D4. Emission Spectroscopy Analysis

> ***The aim of the exercise** is to understand the laws of light absorption and emission in gases, to experimentally determine the spectral lines of a reference gas using a prism spectroscope, and using a so-called dispersion curve, to identify the wavelengths of spectral lines of an unknown gas.*

Atoms absorb electromagnetic radiation at specific frequencies f, i.e., photons with specific energies, given by the formula:

$$E = h\,f, \tag{1}$$

where h is the Planck constant and f is the frequency. These frequencies form an **absorption spectrum**. An atom in its **ground state** (minimum energy) can absorb a quantum of radiation and, as a result of this phenomenon, transit to **the excited state** (higher energy level). Conversely, an atom in an excited state can **emit** a photon and return to a lower energy level. The frequencies of emitted photons form the **emission spectrum**, which matches the absorption spectrum.

In simple atoms (e.g., hydrogen, helium), this behavior is described by the **Bohr model**, which postulates:

Postulate I: An electron orbits the nucleus in discrete circular orbits where the angular momentum is quantized:

$$mvr = \frac{n\,h}{2\pi}, \tag{2}$$

where m is the electron mass, v is the electron's velocity, r is the orbital radius, and n is the principal (main) quantum number.

The orbits of electrons are called stationary states with fixed energy – the energy does not change as long as the electron remains on one of them.

Postulate II: Transition between energy levels (E_n and E_m) involves absorption (for $E_n>E_m$) or emission (for $E_n<E_m$) of energy as a quantum of radiation:

$$\Delta E = E_n - E_m = h\,f. \tag{3}$$

For individual atoms, the emission and absorption of radiation means **electrons' energy change ΔE_e**, forming the **electronic spectrum**. The electronic spectra of atoms consist of **discrete spectral lines**, each corresponding to a transition between energy levels. Each line has a unique frequency f, and hence a unique wavelength $\lambda=c/f$, and an associated color. The spectral line pattern is unique for each element, allowing elemental identification—the core of spectral analysis.

Molecular spectra differ significantly from atomic ones: they appear as **bands** of closely spaced lines due to a more complex energy structure. A molecule's total energy includes: **electron** energy E_e, **vibrational** energy E_v, and **rotational** energy E_r. Each of the above is **quantized**, and transitions can occur between these discrete levels, as a result of emission or absorption of the right amount (quantum) of radiation. Molecular spectra represent energy transitions of each of the abovementioned groups of energy.

Additionally, another case is **continuous spectra** emitted by hot solids or liquids. Those are the most complex spectra.

Spectral analysis enables chemical composition determination because:

- Each element has a characteristic spectral fingerprint.
- The intensity of its spectral lines correlates with its concentration in the substance.

The instrument used for this purpose is a **prism spectroscope**, consisting of (see figure 1):

- A **prism** P (where light is dispersed)
- Two collimators (K_1 and K_2)
- An eyepiece (L)
- A scale placed in the optical path for reading wavelengths

Light from a gas source passes through collimator (K_1), becomes a parallel beam, enters the prism where it is dispersed, and forms colored spectral lines in the eyepiece (L), visible against a scale from (K_2).

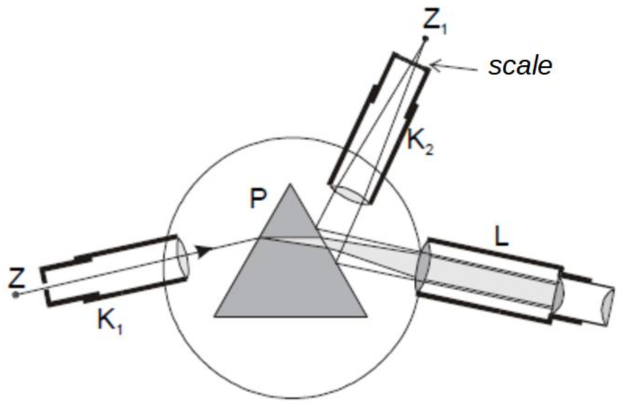

Fig. 1. The scheme of the prism spectroscope

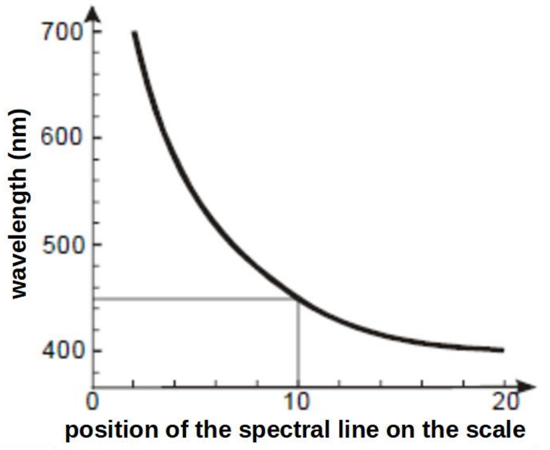

Fig. 2. Dispersion curve

To observe the spectrum of a gas, it's enclosed in a discharge tube at low pressure (~1 mm Hg), e.g., a Plücker tube. Electrodes mounted at both ends are connected to a high-voltage power supply and provide current flow in the gas, exciting the gas to emit light with its characteristic line spectrum.

To identify wavelengths emitted by the unknown gas:

- First, calibrate the spectroscope using a reference (known) gas (e.g., helium),
- Plot a dispersion curve (scale position vs. wavelength) – see figure 2,
- Then, using this curve, determine wavelengths for an unknown gas.

D4. Measurement and calculation protocol

Pair No.:	Student's name and surname:	Field of study: Group:
Date:	Teacher's name and surname:	Passing information:

Measuring protocol:

Equipment: Prism spectroscope, Plücker tubes with helium and unknown gases, Power supply.

Measuring steps:

1. Move the spectroscope away from the power supply. With supervision, place the reference gas tube (helium) in the tube holder.
2. Position the spectroscope correctly. With supervision, turn on the power supply at the rear.
3. The helium gas glows. Look through the eyepiece and adjust it to find the helium emission spectrum. Adjust slit width for brightness. Adjust collimator K_1 length for sharp spectral lines.
4. Illuminate the scale and focus it by adjusting the K_2 collimator length.
5. Align scale "0" with the first visible red spectral line.
6. Read positions of the remaining helium spectral lines and, based on their color, find corresponding wavelengths from a reference table (available in the class).
7. Turn off the power, remove the helium tube, and insert the unknown gas tube. ⚠ Do not move the spectroscope's components during this step!
8. **Turn on the power**, record the scale positions of the unknown gas's spectral lines, and enter data into the table.

   ⚠ Tube operation time is limited to ~10 minutes. Turn off the power after that time.

Data table

Reference gas (helium)			Unknown gas …………………..		
Line color	Position on the scale	Wavelength (read from the table) λ [nm]	Line color	Position on the scale	Wavelength (based on dispersion curve) λ [nm]

Data analysis:

1. On graph paper, plot the dispersion curve for helium:
   a. X-axis: measured scale positions
   b. Y-axis: corresponding wavelengths (from reference table)
2. Using the dispersion curve, read the wavelengths corresponding to the unknown gas's line positions. Fill in the data table.
3. Compare the calculated wavelengths with known line tables to identify the unknown gas.