

FLAME ATOMIC EMISSION SPECTROMETRY

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 equilibria processes in an air acetylene flame which is commonly used in atomic emission spectroscopy.

AIR-ACETYLENE FLAME

Before you begin the experiment, it is extremely important to point out 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

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.
4. Open the oxidant line by turning the switch on the left-hand front panel. With the oxidant switch open, make sure that the oxidant flow gauge ball is even with the red line. Check the air pressure gauge to be sure that the pressure is approximately 60 psi.
5. Open the valve on the acetylene tank. Adjust the fuel flow so that it reads between 3 and 4 on the gauge scale. Once this is adjusted, return to the acetylene tank and check the tank pressure. It should read between 8 and 10 psi with the fuel valve open on the instrument.
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. Adjust the fuel control so that less acetylene is allowed into the combustion mixture. You should continue the adjustment until you see a crisp blue feather and non-luminous flame (The feather should be sharp and well-defined).
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 SHUT-DOWN

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

1. Increase the acetylene flow until the flame becomes fuel rich (bright white).
2. Turn the oxidant toggle from nitrous oxide to air.
3. IMMEDIATELY reduce the acetylene flow to get a fuel lean air/acetylene flame.
4. Aspirate water for approximately 5 minutes before shutting the flame off.

EXPERIMENTAL PROCEDURE

I. Condensed Phase and Sensitivity Interferences with some Additional Complications

Turn on the hollow cathode by pressing "lamp 1", followed by typing 3 on the keypad. Adjust the vertical burner control so that the burner head is about 4 mm below the hollow cathode beam. Turn the hollow cathode off. With the air-acetylene flame lit, set up the instrument for the 422.7-nm line of Ca. Maximize the emission signal with the horizontal burner head control. Aspirate all solutions in the following table, but do so while scanning the wavelength. Scan the region from 421.5 to 423.5 nm. Initiate the scan on distilled, deionized water at 421.5 nm. Then when the wavelength dial reaches about 422.0 nm, begin aspirating the sample. Once the line has appeared and the dial has reached 423.0 nm, return the aspiration to distilled water and allow the scan to continue. Terminate the scan at 423.5 nm. The same procedure should be followed for all samples on the table.

	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	

Now readjust the burner control so the burner head is about 10 mm below the hollow cathode beam. At this position, remeasure solutions 1, 2, and 8. 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?

Consider the effects of a hotter flame upon condensed phase interferences. During lab you will be given a copy of wavelength scans performed on each of the solutions in this section. These scans were performed using the nitrous oxide/acetylene flame. Please use them to aid in your discussion of condensed phase interferences.

II Atomic Transitions

Using the 10 ppm Na standard and the air/acetylene flame, scan the sodium wavelength range using a slit setting of 1. Scan the region between 588.0 nm and 591.5 nm. Reduce the slit settings to 0.5 and 0.2 and repeat the scans (the actual slit widths can be found in the instrument manual). 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.

Using the 10 ppm standard of Cd, attempt to scan the 228.8 nm line. I doubt you will have any success. Why is this? Try again with the 100 ppm Cd standard. In order to determine the effect of flame temperature on the Cd signal, you will be given the scans of the Cd standards in this section as observed using the nitrous oxide/acetylene flame.

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

III Ionization: Atomic and Ionic Spectra

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. Also run the Cs blank. 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?

THE FOLLOWING SECTIONS WILL REQUIRE YOU TO USE THE NITROUS OXIDE ACETYLENE FLAME. BE SURE TO USE THE CORRECT BURNER HEAD FOR THIS SECTION.

IV Atomic and Ionic Spectra Revisited

After finishing III, **do not** change the wavelength setting on the instrument. 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 ppm 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 (You must readjust the wavelength setting when you narrow a slit, but you do not need to when you widen the slit). 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 548 nm and 568 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. During the scan periodically record the wavelength positions on the chart paper. 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.