Experiment No. 54

Measuring of light intensities (spectroscopic properties of light sources)

Keywords:
Atomic and molecular spectra, emission spectra, black body (emitter), gray emitter, Planck's radiation law, Stefan-Boltzmann's law, fluorescence, phosphorescence, chemiluminescence, photoelectric effect, photomultiplier (secondary electron multiplier - SEV), monochromator

Literature:
Textbooks of physical chemistry:
Atkins, "Physical Chemistry"
Gerthsen, Kneser, Vogel: Physics
Textbooks of experimental physics, e.g.:
Demtröder: Experimental physics 2
Bergmann, Schäfer: Textbook of experimental physics 3, optics
Haken, Wolf: Atomic and quantum physics

Basics:
Spectroscopy is an important analytical method that is used in practically every area of chemistry. A wide variety of quantitative and qualitative analyses are carried out in numerous variants (e.g. NMR, MW, IR, UV/VIS, photometry, AAS, and many more). What these applications have in common is that spectroscopic experiments involve an interaction between electromagnetic radiation (light) and matter (atoms or molecules in the gas phase, liquids or solids). The result of these interactions is recorded in spectra in which the intensity of the absorbed or emitted radiation is recorded as a function of its energy (wavelength, wave number or frequency). Depending on the two options, a distinction can be made between absorption and emission methods.

Absorption spectroscopy:
Here a constant, preferably continuous light source is used, the radiation of which is partially weakened by a substance introduced into the beam path. The absorbed radiation increases the internal energy of the molecules and is usually converted into heat. The strength of the absorption and its dependence on the wavelength is characteristic for each substance. The mathematical formulation of absorption goes back to H. Lambert (1760) and A. Beer (1852) and is described by the "Lambert-Beer law".

(1) $I = I_0 \bullet \exp (-\varepsilon \bullet c \bullet l)$

I_0 = initial intensity, ε = molar absorption coefficient,
c = concentration, l = layer thickness of the absorber

Emission spectroscopy:
Here the light-emitting source is directly characterized. Matter can absorb energy in a variety of ways (inelastic collisions with atoms, molecules, ions, electrons, etc., absorption of photons, chemical reactions). If this energy is released again in whole or in part by emitting radiation, this is called fluorescence. If the radiation occurs with a time delay, this is called

phosphorescence. If the energy of the emissions comes from a chemical reaction (e.g. in flames), this is called chemiluminescence.

Spectra can also be classified into different types according to their appearance: A distinction is made between continuous spectra and discontinuous spectra. The latter can be divided into line spectra and band spectra. The occurrence of continuous spectra can be observed, for example, in metallic solids (electron gas model within a metal lattice), which can be excited to glow and further to brightly shining by intense heating.
Theoretically, the intensity of this thermal emission, which is called thermal radiation, can be described by Planck's radiation law, which strictly only applies to the model of black cavity radiation. The following equation applies to the radiation density ρ of this radiation:

$$(2) \qquad \rho(\nu, T)\, d\nu = \frac{8\pi h}{c^3} \bullet \nu^3 \bullet \frac{1}{e^{\frac{h\nu}{kT}} - 1}\, d\nu$$

$\rho(\nu,T)\, d\nu$ = radiation energy per unit volume in the frequency range from ν to $\nu + d\nu$ at temperature T, c = speed of light, h = Planck`s constant, k = Boltzmann constant

The strong dependence of the total emission intensity J on the temperature is reflected by the Stefan-Boltzmann law:

$$(3) \qquad J(T) = \sigma \bullet T^4$$

σ = proportionality constant

Wien's displacement law describes the shift of the maximum to higher energy with increasing temperature

$$(4) \qquad \nu_{max} = 5.879 \bullet 10^{10}\ [s^{-1}/K] \bullet T\ [K]$$

Bodies that absorb all incident radiation are called black bodies. Some practically important light sources correspond to the black bodies according to equation (2) in terms of the dependence of their intensity on the wavelength, but show an intensity that is smaller by an almost constant factor. They are called gray bodies (e.g. tungsten lamps).

Discontinuous spectra (line and band spectra) are synonymously referred to as atomic spectra or molecular spectra. The reason for the appearance of these types of spectra lies in the different forms of energy that can be excited in the respective material. The simplest type of spectra, the line spectrum, results from the fact that only one form of energy can be excited in atoms, namely electronic energy (E_{el}). The observed atomic lines in an emission spectrum thus correspond to the energy differences that are released during electron transitions within an atom.
In a molecule, two other forms of energy can be excited in addition to (E_{el}):
Vibrations along chemical bonds (E_{Vib}), and rotations of the entire molecule (E_{rot}).
Normally, the spectrum of a molecule in the visible light range is based on three forms of energy:

$$(5) \qquad E_{ges} = E_{el} + E_{vib} + E_{rot}$$

This leads to the band spectra of molecules, which are far more complex than the line spectra.

Light sources in spectroscopy:
A variety of lamps are available for producing more or less strong emissions at individual wavelengths or over larger wavelength ranges: tungsten filament lamps, metal vapor lamps (mercury, sodium), fluorescent tubes. Tungsten lamps have a continuous emission spectrum over a wide wavelength range. Mercury vapor lamps emit a multi-line spectrum that broadens to a quasi-continuum at high pressures. Fluorescent tubes are gas discharge lamps whose inner coating consists of fluorescent materials that convert predominantly ultraviolet light into visible light.
In physical chemistry, intense light sources play an important role in the investigation of gases, liquids and solids (spectroscopy) and in the generation of high-energy particles whose reactions are to be investigated or used in photochemistry.

Task:
A spectrum is recorded from various light sources (tungsten lamp, low-pressure mercury vapor lamp, natural gas flame and fluorescent lamp ("neon tube"). The emission intensity is recorded as a function of the wavelength in the range from 200 nm to 700 nm and the various manifestations are discussed.

Experimental setup:
The setup for recording emission spectra consists of four components
- a light or emission source to be examined,
- a dispersive element (e.g. monochromator),
- a detection system (e.g. photomultiplier (SEV)) and
- a data recording device (e.g. recorder (analog signals), computer (digital signals))
and is shown schematically in Fig. 1.

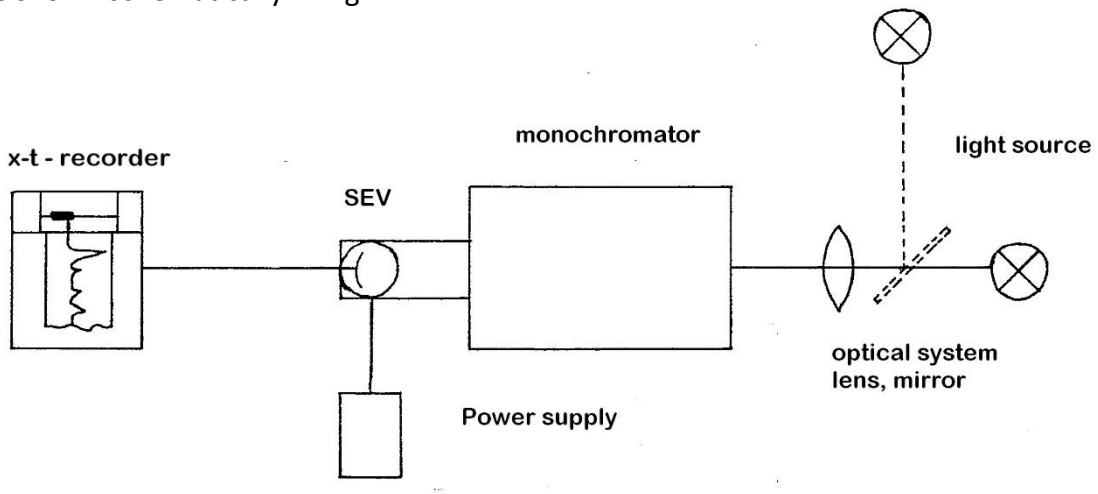

Fig. 1: Schematic structure of the experimental apparatus

A grating monochromator is used as a dispersive element: It consists of 2 slits and a diffraction grating, whereby only light of one wavelength (monochromatic light) passes through the exit slit from the incident polychromatic light, depending on the angle of incidence. By rotating the grating, different wavelengths can be selected one after the other

and a spectrum can be recorded. When working with a grating monochromator, it should be noted that due to the way it works, higher order light can also be created that is not emitted by the light source.
A photomultiplier is used as a detection system: If a photon with sufficient energy hits a photocathode, a primary electron emerges according to the principle of the photoelectric effect (Albert Einstein). This can be accelerated so much by applying a high voltage of 780 V (acceleration voltage) that several more electrons are knocked out of the next dynode by one electron. If this process is repeated several times on a cascade of dynodes, a measurable electron current (photocurrent) is finally obtained. This current can be recorded on paper using a compensation recorder as a result of the voltage drop occurring across a resistor. Alternatively, the photocurrent can be recorded using a digital voltmeter and a computer.

Preparatory questions on theory and implementation:
- Why do we get lines from atoms but bands from molecules?
- What type of spectrum can we expect from the light sources used in this experiment?
- What does Planck's radiation law say in words and how can it be represented graphically?
- Where can the quantity J(T) (Stefan-Boltzmann law) be found in Planck's radiation law?
- Are there light sources that show the emission spectrum of a black body?
- What gas is used in fluorescent tubes?
- What happens in a Bunsen burner flame and what type of spectrum can we expect here?
- How can higher order light be recognized in a spectrum?
  What law applies to the wavelengths of this light?
- How do photomultipliers and monochromators work?
- What limits the sensitivity of a photomultiplier when taking measurements?

Procedure:
1) The photomultiplier is extremely sensitive to ultraviolet and visible light:
Therefore, only switch it on when it is certain that no overload can occur (narrow gap on the monochromator, light-tight connection of the housing)
2) Make sure that no light from other light sources interferes with the measurement!
3) First look at the spectra through the hand-held spectroscope.
4) To record a spectrum, various parameters must first be optimized so that the spectrum fills the chart paper sensibly. To do this, the wavelength at which the strongest intensity occurs must be found for each light source in the wavelength range to be measured. If the monochromator is set to this wavelength, the amount of light entering is regulated by carefully opening or closing both slits (entrance and exit slits) so that the recorder just does not hit the top at the set measuring range (500-20 mV). To record the spectra, the sensitivity of the recorder is set so that it is no longer necessary to switch the measuring range to record the entire spectrum.
5) Record the emission spectra for the four light sources in the range from 200 nm to 700 nm, repeat the measurement of the Hg lamp with the edge filter.

Caution! The drive of the monochromator is very sensitive. Do not adjust the speed or direction of travel until the device has been stopped. Do not let the monochromator continue to run significantly below 200 nm or above 700 nm, otherwise the grating will hit!

Important:
1) Do not look into the mercury lamp with an unprotected eye!
2) Note all test conditions on the spectra!
3) Make sure that the two slots are set the same.

Evaluation:
1) Make a clear sketch on graph paper as shown in Fig. 2, showing the main spectroscopic characteristics of the individual light sources (on 1 sheet).
2) Briefly explain for each spectrum how the light source works and how the corresponding spectra type comes about.
3) Create a table for the mercury vapor lamp in which you compare the line positions found with the corresponding values from the literature (see experiment 61).
4) What effect does the edge filter used in the experiment with the mercury lamp have?
5) Which bands can be assigned to the Bunsen burner flame in the spectrum?
6) Discuss the function of equation (2)!

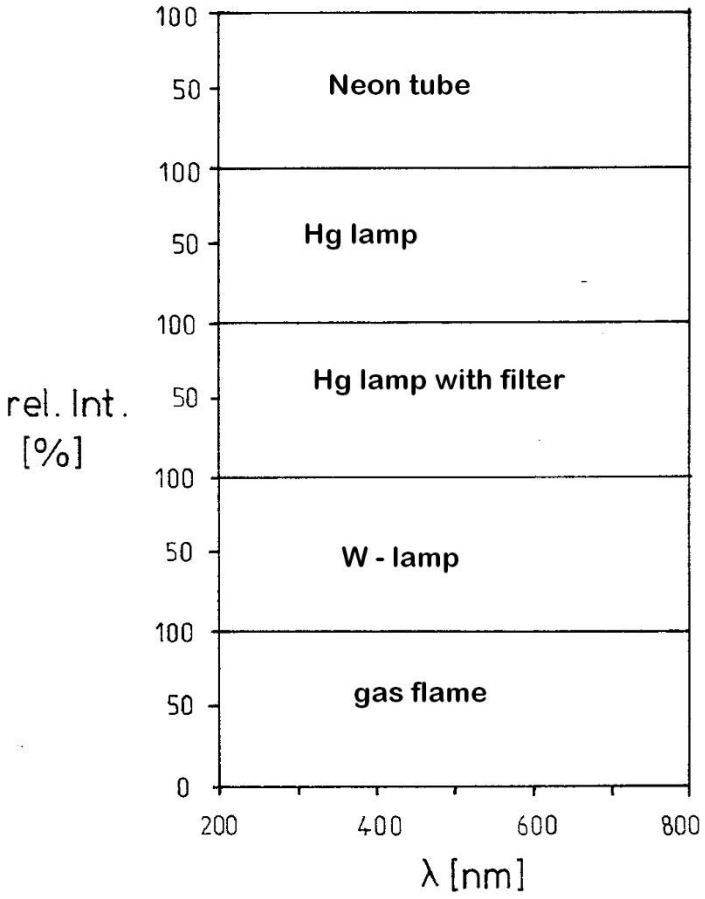

Fig. 2: Comparison of the emission spectra of the light sources

Accessories:
Flashlight, low-pressure mercury vapor lamp with power supply and protective tube, Bunsen burner, grating monochromator, photomultiplier with power supply, flat recorder, hand-held spectroscope, edge filter