SPECTROSCOPY: QUALITATIVE ANALYSIS WITH LIGHT

Waves, Light, and Atomic Spectra

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OBJECTIVES

After completing this experiment, one should be able to:

➤   Define the following properties of waves:

• Frequency   • Wavelength   • Velocity   • Interference

➤   Determine the relationship between the colors of the visible spectrum of light and their corresponding wavelengths and frequencies.

➤   Identify band and line spectra, and relate the physical state of a light-emitting substance to the type of spectrum observed.

➤   Identify an unknown element by measurement of its emission spectrum.

➤   Use Bohr's planetary electron model for the hydrogen atom to predict the colors or wavelengths of light that hot hydrogen atoms should emit, and check your predictions by measuring the wavelengths of the emission spectra lines for hydrogen gas.

BACKGROUND AND EXPERIMENTAL PROCEDURES

The Importance of Spectra

Atoms, as we have learned, are composed of tiny, very heavy positively charged nuclei surrounded by a swarm of light, negatively charged electrons.   An atom by itself is not of great use, but when atoms connect together to form *molecules*, a host of new properties appear. Hydrogen and oxygen atoms combine to form water. Carbon, hydrogen, oxygen, and nitrogen combine in countless different ways to form the molecules that make our bodies and the food we eat.

When two or more atoms join to form a molecule, what binds them together? The clouds of electrons must somehow mesh to form a *chemical bond.*

An understanding of the structure of molecules must, then, be prefaced by some understanding of the behavior of electrons in atoms. How can we learn of this behavior?   Electrons speak the language of light. When atoms are heated, electrons are pushed out away from the nucleus and then fall back. As these returning electrons accelerate, they give back some of this energy as little bursts of light. The colors of light produced provide both a fingerprint of the atom, and a clue to the way the atom's electrons are arranged.

An Overview of this Experiment

To understand the language of electrons, we first have to learn a little about its words. These words are the colors of light, which are actually *electro-magnetic* waves of different wavelength. We will see how the colors or *spectra* of light produced by hot atoms serve as a unique fingerprint for the atom, and finally will look at some of the experimental evidence that caused Niels Bohr to believe that electrons run in planetary orbits around their nuclei.

This experiment is divided into several small experimental modules. Some of these you will perform by yourself, and some you and your fellow students will do together with your laboratory instructor. Each section of this experiment develops a new concept.

Some properties of Waves: **Frequency and Wavelength**

There are several different kinds of waves. We have all seen water waves rolling across a lake or in the ocean surf. We are familiar with sound waves, which are alternating areas of high and low pressure transmitted through the air. As children, many of us made waves in a jump rope. Light, it turns out, is also a wave, but is made up of alternating electrical and magnetic fields that move through space.

To understand waves, we need to understand something about their basic properties — frequency, velocity, wavelength, and interference. **Frequency** is how rapidly a wave changes from its "high" value to its "low" value — or stated in another way, how many waves are produced in a second. **Velocity** is how rapidly a wave moves through the material in which it travels. In general, the rate at which a wave moves is determined by the material — sound waves, for example, move about four times as fast in water as in air. The speed of a wave is not affected by its frequency. Sound waves traveling through air move at the same speed whether they are high frequency waves (produced by a piccolo, for example), or low frequency waves produced by a tuba. When one listens to a band at a football game, sounds from all of the instruments arrive at the same time.
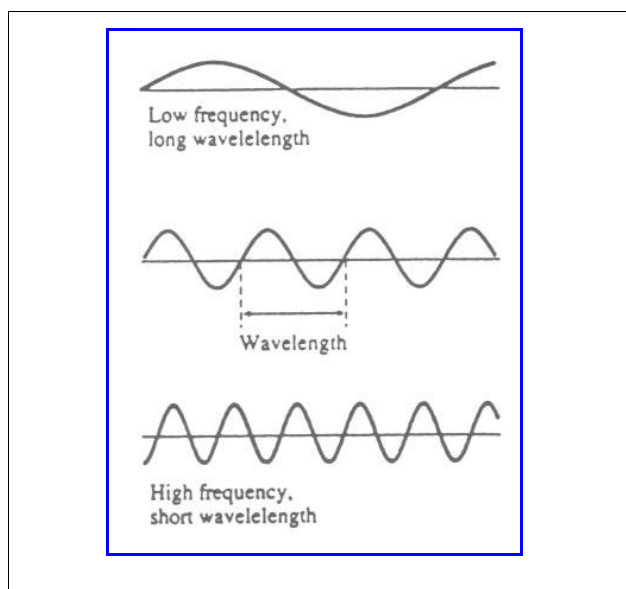

Figure 1. The frequency of a wave is determined by how often it repeats. Its wavelength is how much space it occupies. For a given type of wave in a given material, the speed or velocity is practically constant regardless of wavelength or frequency.

Wavelength is the space occupied by one wave. Since a given type of wave will move at the same speed in a material, waves produced more often (higher frequency) are shorter than lower frequency waves.

Demonstration:

Your lab instructor will show you how to make waves in a long coiled spring (a "slinky") as it lies on the laboratory floor. A question to consider:

■　　　　When the laboratory instructor moves the end of the spring rapidly, producing high frequency waves, is the wavelength shorter or longer than when it is moved more slowly to produce lower frequency waves?

Some Properties of Waves: Constructive and Destructive Interference

An important characteristic of waves is that of "interference." All forms of wave motion interfere. As waves cross, the individual disturbances add algebraically. If two wave crests (positive displacements) cross, a large crest will result. If two wave troughs (negative displacements) cross, a large trough will result. *If a crest and a trough of comparable size cross, the positive and negative displacements will cancel, resulting in no displacement at all.*

Figure 2 presents a series of sketches that illustrate the crossing of small waves on a jump rope. Notice that when both waves have the same sign (positive or negative), they add when they cross, but when the displacements are of opposite sign, they cancel.
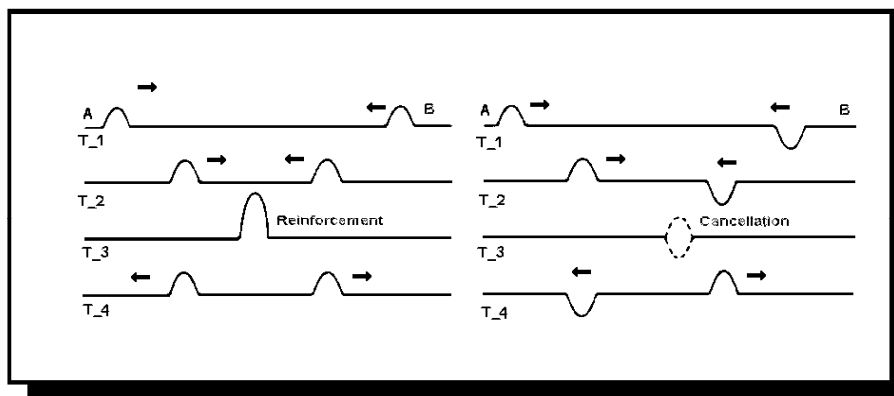

Figure 2. Waves formed by shaking a jump rope behave in the same manner as water waves and other forms of wave motion. These time-lapse sketches illustrate "interference," the algebraic addition of waves as they cross. When waves of the same algebraic sign cross, the displacements add. When waves of opposite signs cross, the displacements cancel.

Demonstration:

Your laboratory instructor will use the slinky to demonstrate wave interference. Watch closely as two waves cross.

■   What happens when two waves, both on the same side of the spring, begin at opposite ends of the spring and cross in the middle? This is called *constructive interference.*

■   What happens when two waves, one on each side of the spring, begin at opposite ends of the spring and cross in the middle?   This is called *destructive interference.*

■   What happens when waves are started at one end of the spring and reflected off the other end to return?   Hold the fixed end of the spring tightly and do not let it move for this experiment. Note that the reflected wave is of the opposite polarity or "phase" than the wave that comes down the spring. If one keeps starting new waves at a constant frequency, a *standing wave* will result.

Light is a Form of Wave Motion

One of the more convincing bits of evidence supporting the wave model for light is the star pattern observed when a light is viewed through a close-mesh screen such as a window screen or the threads of a handkerchief. (See Figure 3).   The pattern of alternating light and dark bands radiating from each light source is called an "interference pattern," and the spacing of the bands is related to the wavelength of the light.   This commonly observed phenomenon may be explained by assuming that light has some properties normally attributed to waves, be they water waves, sound waves, or just waves on a jump rope.

Consider a wave striking a barrier with two small slits. When this occurs, two adjacent waves begin on the other side of the barrier. These two waves interfere in a very predictable pattern, resulting in the occurrence of constructive interference, or wave reinforcement, along a "centerline" drawn between the two slits and perpendicular to the barrier.   In this region, wave crests cross and reinforce wave crests from the other source, and wave troughs cross and reinforce wave troughs.

At a small angle from the centerline a region of destructive interference or cancellation exists (See Figure 4). Along this line wave crests cross wave troughs, and wave troughs cross wave crests. This line of minimum disturbance is called a "nodal line." Farther out from the center is another region of constructive interference or wave reinforcement.

A difference in the interference pattern will be observed if the wavelength is changed.   Figure 5 presents another sketch of this experiment, this time with a higher frequency wave (shorter wavelength) striking the slits.

Note that waves with shorter wavelength form interference patterns closer to the centerline than do longer wavelength waves.

At this point it seems that interference patterns may be used to determine the wavelength of light, provided that one could obtain a satisfactory slit assembly. Such an assembly is available in the form of a *diffraction grating*.   This is a plastic material with approximately 14,000 slits ruled on its surface per inch. A simple diffraction grating spectroscope can be constructed utilizing about one cent worth of this material and an empty toothpaste tube box. A commercial version of such an instrument is sketched in Figure 6.   Your laboratory instructor will have a supply of these simple spectroscopes on hand for your use in the laboratory.
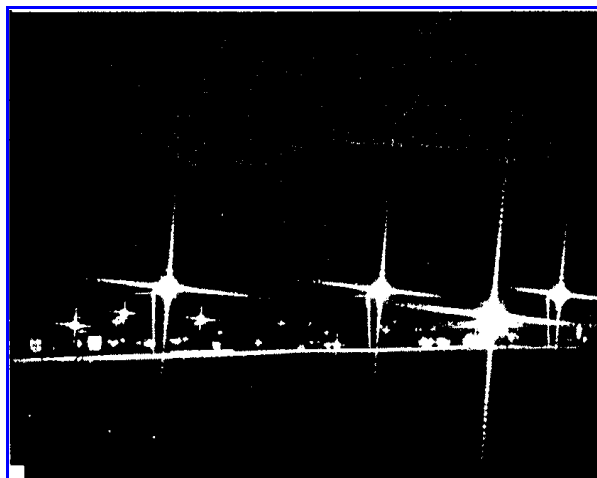

Figure 3. The "star" patterns one observes when you view light through a screen door is a clue to the nature of light. Waves, when they cross, produce areas of alternating cancellation and reinforcement, much as the dark and bright "star" images surrounding each of the streetlights in this photograph.
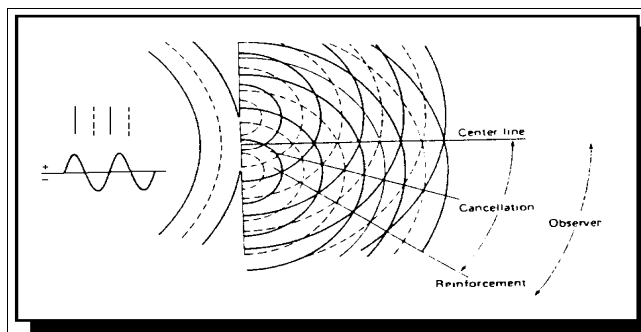

Figure 4.   Areas of wave reinforcement and areas of wave cancellation result when waves cross. The location of regions of constructive and destructive interference is related to the wavelength of the wave.
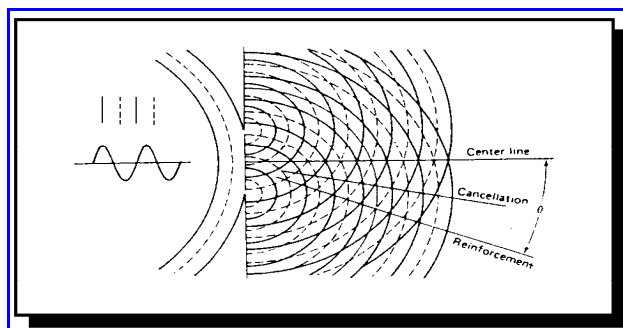

Figure 5. A two-source interference pattern with shorter waves. Regions of reinforcement and cancellation are closer to the center when the wavelength is short.

Using the Spectroscope

Look toward an incandescent light bulb through your spectroscope. You should see a spectrum by centering the slit on the light source and then looking to either side inside the spectroscope. The spectrum is formed by the bright lines of the interference patterns of the various wavelengths making up the spectrum. You may be able to see a second-order spectrum by looking off at still a greater angle from the centerline.

Topic I: Color and Wavelength

Look carefully at the arrangement of colors in the spectrum seen through your spectroscope, beginning on the outside and moving toward the center. Look again at Figures 4 and 5, and review the discussion associated with these figures. Now use what we have just learned about the distance from the

Figure 6: Line up your spectroscope so you can see the light source through the slit. Then look to to the right (or left) to see the spectrum displayed.

center line at which short and long waves will constructively interfere. You will see bright light at these points. Which colors reinforce closer to the center? These are the short waves. Which are farthest out from the center? These are the long waves. List the colors in order of wavelength and frequency in Table 1 below, and also in your lab report.
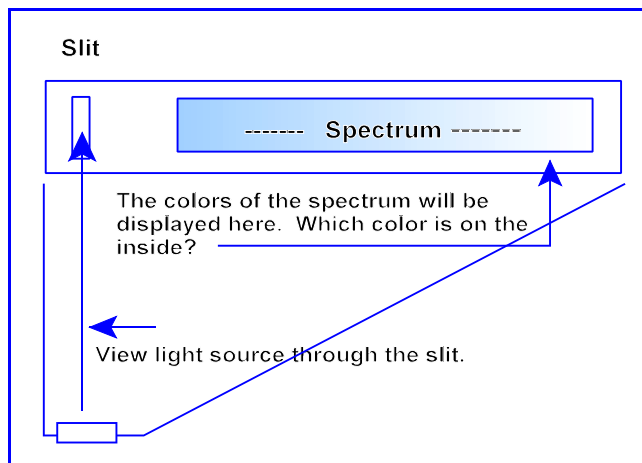

List the colors you see in the spectroscope, in order of increasing frequency and decreasing wavelength:

_____   _____   _____   _____   _____   _____

Increasing **frequency**   ────────────

➤

Decreasing **wavelength**

Table 1. The relationship between frequency and wavelength of visible light.   Which color has the shortest wavelength? Which has the longest wavelength?

Topic II: The Fingerprint Nature of Spectra

Your laboratory will be equipped with bottles containing sodium compounds (sodium chloride, sodium bicarbonate, or other sodium salts). These bottles have corks with flame test wires mounted in them. Take the sodium flame test wire and place its loop at the hottest part of the flame. What do you observe? Look at the flame through the spectroscope. What do you observe? (You may have to replenish your supply of material on the flame test wire periodically.) It works well to have one person hold the flame test wire in the flame and the other observe through a spectroscope. **CAUTION**! DO NOT HOLD YOUR SPECTROSCOPE TOO CLOSE TO THE FLAME. The spectroscopes are plastic and will melt or catch on fire! Your lab partner or the person holding the wire can watch to make sure you keep the spectroscope far enough away from the flame. Obtain a flame test sample of a compound containing lithium, and repeat the observation described above.

Is the flame spectrum you observe dependent on the identity of the compound, or only on the identity of the metallic ion of the compound? Try different compounds of sodium. What do you observe? If several compounds of the other elements are available, compare them also. Can you draw a generalization?

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Your laboratory instructor will set up gas discharge tubes containing argon, helium, and neon gases. Observe the emission spectra of these elements with your spectroscope, and record your observations on a chart similar to that in Figure 7. Note that this chart correlates color with the wavelength of light. Textbooks and reference books list wavelength of light using nanometer (nm) units, or Angstroms (Å). One nanometer (nm) is equal to 1×10^{-9} meters, while one angstrom is equal to 1×10^{-10} meters. More recent writings use nanometers exclusively. Look carefully at the spectrum of a mercury vapor yard light, then at the spectrum of the overhead fluorescent lamp. Can you identify an element present in the fluorescent lamp?
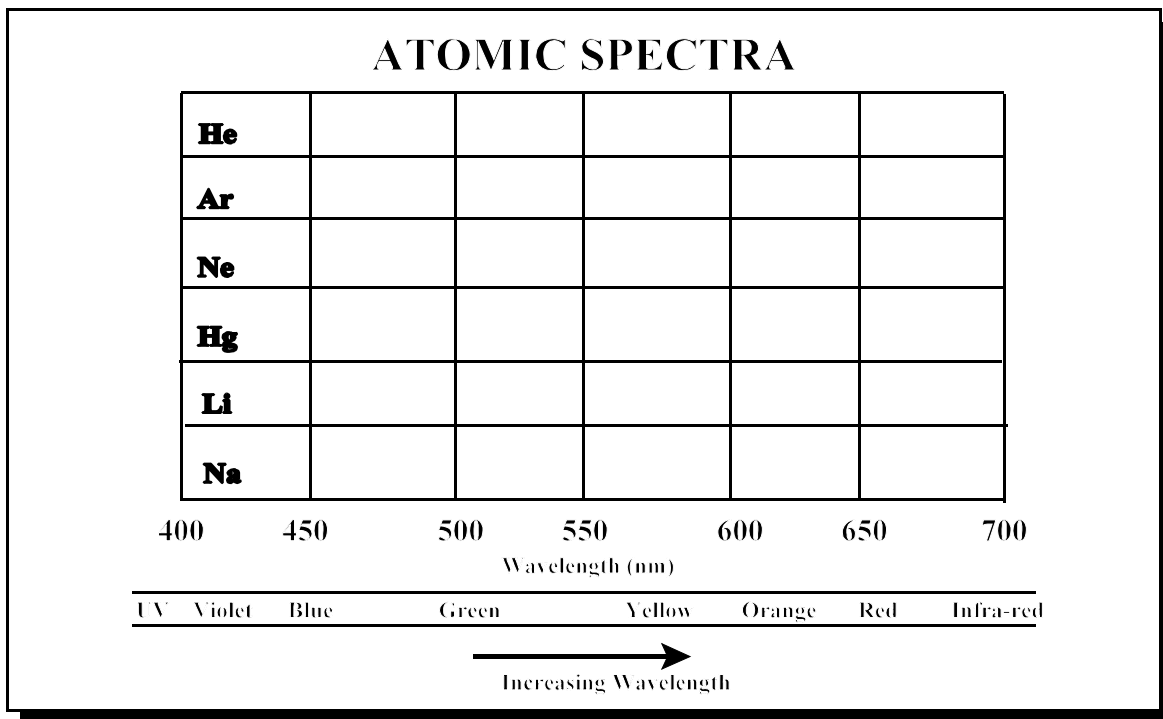
ATOMIC SPECTRA

He					
Ar					
Ne					
Hg					
Li					
Na					

400   450   500   550   600   650   700

Wavelength (nm)

UV   Violet   Blue   Green   Yellow   Orange   Red   Infra-red

Increasing Wavelength

Figure 7. Sample data chart. (A tear-out data chart is provided at the end of this experiment.)

Topic III: Solid vs. Gaseous Spectra

Compare the spectrum of one of your flame tests -- sodium or lithium, for instance, with that of an incandescent lamp and with that of a fluorescent lamp. What do you observe? Look at a clean glowing nichrome wire held in a Bunsen flame. What do you observe? Can you identify a basic difference between the spectrum observed from a heated solid and the spectrum from a highly heated gas? Continuous spectra comprised of all colors are called *band spectra. Line spectra* are comprised of only certain colored lines. Record your observation of the difference between the spectra of a hot solid and a hot gas in Table 2, as well as in your laboratory report.

What do you think causes the light in the overhead fluorescent lamps -- a gas or a solid, or both? Look at a fluorescent lamp with your spectroscope, and decide which is true.

Solids produce a _____ spectrum.

Gases produce a _____ spectrum.

Obtain a yellow flame with your Bunsen burner by closing off the air supply. Look at the flame with your spectroscope. Do you think it is composed of small bits of heated solid or matter in the true gaseous state?

Table 2. The physical state of a light source can be determined by looking at its spectrum. Record your observation — line or band — in this table.

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Photographic Measurement of Spectra

It is possible to make a permanent record of spectra by using a camera behind the spectroscope in place of your eye. Figure 8 shows a sketch of this situation for a simple prism spectroscope. When the spectrum is recorded on film instead of being viewed with the eye, the instrument is usually called a spectrograph rather than a spectroscope. If one uses a photoelectric cell as a detector, the instrument is called a spectrophotometer. Figure 8 also shows a sketch of the spectrum of a sample of mercury that had been heated to vaporization and then excited with an electrical discharge. The color slides to be used in this section of the experiment were taken with similar equipment and color film.
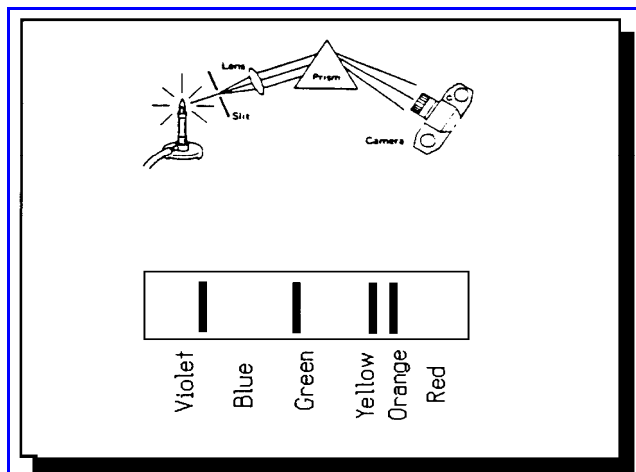

Figure 8:. Spectra can be recorded on film using simple equipment. This figure shows the visible spectrum of mercury.

Note that the mercury spectrum contains several predominant colors or spectral lines. These colors range from yellow for the two closely-spaced lines on the right to violet for the left line. In some spectra you may see lines further in the ultra-violet. Film is more sensitive to ultraviolet than the human eye, and can "see" spectral lines in the ultraviolet that are not visible when one observes the spectrum.88

When a different element is substituted for mercury and the spectrum is observed, a different set of spectral lines is present. Each element has a different set of spectral lines, and this set is always unique enough that it will be characteristic of only one particular element and no other. The predominant visible lines emitted by mercury are listed in Table 3.

Violet	**404.6**	**nm**
Violet	**407.7**	
Blue	**435.8**	
Green	**546.0**	
Yellow	**576.7**	
Yellow	**579.0**	

Table 3. The visible emission spectrum of mercury.

It is possible to identify elements and even mixtures of elements by observation of their spectra. In this part of this experiment you will be asked to identify one or two unknowns.

Unfortunately, it is difficult to determine the wavelength of the various spectral lines directly from a photograph or slide, since the camera has no calibration scale. However, if a known spectrum is included with the unknown it is possible to project the slide onto a wavelength scale and construct a calibration graph which relates position on the scale to wavelength.

Slides of other emission spectra have been scanned onto computer image files which can be displayed on your computer screen using the program *Atomic Spectra*. The unknown elements on the scanned spectra are also listed in Table 5. To run *Atomic Spectra* you will need to exit from LabWorks and double click on the *Atomic Spectra* icon. After clicking the "OK" button on the opening screen, the *Atomic Spectra* window will appear on the screen.

The program should be in the "Calibration Mode" (indicated by the tab in the upper left corner). Select an unknown (W, X, Y or Z) from the sample boxes at the top of the screen. Two spectra will appear across the bottom, the mercury spectrum and the unknown. You will need to make a calibration graph from the mercury spectrum, just as you did with the projected slide. In this case the positions of the mercury lines on the screen will be measured by clicking on them with a mouse.

Just below the "calibrate" tab there should be six boxes, corresponding to the six observable lines in the mercury

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spectrum. The color reproduction on the scanned slides colors may not appear to match exactly the labels on the boxes. The green line at 407.7 nm may look yellow and the two yellow lines may look orange.

Double click on the first calibration box, violet at 404.6 nm. The "Scale" box (upper left) will indicate the position of the mouse pointer on the slide. As you move the pointer across the spectrum, this number will change. It is recording the pixel number from the left edge of the screen. Place the mouse pointer on the far left line of the mercury spectrum and double click. The scale value will be recorded and a point plotted on the calibration graph. Repeat this process for each of the mercury lines. The second violet line at 407.7 nm is very faint and appears just to the right of the first. Slides of other emission spectra have been scanned onto computer image files which can be displayed on your computer screen using the program *Atomic Spectra*. The unknown elements on the scanned spectra are also listed in Table 5. To run *Atomic Spectra* you will need to exit from LabWorks and double click on the *Atomic Spectra* icon. After clicking the "OK" button on the opening screen, the *Atomic Spectra* window will appear on the screen.

The program should be in the "Calibration Mode" (indicated in the upper right corner). Select an unknown (W, X, Y or Z) from the sample boxes at the top of the screen. Two spectra will appear across the bottom, the mercury spectrum and the unknown. You will need to make a calibration graph from the mercury spectrum, just as you did with the projected slide. In this case the positions of the mercury lines on the screen will be measured by clicking on them with a mouse.
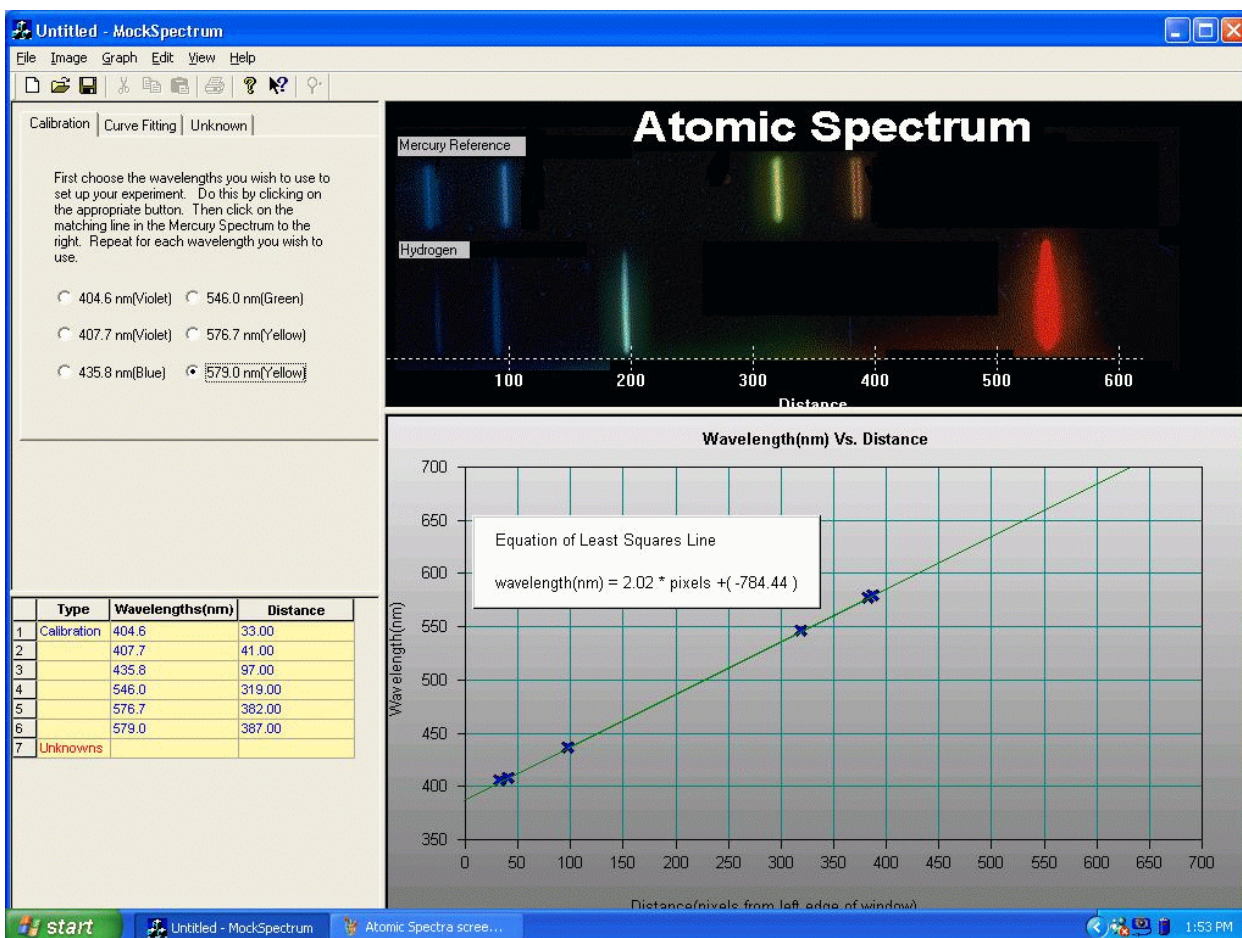

Figure 9: The Atomic Spectra calibration chart relates the wavelength of a spectral line to its position on the photograph.

Double click on the first calibration box, violet at 404.6 nm. The "Scale" box (upper left) will indicate the position of the mouse pointer on the slide. As you move the pointer across the spectrum, this number will change. It is recording the pixel number from the left edge of the screen. Place the mouse pointer on the far left line of the mercury spectrum and double click. The scale value will be recorded and a point plotted on the calibration graph. Repeat this process for each of the mercury lines. The second violet line at 407.7 nm is very faint and appears just to the right of the first.

When all of the mercury lines have been identified and marked on the calibration graph, switch to the "curve fit" mode using the tab in the upper left corner of the screen. A linear regression fit will be drawn through the calibration data points and the equation for the line will be displayed at the top of the graph.

Now switch to the "unknown" tab. When the mouse pointer is moved across the unknown spectrum, its position will be tracked in the "Scale" and "Wavelength" boxes in the upper left corner of the screen. When you double click on a line in the unknown spectrum, scale position and wavelength are entered into the data table on the right.

Mark all of the unknown spectral lines and record their wavelengths in your lab notebook. You should be able to identify the unknown element by comparing your list of wavelengths to those given in Table 4. You can clear the data and select another unknown by switching back to the "Calibration Mode."

You can also bring up an interactive chart showing spectral lines of ten different elements together with those for your unknown.   Using the box in the lower left corner of the screen, select which spectral line you would like to check and the width of the window you would like to explore. For example, if you choose 5 nm for the window, the interactive chart will highlight all spectral lines within +/- 5 nm of your measured line.   Continue this for all of your spectral lines, and then check to see which of the ten known elements best fits your set of spectral lines. Note that you may not be able to see all of the spectral lines – some may be too faint, and some may be outside the range of the colored slide.
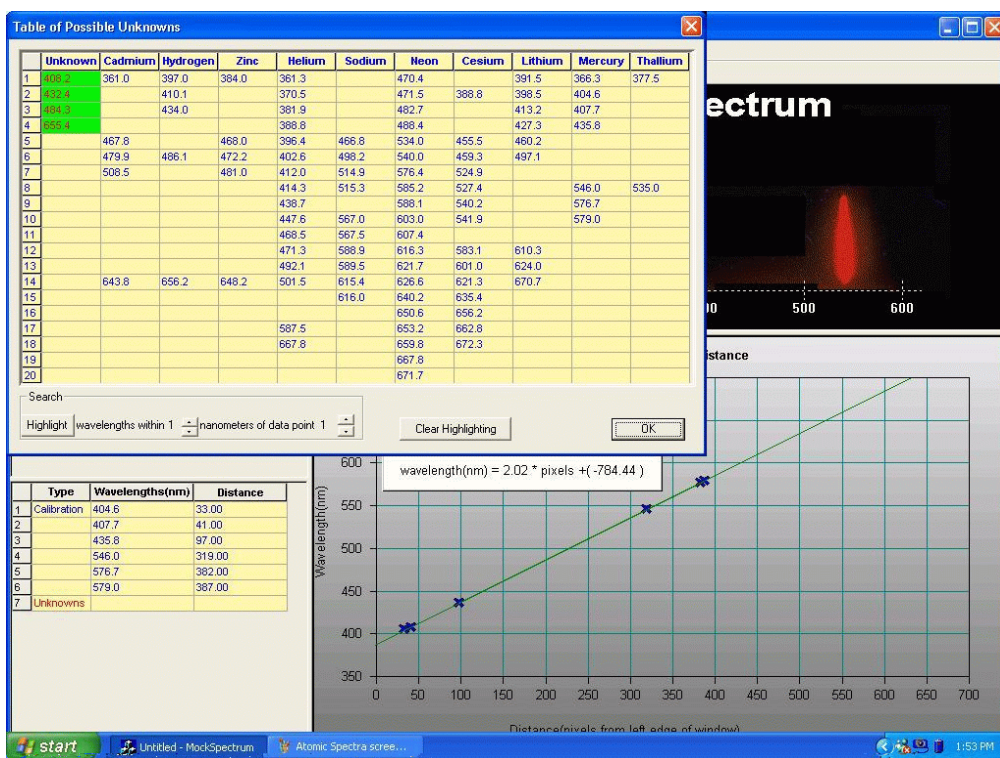

Figure 10: Once the wavelengths of the atomic spectra of an unknown element are determined, you can use the interactive chart to match these with know lines for ten different elements.

Thallium	Cadmium	Hydrogen	Zinc	Helium	Sodium	Neon	Cesium	Lithium	Mercury
378	361	397	384	361	467	470	389	392	366
535	468	410	468	371	498	472	456	399	405
	480	434	472	382	515	483	460	413	408
	509	486	481	389	567	488	525	427	436
	644	656	638	396	568	534	527	460	546
				403	589	540	540	497	577
				412	590	576	542	610	579
				414	615	585	583	624	
				439	616	588	601	671	
				448		603	621		
				469		607	635		
				471		616	656		
				492		622	663		
				502		627	672		
				588		640			
				668		651			
						653			
						660			
						668			
						672			

Table 4 Emission spectra of some common elements. (Wavelengths are given in nm). Mercury lines are used as calibration reference points on the photographic spectra.

Level II: Some Support for Bohr's Planetary Electron Model (Optional)

Neils Bohr was a young Danish post-doctoral student working for Earnest Rutherford when Rutherford's research group discovered the nucleus of the atom.   Bohr returned to Denmark, intent on figuring out how electrons were arranged around the atom's nucleus. Because only certain colors of light were emitted by hot atoms, and because it was known at that time that light or electromagnetic radiation was produced by accelerating or decelerating electrons, Bohr proposed that electrons run in "planetary orbits" around atomic nuclei. (Figure 11). Each atom has a number of possible electron orbits. Electrons can be pushed to outer orbits by heating the atom, and give off light when they fall back to inner orbits. Bohr used known laws of physics that governed circular motion, electrical attraction, gravitational attraction, and the relationship between energy and frequency or wavelength of electromagnetic radiation to develop an equation that should

Figure 11. Bohr predicted that electron jumps from outer orbits to inner orbits would produce light as the electron changed to lower energy.

be able to predict the wavelength of light produced as an electron falls from an outer, higher energy orbit to an inner, lower energy orbit. Bohr figured this only for the element hydrogen, the simplest element in the periodic table. Bohr's equation is illustrated in Figure 12 In this equation, n_1 is the orbit on which the electron stops, and n_2 is the orbit on which it starts its jump.
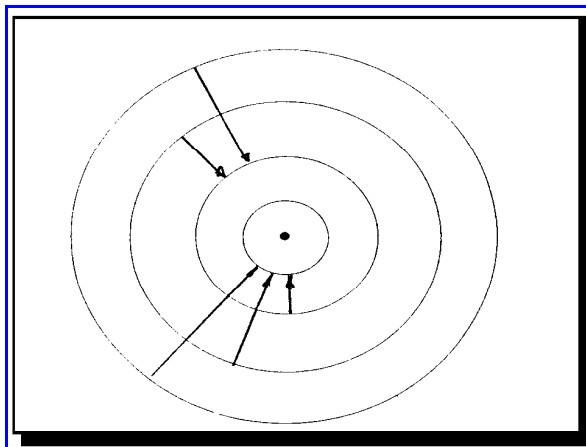
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For wavelength values in nanometers, the term that contains all of the constants in the equation (2 π^2, Z^2, etc) evaluates to 0.0109678 nm^{-1}. Thus to figure out an electron jump from orbit 3 to orbit 2 would involve setting **n₁** to 2 (inner orbit number) and **n₂** to 3 (outer orbit number).

Bohr predicted that electron jumps ending on the second orbit would produce spectral lines in the visible region of the spectrum (See Table 5, next page).

Table 5 gives the wavelengths of light predicted for 3–> 2 and 4 –> 2 transitions. Use the formula below to predict wavelengths of light expected from excited hydrogen atoms for transitions 5 –> 2 and 6 –> 2.

BOHR'S MODEL

Predicting Hydrogen Spectral Lines

$$\frac{1}{Wavelength} = \left(\frac{2\ pi^2\ Z^2\ m\ e^4\ M}{(h^3 c)\ (m + M)}\right)\left(\frac{1}{n^2_1} - \frac{1}{n^2_2}\right)$$

Z = charge of nucleus h = Planck's constant (6 x 10^{-34})

m = mass of electron c = speed of light

M = mass of nucleus e = charge of electron

Figure 12. Bohr's equation, based on predicted electron jumps from outer, higher energy orbits to inner, lower energy orbits would produce different colors or wavelengths of light. The constants in the first term evaluate to 0.0109678 nm^{-1} .

Measure the spectral lines of hydrogen gas using the hydrogen spectra slide mounted in your laboratory or by using *Atomic Spectra*, and consider these two questions in your report:

$$\left(\frac{1}{N_1^2}\right) - \left(\frac{1}{N_2^2}\right) =$$

$$\left(\frac{1}{2^2}\right) - \left(\frac{1}{3^2}\right) =$$

$$\left(\frac{1}{4}\right) - \left(\frac{1}{9}\right) =$$

$$(0.2500) - (0.1111) = 0.1389$$

$$\frac{1}{Wavelength} = (0.0109678\,nm^{-1})\,(0.1389)$$

$$Wavelength = 656.4\ nm$$

1. Does Bohr's model appear to accurately predict the visible region spectral lines of hydrogen, as measured in your experiment?

2. Why are some of the hydrogen spectral lines brighter than others? Although a hydrogen atom has only one electron, that electron can be in any of the possible orbits. Is it possible more hydrogen atoms might have their electrons

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in lower energy (inner) orbits than in outer, higher energy orbits?   Would one be more likely to see atoms performing the 3->2 electron transition than a 4->2 electron transition?   Would this hold for occupancy of higher energy orbits as well?   Would you predict an increasing or decreasing intensity as the spectral lines moved to higher energy?

Hydrogen Spectral Lines predicted by Bohr's planetary electron model for electron jumps ending on orbit two.

Electron transition	Wavelength of emitted light	Color of emitted light.
3 → 2	656.4 nm	Red
4 → 2	486.3 nm	Blue-Green
5 → 2	_____nm	Violet
6 → 2	_____nm	Violet (difficult to see)

Table 5 Electron transitions, wavelengths, and colors of hydrogen spectral lines predicted by Bohr's planetary electron model. The wavelengths predicted for the 5->2 and 6 -> 2 electron transitions are not included in this table. They are left for you to compute.

LABORATORY REPORT

Your report should include your data and conclusions derived for each of the experimental topics. Be sure to include your spectra chart, your mercury calibration graph, and the measurements you made on the unknown colored slides.

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ATOMIC SPECTRA

He					
Ar					
Ne					
Hg					
Li					
Na					

400   450   500   550   600   650   700

Wavelength (nm)

UV   Violet   Blue   Green   Yellow   Orange   Red   Infra-red

→

Increasing Wavelength