SPECTRA

REFERENCES
D. Halliday and R. Resnick, *Fundamentals of Physics*
M.M. Sternheim and J.W. Kane, *General Physics*

INTRODUCTION

In this experiment you will calibrate a prism spectrometer and use this calibration curve to obtain a number of numerical results. You can study the Balmer series of atomic hydrogen spectral lines and determine the Rydberg constant R_H. You can also use the calibration curve to identify an "unknown" gas by measuring its spectral lines. The apparatus is essentially a spectrometer and a variety of spectral "tubes" which are the sources of the line spectra to be studied.

Notes: **A. If you have not studied Discrete Spectra or the Bohr Atom, you should certainly take some time to consult a first year text before you read any further.**
B. The procedure for setting up the spectrometer and also the method for taking measurements is outlined in Appendix 1.

CALIBRATION

Calibrating the spectrometer means determining the relationship between the wave-length of a spectral line and the scale-reading on the spectrometer. Once this relationship is obtained you can use it to convert the scale reading of an unknown line to the corresponding wavelength. The precision of your calibration curve limits the accuracy of everything you do subsequently. It is well worth spending a lot of effort on the calibration.

Use the helium lamp and the helium spectral line tables in Appendix 2 to calibrate the spectrometer using the two methods outlined below. **For both of these methods the calibration curve must be drawn as you make observations**. Do not just copy down the readings for plotting later.

THE SMOOTH CURVE METHOD

In this method you draw the simplest of calibration curves. Make a plot of wavelength against scale reading. If you have correctly identified the wavelength of the lines you chose to measure you should obtain a *smooth* curve. If it is not smooth, go back and check both your measurements and the wavelengths you assigned each line. The advantage of this method is that you need not make any assumptions nor do you need to rely on measurements made by anyone else. The disadvantage is that there is some difficulty in drawing the correct smooth curve between the calibration points and this limits the accuracy of your results. Note that the polynomial fitting programme on the lab computer cannot be used for fitting this smooth curve because (as you may see in the next section) the expected calibration curve is an hyperbola which cannot be suitably expressed by the polynomial $y = A(0) + A(1)\lambda + A(3)\lambda^2 + \dots$.

THE HARTMANN RELATION METHOD

The relationship between the scale reading y and the wavelength λ is given by the Hartmann dispersion relation which is:

$$y = \frac{m}{\lambda - \lambda_o} + b \tag{1}$$

where λ_o, m and b are constants. For your convenience, the constant λ_o, which is a function of the optics of your spectrometer, has been measured by the technicians for each spectrometer and is marked on the side of the spectrometer. By plotting y against $(\lambda - \lambda_o)^{-1}$, a straight line can be obtained from which m and b can be deduced. The advantage of this method is that since the calibration curve is a straight line, you need fewer calibration points, it is easier to draw and it is more accurate. The disadvantages are that you must rely on the observations made by someone else and also readings from your straight line do not give λ directly. This latter drawback is not too serious if you have a calculator with you, especially a programmable one. The polynomial fitting programme available on the lab computer is suitable for this plot; use the values of A(0) and A(1) which the programme provides for the fit to calculate all other values of λ that you need.

THE RYDBERG CONSTANT

Use your calibration curve to measure the wavelengths of the bright lines in the visible spectrum of hydrogen known as the Balmer series. Since hydrogen is a molecule you will see a number of molecular bands in the visible range as well but these will in general be much fainter than the bright atomic lines.

In 1885 Balmer showed that the wavelengths of the atomic lines in the visible part of the Hydrogen

spectrum satisfied the relation $\quad \dfrac{1}{\lambda} = R_H \left(\dfrac{1}{2^2} - \dfrac{1}{n^2} \right)$ \hfill (2)

for the integral values of $n \geq 3$, where R_H is the Rydberg constant.

There are four lines that you should see in the hydrogen spectrum that satisfy the Balmer relation. These include a red line, a blue-green line and two violet lines. Measure their wavelengths, verify that the above equation is satisfied and determine a "best value" for R_H. What are the units of this number? (**Hint**; if you are doing your plot on the computer, you will find that the evaluation of the error in λ is rather complicated, involving as is does the errors in the constants in the Hartmann relation that you have found in the earlier part of the experiment. You should make one sample calculation to show that you know how to do it; then, for the fit use a value of $\Delta\lambda \approx 3$ nm.)

GAS IDENTIFICATION SLEUTHING

You can now test your skill as a spectroscopist by measuring the wavelengths of the spectral lines of "unknown" substances conatined in the spectral tubes placed near the various spectrometers. Identify a couple of "unknowns" by using Appendix 2 which lists the spectral lines of many common substances. There are also various coloured spectral charts around the walls of the lab. (Also the colour of the light given off by the spectral light source often gives a hint to the gas contained.)

EXERCISE

Evaluate $hc\,R_H$ (h = Planck's constant, c = velocity of light). This has units of energy. Convert to eV (electron volts) and compare this to the ionization energy of atomic hydrogen. What is the physical significance of $hc\,R_H$? HINT: the lines of the Lyman series which are in the ultraviolet

obey the relation $$\frac{1}{\lambda} = R_H \left(\frac{1}{1^2} - \frac{1}{n^2} \right) \quad \text{for integral values of } n \geq 2 \tag{3}$$

APPENDIX 1 - USE OF THE SPECTROMETER
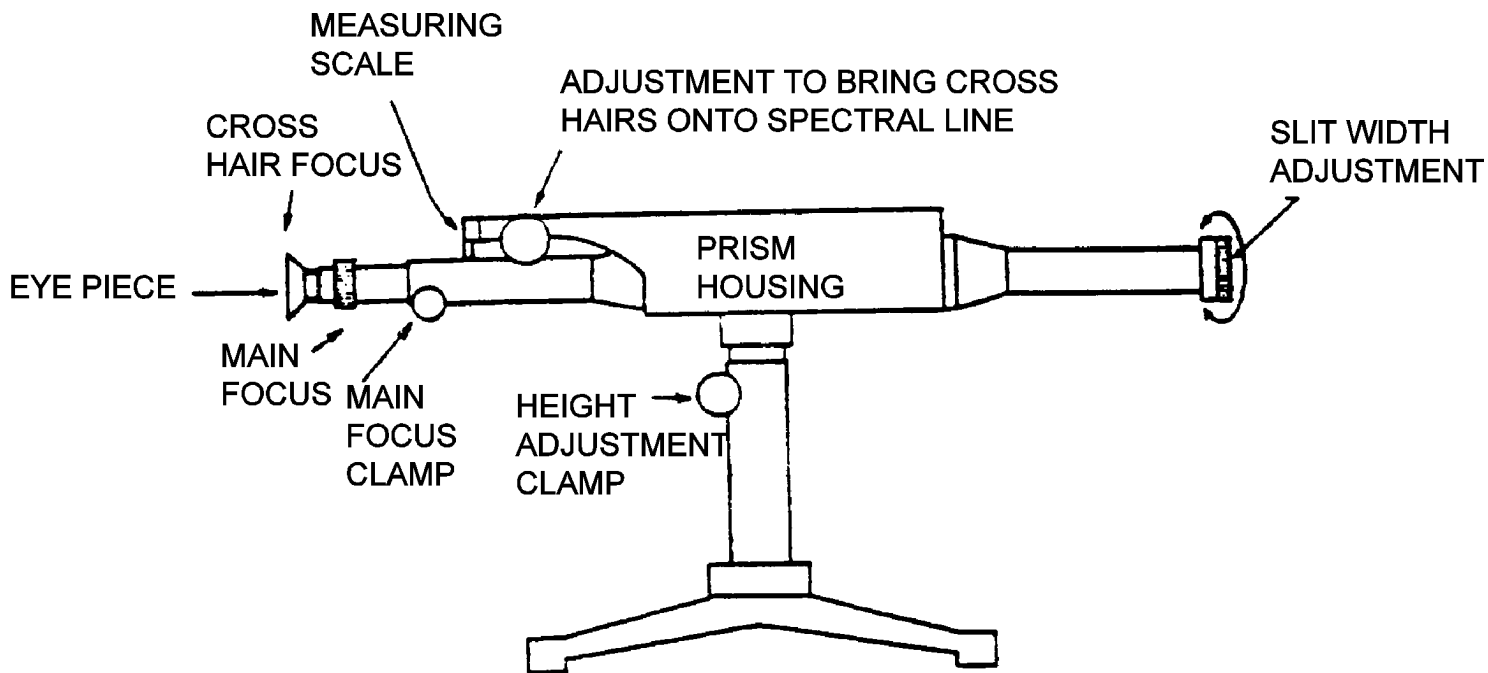
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DESCRIPTION

The tri-prism optical spectrometer is capable of resolving to about 0.1 nm (1 Angstrom unit). The instrument reads the wavelength of the light in arbitrary units. The visible spectrum is contained in 20 of the 50 divisions, with resolution by the vernier to 0.01 divisions. Repeatability is about ±0.02 divisions. A calibration chart is required to convert scale readings to wavelength. Setting of the instrument is accomplished by aligning a cross-hair precisely on an image of the spectral line seen in the eyepiece.
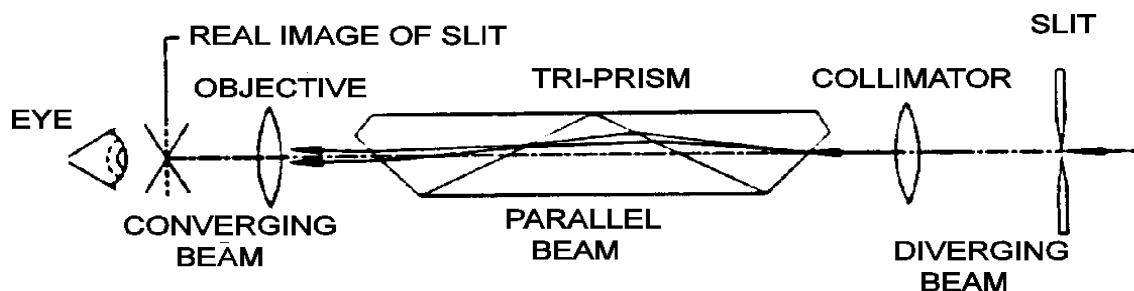
PRINCIPLE OF OPERATION

The light to be analyzed enters the slit, and due to diffraction, it diverges from the slit opening. The slit is situated at the focal point of the collimator lens, so after passing through it, the light is in a parallel beam. It then passes through the tri-prism. The central prism is the one which disperses the light. The first and third prisms are employed to straighten the beam and thus make the spectrometer easier to handle. After leaving the prism the dispersed beam passes into the measuring telescope. Real images of the slit are created in the plane of the cross-hairs, and these are examined using the eyepiece as a simple magnifier.

OPERATING INSTRUCTIONS

(1) Focusing: Using an incandescent light source and with the spectrometer set at about 9 divisions (yellow), focus the cross-hairs by moving the eyepiece in and out. Use the slit width adjustment to get an appropriate amount of illumination. Loosen the main focus adjustment and using the knurled part of the eyepiece tube, rotate the cross-hairs to obtain an "×" rather than a "+".

(2) Slit adjustment and line focus: Use a sodium lamp as source and find the bright yellow line. Focus the spectrometer optics on the spectral line by moving the eyepiece assembly in or out of the black main frame with the knurled knob. Reduce the slit width until the sodium line resolves into two. (Refocus if necessary). When the line is clearly focused, tighten the focusing clamp. The paint dot on the slit adjustment should be kept on the upper side of the spectrometer to maintain calibration. The spectrometer is now ready for use.

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(3)   When observing spectra the slit may be opened or closed, as desired. Opening the slit will increase the brightness but decrease the resolution.

(4)   Measure the wavelength of lines by precisely splitting the line with the centre of the cross-hairs, and then reading the scale and vernier.

Precaution: The vernier has only 50 divisions. Remember to add 50 to the vernier reading when the point is in the second half of a main division.
When making observations in the violet it may be necessary to push-in the eyepiece slightly to keep the cross-hairs in focus.
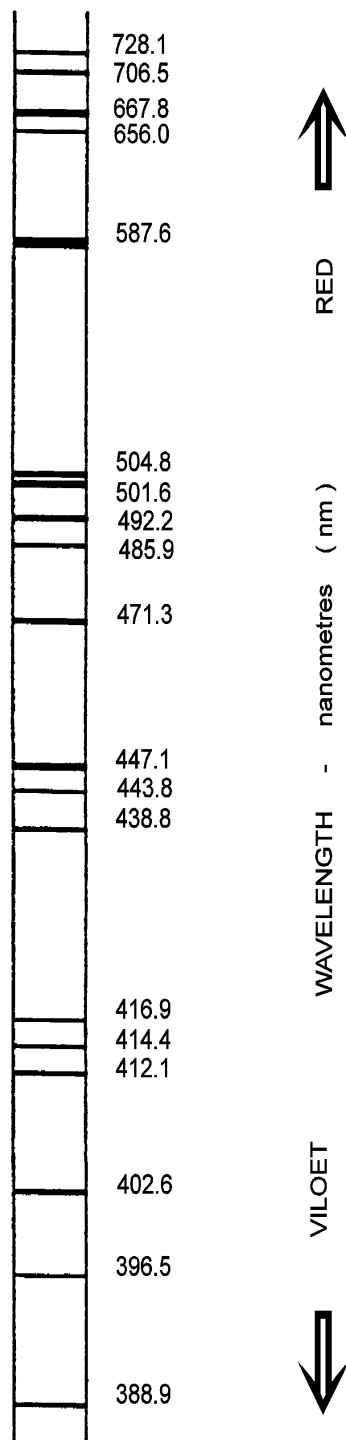
APPENDIX 2 - SPECTRAL WAVELENGTH TABLES

Remarks On The Use Of The Tables

(1)   use the intensity indications with caution. They are meant only as a general guide. Relative intensities vary widely depending on the mode of excitation and so the source that you are using may have lines with different intensities. However, the very bright lines should appear bright in all sources.

(2)   These tables give most of the lines that you will be able to see (and many that you won't be able to see if you are using a narrow slit width). However, the tables are not complete and lack some faint lines.

(3)   Lines separated by less than one nanometre will not be resolved if the slit is wide. If the slit is too narrow, weak lines won't be seen.

(4)   You may assume that the errors in these values is negligible in comparison to the other errors in this experiment.

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HELIUM

WAVELENGTH nm	RELATIVE INTENSITY	COLOUR
728.1	2	RED
706.5	4	RED
667.8	6	RED
656.0	1	RED
587.6	10	YELLOW
504.8	4	GREEN
501.6	6	GREEN
492.2	5	GREEN
485.9	2	GREEN
471.3	5	BLUE
447.1	6	BLUE
443.8	1	VIOLET
438.8	4	VIOLET
416.9	1	VIOLET
414.4	2	VIOLET
412.1	3	VIOLET
402.6	4	VIOLET
396.5	1	VIOLET
388.9	3	VIOLET

728.1
706.5
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471.3

447.1
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416.9
414.4
412.1

402.6

396.5

388.9

RED

WAVELENGTH - nanometres (nm)

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ARGON				KRYPTON		
WAVELENGTH *nm*	*RELATIVE INTENSITY*	*COLOUR*		*WAVELENGTH* *nm*	*RELATIVE INTENSITY*	*COLOUR*
574.0	2	GREEN		645.6	5	RED
565.0	3	GREEN		642.1	5	RED
560.7	3	GREEN		605.6	2	RED
557.3	3	GREEN		601.2	2	ORANGE
549.6	3	GREEN		599.4	2	ORANGE
522.1	2	GREEN		588.0	1	ORANGE
518.8	3	GREEN		587.1	10	ORANGE
516.2	3	GREEN		584.1	1	YELLOW
470.2	1	BLUE		583.3	1	YELLOW
462.8	1	BLUE		570.8	1	GREEN
459.6	1	BLUE		567.2	1	GREEN
452.2	1	VIOLET		565.0	1	GREEN
451.1	2	VIOLET		558.0	1	GREEN
433.5	2	VIOLET		557.0	10	GREEN
433.4	2	VIOLET		556.2	2	GREEN
430.0	3	VIOLET		450.2	5	VIOLET
426.6	3	VIOLET		446.4	5	VIOLET
425.9	3	VIOLET		445.4	5	VIOLET
420.1	2	VIOLET		440.0	2	VIOLET
419.8	2	VIOLET		437.6	5	VIOLET
416.4	3	VIOLET		436.3	4	VIOLET
415.9	2	VIOLET		432.0	3	VIOLET
				431.9	2	VIOLET
				427.4	5	VIOLET

Argon has many faint lines in the red and yellow
which vary in intensity depending on the source
and because of the confusion that this can lead
to only wavelengths less than 580 nm are given.
In this region there are a very large number of
lines. Only relatively brighter ones are listed.
Fainter ones may provide a haze in the
background.

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MERCURY			XENON		
WAVELENGTH nm	RELATIVE INTENSITY	COLOUR	WAVELENGTH nm	RELATIVE INTENSITY	COLOUR
708.2	1	RED	647.3	2	RED
704.5	2	RED	647.0	3	RED
690.7	1	RED	631.8	5	RED
671.6	1	RED	620.1	1	RED
658.5	1	RED	619.8	1	RED
638.3	2	RED	618.2	3	RED
623.4	2	RED	618.0	1	RED
612.3	2	RED	617.8	2	RED
607.3	2	ORANGE	616.4	1	RED
602.4	2	ORANGE	593.4	2	ORANGE
601.7	1	ORANGE	593.1	1	ORANGE
589.0	1	YELLOW	589.5	2	ORANGE
579.1	8	YELLOW	587.5	1	ORANGE
577.0	6	YELLOW	582.5	2	YELLOW
567.7	1	YELLOW	582.4	3	YELLOW
567.6	1	YELLOW	571.6	1	YELLOW
546.1	10	GREEN	569.7	1	YELLOW
536.5	1	GREEN	569.6	1	YELLOW
520.5	1	GREEN	546.0	1	GREEN
519.6	1	GREEN	539.3	1	GREEN
512.1	1	GREEN	502.8	3	GREEN
504.6	1	GREEN	492.3	4	GREEN
502.6	1	GREEN	491.7	4	GREEN
496.0	1	GREEN	484.3	4	GREEN
491.6	5	BLUE	483.0	4	GREEN
452.3	1	BLUE	480.7	5	GREEN
435.8	6	VIOLET	479.3	1	BLUE
434.8	2	VIOLET	473.4	5	BLUE
433.9	1	VIOLET	469.7	4	BLUE
421.2	1	VIOLET	467.1	10	BLUE
420.6	1	VIOLET	462.4	5	BLUE
415.7	1	VIOLET	458.3	1	VIOLET
407.8	5	VIOLET	452.5	2	VIOLET
414.7	5	VIOLET	450.1	2	VIOLET

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NEON

WAVELENGTH nm	RELATIVE INTENSITY	COLOUR
724.5	1	RED
717.4	1	RED
703.2	5	RED
702.4	3	RED
692.9	6	RED
667.8	7	RED
659.9	7	RED
653.3	7	RED
650.7	7	RED
609.6	5	ORANGE
607.4	7	ORANGE
603.0	5	ORANGE
596.5	4	ORANGE
588.2	6	YELLOW
585.2	10	YELLOW
540.1	5	GREEN

Many orange and yellow lines have been omitted as well as all lines of wavelength less than 540 nm (hundreds). Most of these are faint but some overlap to give the appearance of bright lines.

NITROGEN

WAVELENGTH nm	RELATIVE INTENSITY	COLOUR
497.6	3	GREEN
491.7	3	GREEN
481.5	3	GREEN
472.4	3	BLUE
466.7	3	BLUE
464.9	3	BLUE
457.4	3	BLUE
449.0	3	BLUE
441.7	3	VIOLET
435.5	3	VIOLET
434.4	2	VIOLET
427.0	2	VIOLET
420.1	2	VIOLET
414.2	2	VIOLET
409.5	1	VIOLET
406.0	1	VIOLET
399.8	1	VIOLET
394.3	1	VIOLET

Since **nitrogen** is a molecule, the spectrum consists of bands rather than lines. This is due to rotation of the molecules. In the visible the most prominent structure is the First Positive series with about 30 regular spaced bands in the region 500-700 nm. Only the band heads of the Second Positive series are tabled above. The bands trail off to shorter wavelengths. As indicated by the relative intensities on a scale of 10, the Second Positive series is less intense than the First Positive series.

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Preparatory Questions.

Note: We hope that the following questions will guide you in your preparation for the experiment you are about to perform. They are not meant to be particularly testing, nor do they contain any "tricks". Once you have answered them, you should be in a good position to embark on the experiment.

1. What is your estimate of the reading error on the spectrometer?

2. In order to use the Hartmann relation you will want to plot a straight line. What variables will go on the x- and y- axes? If you use the lab computer to fit your values to the equation $y = A_0 + A_1 x$, to what do A_0 and A_1 respectively correspond in the Hartmann relation?

3. If you can assume that the errors in the provided values of wavelength for the known gases are negligibly small, write down an expression for the error in the quantity $\frac{1}{(\lambda - \lambda_0)}$, if the error in λ_0 is $\Delta\lambda_0$.

4. Bohr's theory of the atom says that the electron can only be in certain energy levels. The energy of the n'th level is given by $E_n = -hcR_H / n^2$. (The negative sign indicates that this is a binding energy - the energy of a free electron would be zero or positive). (A) For the Balmer series, an electron drops from a higher energy level to the n=2 level. What would be the energy difference between these levels? (B) What is the minimum amount of energy required to remove the lowest energy electron (i.e. the one "deepest" in the atom where n=1) from the atom? This is called the *ionisation energy.*

5. When an electron "jumps" from a higher to a lower energy level it emits a photon whose energy is equal to the energy difference between the levels. For the Balmer series, for example, this would be $E_{photon} = E_n - E_2$. Given your answer to question 4(A) and the fact that the energy of the photon is $E_{photon} = hf = hc/\lambda$ derive equation (2) in the guide sheets to this experiment.

n=6
n=5
n=4
n=3
n=2

Photon energy Increasing $\longrightarrow$

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