

# 1. Atomic Spectroscopy

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## Objective

The emission and absorption of light energy of particular wavelengths by atoms and molecules is a common phenomenon. The emissions/absorptions are characteristic for each element's atoms and arise from transitions of electrons among the various energy levels of the particular atom under study. The apparatus used to study the wavelengths of light emitted/absorbed by atoms is called a **spectroscope**. In this experiment, you will first calibrate a spectroscope (Choice I). Then you will use the calibrated spectroscope to determine the wavelengths of the emission lines of hydrogen and nitrogen (Choice II) and of a number of metal salts (Choice III).

## Choice I. Calibration of the Spectroscope

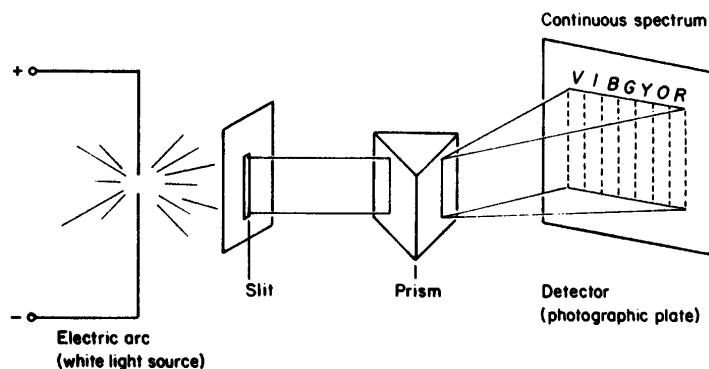
### Introduction

The radiant energy emitted by the sun (or other stars) contains *all* possible wavelengths of electromagnetic radiation. The portion of this radiation to which the retina of the human eye responds is called the **visible light region** of the electromagnetic spectrum. The fact that the radiation emitted by the sun contains a *mixture* of radiation wavelengths may be demonstrated by passing sunlight through a prism. A prism *bends* light; the *degree* to which light is bent is related to the wavelength of the light. When sunlight (or other "white" light) containing all possible wavelengths is passed through a prism, each component color of the white light is bent to a different extent by the prism, resulting in the beam of white light being spread out into a complete rainbow of colors. Such a rainbow pattern is called a **continuous spectrum**.

It was discovered that the use of a narrow *slit* in the spectroscope between the prism and the source of white light sharpened and improved the quality of spectra produced by a beam of white light. See Figure 1-1.

FIGURE 1-1

The spectrum of "white" light. When light from the sun or from a high-intensity incandescent bulb is passed through a prism, the component wavelengths are spread out into a continuous rainbow spectrum.



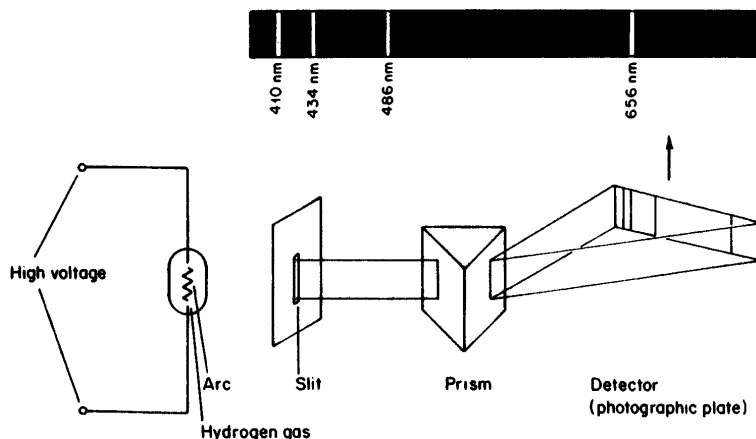
Most substances will emit light energy if heated to a high enough temperature. For example, a fireplace poker will glow red if left in the fireplace flame for several minutes. Similarly, neon gas will glow with a bright red color when excited with a sufficiently high electrical voltage; this is made use of in neon signs. When energy is applied to a substance, the atoms present in the substance may *absorb* some of that energy. Electrons within the atoms of the substance move from their normal positions to positions of higher potential energy, farther away from the nuclei of the atoms. Later, atoms which have been excited by the application and absorption of energy will “relax” and will *emit* the excess energy they had gained. When atoms re-emit energy, more often than not, at least a portion of this energy is visible as light.

However, atoms do *not* emit light energy *randomly*. In particular, the atoms of a given element do *not* generally emit a continuous spectrum, but rather emit visible radiation at only certain discrete, well-defined, fixed wavelengths. For example, if you have ever spilled common table salt, NaCl, in a flame, you have seen that sodium atoms emit a characteristic yellow/orange wavelength of light.

If the light being emitted by a particular element’s atoms is passed through a prism and is viewed with a spectroscope, only certain sharp bright-colored *lines* are seen in the resulting spectrum. The positions of these colored lines occur in the corresponding location (wavelength region) as in the spectrum of white light. See Figure 1-2, which illustrates the bright line spectrum of hydrogen.

FIGURE 1-2

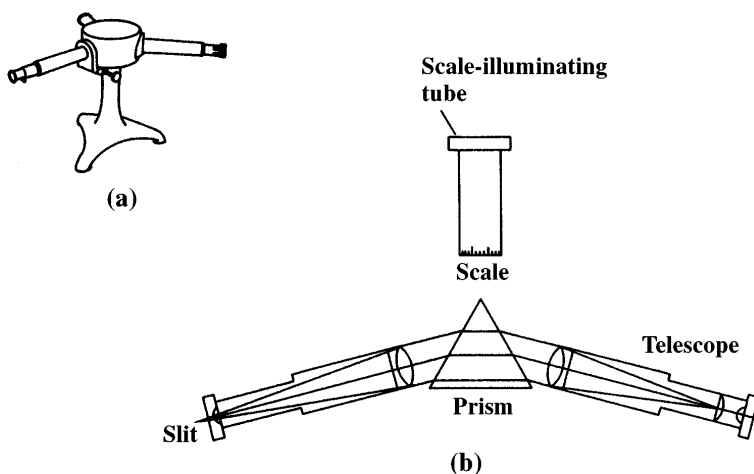
The line spectrum of hydrogen. The location of colored lines in the spectrum corresponds to the location of the same color in the spectrum of white light.



The fact that a given atom produces only *certain* fixed bright *lines* in its spectrum indicates that the atom can only undergo energy changes of certain fixed, definite amounts. An atom cannot continuously or randomly emit radiation but can only emit energy corresponding to definite, regular changes in the energies of its component electrons. The experimental demonstration of bright line spectra implied a regular, fixed electronic microstructure for the atom and led to an enormous amount of research to discover exactly what that microstructure is.

FIGURE 1-3

(a) a view of the spectroscope to be used.  
(b) A schematic representation of the spectroscope, showing its component parts. When viewed through the telescope, the spectrum will appear superimposed on the numerical scale.



In later choices of this experiment, you will examine the line spectra of a number of elements, using a simple spectroscope of the sort indicated in Figure 1-3. The spectroscope includes four major features: a *slit* for admitting a narrow, collimated beam of light; a *prism* or *diffraction grating* that spreads the incident light into its component wavelengths; a *telescope* for viewing the spectrum; and an illuminated *reference scale* against which the spectrum may be viewed (as an aid in locating the positions of the lines in the spectrum).

The scale of the spectroscope is provided merely as a convenience, and the divisions on the scale are arbitrary. For this reason, the spectroscope must be *calibrated* before it is used to determine the spectrum of an unknown element. This is accomplished by viewing a known element that produces especially sharp lines in its spectrum and whose spectrum has been previously characterized (with the emission wavelengths being known with great precision). The positions on the spectroscope scale of the lines in the spectrum of the known element are recorded. Then a **calibration curve** that relates the wavelength of a spectral line of the known element to its position when viewed against the spectroscope scale is prepared. This calibration curve may then be used to calculate the wavelengths of emission lines in the spectra of unknown elements when viewed through the same spectroscope under the same conditions.

In this option, you will calibrate the spectroscope by viewing the spectrum of mercury. The spectrum of mercury has been intensively studied. It has several bright lines in the visible region (400–700-nanometer wavelength):

404.7 nm	violet
435.8 nm	blue
546.1 nm	green
579.0 nm	yellow

A calibration graph will then be prepared, with the apparent position of the spectral line on the scale of the spectroscope, plotted against the known wavelength of that spectral line. This calibration graph should be kept if any additional measurements are to be made with the spectroscope.

## SAFETY PRECAUTIONS

- **Wear safety glasses at all times in the laboratory.**
- **In addition to visible light, the mercury vapor lamp emits radiation at ultraviolet wavelengths. Ultraviolet radiation is *damaging* to the eyes. Wearing your safety glasses while taking readings with the spectroscope will absorb most of this radiation; nevertheless, refrain from looking at the source of radiation for any extended period of time.**
- **The power supply used with the mercury lamp develops a potential of several thousand volts. *Do not touch* any portion of the power supply, wire leads, or mercury lamp unless the power supply is unplugged from the wall outlet.**
- **Always *unplug* the power supply before adjusting the position of the mercury lamp or any other part of the apparatus.**

## Apparatus/Reagents Required

Spectroscope with illuminated scale, mercury vapor lamp (discharge tube), high-voltage power pack with lamp holder

## Procedure

Record all data and observations directly in your notebook in ink.

Check to make sure that the power supply pack is *unplugged*. Remember that this pack operates at high voltages and is dangerous.

Turn on the illuminated scale of the spectroscope, and look through the eyepiece to make sure that the scale is visible but not so brightly lighted as to obscure the mercury spectral lines.

Position the power supply pack containing the mercury vapor lamp so that the lamp is directly in front of the slit opening of the spectroscope.

With the instructor's permission, plug in the power supply and turn on the power supply switch to illuminate the mercury lamp.

Look through the eyepiece, and adjust the slit opening of the spectroscope so that the mercury vapor spectral lines are as bright and as sharp as possible. If necessary, adjust the illuminated scale of the spectroscope so that the numbered scale divisions are easily read but do not obscure the mercury spectral lines.

Record the *color* and *location* on the numbered scale of the spectroscope for each line in the visible spectrum of mercury.

Using the line positions you have recorded with the spectroscope and the known wavelengths of the emissions of the mercury atom given earlier, construct a calibration curve for the spectroscope using fine-scale graph paper.

Plot the *observed scale reading* for each bright line versus the *wavelength* of the line.

## Choice II. Spectra of Atomic Hydrogen and Nitrogen

### Introduction

Hydrogen is the simplest of the atoms, consisting of a single proton and a single electron. The emission spectrum of hydrogen is of interest because this spectrum was the first to be completely explained by a theory of atomic structure, by the Danish scientist Niels Bohr.

As described in Choice I, we know that atoms absorb and emit radiation as light of fixed, characteristic wavelengths when excited. This absorption and emission of light is now known to correspond to electrons within the atom moving away from the nucleus (energy absorbed) or closer to the nucleus (energy emitted). Atoms emit and absorb energy of only certain wavelengths (bright or dark lines in the spectrum) because electrons do not move randomly away from and toward the nucleus, but may only move between certain fixed, allowed “orbits,” each of which is at a definite fixed distance from the nucleus. When an electron moves from one of the fixed orbits to another orbit, the attractive force of the nucleus changes by a definite amount that corresponds to a specific change in energy. The quantity of energy absorbed or emitted by an electron in moving from one allowed orbit to another is called a **quantum (photon)**, and the energy of the particular quantum is indicated by the wavelength (or frequency) of the light emitted or absorbed by the atom. The energy of a photon is given by the Planck equation

$$\Delta E = h\nu = hc/\lambda$$

where  $\nu$  is the frequency of light emitted or absorbed and  $\lambda$  is the wavelength corresponding to that frequency.

Bohr postulated that the energy of an electron when it is in a particular orbit was given by the formula

$$E_n = -(\text{constant})/n^2$$

where  $n$  is the number of the orbit as counted out from the nucleus ( $n = 1$  means the first orbit,  $n = 2$  means the second orbit, etc.) and is called the **principal quantum number**. The proportionality constant in Bohr’s theory is called the Rydberg constant (given the symbol  $R_H$ ) and has the value  $2.18 \times 10^{-18}$  J. According to Bohr’s theory, if an electron were to move from an outer orbit (designated as  $n_{\text{outer}}$ ) to an inner orbit (designated by  $n_{\text{inner}}$ ), a photon of light should be emitted, having energy given by

$$\Delta E = E_{\text{inner}} - E_{\text{outer}} = -R_H[(1/n_{\text{inner}})^2 - (1/n_{\text{outer}})^2]$$

The wavelength ( $\lambda$ ) of this photon would be given by the Planck formula as

$$\lambda = hc/\Delta E$$

Bohr performed calculations of wavelengths for various values of the principal quantum number,  $n$ , and found that the predicted wavelengths from theory agreed exactly with experimental wavelengths measured with a spectroscope. Bohr even went so far as to predict emissions by hydrogen atoms in other regions of the electromagnetic spectrum (ultraviolet, infrared) that had not yet been observed experimentally but that were confirmed almost immediately.

Bohr's simple atomic theory of an electron moving between fixed orbits helped greatly to explain observed spectra and formed the basis for the detailed modern atomic theory for more complex atoms with more than one electron. The spectra of larger atoms are considerably more complicated than that of hydrogen, but generally a *characteristic* spectrum is seen. Bohr's theory for hydrogen accounted on a microscopic basis for the macroscopic phenomena of spectral emission lines.

In this experiment, you will measure the wavelengths of the lines in the emission spectrum of hydrogen with a spectroscope and then determine by calculation to which atomic transition (of the electron between the various orbits) each of these spectral lines corresponds. You will also examine the emission spectra of nitrogen, which as a multi-electron atom is considerably more complicated to interpret.

## SAFETY PRECAUTIONS

- **Wear safety glasses at all times in the laboratory.**
- **In addition to visible light, the hydrogen lamp and nitrogen lamps emit radiation at ultraviolet wavelengths. Ultraviolet radiation is *damaging* to the eyes. Wearing your safety glasses while taking readings with the spectroscope will absorb most of this radiation. Refrain from looking at the source of radiation for any extended period of time.**
- **The power supply used with the lamps develops a potential of several thousand volts. *Do not touch* any portion of the power supply, wire leads, or lamps unless the power supply is unplugged from the wall outlet.**
- **Always *unplug* the power supply before adjusting the position of the lamps or any other part of the apparatus.**

## Apparatus/Reagents Required

Spectroscope with illuminated scale, hydrogen lamp (discharge tube), nitrogen lamp, high-voltage power pack with lamp holder

## Procedure

Record all data and observations directly in your notebook in ink.

Check to make sure that the power supply pack is *unplugged*. Remember that this power supply operates at high voltages and is dangerous.

Turn on the illuminated scale of the spectroscope. Look through the eyepiece to make sure that the scale is visible but not so brightly lighted as to obscure the hydrogen spectral lines.

Position the power supply pack containing the hydrogen vapor lamp so that the lamp is directly in front of the slit opening of the spectroscope.

With the instructor's permission, plug in the power supply and turn on the power supply switch to illuminate the hydrogen lamp.

Look through the eyepiece, and adjust the slit opening of the spectroscope so that the hydrogen spectral lines are as bright and as sharp as possible. If necessary, adjust the illuminated scale of the spectroscope so that the numbered scale divisions are easily read but do not obscure the hydrogen spectral lines.

Record the color and location on the numbered scale of the spectroscope for each line in the visible spectrum of hydrogen. You should easily observe red, blue-green, and violet lines. A second very faint violet line may also be visible if the room lighting and illuminated scale lights are not too bright.

Use the calibration plot prepared in Choice I for mercury vapor to determine the wavelengths of the lines in the hydrogen emission spectrum. Look up the true wavelengths of these lines in your textbook or a chemical handbook, and calculate the percent error in the determination of each line's wavelength.

Use the equations provided in the introduction to this choice to calculate the predicted wavelengths in nanometers (according to Bohr's theory) from the electronic transitions in the hydrogen atom corresponding to the following:  $n = 3 \rightarrow n = 2$ ;  $n = 4 \rightarrow n = 2$ ;  $n = 5 \rightarrow n = 2$ ;  $n = 6 \rightarrow n = 2$ . How do these predicted wavelengths correspond to those you have measured for hydrogen?

Turn off and unplug the power pack containing the hydrogen lamp. Position the power pack containing the nitrogen lamp in front of the slit opening of the spectroscope. Adjust the spectroscope and scale, and record the location of the bright lines in the nitrogen spectrum. A portion of the emission spectrum of nitrogen appears as a band of several colors. Record the position of this band on the spectroscope scale. Using the calibration curve prepared in Choice I, determine the wavelengths of the bright lines in the nitrogen spectrum, and also the approximate wavelength range covered by the band.

### **Choice III. Emission Lines of Some Metallic Elements**

#### **Introduction**

A number of common metallic elements emit light strongly in the visible light region when ions of the metals are excited. The spectra can be studied using the same sort of simple spectroscope as has been used in Choices I and II.

A number of metallic elements from Groups IA and IIA have especially bright emission lines in the visible light region. The emissions are so strong and

characteristically colored that these elements can often be recognized by the gross color they impart when aspirated into a burner flame, even without use of a spectroscope. For example, lithium ions impart a red color to a burner flame, sodium ions a yellow/orange color, potassium ions a violet color, calcium ions a brick red color, strontium ions a brighter red color, and barium ions a green color. Upon examination with the spectroscope, it is noted that the spectra of these ions contain several additional lines, but generally the *brightest* line in the spectrum when viewed through the spectroscope corresponds to the gross color imparted to a flame when the spectroscope is not used. Naturally, when several of these ions are present together in a sample (as happens with real samples very commonly), one color may mask another so that direct visual identification of the ions may not be possible. In this case, only a calibrated spectroscope can determine what elements are present. This is done by comparing the position of lines in the spectrum of the unknown mixture with the position of lines in known single samples of the ions in question.

In this Choice, you will excite the ions of each of the elements listed earlier, using a Bunsen burner. You will observe both the gross color imparted to the flame and the spectral lines emitted by the elements as viewed through the spectroscope. You will then determine what elements of those tested are present in an unknown mixture.

Two alternative procedures may be available for introducing the metal ion samples into the burner flame. In the first method, a wire loop is used to pick up a drop of metal solution, and the drop is then placed into the flame for vaporization. This method is simple and requires little equipment, but it only produces a brief burst of color before the sample evaporates completely. This makes it difficult for one person to both introduce the sample and record the spectrum. The second method uses a spray bottle to introduce a fine mist of sample solution into the flame. This method allows for a longer lifetime for the color of the ion in the flame but requires separate sprayers for each of the ions (because of the difficulty in cleaning the sprayer between samples).

### **SAFETY PRECAUTIONS**

- **Wear safety glasses at all times in the laboratory.**
- **Some of the metal salts used in this experiment are *toxic*. Wash your hands after using them. If the spray method is used, wash down the lab bench to remove all traces of the metal salts.**
- **Avoid having the burner flame too close to the spectroscope, to avoid damaging the apparatus.**
- **6 M HCl can burn skin and clothing. Exercise caution in its use, and inform the instructor of any spills.**

### **Apparatus/Reagents Required**

Spectroscope with illuminated scale; burner; nichrome wire or spray bottles; 6 M HCl; 0.10 M solutions of the following metal chlorides: lithium, sodium, potassium, calcium, and strontium; unknown solution containing one of these ions; unknown mixture containing two of these ions

## Procedure

Record all data and observations directly in your notebook in ink.

Your instructor will tell you which method for introducing the metal ions into the flame to use. In either case, you will be determining the spectra of solutions of lithium chloride, sodium chloride, potassium chloride, calcium chloride, and strontium chloride.

If the wire method is to be used, obtain several 6-inch lengths of nichrome wire and a small amount of 6 M HCl (*Caution!*). Bend the last quarter-inch of each wire into a small loop for picking up the sample solutions. Dip the loops into 6 M HCl to remove any oxides present, rinse in distilled water, and then heat in the oxidizing portion of a burner flame until no color is imparted to the flame by the wires.

If the spray method is to be used, using the sink, check to make sure that the sprayers deliver a very fine mist. If the sprayer nozzle is adjustable, try adjusting the nozzle to improve the character of the spray. If the nozzle cannot be adjusted, consult your instructor for a method of cleaning the sprayer.

Set up a laboratory burner directly in front of the slit of the spectroscope but far enough away from the spectroscope to avoid damaging the instrument. Adjust the flame of the burner so that it is as hot as possible. Adjust the illuminated scale of the spectroscope so that approximate positions of the spectral lines can be noted (exact measurements will not be made).

Using the wire method, introduce a drop of one of the metal ion solutions into the oxidizing portion of the flame and note the gross color imparted to the flame by the solution. Then introduce a second drop of the same metal ion solution into the flame while looking at the flame through the eyepiece of the spectroscope. Note the color, intensity, and approximate scale position of the brightest few lines in the metal ion's spectrum. It may be necessary to repeat the introduction of a drop of the metal ion solution to the flame to permit recording of all the spectral lines shown by the metal ion.

Using the spray method, spray a fine mist of one of the metal ion solutions into the flame and note the gross color imparted to the flame by the metal ion. Then while looking through the eyepiece of the spectroscope, spray additional bursts of the same metal ion solution into the flame, noting the color, intensity, and approximate scale position of the brightest few lines in the metal ion's spectrum.

Repeat the determinations (by either method) using the other metal ion samples. If using the wire method, use a new length of wire for each successive sample. If using the spray method, allow the burner to heat for a few minutes between samples to make sure that the previous sample has been evaporated completely.

When each of the known samples of metal ions has been determined, obtain an unknown sample containing just one of the metal ions. Determine the spectrum of the unknown sample, and by matching the colors, intensities, and positions of the spectral lines, identify the unknown sample.

Obtain an unknown sample containing a mixture of two of the metal ions. Determine the spectrum of the mixture, noting the color, intensity, and position of all the brightest lines in the spectrum. Compare the spectrum of the mixture with the spectra of each of the individual known ions, and determine which ions are most likely to be present in the unknown mixture.

# Atomic Spectroscopy

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Date: ..... Student name: .....  
Course: ..... Team members: .....  
Section: .....  
Instructor: .....

## Prelaboratory Questions

### Choice I. Calibration of the Spectroscope

1. Given the wavelengths and colors of the major mercury emission lines listed in the introduction to this experiment, construct a graph (on a sheet of graph paper) which will approximate the spectrum to be determined. Lay out the horizontal axis of the graph in terms of the wavelength of the lines (in nanometers), and make the vertical axis about 2 inches high to approximate the appearance of the lines to be measured. Using colored pens that correspond to those colors listed, sketch in the emission lines. Compare your sketch of the spectrum to the actual spectrum recorded. Attach your sketch to this page.
2. What are the approximate wavelengths (in nanometers) in the spectrum of visible sunlight that correspond to the following colors?  
  
Red ..... Yellow .....  
  
Green ..... Blue .....
3. What are the frequencies (in Hz) corresponding to the wavelengths you have listed?

### Choice II. Spectra of Atomic Hydrogen and Nitrogen

1. The spectral lines observed in the visible spectrum of hydrogen arise from transitions from upper states back to the  $n = 2$  principal quantum level. Calculate the predicted wavelengths for the spectral transitions of the hydrogen atom from the  $n = 6$  to  $n = 2$ , for the  $n = 5$  to  $n = 2$ , for the  $n = 4$  to  $n = 2$ , and for the  $n = 3$  to  $n = 2$  levels in atomic hydrogen.



# Atomic Spectroscopy

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Date: ..... Student name: .....  
Course: ..... Team members: .....  
Section: .....  
Instructor: .....

## Results/Observations

### Choice I. Calibration of the Spectroscope

Description of the spectrum

#### *Lines observed:*

<i>Color</i>	<i>Location on spectroscope scale</i>
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Attach your graph to this report sheet.

## Questions

1. What is the purpose of the slit in the spectroscope?
2. Why is *mercury* used to calibrate the spectroscope?
3. Why should you *not* look at the emissions from the mercury tube for a prolonged time period?

# Atomic Spectroscopy

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Date: ..... Student name: .....  
Course: ..... Team members: .....  
Section: .....  
Instructor: .....

## Results/Observations

### Choice II. Spectra of Atomic Hydrogen and Nitrogen

#### Hydrogen Emission Spectrum

Description of the spectrum

#### *Lines observed:*

<i>Color</i>	<i>Location on spectroscope scale</i>
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*Wavelengths of the lines* (from calibration graph, Choice I)

<i>Color</i>	<i>Wavelength</i>
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Calculate the percent error in the determination of the wavelengths (comparing the wavelengths you have determined with those given in your textbook).

<i>Color</i>	<i>Percent error in wavelength</i>
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**Nitrogen Emission Spectrum**

Description of the spectrum

*Lines observed:*

<i>Color</i>	<i>Location on spectroscope scale</i>
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# Atomic Spectroscopy

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Date: ..... Student name: .....  
Course: ..... Team members: .....  
Section: .....  
Instructor: .....

## Results/Observations

### Choice III. Emission Lines of Some Metallic Elements

Which method did you use for introducing the metal ion samples?

<i>Metal ion</i>	<i>Gross color</i>	<i>Lines observed</i>
Li	.....	.....
Na	.....	.....
K	.....	.....
Ca	.....	.....
Sr	.....	.....
Ba	.....	.....
Unknown 1 (single)	.....	.....
Unknown 2 (double)	.....	.....
ID number of Unknown 1 .....	Identity? .....	
ID number of Unknown 2 .....	Identity? .....	

