Matrix Effects in ICP-AES Analysis

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The sample "matrix" is the bulk composition of the sample such as water, organic compounds, acids, dissolved solids, and salts. Matrix effects can influence the ability of an analytical method to qualitatively identify and quantitatively measure target compounds in environmental and other samples by indirectly affecting the intensity and resolution of observed signals. To obtain defensible results, the analyst must account for all matrix effects.

In ICP-OES analysis, the ionic-to-atomic line intensity ratio can be used as an indicator for determining plasma-related matrix effects. Elements such as sodium and calcium, which are ubiquitous in nature, have low ionization potentials and as a consequence are some of the most easily ionized elements. In this study, the influence of sodium as well as the acid concentration on the ionic and atomic intensity of chromium, cadmium, and lead has been investigated.

Experimental

Technique: Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) — PerkinElmer Elan DV 3300

Operating Conditions:

RF Generator Power: 1450 W
Plasma Gas flow rate: 15 L/min
Auxiliary gas flow rate: 0.5 L/min
Nebulizer flow rate: 0.65 L/min
Sample uptake: 1 mL/min
Nebulizer: Concentric
Spray chamber: Cyclonic
Injector tube diameter: 1.5 mm

Sample Preparation:

SPEX CertiPrep standard CLMS-2 was diluted to 1.0 ppm by 10X dilution with 5% nitric acid and aspirated through channel 1. Various concentrations of sodium (0, 50, 100, 200, 500, and 1000) were prepared and aspirated through channel 2. Both solutions were mixed through a "T" tube connector and further mixing through a coil before entering the nebulizer.

Results

Figure 1 represents the relative intensity of ionic lines and atomic lines as well as the ionic/atomic ratio in the presence of varying concentrations of sodium. The matrix effect due to varying the concentration of nitric acid and hydrochloric acid is shown in Figure 2 and Figure 3.

Discussion

Effect of Sodium Concentration

We observed a considerable change in the recovery of cadmium and chromium in the presence of varying concentrations of sodium. The relative intensity of chromium and cadmium atom lines was much higher than the respective ionic lines for these analytes. The effect is significant even at 50 ppm sodium. The lead concentration is affected, relatively, less by the change in the sodium concentration.

Effect of Acid Concentration

The matrix effect due to changes in acid concentration was very significant for cadmium and lead in nitric acid; atom line and ion line for both of them showed lower intensity. The higher the acid concentration, the lower was the intensity for these two elements; hence, it has poorer detection limits. While the chromium atom line was somewhat less affected, we observed a decrease in intensity for the chromium ion line.

We also observed a much smaller, though significant, change in analyte recovery with increase in hydrochloric acid when compared with nitric acid. Here again, effect of acid on chromium atom line was minimal when compared to chromium ion line; however the acid concentration impacted lead differently. The recovery for lead ion line was better than the atom line.

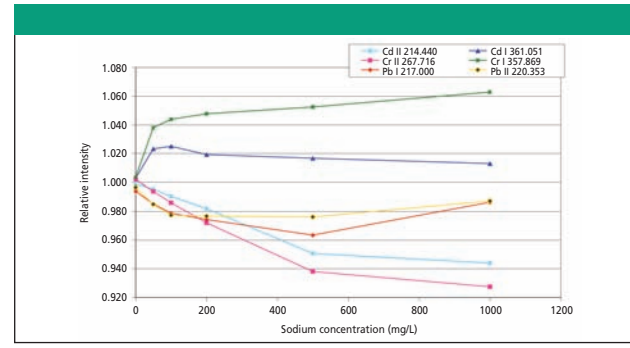

Figure 1: Effect of sodium concentration.

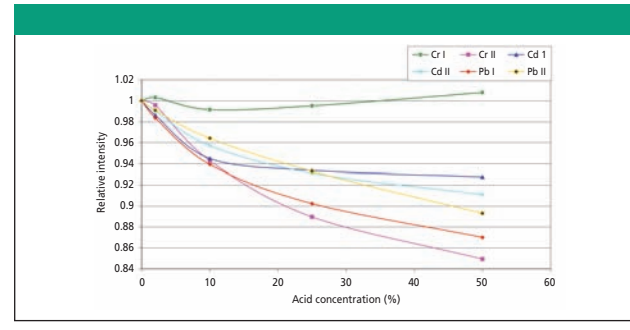

Figure 2: Effect of nitric acid concentration.

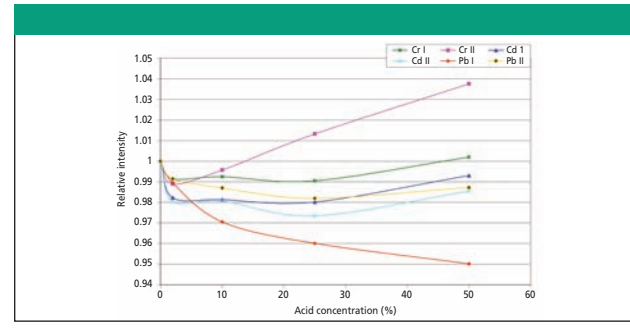

Figure 3: HCl matrix effect.

Results

Sample matrix has a profound effect on the accuracy of trace elemental analysis by ICP. Excess acid from acid digestion can be a source of error in the analysis. Because of the different behavior of the atomic and ionic lines, at least two internal standards are needed to compensate for matrix effects. It is absolutely essential to match the sample matrix to the standard to ensure accurate and defensible data.

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