

# Visualizing the Solute Vaporization Interference in Flame Atomic Absorption Spectroscopy

**Christopher R. Dockery**

Department of Chemistry and Biochemistry, Kennesaw State University, Kennesaw, GA 30144

**Michael J. Blew and Scott R. Goode\***

Department of Chemistry and Biochemistry, The University of South Carolina, Columbia, SC 29208; \*Goode@sc.edu

For a number of years, scientists have known that the signal from calcium in analytical atomic spectroscopy is influenced by the presence of aluminum (1–4). As droplets of the analyte vaporize, refractory calcium aluminates form, so not all of the calcium is vaporized in the presence of aluminum. This type of interference is known as a solute vaporization interference. One method used to reduce the solute vaporization interference is to add a releasing agent such as lanthanum. Lanthanum aluminate forms preferentially to calcium aluminate, ensuring that the calcium is present as free atoms (5, 6).

Students have studied solute vaporization interferences in the undergraduate laboratory by investigating the effectiveness of releasing and chelating agents (3) and by varying observation height and flame stoichiometry (4). Also, numerous articles address optimization of operating conditions and a characterization of a spectrometer (7–12). From such experiments, students learn that the analytical response from a 1 µg/mL sample of calcium depends on whether the calcium is present in distilled water, industrial waste, blood serum, aluminum, lanthanum, and so forth. The effect of the matrix on the calcium signal is the subject of this investigation.

In this experiment, flame atomic absorption spectroscopy (FAAS) is used to systematically investigate calcium atomic absorption and the solute vaporization interference. Calcium atomic absorption measurements are performed on solutions that contain only calcium, calcium plus aluminum, and calcium plus aluminum with lanthanum added as a releasing agent. We visualize the solute vaporization interference using modern response surface methods and evaluate the efficacy of adding lanthanum to suppress this interference. These interferences are affected by flame temperature, so measurements were made under conditions of varied flame stoichiometry and observation height. Results are displayed using response surfaces generated by regression analysis of absorbance generated by a factorial design in which burner height varied over five levels and fuel ratio varied over four levels.

This mode of presentation allows the student to visualize the influence of flame conditions on the instrumental response. The user can choose to optimize operating conditions based on minimizing the solute vaporization interference, maximizing the absorbance, optimizing signal-to-noise ratio, or any combination of these three diagnostic parameters. Students can analyze the response surface plots to find regions (observation height and flame stoichiometry) that are least influenced by chemical interferences and determine the tradeoffs required to optimize instrumental response. Conditions producing maximum absolute calcium absorption and the lowest limits of detection are not the same as those needed for stable, reproducible chemical analyses.

## Experimental

All experiments were performed using a Perkin-Elmer (Norwalk, CT) model 3110 atomic absorption spectrometer (AAS) set to atomic absorption mode using a calcium hollow cathode lamp (Fisher Scientific, Fair Lawn, NJ). The manufacturer's recommendations are acetylene/air pre-mixing slot burner, 422.7 nm wavelength, and 0.7 nm spectral slit width (5). Calcium atomic absorption was optimized following the manufacturer's recommendations for adjusting the burner horizontal and rotational positions (6). The vertical positioning of the burner (observation height) and the fuel stoichiometry are not optimized during the startup procedures as these factors will be investigated during the course of the laboratory.

Students systematically investigate the influence flame stoichiometry and observation heights have on calcium atomic absorption and the solute vaporization interference. Fuel to oxidant ratio is varied by changing the fuel setting on the flow meter. The oxidant (air) remains constant at a setting of 4 units (6.25 standard liters per min, SLPM), so the aspiration parameters remain unchanged. The fuel (acetylene) may safely be run as low as 1.5 units (1.0 SLPM) and as high as 4 units (2.2 SLPM). Burner height is measured from the top of the burner slot to the center of the observation window. We suggest that students investigate conditions in which burner height varied over five levels (1, 4, 7, 10, 13 mm) and fuel ratio varied over four levels (1.5, 2.0, 2.5, 3.0 fuel setting).

Students generate surface response plots predicting the behavior of calcium in the flame at varied observation heights and fuel stoichiometry. A quadratic model of the following form is fit to the data

$$Y = \beta_0 + \beta_1 X_1 + \beta_{11} X_1^2 + \beta_2 X_2 + \beta_{22} X_2^2 + \beta_{12} X_1 X_2 + \text{residuals}$$

where  $X_1$  is the burner height and  $X_2$  is the fuel setting.

A detailed discussion on generating quadratic model surface response plots using Microsoft Excel appears in the online supplement. Unless otherwise noted, surface response plots were generated using Design-Expert, version 5 (Stat-Ease Corp., Minneapolis, MN).

## Hazards

Take caution not to drop the fuel lower than 1.5 units or change the oxidant setting from 4 units as excess acetylene can build up in the burner head and cause a flashback explosion. To minimize damage in the event of a flashback, the burner head should be secured to the instrument casing with heavy gauge wire, which is a standard safety feature on most modern flame AA spectrometers.

## Results and Discussion

Response surfaces for a 10 ppm calcium solution in deionized water generated using Design-Expert and Microsoft Excel are compared in Figure 1. The regression parameters are identical and both predict a diagonal ridge of maximum atomic absorption.

### Absorbance Signal

Figure 2 shows the absorbance response surfaces for 10 ppm calcium, 10 ppm calcium in the presence of 10:1 mole ratio

aluminum as a solute vaporization interference, and 10 ppm calcium in the presence of 10:1 mole ratio aluminum plus 0.5% lanthanum added as a releasing agent. Students analyze the plots to find regions (observation height and flame stoichiometry) that are least affected by the chemical interferences. Aluminum suppresses the calcium atomic absorption 20–30% (Figure 2B) while adding lanthanum corrects in some regions but shows signal enhancement at high fuel settings and low observation heights (Figure 2C). Ideally, operating conditions should be chosen to minimize enhancements or suppression caused by matrix effects.

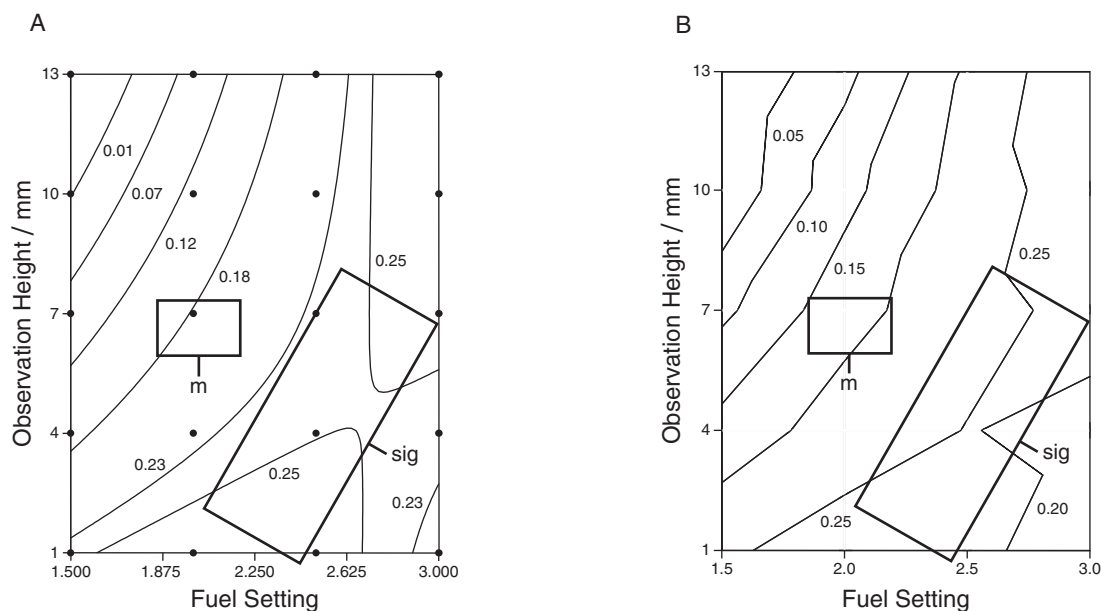


Figure 1. Calcium atomic absorption surface response plots generated by (A) Design-Expert and (B) Microsoft Excel. The surfaces predict a diagonal ridge of maximum atomic absorption. The manufacturer's suggested optimum is indicated with **m**. The region of highest analytical signal is shown with the box labeled with **sig**. Note that the fuel settings are the settings on the flow meter and are related to standard liters per minute.

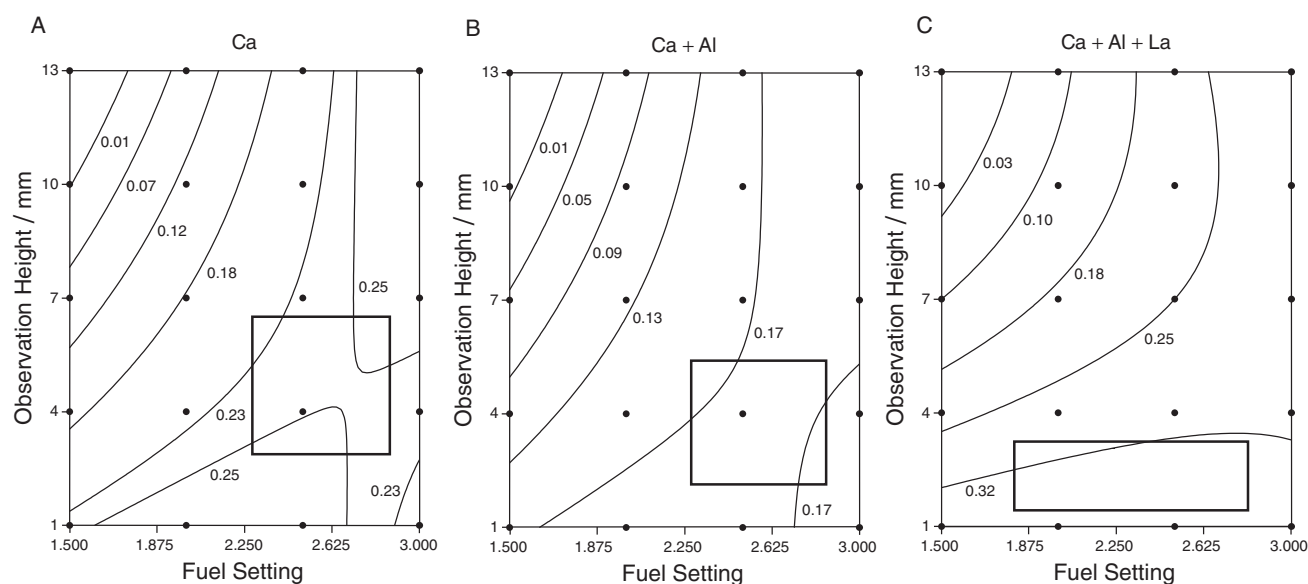


Figure 2. Atomic absorption signal for (A) 10 ppm Ca in deionized water, (B) 10 ppm Ca in a 10:1 mole ratio aluminum solute vaporization interference, and (C) 10 ppm Ca in a 10:1 mole ratio aluminum solute vaporization interference plus 0.5% lanthanum added as a releasing agent. Boxes show the regions of highest analytical signal.

### Signal-to-Noise Ratio

Students obtain response surfaces of signal-to-noise ratio (S/N). The S/N is calculated by the reciprocal of the relative standard deviation of the triplicate measurements of absorbance. The S/N is related to the limit of detection, which is generally defined as the concentration that produces a S/N equal to 3. Typical results are shown in Figure 3.

### Solute Vaporization Interference

Students can visualize the conditions producing minimum suppression or enhancement by generating difference plots (Figure 4). The difference plots are generated by subtracting the interference free response from the response in the presence of the chemical interference. The solute vaporization interference may be minimized by optimizing the experimental factors. Fig-

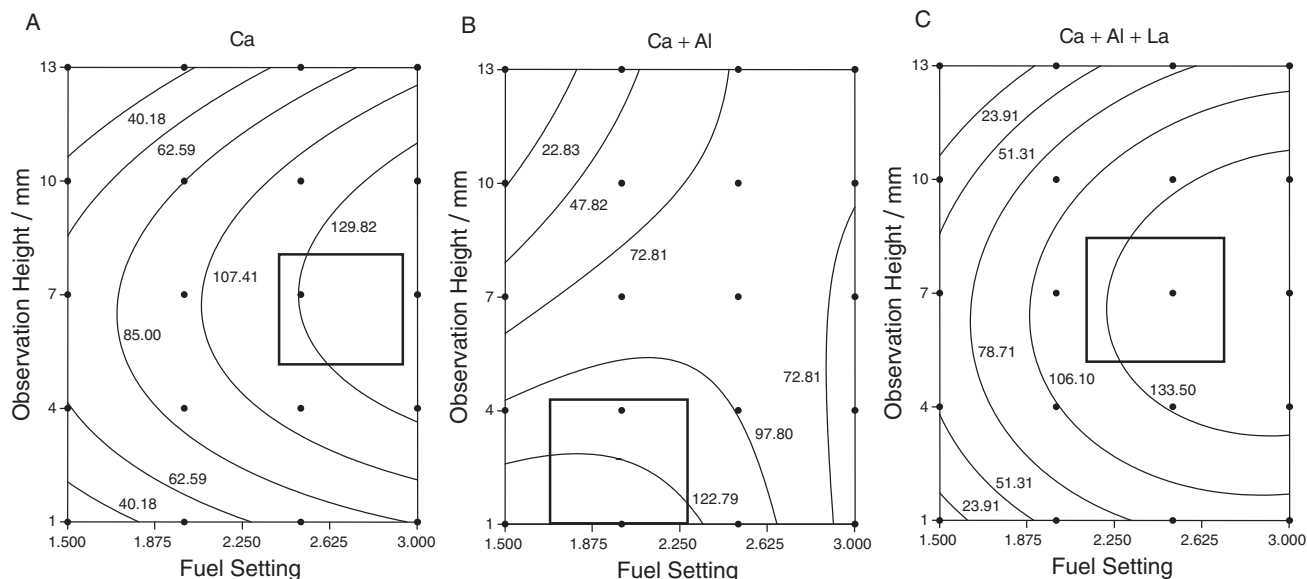


Figure 3. Signal-to-noise ratio (S/N) plots for (A) 10 ppm Ca in deionized water, (B) 10 ppm Ca in a 10:1 mole ratio aluminum solute vaporization interference, and (C) 10 ppm Ca in a 10:1 mole ratio aluminum solute vaporization interference plus 0.5% lanthanum added as a releasing agent. Boxes indicate regions of highest S/N.

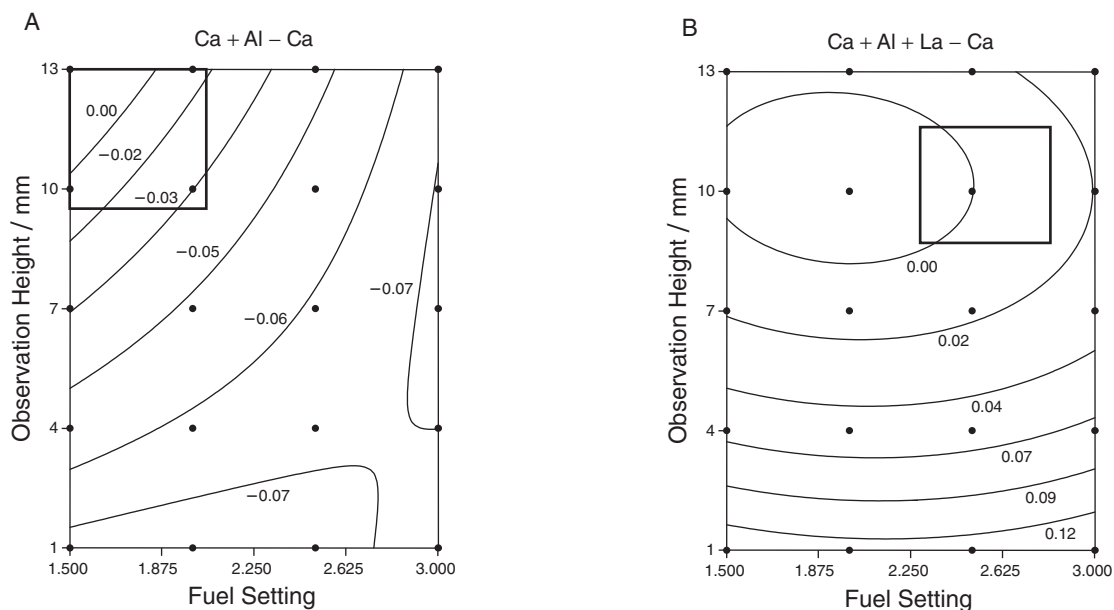


Figure 4. Difference plots: (A) 10 ppm Ca in a 10:1 mole ratio aluminum solute vaporization interference minus 10 ppm Ca in deionized water and (B) 10 ppm Ca in a 10:1 mole ratio aluminum solute vaporization interference plus 0.5% lanthanum added as a releasing agent minus 10 ppm Ca in deionized water. Boxes show regions of minimum solute vaporization interference.

ure 4A shows that aluminum decreases the calcium atomic absorption, thus producing negative values on the difference plot. The depression is minimized in a fuel-lean flame 13 mm above the burner slot. However, these operating conditions produce very little absorption (see Figure 2A); the lack of suppression results from signals that are near zero rather than discovery of optimized operating conditions. The solute vaporization interference of aluminum on calcium cannot be eliminated by adjusting settings of fuel or observation height.

Figure 4B shows the difference between the calcium atomic absorption signal and calcium in the presence of aluminum and lanthanum added as the releasing agent. Under certain conditions, the presence of lanthanum increases the calcium atomic absorption. The difference plot (Figure 4B) shows that the lanthanum solution eliminates much of the interference over a wide range of operating conditions 7–13 mm above the burner slot. Operating within this range of physical parameters minimizes artificial signal enhancements caused by matrix effects in the releasing agent solution.

### Optimum Conditions

Using response surface methods, students investigate the tradeoffs required to optimize instrumental parameters, comparing regions producing the maximum calcium signal (Figure 2), the maximum S/N (Figure 3), and the minimum chemical interference (Figure 4). Students are asked to select optimum conditions and justify their choices. They are expected to notice that conditions producing maximum absolute calcium absorption may not be ideal for stable, reproducible chemical analyses. A summary of the experimental optimization of minimized solute vaporization interference, maximum signal, and maximum S/N is presented in Figure 5.

Once optimum conditions have been determined, students run calibration standards at optimum operating conditions and at conditions that produce significant interferences. These results are shown in Figure 6. At optimum operating conditions (Figure 6A) the aluminum suppression is minimized and the added

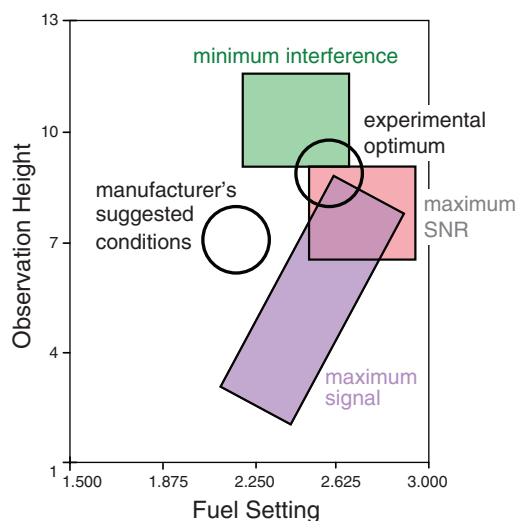


Figure 5. Summary of experimental optimization.

lanthanum does not produce calcium signal enhancements. Observation low in a slightly lean flame (Figure 6B) produces acceptable calibration in interference free solutions, but these conditions show a significant solute vaporization interference that cannot be corrected by adding lanthanum. From these calibrations, students are asked to assess the error associated with calibration at unoptimized conditions.

### Conclusion

Through visualization of experimental results via generation of surface response plots, students recognize the tradeoffs required to optimize instrumental parameters in the presence of known chemical interferences. Students find that the analytical response from 1  $\mu\text{g}/\text{mL}$  calcium in solution will differ depending on the matrix. Also, students gain better understanding and

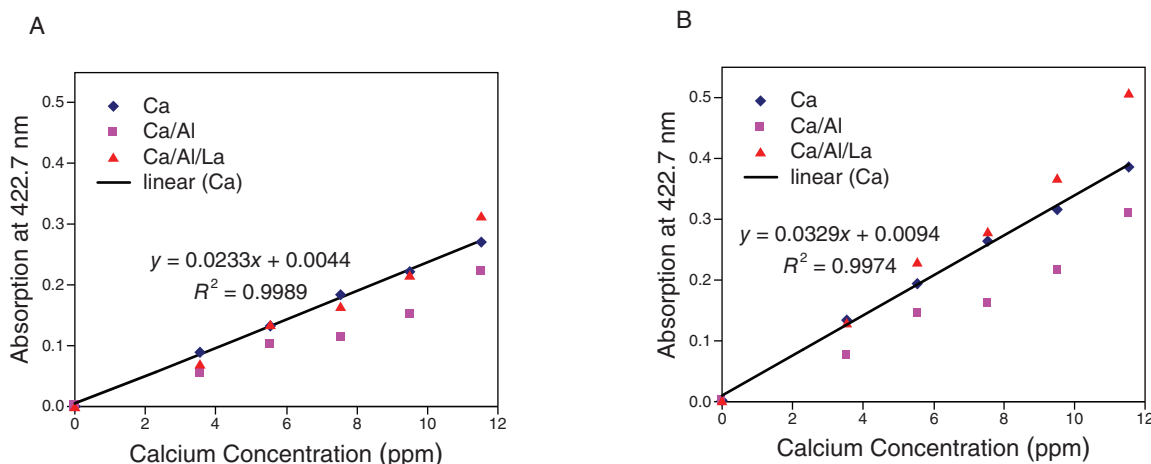


Figure 6. Calibration curves in the presence of chemical interferences at (A) optimum and (B) unoptimized conditions chosen to accentuate solute vaporization interference. At optimum operating conditions, the aluminum suppression is lower and the added lanthanum does not produce calcium signal enhancements.

appreciation for the spectrometer and realize the tradeoffs in signal, signal-to-noise, and freedom from interference that must be made when developing an analytical method.

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