

FLAME ATOMIC EMISSION SPECTROMETRY Using the Varian SpectrAA-200

The objective of this laboratory experiment is to introduce the concept of flame emission as applied to analytical atomic spectroscopy, and to explore the working concentration ranges, interferences, and basic equilibrium processes in air-acetylene and nitrous oxide-acetylene flames which are commonly used in atomic emission spectroscopy.

Before you begin the experiment, it is extremely important to understand the precautions and rules to follow when using the Varian atomic absorption/emission spectrophotometer. **FAILURE TO OBSERVE ANY OF THE FOLLOWING PRECAUTIONS CAN AND WILL RESULT IN A VIOLENT EXPLOSION!**

FLAME START-UP: AIR-ACETYLENE FLAME

1. Pull off the burner head to check if the liquid trap is filled. Check by pouring distilled water into the spray chamber through the burner head collar until you observe water running through the drain tube into the waste bucket. Replace the burner head, making sure that it is secure.
2. Make certain that the waste bucket has been emptied before you start. After emptying the bucket, replace the drain tube. When replacing the tube, make sure that the end of the tube is NOT submerged.
3. Turn on the exhaust hood before any fuel or oxidant lines have been opened. Also, turn on the power switch on the Varian spectrophotometer. *Power up the instrument before starting the SpectrAA Software on the computer.*
4. Open the air line using the bench-mounted spigot. Check the air pressure gauge mounted on the wall behind the instrument to be sure that the pressure is approximately 60 psi.
5. Open the valve on the acetylene tank. Check the tank pressure. It should read between 8 and 10 psi.
6. With both the air and acetylene lines open, press the ignite button on the instrument's front panel. A bright yellow-white flame should result. Provided the fuel and oxidant purity is sufficient, the default gas flow settings on the instrument should produce an acceptable flame. The flame should have a crisp blue feather and non-luminous flame (The feather should be sharp and well-defined). Adjustments to the fuel to oxidant ratio can be made in **Analysis...Optimize** window in the SpectrAA software.
7. Aspirate distilled, deionized water for approximately 5 minutes to allow the flame and instrument to stabilize. Aspiration of water also serves to clean out the spray chamber and nebulizer from previous sample residues.

FLAME START-UP: NITROUS OXIDE-ACETYLENE FLAME

BEFORE LIGHTING AN N₂O-ACETYLENE FLAME, BE SURE THE APPROPRIATE BURNER HEAD IS INSTALLED!! ASK YOUR INSTRUCTOR IF YOU ARE UNSURE.

1. Ignite the flame using air-acetylene by following steps 1-6 above. The air acetylene flame must be lit prior to switching to nitrous oxide.
2. In the SpectrAA software, develop a method for the analyte of interest. When editing the method, select N₂O/Acetylene in the **Flame Type & Gas Flows** box in the **Type/Mode** tab.
3. Once you have created the method, go to the **Analysis** tab and click the **Optimize** button. Once the optimization window opens, the system will switch from air oxidant to nitrous oxide. The flame should appear more white with a rose colored area at the feather. Adjustments to the fuel to oxidant ratio can be made in this window.
4. Aspirate distilled, deionized water to allow the flame and instrument to stabilize. Aspiration of water also serves to clean out the spray chamber and nebulizer from previous sample residues.
5. When you have finished with the nitrous flame, open or create a method for air-acetylene flame and select **Optimize** in the **Analysis** tab to convert the flame back to air oxidant before following the shut down procedure below.

FLAME SHUT-DOWN

To shut the instrument down when necessary, the following procedure is used:

1. Aspirate water for approximately 5 minutes before shutting the flame off.
2. Close the main valve on the acetylene tank and allow the line to bleed out. The flame will extinguish on its own.
3. After the flame has gone out, close the air valve.

EXPERIMENTAL PROCEDURE

I. Condensed Phase and Sensitivity Interferences with some Additional Complications

Align the burner so that the optical field of view is roughly 4 mm above the burner head. In the SpectrAA software, create a new method for calcium. While aspirating solution 1 below, scan the region from 423.5 nm to 421.5 nm to observe the 422.7 nm line for calcium. Scan parameters are set by selecting **Wavelength Scan** from the **Instrument** menu. After aspirating the sample, aspirate distilled water. Set the instrument to record the emission signal that corresponds to the wavelength of maximum emission for the scan above. For each of solutions 2-8 below, aspirate the solution and use the **Read** button to record the emission at this wavelength. Follow the software prompts for each measurement. After aspirating each solution, aspirate distilled water. Adjust the burner control so that the burner head is roughly 10 mm below the optical field of view and repeat the measurement for solutions 1, 2, and 8.

	Ca ²⁺ ppm	PO ₄ ³⁻ ppm	Al ³⁺ ppm	La ³⁺ ppm
1	10			
2	10	100		
3	10	100		1000
4		100		
5				1000
6	10		100	
7	10		100	1000
8			100	

Return the burner to its original position so that the optical field of view is roughly 4 mm above the burner head. In the SpectrAA software, create a new method for calcium, this time using the N₂O/acetylene flame. Aspirate solutions 1-8 again, recording the emission of the 422.7 calcium line.

What effect does the analytical observation zone have on the sensitivity and degree of condensed phase interferences encountered? What other factor which we have not addressed in this experiment could we use to reduce the degree of condensed phase interferences and increase the sensitivity of our measurements? What was the impact of a hotter flame on the condensed phase interferences?

II Atomic Transitions

Align the burner so that the optical field of view is roughly 4 mm above the burner head. In the SpectrAA software, create a new method for sodium using an air/acetylene flame. While aspirating the 10 ppm Na solution, scan the region from 591.5 nm to 588.0 nm using a slit setting of 1 to observe the emission of the sodium D line. Reduce the slit setting to 0.5 and repeat the scan. Reduce the slit setting to 0.2 and repeat the scan again. Report the line width (full width at half height) at each slit setting and the effects of reduced slit settings on resolution. Can you find any information on the transitions involved here? If so, compute the theoretical intensity ratio and compare it to the actual intensity ratio for the sodium doublet.

In the SpectrAA software, create a new method for cadmium using an air/acetylene flame. While aspirating the 10 ppm Cd solution, attempt to measure the emission of the 228.8 nm line using a slit setting of 0.5. I doubt you will have any success. Why is this? Repeat the measurement with the 100 ppm Cd solution. Create a new method for Cd using the N₂O/acetylene flame and measure the emission of the 10 ppm and 100 ppm solution at 228.8 nm.

In your report justify the relative intensities you have observed for Na and Cd.

III Ionization: Atomic and Ionic Spectra

In the SpectrAA software, create a new method for potassium using an air/acetylene flame. Peak the instrument on the 767 nm emission of K and run the 60 ppm K standard followed by the 60 ppm K + 1000 ppm Cs standard. Measure the emission of the Cs blank at this wavelength as well.

What effects are observed? From your observations, make a conclusion about the cause of the problem that you have observed. Speculate what the effects of a hotter flame, such as the nitrous oxide/acetylene flame, might bring to the observations of the same three solutions. What about the effects of a cooler flame?

IV Atomic and Ionic Spectra Revisited

After finishing III, create a new method for K using an N₂O/acetylene flame. Optimize the K signal using the 60 ppm K + **1000** ppm Cs solution. Record the relative intensity of the 60 ppm K solution and the 60 ppm K + 1000 Cs solutions. What effects of changes are seen with the hotter flame? Discuss and comment on the role that easily ionizable elements play in analysis using flame spectrometry.

V. Spectral Interferences

Using the 553.6-nm line of Ba, the nitrous oxide/acetylene flame and a slit setting of 1.0, aspirate a 40 ppm solution of Ba. Record the intensity. Follow by aspirating a 200 ppm solution of Ca standard. What did you see?

Your goal in this section is to determine the cause of the observed dilemma. It could be due to a) Ba contamination in the Ca standard, b) direct spectral overlap of a Ca line, c) direct spectral overlap of a molecular band, or d) stray light. All of these interferences are possible and do often appear in flame emission spectrometry.

Before you determine the nature of the interference, repeat the aspiration of Ba and Ca standards with the instrument slit setting at 0.2. What effects did the reduction of the slit width cause upon this interference? Return the slit setting to 1 before continuing with the next part.

In order to determine the origin of the interference, scanning the wavelength region around 553.6 nm will be necessary. You will need to scan the region between 568 nm and 548 nm. Do this for a 40 ppm Ba standard, a 200 ppm Ca standard, a 200 ppm Ca + 40 ppm Ba standard and distilled, deionized water. Decrease the slit settings to 0.2 and repeat the scans of all but the distilled water. What effect is observed when this is done? What could be done to reduce or eliminate this interference if an analysis of Ba in a high Ca matrix were desired? Three or four possible solutions to this problem exist.