OPTICAL SPECTROSCOPY | GP II

Key Words

Dispersion; Prisms. Diffraction and Interference; Diffraction Grating. Spectral Equipment and Spectral Analysis.

Aim of the Experiment

Phenomenological and experimental introduction into the fundamentals of optical spectroscopy as an important scientific and applied analytical tool in many areas of the natural sciences.

Literature

Standard literature (see list of standard text books).

Exercises

Performing experiments either with the prism spectrometer or grating spectrometer:

Prism Spectrometer

1. Setting up and adjusting the spectrometer (illumination, collimator, telescope).
2. Measuring the angle of the refracting edge of a prism.
3. Recording the spectrum of a mercury lamp to calibrate the spectrometer.
4. Performing one of the following experiments.
5. Plotting the dispersion curve $n(\lambda)$ and determining the differential dispersion $dn/d\lambda$ for the 577/579 nm line of mercury.
6. Determining the resolving power of the prism and comparing the result with the theoretical expectation.
7. Qualitative observation and discussion of the diffraction spectrum of a grating.

Grating Spectrometer

2. Recording the spectrum of a mercury lamp in the first and second order and determining the grating constant.
3. Performing one of the following experiments.
4. Determining the resolving power of the grating in the first and second order and comparing the result with the theoretical expectations.
5. Qualitative observation and discussion of the dispersion spectrum of a prism.

Spectroscopic Tasks

Spectroscopic analysis of an unknown lamp and determining its gas content.

Physical Principles

Prism

The transmission of light through transparent media represents a resonance phenomena with a frequency- or wavelength dependence of the refractive index *n* known as *dispersion*. Consequently, light of different wavelengths is refracted differently at a boundary surface and thus resolved into its spectral parts. The total deflection angle when light passes through both boundary surfaces of a prism depends not only on the refractive index but also on the direction of the incident light. Simple conditions result for the special case when a light ray passes through the prism parallel to the base and is thus symmetric with respect to entrance and emerging angles. In this case, the total deflection angle is minimal (*minimal deflection*). The entrance and emerging angle at one of the boundary surfaces follows from the geometrical ratios (see diagram below):

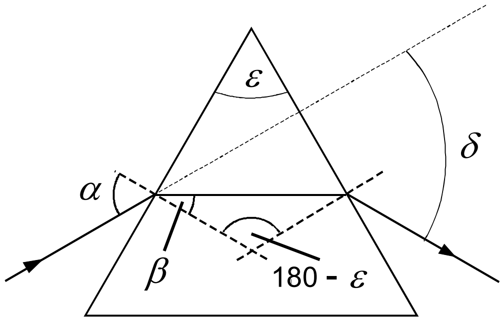


Fig. 1: Refraction of Light at a Prism

(1) $\beta = \frac{\varepsilon}{2}$ (inner triangle) and

$$\delta = 2\,(\alpha - \beta) \quad \text{or} \quad \alpha = \frac{\delta + \varepsilon}{2} .$$

From the law of refraction we then have

$$\frac{\sin\alpha}{\sin\beta} = \frac{c_0}{c_P} = \frac{n_P}{n_0} \quad \text{or}$$

(2)
$$n_P = n_0 \frac{\sin\frac{\delta+\varepsilon}{2}}{\sin\frac{\varepsilon}{2}}$$

where ε is the angle between the refracting surfaces and n_p and n_o are the refractive indices of the prism and the surrounding medium respectively (for air n_o = 1.0003).

Prisms find application is spectroscopy and light filtering. The dispersion power and the refractive index are independent of one another. For example, the refractive index of flint glass is only slightly higher than that of crown glass, however, the dispersion power is almost twice as high. The different behavior of various types of glass allows the construction of prisms with strong deflection properties but do not disperse (deflection prism, *achromatic prism*) or prism with strong dispersion properties but do not deflect (*direct vision prism*).

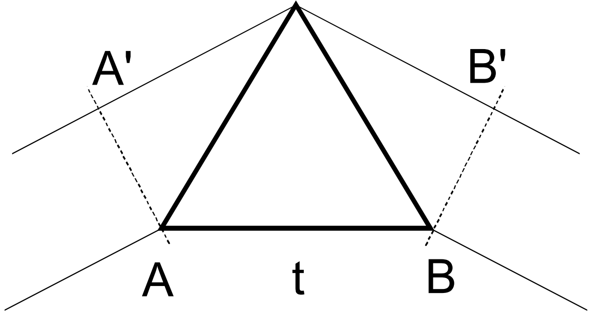
Resolution Criterion

The determination of the resolving power of spectral equipment requires a conventional agreement as to when two spectral lines can be considered as separated. In general, the most practical criterion is the *Sparrow criterion*, whereby two lines are seen as separated when they possess a relative minimum. Quantitative more accurate is the *Rayleigh criterion* (*John William Strutt*, since 1873 *Baron Rayleigh*; 1842-1919; Engl. physicist), stating that lines can then be considered as separated the diffraction maximum of the one line coincides with the first diffraction minimum of the other (see figure below). The intensity in the minimum of this double line then falls to the value of $8/\pi^2$ of the maximum.

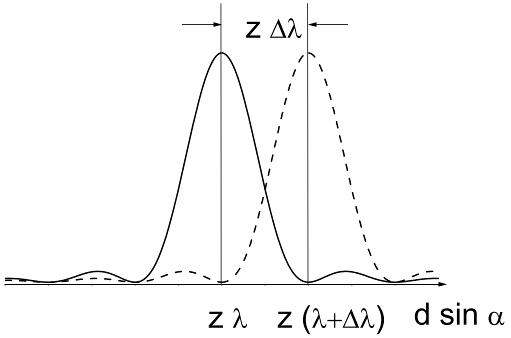
Resolving Power of a Prism

The finite resolution of a prism is conditional on the diffraction since it represents a limitation for the ray path. It is derived from a consideration of the optical path length in the prism (see figure below).

A-A' and B-B' represent two wave fronts ahead and behind the prism belonging to a direction of deflection under which, corresponding to the *Rayleigh criterion* for the wavelength λ and for the wavelength λ+Δλ, the main maximum and the first adjacent minimum lie.



Resolution of the Prism



Rayleigh Criterion

For the main maximum (to λ) the rays should not exhibit a path difference, whereas the first adjacent minimum originates in the diffraction pattern (to λ+Δλ) when the rays at the edges exhibit a path difference of just one wavelength (see experiment *DIFFRACTION AND INTERFERENCE*).

For small differences in wavelength, the dependence of the refractive index on λ is approximately given by a linear relation:

(2) $n(\lambda) = n$ and $n(\lambda + \Delta\lambda) = n + \frac{dn}{d\lambda}$

Since the optical path from A' to B' is the same for both wavelengths because n ≈ 1, a path difference of λ must arise at the base of the prism (base length *t*):

$$\left(n + \frac{dn}{d\lambda}\Delta\lambda\right) t - n\,t = \lambda \tag{3}$$

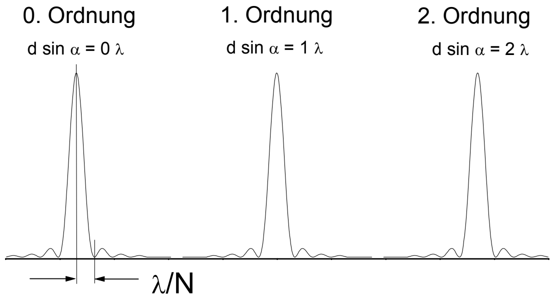
Consequently, the resolving power of the prism is determined by the base length *t* (representing the opening of the prism) and the *differential dispersion* d*n*/dλ.

Diffraction Grating

A grating can be simply conceived as an aperture with a periodic sequence of sharp and impermeable bounded slits. Normal gratings used in practice, e.g., made by scribing on a glass plate do not correspond to this picture. In general, one speaks of a grating when at an object a transmission (or reflection) recurs periodically at a spacing *d*, the *grating constant*.

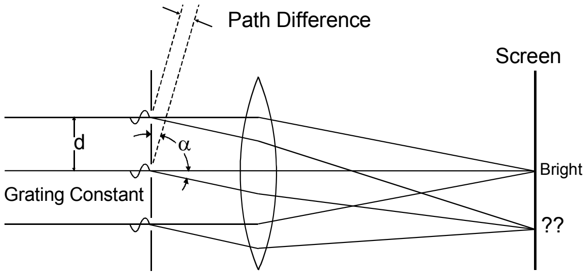
If one shines coherent light onto a grating or, as a model, monochromatic plane waves, one observes behind the grating a periodic intensity distribution explained by diffraction and interference effects. Comparatively simple relations are found in the *plane of observation* at infinity which can be realized in practice by placing a convex lens behind the grating. The resulting intensity distribution is termed the *Fraunhofer Diffraction Pattern* (*Joseph Fraunhofer*, 1787-1826, German optician and physicist).

The patterns are in the form of sharp *diffraction maxima* (main maxima), separated by wide extinction zones (see diagram below; in extinction zones in the diagram are not to scale in order to clearly show the adjacent maxima):



The main maxima can be simply derived from the condition that the path difference of rays of neighboring slits must be a whole multiple of the wavelength for *constructive interference* to occur see diagram below):

$$d \sin \alpha = z \lambda \quad \text{with} \quad z = 0, 1, 2, \ldots \tag{4}$$



The number *z* labels the *Order* of the diffraction maxima. Since for a given grating constant, the position of the maxima, aside from the order, is dependent on the wavelength, a grating can be used to perform (absolute) wave measurements.

Resolution of a Grating

Besides the main maxima given by (4) there exists a series of adjacent maxima, whose intensity rapidly approaches zero with increasing distance from the main maxima. The position of the first adjacent minimum of order *z* is given by:

$$d \sin \alpha_{\text{min}} = \left(z + \frac{1}{N} \right) \lambda \tag{5}$$

where *N* is the total number of contributing slits. (For even N this relation can be derived rigorously, by imagining the grating composed of two equal parts with half the number of slits and allowing pairs of slit to interfere destructively, i.e., with a path difference of λ/2).

If one sets, according to the *Rayleigh criterion,* condition (4) for the main maximum with a wavelength λ+Δλ and for the adjacent minimum condition (5) with a wavelength λ then for the resolution of the wavelength difference or for the resolving power it follows that:

(6)

$$\Delta\lambda = \frac{\lambda}{z\,N} \quad \text{or} \quad \frac{\lambda}{\Delta\lambda} = z\,N$$

i.e., the resolving power increases with the growing number of slits and with increasing order number.

Hydrogen Spectrum and the Rydberg Constant

In 1885 the Swiss mathematician and physicist *Johann Jakob Balmer* (1825-1898) found, while conducting an empirical analysis of the characteristic line series of hydrogen (*Balmer-Serie*), that the wave number of the lines could be described as the difference of two terms:

(7)

$$\bar{\nu} = \frac{1}{\lambda} = R \left[\frac{1}{2^2} - \frac{1}{n^2} \right] \quad \text{with} \quad n = 3, 4, 5, \ldots$$

This discovery was later to become an important support for the *Bohr model of the atom* (*Niels Bohr*; Danish physicist; 1885-1962), according to which the radiation of atoms is the result of electron transitions between atomic levels. The constant *R* in the relationship is the *Rydberg constant* (*Johannes Rydberg*; 1854-1919; Swedish.physicist):

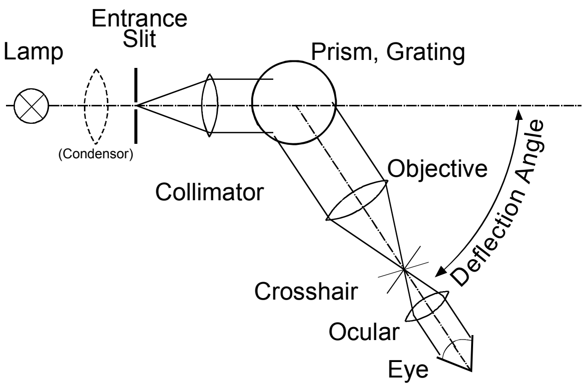
$$R = \frac{2\pi^2 m_e e^4}{h^3 c} \tag{8}$$

Apparatus and Equipment

Goniometer assembly (angle measuring equipment) on rails, including a tiltable and rotatable table for a prism or grating.
Optical components: Entrance slit, collimating lens, objektive lens, ocular with crosshairs. adjustable crosshairs (for angular measurements on the prism), measurement slit (to determine the resolution). Spectral lamps with power supply Hg lamp, unknown lamps.

Experiment and Evaluation

The spectrometer consists of a goniometer for angular measurements, an entrance slit with a collimator to produce parallel light, the dispersive element (prism, grating) and a telescope. Usually a condenser lens is placed between the lamp and the entrance slit. See diagram below.



Adjustment

The prerequisite for quantitative proper results in optical experiments is very careful adjustment of the optical assembly. Furthermore, this also conveys an understanding of the fundamentals of geometrical optics

The collimator lens and the objective lens are fixed at a certain height. This sets the height axis of the assembly. The other components must be aligned to this height

Illuminating equipment is not necessary because of the high light density of the lamps and the Hg lamp is placed directly behind the entrance slit. The slit represents (in one spacial direction) an approximately point shaped, *secondary light source*.

Adjustment of the collimator is done by *autocollimation*. The light from the collimator is reflected by a mirror placed on the prism table. When the collimator is correctly adjusted one sees a sharp image of the slit reflected back at the slit. The image can be slightly shifted to one side of the slit mechanism to get a better view.

The crosshairs of the ocular are focused against diffuse background lighting with the eye relaxed. The ocular is then placed in the swivel arm of the goniometer.

Finally, the objective lens is adjusted so that a sharp image of the slit is seen in the image plane of the ocular. The criterion for proper adjustment is freedom of parallax error, i.e., that the slit image and the crosshairs are not shifted against each other by a sideways movement of the eye. Causes for a poor slit image, aside from incorrect adjustment of the collimator- or objective lens, may be that the slit is opened too wide or is too narrow or the slit is not positioned vertically or is dirty. A slight over-illumination of the slit is unavoidable under the given circumstances.

The angle between the collimator- and telescope axis is read on an angle scale with 1/100 degree divisions (vernier scale). To ensure correct reading it is recommended to practice using the vernier scale before performing the measurements.

Error Estimations

In particular with optical experiments, one should make control measurements of the settings in order to check the reproducibility or observed deviations, thus allowing statements to be made on possible errors (estimated errors).

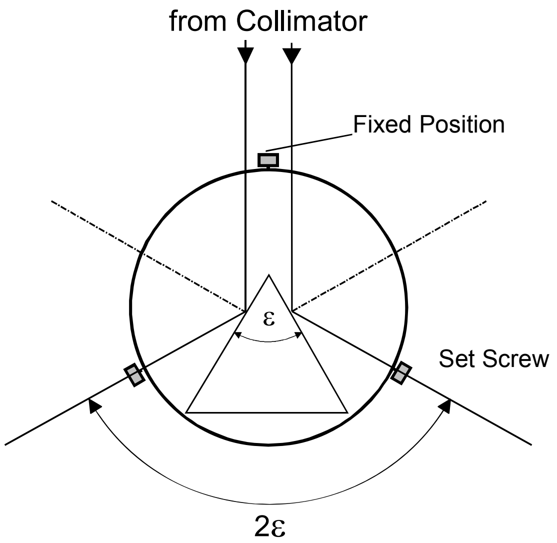
Prism Spectrometer

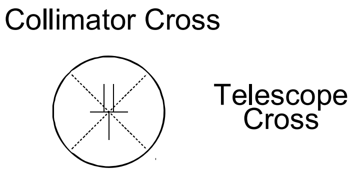
To Exercise 1 (Angle of the Refracting Edge; see diagram below)

The angular measurement is performed by placing a ground glass screen with crosshairs in the ray path where the entrance slit is normally positioned (crosshairs facing the telescope), the image is focused and adjusted in height, so that both crosshairs (in the collimator and in the ocular) can be made to cover each other.

The prism table is first visually aligned to a horizontal position so that one of the three set screws points to the collimator and the other two point in the respective directions of observation.

The prism is then placed on the table so that the light reflected from both side faces can be observed with the crosshairs in the telescope.





The prism must be placed as far as possible towards the telescope because the illumination is very narrow and the side faces meet only at the tip of the prism.

Now fine alignment is made of the prism side faces perpendicular to the optical axis. This is done by successively observing both sides of the crosshairs and adjusting the respective opposite set screw to achieve the same height. The adjustments are performed until the height on both sides coincides.

Finally, the angular difference of the intercept points of both reflected crosshairs is measured, thus giving the angle of the refractive edge.

To Exercise 2 (Calibration Curve)

The prism is now positioned in the deflection position, again ensuring good illumination. The minimal deflection for the 546 nm is now set and the complete spectrum of the mercury lamp recorded. The positions of the optical components on the rail and, in particular, that of the prism must not be changed for this and subsequent measurements, otherwise the assignment between wavelength and deflection angle would be lost.

Evaluation is made by plotting wavelength against deflection angle on DIN-A4 mm paper to match the accuracy of the measurements!

To Exercise 3 (Spectroscopic Experiments)

See the following notes on the exercises.

To Exercise 4 (Dispersion Curve and Differential Dispersion)

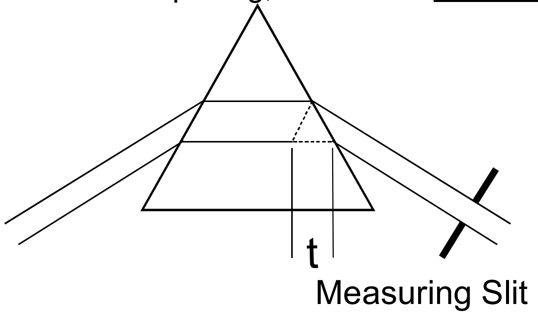
The minimal deflection is set and the deflection measured for each of the main lines of the Hg-spectrum (579, 577, 546, 492, 436 and 405 nm). From the measurements one can calculate the refractive indices and plot the dispersion curve $n(\lambda)$ employing equation (2). The differential dispersion for the 579/577 nm lines is determined by constructing a tangent to the dispersion curve at these wavelengths.

To Exercise 5 (Resolving Power)

Since the wavelengths of the lines cannot be changed, the optically effective base length *t* of the prism must be shortened. This is done by placing an additional measuring slit in the collimator ray path directly in front of the prism and closing the slit so far until one observes two lines adjusted to minimal deflection that can just be separated under the subjective resolution criterion (*Sparrow* or *Rayleigh*).

The investigation is carried out on the 579.1/577.0 nm pair of lines of mercury. The experimentally observed resolution results from the ratio of the mean value of the lines to the difference, and the theoretically expected value from equation (4).

The effective base length *t* is calculated from the set slit opening *b*, the deflection angle γ and the prism angle ε. Note that when reading the scale on the micrometer to determine the width of the slit, take into account that the zero point is arbitrarily shifted and that the scale, with respect to the slit opening, counts backwards.



To Exercise 6 (Grating Spectrum)

The prism is replaced by a grating. The characteristic differences of the spectra are to be observed and recorded and a short discussion presented in the report.

Grating Spectrometer

To Exercise 1 (Grating Constant)

The grating is placed in the ray path (see lab bench script for the orientation of the grating). The grating is carefully adjusted perpendicular to the ray path by autocollimation, i.e., observing the surface of the grating reflected back on the slit.

The grooves of the grating are asymmetrically scribed (*blazed grating*), whereby, for a certain range of wavelengths the largest intensity is available for a certain direction of deflection and a certain order. The complete observable spectrum of the Hg - lamp is to be recorded in the 1.order and in the 2.order the main lines (579, 577, 546, 492, 436 and 405 nm). Because of the high accuracy of the measurement, graphical evaluation is unsuitable in this case.

To Exercise 2 (Spectroscopic Experiments)
See the following notes on the exercises.

To Exercise 3 (Resolving Power)

Since the wavelengths of the lines cannot be changed, the effective width of the grating must be shortened to determine the limit of resolution. This is done by placing an additional measuring slit in the collimator ray path directly in front of the grating and closing the slit so far until one observes two lines that can just be separated under the subjective resolution criterion (*Sparrow* or *Rayleigh*).

The investigation is carried out on the 579.1/577.0 nm pair of lines of mercury. The experimentally observed resolution results from the ratio of the mean value of the lines to the difference, and the theoretically expected value from equation (7).

The number of grating slits can be calculated from the effective grating width governed by the limitation due to the measuring slit and from the grating constant. Note that when reading the scale on the micrometer to determine the width of the slit, take into account that the zero point is arbitrarily shifted and that the scale, with respect to the slit opening, counts <u>backwards</u>.

<u>To Exercise 5</u> (Prism Spectrum)

The grating is replaced by a prism. The characteristic differences of the spectra are to be observed and recorded and a short discussion presented in the report.

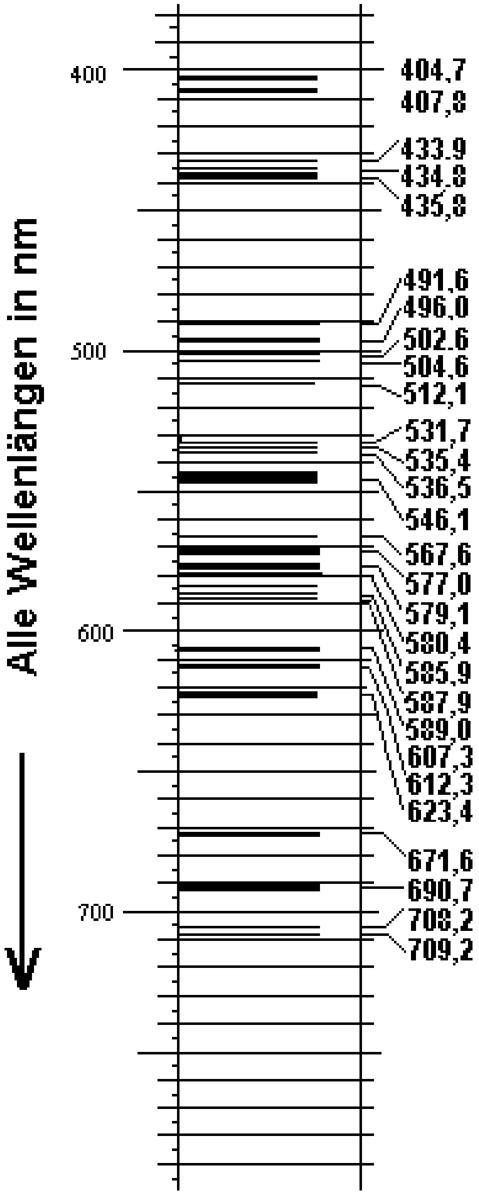
Spectroscopic Experiments

<u>Unknown Lamps</u>
The spectrum of one (of the three available) unknown lamps is recoded and the observed wavelengths determined from the calibration curve or the grating constant. The results are analysed using the table of selected spectral line attached to this script.

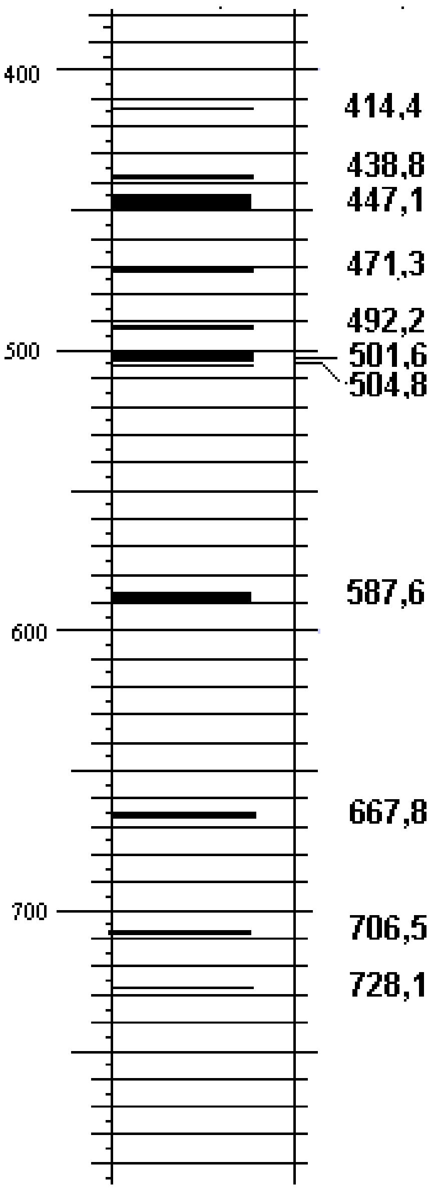
Spectral Lines

See the following page for the spectrum of the Hg-lamp and the lines of Cd, He and Zn.

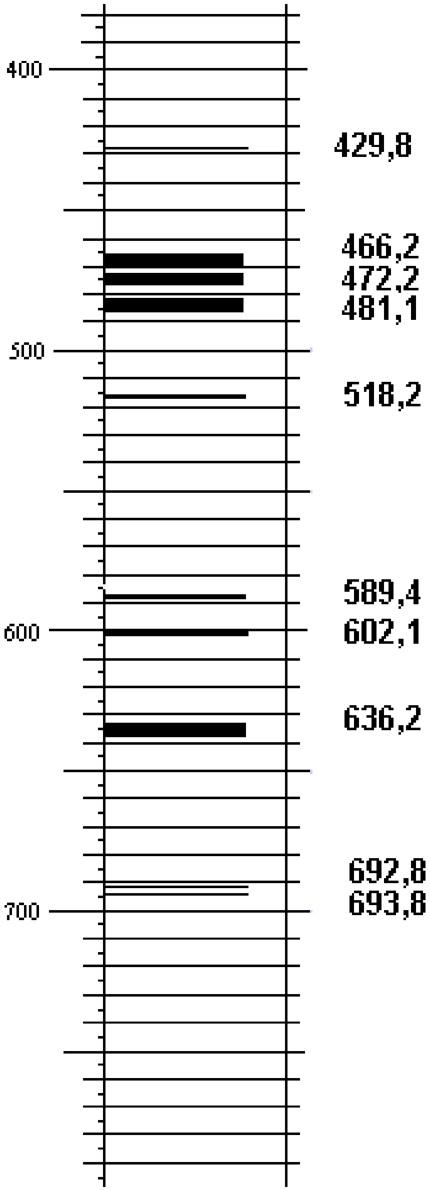
Spectrum of the Hg-Lamp



Spetrum of the He-Lamp



Spectrum der Zn-Lamp



Spectrum der Cd-Lamp