

In Maine we have a saying that
there's no point in speaking
unless you can improve on silence.
--Edmund Muskie

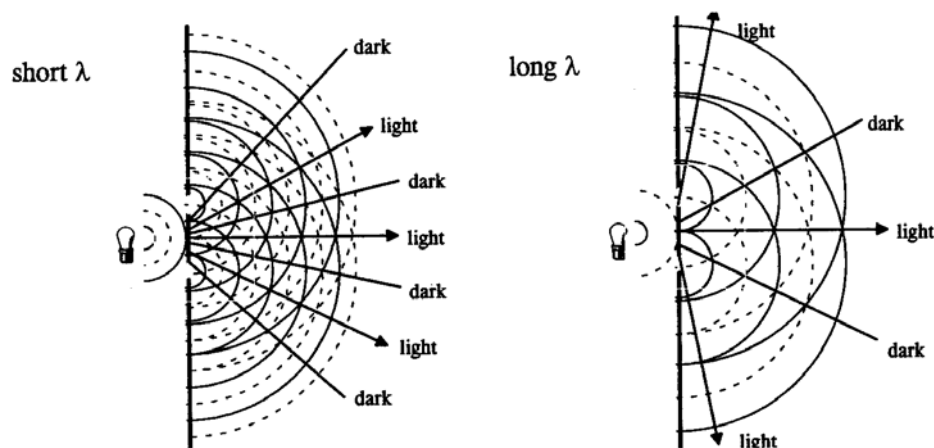
Emission Spectra

The first evidence supporting the Bohr model of the hydrogen atom came from the striking spectrum produced by gaseous hydrogen atoms under conditions of electrical excitation. The series of visible lines known as the *Balmer series* (one of a set for hydrogen) is a kind of after-the-fact road map which indicates to what energy levels the single electron in the hydrogen atom has been excited. Electrons excited to higher energy levels give off energy when they 'relax' and return to lower levels. This energy is equivalent to a certain frequency of electromagnetic radiation, as illustrated by Max Planck:

$$\Delta E = h\nu$$

If this frequency, ν , happens to fall within the visible spectrum we perceive it as a color. In studying this phenomenon the diffraction grating is particularly useful because it enables us to split up what *appears* to be monochromatic light into any component colors (much the same way a prism splits up white light). How does it do that?

The transmission grating you will be using consists of a sheet of transparent plastic that has thousands of tiny parallel grooves ruled on it (around 5300 per cm). If you imagine light waves approaching the grating like waves in the ocean breaking on the shore, the lines on the grating act like little gates that the waves must pass through. Forcing the waves to pass through these "gates" causes a complex interference pattern (diagram below).



Where the crests (solid lines) from the "ripples of light" emerging from the gates are in the same place, the waves add to give a more intense wave (brighter). Where crests and valleys (dotted lines) meet, waves cancel and darkness results. If light of one wavelength (such as laser light) passes through a transmission grating, we see the undiffracted beam as well as a series of diffracted beams at angles depending on the *wavelength* (λ) of the light and the *spacing* of the rulings on the grating (the "gates"). In the diagram on the left, the wavelength of light is shorter than on the right. Note that the beams of light that emerge from the grating are spaced more closely together than on the right where the wavelength of light is longer.

Thus when light composed of *several* wavelengths passes through the grating it is "broken up" into its component wavelengths since the different wavelengths emerge at slightly different angles from the gates. So when the light from excited hydrogen atoms (which appears to us as purplish) passes through the grating, four sharp lines of light emerge separated by darkness.

The wavelengths (and therefore *colors* and *spacing*) of lines in a spectrum are characteristic of a substance and can be used to identify it. The science of **spectroscopy** is based on these principles.

Preparing to experiment

You will be provided with the following materials:

1. a grating spectroscope [see **Technique** section]
2. solutions containing the following metal ions:
 Na^+ , Li^+ , Ca^{2+} , Sr^{2+} , unknown
3. gas discharge tubes containing three of the noble gases

Each solution sample is provided with a wire flame test loop which has stainless steel sponge wrapped around it to help hold more solution.

Calibrate the spectroscope as described in the **Technique** section.

Design an experiment to observe and record the visible lines of the metal ions in the solutions and use this information to identify the unmarked solution. **You will be helping the person who works next to you in lab (introducing the solution into the burner flame) but each student should record his/her observations.** Finally, observe and record the spectra of the gas discharge tubes.

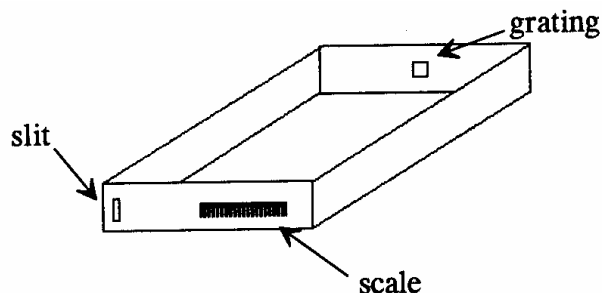
(*hint*: begin with NaCl first since its single line near 600 nm is very persistent and easy to observe)

Technique

1. The spectroscope

The spectroscope has been constructed from an ordinary cardboard box according to the diagram below (the cover has been removed for clarity):

How does it work?



Light enters through the slit (defined by the edges of electrical tape). It strikes the transparent grating at an angle and passes through it to the back of your eye, separated into its component wavelengths. As you look through the grating at the arbitrary scale on the opposite end of the box, the image in your eye is superimposed on the scale and you see the lines of the spectrum on the scale!

2. Calibration of the spectroscope

To use your spectroscope to identify substances you will need to be able to distinguish one red line from another and so forth. That's what the scale on one end of the box is for.

Look at a *fluorescent* light through the spectroscope. The overhead lights in the classroom or lab will not work because of the diffusing plastic covers. You can, however, use the lights over the counters in the lab. You should see three distinct lines superimposed over a dim continuous background spectrum. These lines are produced by transitions of electrons in the mercury (Hg) vapor that is inside the fluorescent tube. When high voltage passes through the mercury vapor it causes it to glow. The light bulb has a white coating on the inside which responds to this glow by giving off a mixture of light that is roughly "white" (thus the two spectra superimposed). Those mercury lines are:

Line 1 (closest to the slit), violet	λ
Line 2	436 nm
Line 3 (sort of smeared), yellow	, green
	546 nm
	580 nm

Record the position of each line as its image appears on the scale. The dispersion of the grating (how much spreading of the different wavelengths occurs) is essentially linear. So if you make a plot of wavelength (in nm) vs. position of the line (in the arbitrary units of the scale) you will have a graph from which you can read off the wavelength of any line you see in the spectroscope!

3. Observing flame emission spectra

You will need a flame that gives off very little of its own light and is of medium heat (small blue cone) and medium length (perhaps 7-10 cm). The hottest part of the flame is just above the blue cone but that will burn off your sample too quickly so you want to place the loop containing the solution in the lower outside part of the flame. This will tend to color the entire flame as the solution evaporates and make observation easier. Even so, these spectra are ephemeral at best. You will probably need to put new sample into the flame several times in order to observe and record each line for a substance. It will be easiest for you to observe the spectra if you have your back to the windows and cup your free hand around your eye so that you shield out stray light from the outside.

Because the air/methane flames don't provide much energy, many lines that might be recorded in handbooks for the elements in this experiment will not be visible to you. But you should be able to get a unique "fingerprint" for each substance provided.

You should also be aware that sodium is a contaminant in the air and therefore is likely to appear (if only dimly) in each spectrum.

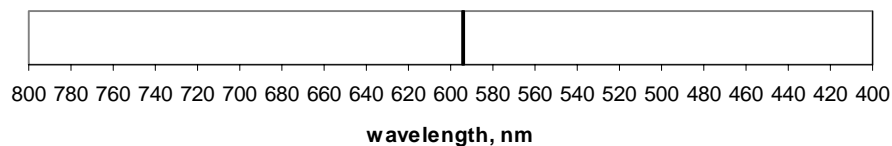
Analysis

1. Plot a calibration graph that extends (on the vertical axis) from 400 to 800 nm. Draw the best straight line among the three points you obtain from the fluorescent light data.
2. Prepare a table of wavelengths for the lines observed in each metal ion spectrum and for each discharge tube using your calibration graph.
3. Compare the wavelengths you get from your data with the wavelengths given on the table attached to this sheet. Remember, you may not have observed all lines.
4. Use the table prepared in #2 to identify the unmarked substance. Be sure to indicate the # of the substance! (see spectrum diagrams on following page)
5. Use the table prepared in #2 to match the discharge tubes with their correct noble gases. (see spectrum diagrams on following page)

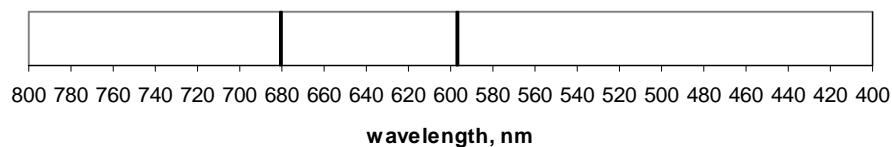
6. Qualitative analysis is a series of techniques and procedures to determine the presence or absence of elements in a sample. You will do some of this later in the course. Most of the procedures involve the judicious use of solubility rules to precipitate, separate and identify elements. However, the alkali metals are almost always identified by flame tests such as you did in this experiment. Why does this make sense? (think about those solubility rules!!)

[in the spectra following, dotted lines are variable and/or dim lines; gray patches are either broad bands or regions with many faint lines]

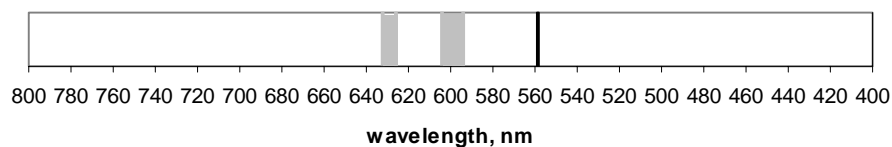
Na



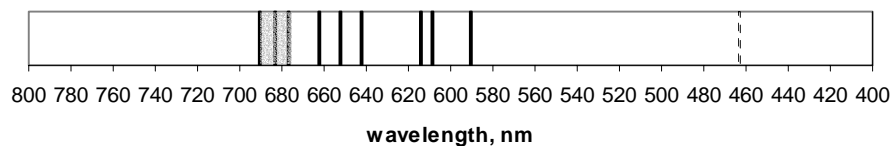
Li



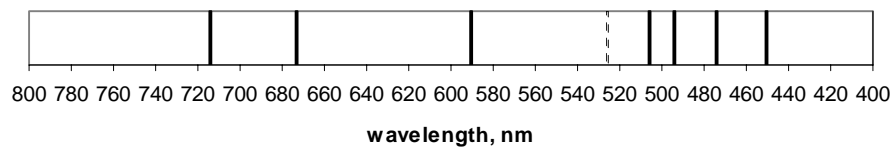
Ca



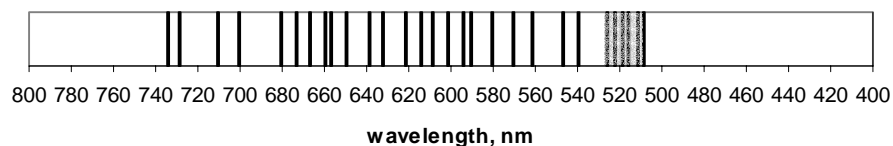
Sr



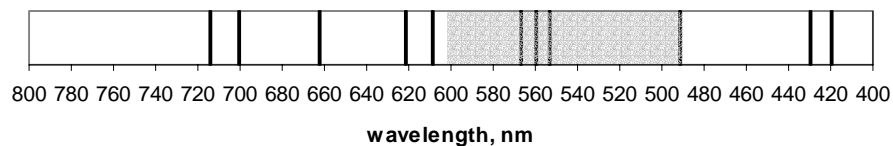
He



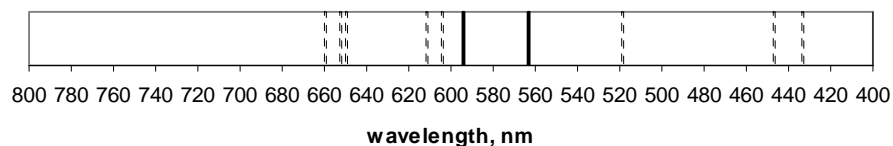
Ne



Ar



Kr



Xe

