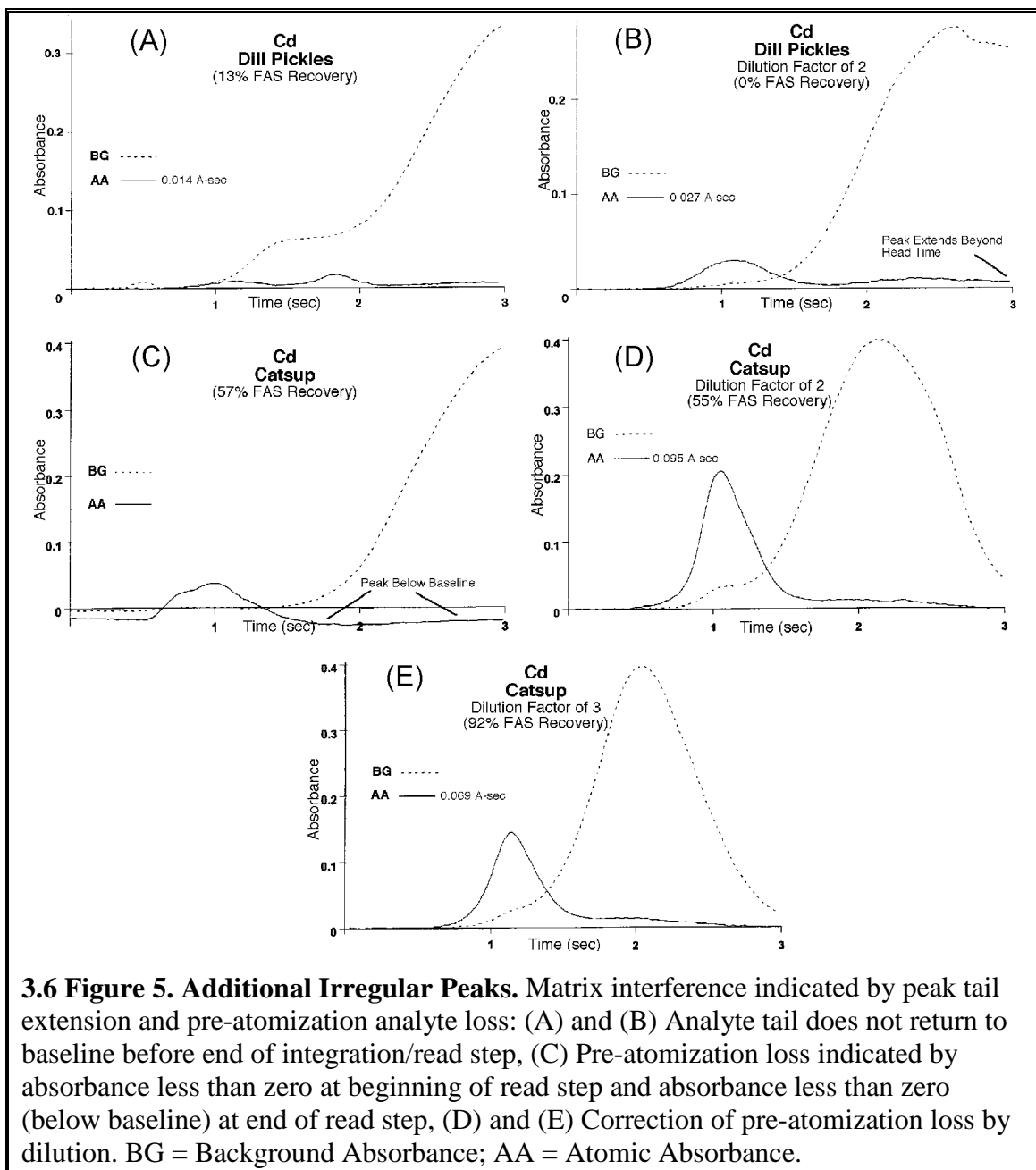
Another phenomenon that has been observed with high-salt samples is pre-atomization analyte loss during the char step. This phenomenon causes an analytical result that is biased low. This loss can occur even when using a matrix modifier and a conservative char temperature. Pre-atomization loss is indicated by an absorbance less than zero at the beginning of the read cycle and ending with the peak's tail dipping below the baseline. Samples displaying this behavior need to be diluted and re-analyzed (3.6 Figures 5C-5E).

Analytes at high levels in the analytical solution may not be volatilized out of the graphite furnace. This residual analyte may have a "memory effect" on the next measurement resulting in a falsely high result (*i.e.*, false positive or high bias). In addition, foods high in salt and minerals can have a matrix memory effect on the next measurement. Use of a clean-out step of a few seconds at maximum temperature should minimize these problems.



3.6 Figure 2. Manifestation of Matrix Interference. Matrix interference indicated by irregular peak profile, low recovery of fortified analytical solutions (FAS) and low recovery of expected value for spinach reference material (NIST SRM 1570): (A) DF 2, 42% RM Recovery, 0% FAS Recovery, (B) DF 2, +400 pg Pb FAS, 0% FAS Recovery, (C) DF 3, 75% RM Recovery, [21% FAS Recovery], (D) DF 4, 102% RM Recovery, [97% FAS Recovery], (E) DF 5, 101% RM Recovery, [95% FAS Recovery]. BG = Background Absorbance; AA = Atomic Absorbance.





3.6 Figure 5. Additional Irregular Peaks. Matrix interference indicated by peak tail extension and pre-atomization analyte loss: (A) and (B) Analyte tail does not return to baseline before end of integration/read step, (C) Pre-atomization loss indicated by absorbance less than zero at beginning of read step and absorbance less than zero (below baseline) at end of read step, (D) and (E) Correction of pre-atomization loss by dilution. BG = Background Absorbance; AA = Atomic Absorbance.

3.6.1.2. Peak Profile

For GF-AAS, peak profile (shape of absorbance vs. time graph) is used to evaluate the quality of the analyte atomization. The profiles of the standard solutions should be very close to the manufacturer's example of an ideal peak for the particular instrument/furnace/tube/element combination. The ratio of peak height to area (H/A) provides for an objective way to judge peak profiles. A narrow peak will have a larger H/A. A wide peak will have a smaller H/A and indicates a slow release of analyte. Matrix suppression should be suspected if the H/A ratio for an analytical solution is <80% of the ratio for a standard solution. If the release is slow enough (low H/A), some analyte might still be present in the tube after the end of the read step resulting in the peak not returning to baseline. Ensure that the read time is sufficient for all analytical solutions. A low H/A can also indicate a doubled peak. Doubled peaks are another manifestation of matrix interference. The degree of matrix interference will be quantitatively assessed by the FAS recovery.

3.6.1.3. INSTRUMENT SETUP

Clean optical windows and replace when the absorbance is 50% greater than manufacturer's specification for new windows.

Inspect and replace tube and platform if necessary. A tube/platform will last between 200-800 firings depending on instrument manufacturer, atomization temperature and sample type. Consult instrument's laboratory records information on tube history. Tubes should be replaced when characteristic mass has increased 10-15%, when peak profiles have degraded (longer tails, doubled peaks, wider peaks) or when laboratory records indicates tube is approaching the end of its performance lifetime. Starting an analysis with a new tube is better than having tube performance degrade during an analytical run.

Check optical alignment of furnace and alignment of autosampler tip.

After instrument has warmed up for at least 30 minutes, record lamp energy for future reference. Suspect a problem if lamp energy is <90% of expected.

Perform instrument sensitivity check. If characteristic mass specification cannot be met, then the standard solution was improperly made or there is a problem with the instrument or furnace program.

Perform instrument stability check. If short term precision is >5% RSD, determine and correct problem.

3.6.1.4. PRE-STANDARDIZATION CHECKS

- (1) Instrument sensitivity check—Adequate instrument sensitivity is demonstrated by analyzing a standard solution and calculating characteristic mass, m_o (see §3.2.1). Choose a standard that results in 0.05–0.1 A-sec. This daily m_o must be within 20% of the expected value as calculated from accumulated m_o results for the same set of conditions. If proper sensitivity cannot be demonstrated, determine and correct problem before standardization.
- (2) Instrument stability check—Instrument stability is demonstrated by analyzing a standard solution a minimum of 5 times. Choose a standard that results in 0.05–0.1 A-sec. The resulting RSD of absorbance signals must be $\leq 5\%$. If RSD >5%, determine and correct problem before standardization.

3.6.1.5. STANDARDIZATION VERIFICATION

To ensure accuracy, instrument standardization is verified initially, during and after an analytical run.

- (1) Initial standardization verification—Analyze ICS and standard blank immediately following instrument standardization. Results for ICS recovery must be $100 \pm 5\%$ of expected value. Analyze standard blank after ICS to check for carry over. Results for the standard blank must be less than the ASDL. If either of these conditions is not met, diagnose and correct the problem(s) and re-standardize GF-AAS instrument.
- (2) Continuing standardization verification—To verify lack of instrumental drift, analyze a check solution at a frequency of 10% of analytical solutions and at end of analytical run. Control limits for check solutions are $100 \pm 10\%$ of expected concentrations. If control limits are not met then analysis must be discontinued, cause of deviation determined and

instrument re-standardized. All analytical solutions following the last acceptable check solution must then be re-analyzed. This procedure ensures that all groups of 10 or less analytical solution analyses are bracketed by valid standardization verification checks.

3.6.1.6. ANALYSIS CHECKS

- (1) Precision—All measurement results of analytical solutions, standard solutions, standard additions, and quality control solutions are based on the mean of at least 2 replicate injections of the solution from the same autosampler cup. Precision between the injections must be 7% RSD or less for all analytical solutions with ≥ 0.012 A-sec. If control limits are not met then re-analyze the analytical solution. If the repeat analysis is still out of control, then suspect instrument problem or matrix interference. Diagnose the problem, make necessary adjustments and re-analyze the analytical solution.
- (2) Standard curve—The value for the correlation coefficient (r) must be ≥ 0.998 . Highest standard must be within the LDR if a linear algorithm is used. A value less than this control limit is an indication of a problem with preparation or standardization due to one or more standard solutions or the standard blank. If display of the standard curve (A-sec vs. concentration) indicates which standard solution is bad, provide re-standardization data for that standard solution. Otherwise, re-standardize with all standard solutions. If re-standardization does not fix the problem, then prepare new standard solutions and re-standardize GF-AAS instrument.
- (3) Standard additions—The value for correlation coefficient (r) must be ≥ 0.995 . A-sec of all analytical solutions plus additions must be within the LDR.

Dilute any analytical solutions with standard blank if integrated absorbance is greater than highest standard solution. Estimate degree of dilution needed from absorbance.

There are limitations to the amount of matrix effect correctable by quantification using the method of standard additions. If the slope of an analytical solution standard addition curve is <50% of the slope standard addition curve of a standard blank (or a standard solution without any matrix effect such as the ICS), then the analytical solution should be diluted by a factor of 2 with standard blank and re-analyzed.

REFERENCES

- (1) Creed, J., Martin, T., Lobring, L., and O'Del, J. (1992) Minimizing Chloride Interference Produced by Combination Acid Digestion Using Palladium and Hydrogen as a Matrix Modifier in Graphite Furnace Atomic Absorption Spectrometry, *Environ. Sci. Technol.* **26**, 102-106.