

Elemental Analysis Manual

for Food and Related Products

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3.6.4 Inductively Coupled Plasma-Mass 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

3.6.4.1. Interferences

Several types of interferences are associated with inductively coupled plasma-mass spectrometry (ICP-MS). Instrument operators must be familiar with the various interferences, the means of detecting interferences and the ways to eliminate or minimize them. Typical quadrupole-based instruments do not have the resolution capabilities to resolve interferences that are less than one nominal mass unit such as ^{75}As (mass 74.9216) and $^{40}\text{Ar}^{35}\text{Cl}$ (mass 74.9312).

- (1) Elemental isobaric interference—is caused by an isotope of an element other than the analyte element that forms a singly charged ion with the same nominal mass-to-charge ratio as the analyte isotope. The recommended isotopes for elements determined by this method are free from elemental isobaric interference. An example of elemental isobaric interference is ^{114}Cd and ^{114}Sn . However, none of the recommended isotopes in this method suffers from an elemental isobaric interference.
- (2) Doubly charged species isobaric interference—is actually a special case of elemental isobaric interference caused by an isotope of an element other than the analyte element that forms a doubly charged ion with the same nominal mass-to-charge ratio as the analyte isotope. The only doubly charged species of concern for this method are $^{150}\text{Sm}^{++}$ and $^{150}\text{Nd}^{++}$. The mass to charge ratio is 75 for $^{150}\text{Sm}^{++}$ and $^{150}\text{Nd}^{++}$, which is the same mass to charge ratio used to determine arsenic. Tuning the instrument to minimize doubly charged species is helpful. However, if neodymium or samarium is present in an analytical solution, correction factors must be applied. Otherwise, arsenic results could have a positive bias.
- (3) Polyatomic isobaric interference—is caused by molecular species with the same nominal mass-to-charge ratio as the analyte isotope. These ions can be formed in the plasma, the interface or the reaction cell. The sources for these molecular ions are the plasma (Ar), the atmosphere (C, O, N, CO_2), the matrix (H_2O) and the sample. The main polyatomic interferences on arsenic are $^{40}\text{Ar}^{35}\text{Cl}$ and $^{40}\text{Ca}^{35}\text{Cl}$. These could be significant because many processed foods are high in salt and dairy products are naturally high in calcium. Additionally, HCl is added to help stabilize Hg so chloride will be present in all analytical solutions. The main polyatomic interference on the recommended Cd isotope (^{111}Cd) is $^{95}\text{Mo}^{16}\text{O}$. The effect should be negligible if the instrument is tuned properly (low oxide formation) and the fact that Mo levels in foods are very low. Lead and mercury should not be affected by polyatomic isobaric interferences in most food and dietary supplement analyses.
- (4) Matrix interference—is caused by various properties of the analytical solution such as dissolved solids content and viscosity. High dissolved solids can affect nebulizer operation, cause deposits on the interface cones, and affect ionization efficiency. Cone deposits will cause the response to drift over time. High dissolved solids/salt in an analytical solution will suppress ionization of elements with high ionization potentials (>9 eV) more than other elements. Therefore, an internal standard element that has a similar ionization potential (IP) as the analyte will probably compensate for this suppression better than one with a greatly different IP. Another type of matrix effect is suppression caused by the space charge effect. Lighter elements will tend to be “knocked around” and not pass through the ion lenses as efficiently as heavier elements. An internal standard element close in mass to the analyte element will help with this type of interference.

The net effect of various matrix effects is a change in response factor for a given element in the food analytical solutions versus the standards thus leading to inaccurate results. Analytical solutions must be limited to <0.2% (2000 mg/L) dissolved solids. Suppression

of the internal standard isotope usually indicates that some type of matrix effect is present. Dilution is required for any analytical solution if the internal standard signal differs by more than 40% from the calibration blank. Although internal standards can compensate for matrix effects, there is a limit to the amount of correction applied before the accuracy of the measurement suffers. Poor fortification recovery of the FAP and FAS quality control analyses can also indicate matrix interference. If the fortification recovery is outside the acceptable range, then a matrix effect should be suspected and the analytical solution must be diluted and reanalyzed or analyzed by method of standard additions.

- (5) Memory effect interference—is caused by a high concentration of an element in an analytical solution that does not fully rinse out of the sample introduction system during the programmed rinse time. Sufficient rinse time must be allowed in the autosampler program to rinse out the highest concentrations of elements expected. Analyzing a blank after the highest standard will confirm if the rinse time is long enough. Mercury is especially prone to memory effects. Therefore, the highest Hg standard should be no higher than 1 µg/L.

3.6.4.2. Instrument Setup

Each laboratory must determine optimum instrument parameters for radio frequency (RF) power, sampling depth, argon flow rates, collision cell gas flow rate, lens voltages and sample uptake rate. Analyst should be aware that small changes in RF power, sampling depth and argon flow rates could greatly affect the instrument performance. Inspect sample introduction system including nebulizer, torch, pump tubes and sampler cone. Inspection frequency will depend on work load and analytical solution composition. Inspect system at each use and clean as needed. Clean cones when deposits are noticed. Allow instrument to become thermally stable before standardization and analyses. This usually requires at least 20-30 minutes of operation. After instrument warm-up, perform tuning. Set up method and autosampler sequence table. Determine any corrections factors needed and enter in method.

Safety Note: Inductively coupled plasmas emit ultraviolet radiation during operation and must be viewed with proper eye protection.

3.6.4.3. Pre-standardization Checks

Instrument sensitivity and precision check—Ensuring that the instrument is operating correctly is essential before spending time standardizing or analyzing samples. Instrument sensitivity and short-term precision must be demonstrated before proceeding with standardization. Run the “Tune Report” after tuning the instrument and while still aspirating the tune solution. Results for sensitivity, oxide lever, double charged species, peak axis and peak height should meet laboratory’s or manufacturer’s specifications. Analyze one of the midlevel standard solutions and check that the RSD is $\leq 5\%$ indicating good precision. Failure of either the sensitivity or precision check usually indicates a solution introduction problem. Correct the problem before proceeding.

3.6.4.4. Standardization Verification

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

- (1) Standard curve—Values for correlation coefficients (r) must be ≥ 0.998 . A value less than this control limit indicates problem with preparation or standardization due to one or more standard solutions or the standard blank. If display of the standard curve (intensity vs. concentration) indicates which standard solution is bad, re-standardization that standard solution. Otherwise re-standardize ICP-MS instrument. If re-standardization does not fix the problem, then prepare new standard solutions and re-standardize instrument.
- (2) IDL verification—immediately after standardization, determine IDLs. Analyze the standard blank 5 times (separate analyses with normal autosampler rinse in between). The IDLs must be within 3 times the normally obtained IDL values.
- (3) Initial standardization verification—Analyze ICS and standard blank immediately following instrument standardization and IDL verification. 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 ICP-MS instrument.

Note: If the fortification solution was used to prepare ICS and ICS is out of control, an error in fortification of the FAP should be suspected and may require the FAP to be re-prepared.

- (4) Continuing standardization verification—To verify lack of instrumental drift and carry over, analyze a check solution and the standard blank 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. Control limits for standard blanks are \leq ASDL. If control limits are not met analysis must be discontinued, cause of deviation determined and instrument re-standardized. All analytical solutions following the last acceptable check solution and standard blank must be re-analyzed. This procedure ensures all groups of 10 or less analytical solution analyses are bracketed by valid standardization verification checks.

3.6.4.5. Analysis Checks

- (1) Precision—All measurement results of analytical solutions, diluted analytical solutions, standard solutions, and quality control solutions shall be based on the mean of 3 replicate integrations. Precision of replicate integrations is usually 7% RSD or less for concentrations above ASQL in all analytical solutions. 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 problem, make necessary adjustments and re-analyze analytical solution. There may be either a problem with the sample introduction system or a physical interference with the analytical solution. Flushing the sample introduction system for several minutes and diluting analytical solution by a factor of 2 may resolve the problem. If the RSD still fails then diagnose the problem and fix before proceeding.
- (2) Standard additions—If quantification is performed by the method of standard additions, the value for correlation coefficient (r) must be ≥ 0.995 .