Spectroscopy:

The Interaction of Light and Matter

"We all know what light is; but it is not easy to tell what it is."

Samuel Johnson
Introduction

In certain parts of South America, there exists a most beautiful and remarkable species called the railroad worm (*Phrixothrix*). Yellowish-green luminous spots are arranged in eleven pairs on the worm’s abdominal segments, and on its head there are two additional red luminous spots. When the worm is disturbed, all the spots give off light, and as it undulates through the night, it looks like a miniature railroad train. Of course, this biological midnight express emits an amazingly small amount of energy in the form of visible radiation (light) compared to the many other natural and man-made sources. Our world is literally inundated with all kinds of radiation, much of it coming from our own sun. Daylight that comes from the sun is a very small part of the spectrum of electromagnetic radiation. From cosmic rays to radio waves, the total electromagnetic spectrum includes all the known types of radiation (see Table 2.1).

Radiation may be described in one of two ways: either as a stream of energy pulses (photons) or as energy waves sent out from a source (worms, suns, etc.) at the speed of light. Scientists dodge the bullet by using whichever interpretation works best to explain an experiment involving radiation. The photon and wave theories are linked by Planck’s law:

\[ E = hv \]

where \( E \) is the photon energy in joules (J), \( v \) is the frequency of the radiation (Hz or s\(^{-1}\)) and \( h \) is Planck’s constant \( (6.63 \times 10^{-34} \text{ J s}) \). Wavelength and frequency are related by

\[ c = \lambda v \]

where \( c \) is the speed of light \( (3 \times 10^8 \text{ m s}^{-1}) \), \( \lambda \) is the wavelength of the radiation (often reported in nm), and \( v \) the frequency. It is useful to note that energy and frequency are directly proportional to each other, whereas energy is inversely proportional to wavelength.

Sources of radiation are extraordinarily diverse, ranging from complex nuclear fusion reactions in supernovae to burning zirconium foil in photographic flash cubes. In spite of this diversity, the amount and type of emitted radiation are intimately related to the chemistry of the processes that produce the radiation. It is this link that forms the basis for the science of spectroscopy. Spectroscopy is the study of the interaction of electromagnetic radiation with matter. When matter is energized (excited) by the application of thermal, electrical, nuclear, or radiant energy, electromagnetic radiation is often emitted as the matter relaxes back to its original (ground) state. The spectrum of radiation emitted by a substance that has absorbed energy is called an emission spectrum, and the science is appropriately called emission spectroscopy.

Another approach often used to study the interaction of electromagnetic radiation with matter is one whereby a continuous range of radiation (e.g., white light) is allowed to fall on a substance; then the frequencies absorbed by the substance are examined. The resulting spectrum from the substance contains the original range of radiation with dark spaces that correspond to the missing, or absorbed, frequencies. This type of spectrum is called an absorption spectrum. In spectroscopy the emitted or absorbed radiation is usually analyzed, i.e., separated into the various frequency components, and the intensity is measured by means of an instrument called a spectrometer.

The resultant spectrum is mainly a graph of intensity of emitted or absorbed radiation versus wavelength or frequency. There are in general three types of spectra: continuous, line, and band. The sun and heated solids produce continuous spectra in which the emitted radiation contains all frequencies within a region of the electromagnetic spectrum. A rainbow and light from a light bulb are examples of continuous spectra. Line spectra (illustrated in Figure 2.1) are produced by excited atoms in the gas phase and contain only certain frequencies, all other frequencies being absent. Each chemical element of the periodic chart has a unique and, therefore, characteristic line
spectrum. Band spectra are produced by excited molecules emitting radiation in groups of closely spaced lines that merge to form bands.

These categories of emission and absorption spectra contain tremendous amounts of useful information about the structure and composition of matter. Spectroscopy is a powerful and sensitive form of chemical analysis, as well as a method of probing electronic and nuclear structure and chemical bonding. The key to interpreting this spectral information is the knowledge that certain atomic and molecular processes involve only specific energy ranges. Table 2.1 shows the regions of the electromagnetic spectrum and the associated energy transitions that occur in atomic and molecular processes.

A simple example of the energy changes involved in particular transitions and the resulting spectrum is the hydrogen emission spectrum. This spectrum is especially interesting for historical, theoretical, and practical reasons. Over a period of 40 years, from 1885 to 1925, all of the lines in the emission spectrum in the ultraviolet, visible, and infrared regions were found experimentally and were identified with various electron transitions. Spectroscopic experiments like the above gave the major experimental evidence for the Bohr theory of the atom and eventually for the modern quantum theory.

Much of the scientific knowledge of the structure of the universe, from stars to atoms, is derived from interpretations of the interaction of radiation with matter. One example of the power of these techniques is the determination of the composition, the velocities, and the evolutionary dynamics of stars. The source of the incredible amount of energy produced by the sun is nuclear fusion reactions going on within the hot interior (temperature $4 \times 10^6$ K). Two fusion cycles, the carbon cycle and the proton cycle, convert hydrogen nuclei into helium nuclei via heavier nuclei, such as carbon 12 and nitrogen 14. The enormous radiation of energy from the hot core seethes outwards by convection. This radiation consists of the entire electromagnetic spectrum as a continuous spectrum. Towards the surface of the sun (the photosphere), the temperatures are much lower, and the cooler atoms of different elements all absorb at their characteristic frequencies. The radiation that shoots into space towards the earth is a continuous emission spectrum with about 22,000 dark absorption lines present in it (Fraunhofer lines), of which about 70% have been identified. These absorption lines — i.e., missing frequencies — prove that more than 60 terrestrial elements are certainly present in the sun.

Stellar spectroscopy via satellites has shown unequivocally that all the known elements of the periodic chart are made in complex sequences of fusion reactions in stars. The absorption lines also have different intensities at different sequences, and the spectra are therefore excellent indicators of the temperature of a given stellar atmosphere. Absorption lines of stellar spectra can also be used to measure star
<table>
<thead>
<tr>
<th>Type of Radiation (i.e. Spectral Region)</th>
<th>Energy Range (E, joule)</th>
<th>Frequency Range (ν, Hz)</th>
<th>Wavelength Range (λ)</th>
<th>Energy Transition</th>
</tr>
</thead>
<tbody>
<tr>
<td>γ-ray</td>
<td>4.0 x 10^{-14}</td>
<td>6.0 x 10^{19}</td>
<td>&lt; 5 x 10^{-3} nm</td>
<td>Nuclear</td>
</tr>
<tr>
<td>X-ray</td>
<td>4.0 x 10^{-14} - 2.0 x 10^{-17}</td>
<td>6.0 x 10^{19} - 3.0 x 10^{16}</td>
<td>5 x 10^{-3} - 10 nm</td>
<td>Inner-shell electrons</td>
</tr>
<tr>
<td>Vacuum UV</td>
<td>2.0 x 10^{-17} - 1.1 x 10^{-18}</td>
<td>3.0 x 10^{16} - 1.7 x 10^{15}</td>
<td>10 - 180 nm</td>
<td>Middle-shell electrons</td>
</tr>
<tr>
<td>Near UV</td>
<td>1.1 x 10^{-18} - 5.7 x 10^{-19}</td>
<td>1.7 x 10^{15} - 8.6 x 10^{14}</td>
<td>180 - 350 nm</td>
<td>Valence electrons</td>
</tr>
<tr>
<td>Visible</td>
<td>5.7 x 10^{-19} - 2.6 x 10^{-19}</td>
<td>8.6 x 10^{14} - 3.9 x 10^{14}</td>
<td>350 - 770 nm</td>
<td>Valence electrons</td>
</tr>
<tr>
<td>Infrared</td>
<td>2.6 x 10^{-19} - 4.0 x 10^{-21}</td>
<td>3.9 x 10^{14} - 6.0 x 10^{12}</td>
<td>770 nm - 50 μm</td>
<td>Molecular vibrations</td>
</tr>
<tr>
<td>Far Infrared</td>
<td>4.0 x 10^{-21} - 2.0 x 10^{-22}</td>
<td>6.0 x 10^{12} - 3.0 x 10^{11}</td>
<td>50 - 1000 μm</td>
<td>Molecular rotations</td>
</tr>
<tr>
<td>Microwave</td>
<td>2.0 x 10^{-22} - 6.6 x 10^{-25}</td>
<td>3.0 x 10^{11} - 1.0 x 10^{9}</td>
<td>0.1 - 30 cm</td>
<td>Molecular rotations</td>
</tr>
<tr>
<td>Radiowave</td>
<td>&lt; 6.6 x 10^{-25}</td>
<td>&lt; 1.0 x 10^{9}</td>
<td>&gt; 30 cm</td>
<td>Nuclear and electron spin</td>
</tr>
</tbody>
</table>

Table 2.1  Spectral Regions in the Electromagnetic Spectrum
velocities (relative to the earth) by measuring the Doppler effect. When a source sends out light of a specific frequency, the frequency remains the same only if the distance between the source and receiver stays the same. If the source is moving towards the earth, the light will appear to be of a higher frequency — i.e., bluer — than the light of a similar source in the laboratory. Conversely, the light of a receding source appears to be of lower frequency and, thus, redder (see Figure 2.2). The Doppler effect is easily measured by comparing the stellar spectrum with the spectrum of matter made luminous in the laboratory.

The science of spectroscopy can take us into the subatomic world or out into the farthest distance of space. The development of lasers is now causing a revolution in many areas of spectroscopy. These coherent, almost monochromatic, sources can be used to study extraordinarily fast chemical processes, as well as such previously inaccessible processes as flames and combustion. Recent research has shown that all living objects emit low-intensity radiation that may be detected and analyzed with modern photoelectronic techniques.

Figure 2.2 Spectral Shifts Due to the Doppler Effect
Background Chemistry

"The most directly compelling evidence for the quantization of energy comes from the observation of the frequencies of light absorbed and emitted by atoms and molecules."

P.W. Atkins

Atoms, ions, and molecules contain electrons that occupy discrete energy levels. The actual energy of each state (level) is dependent upon several factors: the nuclear charge, the distance of the electron from the nucleus, and the number of electrons between the nucleus and the electron in question. The transition of an electron from one level to another must be accompanied by the emission or absorption of a discrete amount of energy. The magnitude of this energy depends on the energy of each of the levels between which the transition occurs.

\[ \Delta E = E_2 - E_1 \]

For energy emission to occur, electrons must first be given energy from some external process — e.g., an electrical discharge, a combustion reaction, or a heated wire. They are then said to move from the ground state to an excited state. The excited electrons then "relax" back to their original levels, and energy is emitted. The number and type of these transitions depend on the particular structure of the energy levels in a given chemical species and on various quantum selection rules. These properties are unique to each individual species and give rise to an emission of energies that characterizes that species. If the value of \( \Delta E \) lies within the visible region of the total electromagnetic spectrum, then the frequency corresponds to visible light, and the emission can be seen by the eye. From a practical point of view, since each electron can undergo many transitions and since many species have many electrons, emission spectra usually consist of a very large number of discrete frequencies.
The wave theory of radiation is particularly useful in providing models for interpreting the behavior of light emitted from atoms. Radiation is a form of energy consisting of oscillating electric and magnetic fields that move the direction of propagation at the speed of light. The wave motion, which is illustrated in Figure 2.4, is described in terms of some fundamental properties such as amplitude $A$, wavelength $\lambda$, and frequency $\nu$.

![A Wave](image)

Figure 2.4  A Wave

The frequency is defined as the number of waves (of wavelength $\lambda$) passing a point per second. The relationship that links $\lambda$ and $\nu$ is

$$c = \lambda \nu$$

The human eye is sensitive only to a tiny band of radiation of the total electromagnetic spectrum. This band, called white light, ranges from about 400 nm to about 800 nm in wavelength and is made up of the colors of the rainbow. Table 2.2 shows the wavelength ranges within the spectrum of white light:

<table>
<thead>
<tr>
<th>Color</th>
<th>Wavelength (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Violet</td>
<td>400 – 430</td>
</tr>
<tr>
<td>Blue</td>
<td>430 – 490</td>
</tr>
<tr>
<td>Green</td>
<td>490 – 570</td>
</tr>
<tr>
<td>Yellow</td>
<td>570 – 590</td>
</tr>
<tr>
<td>Orange</td>
<td>590 – 640</td>
</tr>
<tr>
<td>Red</td>
<td>640 – 750</td>
</tr>
</tbody>
</table>

Table 2.2  Wavelength Ranges of Colors in White Light

The energy of the various colors of light can be easily calculated using Planck's law,

$$E = h\nu$$

where $E$ is the energy (in joules), $h$ is Planck's constant ($6.63 \times 10^{-34}$ J s), and $\nu$ is the frequency of the radiation.

The separation of light into its spectral components can be done by refraction or diffraction. In this series of experiments, the separation of light into its component
colors is accomplished by diffraction in a device called a spectroscope. A *spectroscope* is simply a box, with a slit at one end (to let in light) and a light-separating device at the other end. The separating device you will be using is called a *transmission diffraction grating*, and it consists of a sheet of transparent plastic that has thousands of tiny grooves ruled on it. The way in which the grating works to separate light into colors is by *wave interference*. Imagine that light of one color (monochromatic) is shone on the grating in Figure 2.5.

![Vertical grooves](image)

*Figure 2.5  Diffraction of Laser Light*

The grating device in Figure 2.6 illustrates wave interference. Viewed from above, the light waves can be seen as a series of straight lines representing the crests of the waves and the grooves look like tiny openings in the plastic. As these waves hit the grating, ripples of light come from each hole.

![Light falling on grooves](image)

*Figure 2.6  Light Falling on the Grooves of a Grating*
The ripples move outward and interfere with each other. Where the crests are in the same place (crest lines cross), the waves will actually add to give a higher wave and a bright spot of light, which is called constructive interference. Destructive interference occurs when crests and valleys meet; the waves will almost cancel each other, resulting in darkness. Figure 2.7 illustrates these differences.

Figure 2.7  Constructive and Destructive Interference

The overall cumulative effect is that the light is bent at an angle to the incident beam. This phenomenon is called diffraction and the angle is called the angle of diffraction $\theta$. A quantitative relationship can be derived from the geometry as shown in Figure 2.8.

Figure 2.8  Geometry of Diffraction
where \( d \) is the distance between two adjacent grooves, \( \theta \) is the angle of diffraction and 1 and 2 are two rays of monochromatic light of wavelength \( \lambda \). Now both rays, 1 and 2, are travelling at the same speed (the speed of light), and after hitting the grating, both are bent at an angle \( \theta \). Ray 2, however, has to travel a little bit farther (distance \( x \)) than ray 1 in the same amount of time. This path length difference causes a delay in ray 2, and interference can occur. If the path difference is an integral number of wavelengths, then constructive interference will occur. From simple geometry,

\[
\frac{x}{d} = \sin \theta,
\]

then
\[
x = d \sin \theta,
\]

thus
\[
n\lambda = d \sin \theta
\]

For a given number of grooves per cm and when \( n = 1 \) (said to be first order), the angle of diffraction depends on the wavelength of the light. White light, or any other kind of light composed of a combination of colors, will be separated into the individual component colors.

Three common terrestrial sources of visible radiation are the electrical discharges in gases, thermal energy from combustion, and heated metals. A convenient source in the laboratory is the \textit{electrical discharge tube} — i.e., a glass tube that contains metal electrodes at each end and is filled with a gas, such as hydrogen, helium, or mercury, at a low pressure. A high voltage is placed across the electrodes, and when the current is switched on, a stream of fast-moving electrons shoots through the gas from the cathode to the anode. Energy is transferred from the electrons to the gas atoms, and the electrons in the gas atoms are excited to higher energy levels. The return of excited electrons to the ground state results in the emission of light, which may be analyzed with a spectroscope. A simple discharge tube is pictured in Figure 2.9.
Figure 2.10  A Fluorescent Lamp

Some practical devices are the common fluorescent light, neon signs, and street lights. A fluorescent lamp (such as the one pictured in Figure 2.10) is a discharge tube that is filled with mercury vapor at low pressure. The inside walls of the tube are coated with a phosphor of calcium halophosphate (Ca₅(PO₄)₃F₁₋ₓClₓ) doped with Mn²⁺ and Sb³⁺. Mercury atoms are excited by the process discussed above and emit their characteristic spectrum, which is in both the visible and in the ultraviolet spectrum (mostly UV, at 254 and 185 nm). This UV radiation is absorbed by the Sb³⁺ and passed on to the Mn²⁺. The Sb³⁺ dopant gives off blue light, and the Mn²⁺ gives off orange light; the combination appears as white light.

Many solid substances — e.g., sodium chloride (NaCl) — may be excited by the thermal energy (heat) of flames. The heat comes from the exothermic combustion reactions occurring in the flame, e.g.,

\[ \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} + \text{heat} \]

Solid sodium chloride consists of sodium ions (Na⁺) bonded to chloride ions (Cl⁻). In a bunsen burner flame, these ions are dissociated, and the separated Na⁺ ions combine with free electrons in the flame to form sodium atoms:

\[ \text{Na}^+ + e^- \rightarrow \text{Na} \]

Electrons within the neutral sodium atoms can then be excited to higher energy levels by the heat of the flame:

\[ \text{Na} + \text{heat} \rightarrow \text{Na}^+ \text{ (an excited Na atom)} \]

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The excited atoms then "relax" back to the ground state and emit light:

\[ \text{Na}^* \rightarrow \text{Na} + \text{hv} \text{ (light)} \]

The emitted light is characteristic of all of the electronic transitions that occur with energy differences corresponding to visible radiation. Analysis of the light by means of a spectroscope gives the atomic emission spectrum of sodium. In this series of experiments, you will be able to measure wavelengths of the emitted light, but not intensity. This is because you will be looking at the spectra by eye. Various types of detectors are available for measuring radiative intensities, and if they were used, a quantitative analysis for the amount or concentration of a chemical element could be accomplished.

Continuous emission spectra contain so many emitted frequencies of radiation that the lines overlap and the light looks like a rainbow. Common terrestrial sources of continuous emission are fluorescent lamps, ordinary incandescent light bulbs, heated metals in general, and flames containing soot. Notice that all these sources are solids — e.g., the wire filament in a light bulb and soot particles in a candle flame. The atoms and molecules in heated solids are continuously bumping against each other because they are so close. This dynamic contact results in much of the energy being transferred as kinetic energy which is not quantized. As the temperature of a solid is raised, more and more of the radiation is emitted at shorter wavelengths.

**ADDITIONAL READING**

   Everything you wanted to know about the sun and its emission spectrum.

   A wonderful, readable book about the birth, life, and death of the stars (the nonterrestrial ones!).

   A classic and, in my opinion, still the best book on the subject.

   Feynman's dedication is beautiful — "what one fool can understand, another can." This book should be read by all faculty and students, but particularly faculty!

   A more advanced book, but has all the practical details. Encyclopedic.
Pre-Laboratory Quiz

1. Photon and wave theories of radiation are linked by Planck's Law. Give the law and define the symbols. Give typical units for each.

2. Briefly describe emission spectroscopy.

3. Give 2 examples of sources that emit continuous spectra.

4. What process will produce a line spectrum?

5. What types of radiation will be emitted from atoms in which valence electron transitions are occurring?
6. What is the wavelength range of the visible spectrum?

__________________________________________________________________________

__________________________________________________________________________

__________________________________________________________________________

7. List the colors of the spectrum of white light from the highest to the lowest frequency.

__________________________________________________________________________

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__________________________________________________________________________

8. How do we know that more than 60 terrestrial elements are found in the sun?

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__________________________________________________________________________

9. In the hydrogen emission spectrum, what energy level transitions produce visible light?

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10. What is the Doppler effect?

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__________________________________________________________________________
Laboratory Experiments

Flowchart of the Experiments

Section A. Characterization of a Transmission Diffraction Grating

Section B. Construction of a Spectroscope

Section C. Exploring Spectroscope Specifications

Section D. Wavelength Calibration of the Spectroscope

Section E. A Comparison of Continuous Emission Spectra

Section F. Atomic Line Spectra and Electronic Transitions; Electrical Discharge Tubes

Section G. Flame Emission Spectra

Requires one three-hour class period to complete
Section A. Characterization of a Transmission Diffraction Grating

CAUTION: Lasers are dangerous. Do not stare directly into a laser beam, or into a beam reflected from any mirror surface. Although you are using low-power lasers, exercise caution.

Goals:
1. To use laser light of wavelength 632.8 nm, to determine the number of grooves on a diffraction grating.
2. To be able to calculate the groove distance of a diffraction grating from first and second order diffraction data.

Discussion:
One of the best ways of experimentally determining the number of grooves on a diffraction grating is to use it to diffract light of an exactly known wavelength. This can be done easily if you have access to a Helium-neon laser source. This gas laser is a continuous-wave (CW) source which emits mainly visible radiation at 632.8 nm. The laser is pointed at the grating and the angles of diffraction are calculated form the experimental geometry.

This experiment can be done in any one of three ways depending on how many He-Ne lasers are available in the laboratory. If you have one that you can use, then your instructor will demonstrate the experiment and give you the measurements. If there are none available, you may read through the method and I will give you values that I measured using a Spectraphysics 0.5 milliwatt He-Ne laser. If lasers are available, then work through the following sequence.

Experimental Steps:
1. Set up the diffraction grating (which has been mounted in a 35 mm slide holder). To do this, simply cut an SJ straw through about 1 cm from the end.

2. Mount the straw into a vertical straw in which a hole is punched 5 cm from the end. Place the vertical straw in a microtray and push the diffraction grating into the cut straw.
3. The laser should be set up so that it points normal (at 90°) to the grating. Then place a white card to intercept the diffracted light. Turn the laser on.

You can see an intense undiffracted beam striking the card and on either side — if you have the grating in the right direction — you can see the diffracted spots. If the diffracted spots are in a vertical mode simply rotate the grating 90°.

If the room is dark and the distance between card and grating is not too great then you should be able to see at least two orders of diffraction.

4. Using a ruler or meter stick, measure the appropriate distances to find \( \sin \theta \) for each order of diffraction that you can see.

Here are some measurements I made:

For first-order diffraction, \( a = 15.3 \text{ cm}, b = 45.8 \text{ cm} \). To obtain second-order diffraction, I moved the card closer to the grating and found a faint second-order spot: \( a = 8.5 \text{ cm}, b = 12.7 \text{ cm} \). With the low-intensity beam on my laser, I could not find a third-order spot.

5. Now use the two-dimensional diffraction relationship \( n \lambda = d \sin \theta \) to calculate the groove distance \( d \). Be careful with the units — a good tip is to work in meters. You can now easily find the number of grooves per cm (or inch) on the replicate transmission diffraction grating.
Section B. Construction of a Spectroscope

Goal: To construct a simple but rather accurate spectroscope containing a built-in quantitative calibration system.

Discussion: All of the materials you need for building the spectroscope are located at Reagent Central. Part 1 and Part 2 provide instructions for building a spectroscope from two different types of boxes. Your instructor will determine which of these sets of instructions should be used.

Section B. Part 1. Construction of Box Type A

Experimental Steps: Diagrams of the completed instrument are shown below.

1. Cut off the inside flaps, leaving about 0.5 cm.
2. Outline the slit area and small square with a pencil before you cut them out. Make sure that these holes are in line before you cut them out.

3. Obtain a piece of corrugated cardboard, which will be used as a cutting board.
4. With a razor blade cut out the slit and square.
   
   **CAUTION:** Please be careful, these blades are sharp.

5. Now put the box together tightly using masking tape. The only light permitted in should be through the two holes you have cut.

6. Pencil in 2 points, one on each side of the box exactly opposite each other.

7. Make holes at these points by pushing and rotating a sharp pencil point into the box. The holes should only be large enough to friction-fit the 4 mm glass rod!

8. Lay the glass rod on the table and make a clean scratch in the middle of the rod using a glass scorer or file. Don't cut too deeply or the rod will break.

   **CAUTION:** Be careful — the ends of the rod are sharp.
9. Now use 2 pieces of black electrical tape to define an approximately 1 mm slit.

10. Obtain a piece of plastic diffraction grating and orient it correctly on the box before taping it permanently with transparent tape. To do this, hold the box so that you can look into it through the square hole, and point it vertically so that light from the fluorescent light enters the slit. Hold the grating over the square hole with your index finger while still looking into the box. You should see a visible spectrum (rainbow) to the right of the slit. If it doesn’t look right, rotate the grating 90°.

Once you are satisfied, carefully tape the grating to the box (tape around the edges).

11. Hold the box with the slit facing you on the right side of the box end and carefully insert the glass rod into the box as shown below, gently working it so that it is all the way through.

**CAUTION:** Don’t force it, or it will break and cut you!

You now have a spectroscope with a calibration device.

12. Point the spectroscope vertically and look at the brightest part of the ceiling light. Inside the box you should see a good spectrum and also an outline of the glass rod. The scratch on the rod should be clearly visible to you. If not, carefully rotate the rod until you see it.
13. Now move the rod further into the box, slowly. The scratch will move, allowing you to locate any specific point on the spectrum.

14. The reason you can see the scratch is that light from outside the box is reflected down the rod until it reaches the scratch (as illustrated below). At this point the light is scattered in all directions by the damaged glass. Some of the light will come in your direction and you can see the scratch.

* Do you think that you could see a spectrum without the box?

## Section B. Part 2. Construction of Box Type B

**Experimental Steps:**

1. Obtain a flat bakery box from Reagent Central.
2. Place the box on a piece of corrugated cardboard.

Steps 3 through 5 are illustrated in the diagram below.
3. Using a razor blade, cut a slit about 2 cm from the fold.

4. Using a pair of scissors, cut off the flaps as indicated by the hatched areas.

5. Using a razor blade, cut a hole 1 cm square. Fold the box on the fold lines and tape all the edges with masking tape.

Now go back to Step 6 of Part 1 (Section B) to finish constructing the spectroscope and to complete Part 1.

Section C. Exploring Spectroscope Specifications

Goal: To be able to determine the specifications for your spectroscope.

Discussion: It is always wise to explore the good points and the limitations of any instrument before launching out and spending time and money (tuition!) using it. Obviously, the spectroscope that you have built has many limitations. However, the nice thing about an inexpensive, simple, self-built machine is that you should have no inhibitions about using it, breaking it, changing it, or fixing it. In fact, you have a unique opportunity to write the specifications for your own spectroscopic instrument.

NOTE: If you wear spectacles, you might find it easier to take them off when looking into the spectroscope.

Experimental Steps:

- Were you confused at any step — and where? How could the instructions for building the spectroscope be improved — e.g., can they be made shorter?

- What are the dimensions of your spectroscope?

- How could you measure the actual dimensions of the spectrum? What are they?

- This may seem like a silly question, but it’s not. What is the actual location of the spectrum? Is it really inside the box?

- Predict what differences in the spectrum you would see if the spectroscope were made out of a giant pizza box.

1. Now let’s change some things. Vary the slit width by unpeeling one of the pieces of electrical tape and repositioning it onto the box.

- If you make the slit larger or smaller, what happens to the fluorescent light spectrum?

- Draw a few simple pictures to illustrate what you see.

- Does the slit have to be a long, thin rectangle?

- What is the relationship between the distance of the source from the spectroscope and the characteristics of the spectrum?

- What changes would you have to make in your spectroscope in order to see a second-order spectrum?
Give your spectroscope a rating (1 – 10) for
a) craftsmanship
b) aesthetics
c) spectroscopic efficiency

**Section D. Wavelength Calibration of the Spectroscope**

*Goal:* To carry out a calibration of your spectroscope by using known spectral lines in the emission spectrum of a fluorescent light.

*Discussion:* All scientific instruments must be calibrated before any quantitative measurements can be made. Commercial instruments are almost always calibrated by the manufacturer before they are actually used in the factory or laboratory. The glass rod in your spectroscope is a suitable measurement device, but the only way to calibrate it is to be able to view a visible spectrum that has emission lines of exactly known wavelength. The light emitted from a typical fluorescent light is such a spectrum.

*Experimental Steps:* 1. Make sure that the slit width is about optimum (1 mm), and point your spectroscope directly up at the brightest part of a fluorescent light. It helps if you shut one eye!

The spectrum that you can see is actually composed of two types of spectra: a continuous and a line emission spectrum, superimposed on each other. This superimposition produces a rainbow with 3 fairly prominent lines of light in it.

![View of Spectrum Inside Box](image)

The three lines 1, 2, and 3, are violet, green, and yellow and are the strong emissions from Hg vapor in the fluorescent tube. These lines have well-known wavelengths and we can use them to calibrate the spectroscope:

- Line 1, violet 436 nm
- Line 2, green 546 nm
- Line 3, yellow 580 nm

2. Keep looking at the spectrum and slowly push the rod until the scratch mark is lined up just underneath and exactly in line with the violet line (line 1).
3. Without moving the rod at all, use a ruler to measure the distance from one end of the rod to the side of the box (outside the box). Measure to an estimated 0.1 mm.

![Diagram of a glass rod and measuring distance]

4. Look at the spectrum again and push the rod so that the scratch mark is now lined up with the green line (line 2). Measure the rod distance again (on the same side of the box as before).

5. Repeat the procedure for the yellow line (line 3) and measure the distance.

6. Now plot a graph of wavelength of lines 1, 2, and 3 versus rod distance for each line. Use a wavelength axis from 400 nm to 650 nm. Draw the smoothest curve you can through all 3 points.

NOTE: Graph paper is bound into the back of this book. Simply tear it out and tape it into your laboratory record.

This graph is the spectroscopy calibration line which will enable you to find the wavelengths of unknown spectral lines, bands, etc., in any emission or absorption spectrum.

- Would this calibration line work for your neighbor’s spectroscopy?
- What could you do to ensure that the calibration line was the same for any spectroscopy (with the same size box)?
- How does the slit width affect the calibration line?

NOTE: The next three experiments (E, F, and G) can be done in any order. The sources for these experiments are in various places in the room. Check for accessibility and go ahead!

### Section E. A Comparison of Continuous Emission Spectra

**Goal:**

*To use the spectroscopy to compare various continuous emission sources.*

**Discussion:**

Most people are aware that white light from different sources can look very different. Colors that match in artificial light look very different in daylight. In this experiment you can use the spectroscopy to investigate the difference in spectral characteristics of common sources of white light. Use your spectroscopy to analyze the light from (a) fluorescent light, (b) incandescent light (i.e., 60 watt bulb), (c) candlelight, and (d) daylight. Several methods are described below; try each method!
Experimental Steps:

**Method 1**

1. Look at one source and immediately go to another and back to the first. Differences in the two spectra can then be easily seen.
   - Draw pictures to illustrate these differences.

**Method 2**

1. Determine the total spectral range and the width of each band of color (red, for example) by measuring with the glass rod.

2. Line up the scratch on the edge of the blue side of the spectrum, measuring the rod distance, and then moving the scratch all the way over to the very end of the red side and measuring. By consulting your calibration line you can obtain the spectral range for that light.

3. To obtain a daylight spectrum, point your spectroscope at a bright sky.

**CAUTION:** Do not look directly at the sun.

**Method 3**

Studying the candle flame requires a different observational approach.

1. Look carefully at the flame.
   - Draw a simple picture.

Even though the spectroscope shows one bright continuous spectrum, close inspection reveals several zones which are different intensities or colors. At the base of the flame, the blue light is emitted by the combustion reaction products molecular carbon (C2) and a hydrocarbon (CH). About halfway up the flame, the temperature reaches about 1400°C. Most of the candlelight (and, therefore, the emission spectrum) comes from tiny soot particles that are about 50 nm in diameter. It is the heating of these particles that produces the yellow glow of the flame.

**Discussion:**

The chemical processes that produce the light emitted from the sun, a candle, a 60 watt bulb, and a fluorescent light are all quite different. However, all these sources give a continuous emission spectrum.

- Why is this?

You may take your spectroscope with you at the end of the laboratory.

**CAUTION:** Remove the rod when you are carrying it.

- As a homework project, look at and describe the spectral characteristics of 4 sources different from the ones you studied in lab. Some suggestions are white light from a TV screen, street lights (there are many types), and neon signs.

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<th>Section F.</th>
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**Goals:**

1. To obtain the atomic line spectra of light emitted from electrical discharge tubes.
2. To be able to calculate photon wavelengths, frequencies, and energies from line spectra data.
**Experimental Steps:**

1. The electrical discharge tubes are along one side of the room and are connected to a high-voltage supply. Ask your instructor to switch them on for you.

   **CAUTION:** Be careful not to touch the tubes or metal strands or you will get an electrical shock.

2. View several discharge tubes before making any measurements so that you can get a good idea what line spectra look like. The brighter tubes can be viewed from several feet away.

   **NOTE:** You might find it advantageous to increase the slit width to about 1.5 to 2 mm.
   - Why?

3. Now view the tube containing hydrogen gas. This is not very bright so you must view it quite closely, perhaps about 10 to 20 cm away.
   - Use the glass rod measurement technique and your spectroscope calibration line to determine the wavelength of the spectral lines that are prominent.
   - Be careful to record the color of the lines and the overall color of the emitted light.

4. Study the following diagram which shows the energy level transitions for H atom emission.
   - From your data identify the transitions which correlate with the spectral lines you observed.
5. Select another discharge tube.
   - Find the wavelength, frequency, and photon energy for the prominent spectral lines.

Suppose the tube you selected (Step 5) was contaminated with hydrogen gas. What would the emission spectrum of this mixture look like?

   - Draw the lines and colors on a wavelength grid 450 – 750 nm.

### Section G. Flame Emission Spectra

**Goal:**

To obtain line and band spectra of light emitted from chemical species produced in Bunsen burner flames.

**Discussion:**

Many substances, particularly alkali metal and alkaline earth salts, produce brightly colored flames when they are heated by a Bunsen burner. Flame emission spectroscopy is a powerful method for qualitative identification and quantitative determination of many elements. One of the most common and useful flame emissions is that from atomic sodium.

**Experimental Steps:**

1. Find a partner to hold a glass rod in a Bunsen burner flame.

2. Obtain a wire loop that has been stuck into a cork and one of several solid salts (LiCl, NaCl, KCl, SrCl₂, CaCl₂, or CuCl₂) from Reagent Central.

3. When the flame gets bright, view it through your spectroscope. Get reasonably close to the flame (about 4 inches or so), but try not to set the spectroscope on fire.

   **CAUTION:** Be very careful to keep the spectroscope at a safe distance from the flame so that it doesn't catch fire!

   - Measure the wavelength in the usual way, calculate the frequency and photon energy, and record in your laboratory record.

4. Adjust the Bunsen burner flame so that it is about 4 to 5 inches high and is a hot flame.

5. Heat the loop in the flame until it is red-hot, which will burn off any impurities. While the loop is still red-hot, quickly dip the loop into the solid. Some of the solid will stick to the wire.

6. Place the loop into the outside part of the flame and note the flame color.

7. Clean the loop by dipping in water and reheating and then obtain the flame colors for all of the salts.

   **CAUTION:** Please do not contaminate the salts!

8. Find a partner and select one of the salts.

9. Have your partner hold the loop (with sample) in the flame while you view the flame color through your spectroscope. Flame spectra are not very intense, and in order to get
good measurements of line spectra, you will need to (1) have an optimum slit width, (2) do 1 line at a time, and (3) be fairly close to the flame. Try for the most prominent lines.

10. Obtain one of the unknowns from your instructor and carry out a qualitative analysis.
   • Report the result and the reasons for your answer in your laboratory record.