I. OBJECTIVES
- Understand the principle of atomic emission spectra.
- Know how to acquire emission spectrum and identify the specific spectra of some common materials.
- Figure out the advantages and the disadvantages of this technique.

II. BACKGROUND

1. Bohr’s model

According to Bohr’s model, an atom consists of electrons which revolve around the nucleus in certain orbits corresponding to discrete energy levels. Bohr proposed that angular momentum of electron can take only certain values or in other words angular momentum of electron is quantized. According Bohr angular momentum for electron in atom is given by:

\[ L = n \frac{h}{2\pi} = n\hbar \]  

(1)

here \( n \) is an integer number which is usually called the principle quantum number \((n = 1, 2, 3, 4,\ldots)\), \( h \) is the Plank constant and \( \hbar = \frac{h}{2\pi} \) – reduced Planck constant.

Quantization of angular momentum for hydrogen atom results in allowed energy level given by equation:

\[ E_n = \frac{me^2}{32\pi^2\varepsilon_0^2\hbar^2} \cdot \frac{1}{n^2} \]  

(2)

If electrons are not disturbed by external forces they occupy the highest energy levels (smallest quantum numbers). Absorption of photon can excite electron from low energy lever to higher one. Then electron relaxes from the higher energy level to the lower level it will emit a photon. The wavelength of the emitted/absorbed radiation (photon) is directly related to the difference between two energy levels:

\[ \Delta E = E_i - E_j = \frac{hc}{\lambda} = \hbar \nu \]  

(3)

here \( \nu \) is the frequency of emitted/absorbed electromagnetic wave, \( E_{i,j} \) is the energy level with principal quantum number \( n = i,j \).

![FIG. 1. Transition of an electron between two states](image-url)
Each atom in the periodic element table has unique set of energy levels which gives rise to its characteristic emitted/absorbed radiation. This special feature is used as a fingerprint to identify the presence of the different chemical elements.

2. Experiment methods

2.1. Principle:

Any method that is capable of exciting electrons in atoms between different energy levels can be used to generate the atomic emission spectrum. Only free atoms can produce the atomic emission spectrum, the electronic properties of bulk materials are different, because atoms make chemical bonds and discrete energy levels merge into the allowed energy bands. Thus in order get the atomic spectrum any sample has to be converted into the gas phase. When the electrons in free atoms are excited to higher energy levels, after very short time they will relaxate by emitting electromagnetic waves. If these transitions appear at the energy range of the visible light, VIS light spectroscopy can be applied in order to study the chemical composition. In order to disperse the light beam into different constituents depending on the wavelength, a dispersion component such as prism or grating has to be used (see Fig.3 and Fig.4). The dispersed light (spatially dispersed) is detected and recorded by detector and can be converted into the digital signal, which is used for analysis.
2.2. Measurement techniques

An emission spectroscopic analysis can be divided into three basic steps (also see Fig.5):

- excitation - conversion to gas phase and excitation of atoms;
- dispersion – separation of light into its component depending on wavelength (spatial separation);
- detection.

**a. Excitation**

If the sample is in bulk or liquid phase, at first it must be converted to gas phase containing free atoms. Then electrons of these atoms need to be excited into the higher energy states that allows to generate atomic emission spectrum. To
generate the atomic spectrum of gas, solid and liquid samples, three methods are commonly used:

* **Flame:** Most commonly used to analyze alloys. An alloy can be dissolved in an acid and obtained solution injected into a flame. This flame can be either an acetylene-oxygen flame or an induction heated argon flame. Plasma generated in flame emits spectrum of light which contains characteristic features depending on its chemical composition. This method can also be used to study the composition of flammable gases or liquids.

![Image of flame tests](image)

**FIG. 6.** The flame tests above show (a) strontium, (b) sodium, (c) lead, and (d) potassium.

* **DC arc:** An electric discharge is another method that has been commonly used. Application of high DC-voltage between two electrodes generates a discharge in gases due to ionization of atoms by electric field that leads to the atomic emission spectrum. Moreover this method can be used to study the chemical composition of metals. If sample is conductive it can be used as an electrode for excitation of DC arc. Due to interaction of DC arc with electrode material its atoms will be ejected into the plasma and contribute to the atomic emission spectrum. This method is used in current laboratory work.

* **AC spark:** Another method is to use a resonant LC-circuit that generates a high frequency oscillation of electric field. The LC-circuit is only charged with a few thousand volts which is not enough to initialize a spark on its own so there is an additional low energy high voltage circuit carrying some 20000 volts that strikes the spark at regular intervals. This arrangement is capable of generating very high currents for short time periods and the temperature in the spark can reach 10000K. This high temperature excites electrons to higher energy levels and the spectrum then contains many more lines for electron de-excitations to higher energy levels than the ground state. One drawback is that the total energy is lower than DC-arc excitation and the intensity of the spectral lines are lower. Also this method is mostly suitable for samples which are already in gas phase.
b. Dispersion

Two common methods used to disperse the light beam are prism and diffraction grating. Using prism is quite simple than grating but the resolution is not high due to limited optical dispersion of materials. That’s why for measurements requiring a high resolution, diffraction grating is preferred.

In the case of reflection grating, the relation between the angle of incidence, diffraction angle, wavelength and diffraction grating period is described in the following equations:

\[ d(\sin\alpha + \sin\beta) = m\lambda \]  \hspace{1cm} (3)
\[ \sin\alpha + \sin\beta = Nm\lambda \]  \hspace{1cm} (4)

\( d \): spacing between the slits, called the grating period  
\( N \): number of slits per mm (the groove density), equal to the reciprocal of the grating period (grooves or lines/mm)  
\( m \): diffraction order \((m = 0, \pm1, \pm2, \pm3, \ldots)\)  
\( \lambda \): wavelength

It can be seen that when \( m \neq 0 \) the diffraction angle depends on wavelength. Therefore, we can use gratings to separate (disperse) white light into its constituent. The diffraction angle \( \beta \) also varies with the groove density \( N \) and the incident angle \( \alpha \). Depending on the value of \( N \), the diffraction may not occur. For example, if the angle of incidence is \( \alpha = 30^\circ \) and the groove density \( N = 2400 \) grooves/mm and the wavelength of 700 nm is used, using the equation (4) with \( m = 1 \) (first order of diffraction), we get \( \sin\beta = 1.18 \) (as we know, sine is less or equal to 1). Thus, there is no first-order diffraction does not occur.

\[ \sin\beta = \frac{1}{1.18} \]

FIG. 7. The Principle of Reflection Gratings

In our experiment, rotation of the diffraction grating changes the angle of incidence of the incoming beam that gives change in the reflection angle, thereby the wavelength range recorded by a detector is shifted. The grating can be rotated to cover different parts of the spectrum.
c. Detection

The intensity of light at different wavelengths is detected by a Photo Diode Array (PDA), see in Fig. 8. Each photodiode consists of p-n junction connected to external reverse bias. Ideally when no light reach photodiode, there is no current flowing through it. When photons strike semiconductor, they can excite electrons from the valence band to the conduction band which results in an electron-hole pairs, see in Fig. 8. When electron-hole pairs are excited in photodiode they create current flowing through it. The amount of generated electron-hole pairs depends on the amount of photons (intensity) interacting with the semiconductor. Thus a current flowing through the photo diode depends on the intensity of light. The PDA used in this laboratory work contains of 1024 photodiodes. Spatially dispersed light hits different positions of the PDA depending on a wavelength. External electronic circuit reads the signal coming from each photodiode in PDA and send it to a computer. This read out is done by the control electronics connected to the spectrometer.

FIG. 8. Schematic of photodiode detector
(http://www.files.chem.vt.edu/chem-ed/optics/detector/pd.html)

FIG. 9. 46 element Si photodiode array for UV to NIR

III. PREPARATORY ASSIGNMENTS

1. Assignment
Describe the Bohr’s model

2. Assignment (excitation)
In the compendium three procedures to evaporate and excite a sample are described. Name them? When is one or the other method used?

3. Assignment (dispersion)
Two methods for wavelength separation are described. Which? Which one of the two do you think is most used today?

4. Assignment (diffraction)
In first order diffraction of light of wavelength $\lambda$ diffracted at 45° with the normal and follows the laws of reflection. The grating consists of 1200 lines/mm. What will be the wavelength of light in nm? Assume normal incidence.

5. Assignment (Photodiode array)
Describe the role of slit and grating in a spectrometer.
6. Assignment
Describe in short a function of PDA by diagram.

7. Assignment
Give conversion steps to convert energy in eV to wavelength in Å.

IV. EXPERIMENT
1. Acquire the background spectrum
   - Turn off the light
   - Select Sampling from the Setup, then set up the two parameters: integration time (ms):100 and averaging: 1
   - Select Mode \(\rightarrow\) Spectrum \(\rightarrow\) Pixels (in box X-units)
   - Click \(\mathcal{E}\) button to acquire the spectrum
   - Observe the spectrum, then save the spectrum.

2. Acquire the spectrum of Hg
   - Arrange a lamp, a mirror, a lense and a spectrometer as in a figure below:
     - Connect the Hg lamp to the source.
     - Open the program “SpectraArray SL” (on the desktop).
     - Select Sampling from the Setup, then set up the two parameters: integration time (ms):100 and averaging: 1
     - Select Mode \(\rightarrow\) Spectrum \(\rightarrow\) Pixels (in box X-units)
     - Click \(\mathcal{E}\) button to acquire the spectrum
     - Adjust the angle of mirror until the count of the strongest peak around 3400.
     - Click \(\mathcal{E}\) button again to stop the measurement and capture the spectrum used for analysis.
Notice: The y-axis shows the intensity, when software is not calibrated the x-axis shows the peak position in pixel units NOT in wavelength unit (Å, nm).

3. Calibration

In principle, calibration process includes three main steps as mentioned below:

**Step 1:** Measure the emission spectrum of a standard spectral lamp within the relevant selected spectral range in which strong peaks appear. In our experiment, we use a Hg lamp as a standard lamp.

**Step 2:** Identify the peak position in a unit of pixel along the X-axis. Notice: choose the maximum intensity of peaks in spectrum but avoid saturation of the detector.

**Step 3:** Correlate them with the reference data taken from NIST atomic spectra database or handbook.

In our measurement, we will use the manual calibration.

**Step 1:** Acquire the Hg spectrum

**Step 2:** Determine the pixel position of the high peaks in a whole spectrum.

**Step 3:** Use NIST database or Handbook to determine the wavelength of each peak.

**Tip:**

- You should draw two columns to write down the pixel position and the corresponding wavelength.

<table>
<thead>
<tr>
<th>Pixel Position</th>
<th>Wavelength</th>
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- Hg lamp is often used for calibrating when we study the peaks in visible range, see Fig. 9. For higher range of wavelength, Ne lamp is a preferred one.

- The wavelength region accessible by spectrometer can be adjusted by changing the grating position which is done by turning the micrometer screw (in our lab, we do not need to change this parameter).
Step 4: Click Setup → Wavelength Calibration → Calibrate using spectral lines → Add → Fill the pixel position (from an acquired spectrum) and the corresponding wavelength (from NIST database of Hg I) of each peak used to calibrate.

Step 5: Select Accept button to complete calibration.

Step 6: Change unit of x-axis by selecting Mode → Spectrum → nm (in box X-units)

4. Analysis of spectra using other lamps: Ne, Na

Step 1: Replace the Hg lamp by the Ne or Na lamp.

Step 2: Turn on the lamp and acquire the spectrum

Step 3: Determine the wavelength of each characteristic peak by moving mouse cursor to each peak.

Step 4: Compare with the standard database to see how precise the spectrum is. If it is not good, we have to re-calibrate with higher precision and maybe adding some more known peaks.

Notice: Some peaks of Ne lamp appear in the infrared range above 700 nm. Thus they cannot be seen in the spectrum. Of course, we can shift the spectral range covered by the spectrometer by adjusting the rotation of the diffraction grating. However, then you will have to calibrate again. Note: Adjusting diffraction grating means calibrating again.

4. Analysis of solid material (Copper, Zinc, Steel, Spoon and some coins)

Step 1: Sharpen the carbon electrode by a pencil sharpener and polish the surface of analyzed material.
**Step 2:** Load the carbon electrode (top) and the material (bottom) to DC-arc system. Remember the distance between the electrode and the material must be small (~ 2 mm)

**Step 3:** Turn on the DC-source

**Step 4:** Press the black button (on the left of the DC source) to initialize the arc. If no arc appears, we need to check the electrode and the material again (The distance is OK or not, the electrode is sharp or not…).

**Step 5:** When the arc appears, we have to acquire the spectrum quickly then shut down the DC-source (just open the door of chamber) to protect the electrodes from melting.

**Step 6:** Analyze the acquired spectrum.

**Notice:**

- Never keep the arc appear for more than 10s. It can make the electrode melt.
- When the arc initiates, immediately adjust the distance, the angle of the lens to focus the light on the entrance slit to have a sufficiently high peak on the screen. After that, we have acquire the spectrum and shut down the arc.

**V. GUIDELINES**

- Make a proper protocol so you can keep track of what tests have done.
- Verify that the parameters used by the computer are the same as the spectrometer is set to.
- Clean and sharpen the electrodes and adjust the electrode gap before every measurement.
- Do not touch the electrodes while they carry voltage.
- Do not look directly into the arc. UV-light fogs the lens in your eye.
- Verify that the light is well collimated on the slit before your run the command scan.
- Make use of tables or spectral atlases to find suitable candidates for elements present in the samples and eliminate some by exclusion (if one spectral line is missing the candidate is probably not present in the sample). Note that a sample usually contains more than one element.
- Use and update the calibration curve present in the lab.
- Do not hurry, you have enough time.

http://student.fizika.org/~nnctc/spectra.htm