

Pollution Spectroscopy

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Abstract

We propose the use of emission spectroscopy to study the level and quality of pollution in selected portions of the South.

Contents

1	Project Summary	2
2	Project Description	2
2.1	Background	3
2.2	Plan for Research and Project Management	4
2.3	Broad Impact	4
3	Initial Results and Analysis	5
3.1	Hydrogen, Helium, and Mercury Spectra	5
3.2	Rydberg Constant	5
3.3	Ionization Energy (Hydrogen)	6
3.4	Heat Calculations	6
3.5	Blackbody Curves	6
4	Equipment and Resources	7
5	Appendices	9
5.1	Hydrogen Spectrum	9
5.2	Helium Spectrum	12
5.3	Mercury Spectrum	16
5.4	Incandescent Bulb Spectra	17

1 Project Summary

We are increasingly aware of environmental effects on health. New studies on the effects of something as seemingly innocuous as dust have shown that communities should pay careful attention to the chemical composition of the world around them.¹ More pressing to those of us in Alabama, the prevalence of stroke-related fatalities in the Black Belt has been linked not to diet, to genetics, or to demographics, but to such non-traditional factors as water and air quality.² One promising technique for studying these environmental factors is atomic emission spectroscopy, whereby we can detect the elemental composition of various kinds of samples, allowing us to document contaminant levels all across western Alabama.

To continue our development of the spectroscopic techniques for this ambitious project, we would like to request some funding, mainly for equipment and for paying volunteers to collect samples for analysis, as described below. The additional resources required are minimal, as much of the analyte collection has already been accomplished through the combined volunteer efforts of professors, researchers, students, and concerned citizens. The positive response so far, the encouragement and support of communities who have participated and offered help, convince us that this project holds real value for all concerned.

Our group has been involved for some time in studying atomic emission spectra. Those efforts are detailed below, but to summarize here our credentials for undertaking the sort of project envisioned, we list a few important results. We have accurately identified several known emission and absorption lines from elements such as hydrogen, helium, and mercury excited in gas form, and used these results to arrive at experimental values for the Rydberg constant in several cases. We have studied the so called Fraunhofer lines, deviations of the solar spectrum from that of a theoretical blackbody. We have even characterized the heating of filaments in incandescent lamps as a function of applied voltage, going so far as to compare the emission spectra of such lamps to modern compact fluorescent lighting options. We feel that this background has prepared us to attack a problem of this scope and importance for our communities.

2 Project Description

The elemental composition of any sample—be it a metal, vapor, or soil—proves to be valuable information, for it determines the characteristics of the entire sample itself. Purity is often of utmost importance; seemingly small contaminations can destroy the effectiveness of a pharmaceutical or the performance of a semiconductor. And nowhere is such purity more important than in the world around us. The quality of air, water, and soil not only proves vital to human health, but also to the preservation of the natural environment. Therefore, reliable methods for determining the composition of a substance are absolutely essential, both to uncover areas of previously unnoticed contamination and to dispel rumors of pollution where unjust accusations have been made. For our purposes, atomic emission spectroscopy is the answer. In it the electrons of a particular sample are energized by some external influence, such as a plasma excitation source or a simple flame; as the electrons return to their ground state, light is emitted at wavelengths corresponding to the discrete energy levels characteristic of the elements involved. Measurement of the

intensity at these wavelengths thus facilitates identification of the sample's composition.

Unfortunately, we at present lack the equipment required to perform such precise analysis. Yet our research thus far has indicated much potential value in this work, as is evident by the results noted in the succeeding report. Given the required resources, we are confident that we will be able to apply the principles of atomic emission spectroscopy to obtain accurate readings of contaminants in environmental sources, including air, water, and soil. With this data, we can assist in developing a more complete mapping of local chemical pollutants, which is vital information for policymakers and fellow researchers—and the local population in general.

2.1 Background

The discovery of the spectral nature of light, i.e. that white light is comprised of a continuum of colors, stems from the work of Isaac Newton. Therefore it is he who may be deemed the founder of the science of spectroscopy. Yet its quantitative backing did not truly arise until the work of Joseph von Fraunhofer.³ He developed the first spectroscope and discovered absorption lines in the solar spectrum, now named Fraunhofer lines in his honor. And his invention of the diffraction grating allowed precise measurements of light wavelengths. However, his discoveries did not reach culmination until the work of Gustav Kirchoff and Robert Bunsen, who established that matter absorbs and emits light at discrete wavelengths; each element possesses a unique spectrum. This principle proves the basis for modern atomic spectroscopy, for it implies that the presence of a particular element can be determined solely by a sample's radiation spectrum. Quantum mechanics would later justify and explain this phenomenon, but its usefulness was already established; atomic spectra provide key insights into the composition of materials.

The scientific foundation for the occurrence of spectral lines lies in the quantized nature of atomic energy. Since electrons can only assume particular energy levels, the radiation emitted or absorbed in a transition from one state to another is discrete as well. And the intensity observed at one of these discrete wavelengths depends on the relative probability of the transition required to produce it, allowing analysis of the *amount* of a particular substance present. For if the dominant lines of one element's spectrum are of greater intensities in one sample than in another, the former must possess a greater portion of it. Typically, two basic devices are required to execute this analysis: an excitation source to excite electrons in the sample, and a spectrometer to record the relative emission intensities at each wavelength of the spectrum. This information, coupled with data on common atomic spectra, allows one to determine the sample's elemental composition—with precision contingent on the experimental equipment.

Through this basic process, previous experimenters have completely mapped the spectra of known elements; the ubiquitous CRC Handbook, for example, contains a comprehensive listing. Nonetheless, our preliminary work focuses on the examination of known substances and blackbodies, particularly H, He, and Hg gases; the sun; and light bulbs. Although the ultimate goal of our research—determination of unknown substances—is not achieved in this process, it is a necessary first step; only by comparing our data with accepted values can a conclusion be drawn regarding the accuracy of our equipment and the merit of our methods. And precisely for this purpose our results follow below.

2.2 Plan for Research and Project Management

Our research strategy follows a simple, three-phase plan. First, we will collect soil, air, and water samples throughout west Alabama. Thereafter, we will study these analytes for any abnormal contaminants and impurities using atomic emission spectroscopy. And finally, we will integrate our results to provide a comprehensive overview of the chemical makeup of the local environment. The first objective is presently underway; we have already obtained a wide range of samples from government property and land affiliated with the university, along with commitments from several property owners and farmers willing to grant us access to their land. As word of this project spreads, we expect to find more locations for sample collection throughout the next year.

Actual spectroscopic analysis of the samples must wait, however, pending the acquirement of more precise spectrometers and more powerful excitation sources, such as the ICP spectrometer listed in the resources section of this work. But with these, the second phase can proceed. Each sample will undergo rigorous testing, and we will note its complete elemental composition using established data for atomic spectra; sites with particularly unusual analytes will receive follow-up visits for further collection and analysis. When a full mapping of the western part of the state has been obtained, we will present our results to the public and specialized environmental researchers for the purposes of governmental policy and general information. At this point, we will have accomplished our goal of collecting precise data for the expansion of local environmental knowledge.

2.3 Broad Impact

The research plan we have put forward will require a serious level of time and resources but it will have a far-reaching impact. Perhaps most importantly, its execution will involve the collaboration of a wide range of disciplines and specialists. Physics, chemistry, and geology all play major roles, and accordingly this project necessitates the complete cooperation between experts from each field. For this reason, an immediate result of this venture will be enhanced interdisciplinary interaction between the departments on campus. And therefore any student assistants will be exposed to individuals from other fields and will gain experience collaborating with others to accomplish a task; such experience proves invaluable in preparing graduates for work in industry or on large research projects.

Beyond these immediate consequences, the final data itself will likely bring about a significant outcome. What it may suggest remains unknown; it is for this very reason that such research is needed. But regardless of what conclusions may ultimately be drawn—whether positive or negative—our research will provide the much-needed scientific backing for any future policies. Through diligent sample collection and spectroscopic analysis, we will at the very least provide enhanced insight into the chemical composition of the local environment. Such information is inherently valuable, and we plan to bring it to light.

3 Initial Results and Analysis

3.1 Hydrogen, Helium, and Mercury Spectra

The data tables were given from the spectrometer and graphed accordingly. We were able to find various spectral lines associated with the elements, but sometimes the lines were too close together to be distinguished. (For instance, there were two different expected spectral lines from energy level 3 to 2 in hydrogen, but they were too close together and were counted by our measurements as a single line.) For this reason, it would be helpful to find a more precise spectrometer to distinguish some of the close-proximity lines.

Frequency f was calculated for each of the identified lines using the equation $f = c/\lambda$ (where λ is the measured wavelength and c is, of course, the speed of light in vacuum), taking the values of λ returned by the program (which had an accuracy on the order of 1 nm).

Energy E was likewise calculated taking $E = hf$, where h is Planck's constant.

3.2 Rydberg Constant

To find the Rydberg constant we used

$$\frac{1}{\lambda} = R_{\text{H}} \left(\frac{1}{n'^2} - \frac{1}{n^2} \right)$$

and

$$\frac{1}{\lambda} = R_{\text{He}} \left(\frac{1}{n_1^2} - \frac{1}{(n_2 - \delta_{3p})^2} \right)$$

for hydrogen (R_{H}) and for helium (R_{He}).

We plotted λ^{-1} against n^{-2} (n was found by comparing measured peak wavelengths to an element's spectral wavelengths). The slope was used to obtain values for R_{H} and R_{He} . Standard error was taken to be $\sigma_y \sqrt{N \Delta^{-1}}$, where σ_y was based on the uncertainty in λ taken as the precision error of the spectrometer, on the order of 1 nm. (An estimated average wavelength of 500 nm was used, and projected appropriately: since the x -axis was λ^{-1} , the uncertainty was estimated at λ^{-2} , the derivative's absolute value.) N is the number of data points—5 in the case of H, and 3 in each form of He. In accordance with Taylor⁴

$$\Delta = N \sum \frac{1}{\lambda^2} - \left(\sum \frac{1}{\lambda} \right)^2.$$

Experimental values for the Rydberg constant closely mirror that of accepted results. Hydrogen returned $(1.097 \pm 0.01) \times 10^7 \text{ m}^{-1}$, matching the accepted value of $1.097 \times 10^7 \text{ m}^{-1}$.

Helium values for the Rydberg constant match the accepted value (also $1.097 \times 10^7 \text{ m}^{-1}$ for helium) for both the parahelium and orthohelium data. Parahelium was calculated as $(1.10 \pm 0.01) \times 10^7 \text{ m}^{-1}$ and orthohelium measures as $(1.09 \pm 0.01) \times 10^7 \text{ m}^{-1}$.

For helium, the defect correction δ_{3p} was also calculated using intercept (from graph) = $R_{\text{He}}/(2 - \delta_{3p})^2$, and $\delta q/q$ is on the order of $\sqrt{(\delta x/x)^2 + (\delta y/y)^2}$, where q represents the defect correction, x is the Rydberg constant calculated earlier, and y is the intercept (the

uncertainty of which is found by $\delta_y \sqrt{(\sum((1/\lambda)^2)/\Delta)}$. The data yielded 0.064 ± 0.001 for orthohelium and -0.008 ± 0.001 for parahelium.⁵

3.3 Ionization Energy (Hydrogen)

We know that $\Delta E = E_i(1/n'^2 - 1/n^2)$, and

$$\frac{1}{\lambda} = R_H \left(\frac{1}{n'^2} - \frac{1}{n^2} \right),$$

so, substituting and remembering that $\Delta E = hf$, we find that

$$E_i = R_H hc.$$

After substituting the accepted values, $E_i = 13.7$ eV, closely approximating the accepted ionization energy of 13.6 eV.

3.4 Heat Calculations

The sun's temperature T is measured based on the formula $\lambda_0 T = 2.898 \times 10^{-3}$ K, where λ_0 is the peak wavelength.⁶

Using 555 nm, the measured peak wavelength, we obtain 5200 K for the temperature of the sun's surface, as opposed to 5800 K, which is the expected value. It is fairly obvious from looking at the curve and from having familiarity with blackbody curves that the peak wavelength is "supposed" to be shorter. This is one reason more advanced equipment is needed; it is possible that our equipment is missing some of the peak wavelengths, or else that it is lumping together wavelengths later in the spectrum and causing a false peak. Either way, we need equipment that can measure more precisely, so we can obtain clearer results for peak wavelengths than the ones measured here.

Similar calculations were made for the incandescent bulb, though an outlier data point had to be discarded at 120 V. After plotting, a very good linear relationship was found between average temperature and voltage.

The following values were used to obtain the heat/voltage relationship:

Voltage [V]	Peak Wavelength [nm]
60	706
80	668
100	635
120	609

3.5 Blackbody Curves

Solar radiation approaches a blackbody curve.⁷ Certain wavelengths are lower than expected, particularly ones associated with the Balmer series (434 nm, 486 nm, and 656 nm from the Balmer series, because these are more easily absorbed by atoms). This is one reason we need better equipment. It would be helpful to investigate these Fraunhofer

lines in greater detail, but the resolution is not currently good enough to make precise measurements. Since the resolution is only about to 1 nm, it is difficult to say which wavelength precisely is represented by a given Fraunhofer line, or if more than one is represented. For instance it was initially thought that the 435 mercury line was visible, but later decided that the 434 hydrogen line was primarily the line observed. Greater resolution could make these details more clear, and aid to avoid overlapping Fraunhofer lines—or other lines, for that matter.

The incandescent light also approximated a smooth blackbody curve, but the fluorescent curve was far from this, having great intensity only at a few discrete wavelengths. The fact that its curve is far less continuous makes it seem somewhat “unnatural.”⁸⁹¹⁰

4 Equipment and Resources

Our research has already acquired access to the necessary equipment for analyte collection, including soil core samplers, air sample bags and pumps, and water sampling bailers; we should require no further resources for this portion of our research plan. However, we do need improved equipment for spectroscopic analysis. Although the required SpectraSuite software is already installed on our equipment, we must obtain a general-purpose spectrometer with much greater resolution than what we currently have. In order to match the current computer platform, we recommend the Ocean Optics HR4000 High-Resolution Spectrometer with a UV4 detector upgrade. Below is a depiction of the device. The estimated total cost is approximately US\$5100.

For the precise sample analysis essential to our research, we suggest the SPECTRO ARCOS ICP Spectrometer, accompanied by SPECTRO Smart Analyzer Vision software. This covers the entire analysis process, using high-temperature plasma to excite electrons in the given sample, and measuring the emitted wavelengths with an optical spectrometer. The cost of the device, which is pictured below, is unknown awaiting SPECTRO’s reply to our estimate quote request. And upon receiving the devices listed here, our group will possess all it needs to proceed as planned with the proposed research.

Notes

¹D. W. Layton and P. I. Beamer *Environ. Sci. Technol.*, **2009**, 43 (21), pp 8199–8295.

²G. Howard, *et al.*, *Prev. Med.* 2009 Aug-Sep; **49** (2-3): 129–32.

³A somewhat more complete history of the field can be found online from the MIT Spectroscopy Laboratory at <http://web.mit.edu/spectroscopy/history/history-classical.html>

⁴J. R. Taylor, *An Introduction to Error Analysis*, 2ed., 184–188.

⁵The distinction between orthohelium and parahelium lines refers to the spin-state of the upper level (i.e. excited) electron, which can be either parallel or antiparallel, respectively, to that of the ground state electron left in the S orbital.

⁶N.B.: The sun does not necessarily appear to be the same color as its peak wavelength. As the peak wavelength shortens, the spectrum broadens, so that we see a mixture of a whole range of colors. As an object is heated from red-hot, to orange-hot, &c., the colors mix until we finally reach white-hot (without, for instance passing through a green-hot phase).

⁷We call such a smoothly varying intensity v. wavelength curve ‘continuous’, in contrast with ‘line’ spectra such as atomic emission spectra.

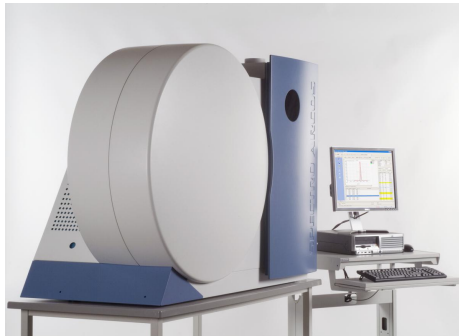
⁸http://en.wikipedia.org/wiki/Rydberg_constant

⁹prola.aps.org/abstract/PR/v30/i5/p608_1

Figure 1: Ocean Optics HR4000 Spectrometer.¹¹



Figure 2: SPECTRO ARCOS ICP Spectrometer.¹²



¹⁰<http://www.egglescliffe.org.uk/physics/astronomy/blackbody/bbody.html>

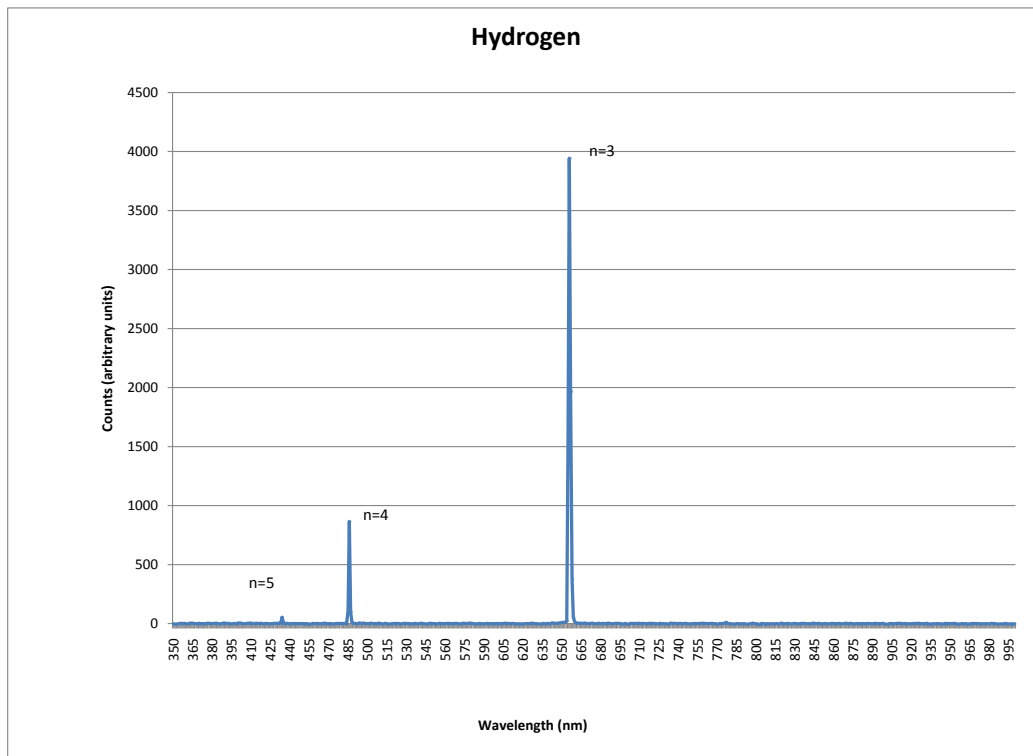
¹¹Image obtained from Ocean Optics website <http://www.oceanoptics.com/Products/hr4000.asp>

¹²Picture acquired from <http://www.spectro.com/pages/e/p010304.htm>

5 Appendices

5.1 Hydrogen Spectrum

Figure 3: Displayed are the highest peaks in the Balmer series. (For instance, $n = 3$ implies transition from 3 to 2 in the Balmer series, $n = 4$ implies transition from 4 to 2, &c.)



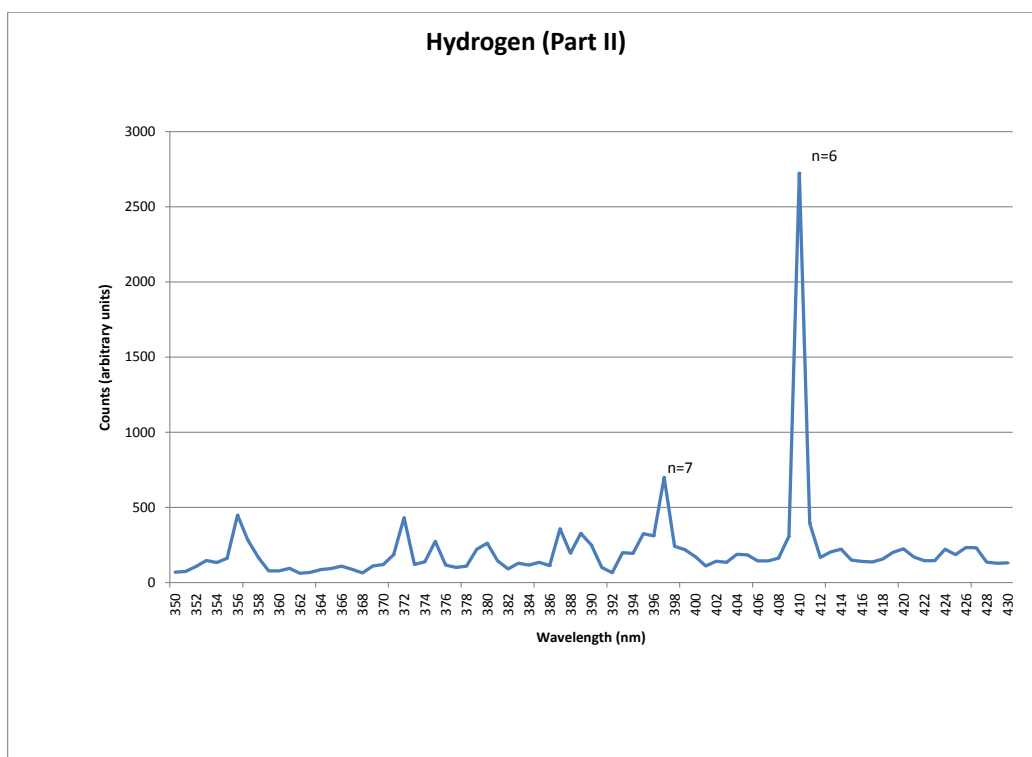
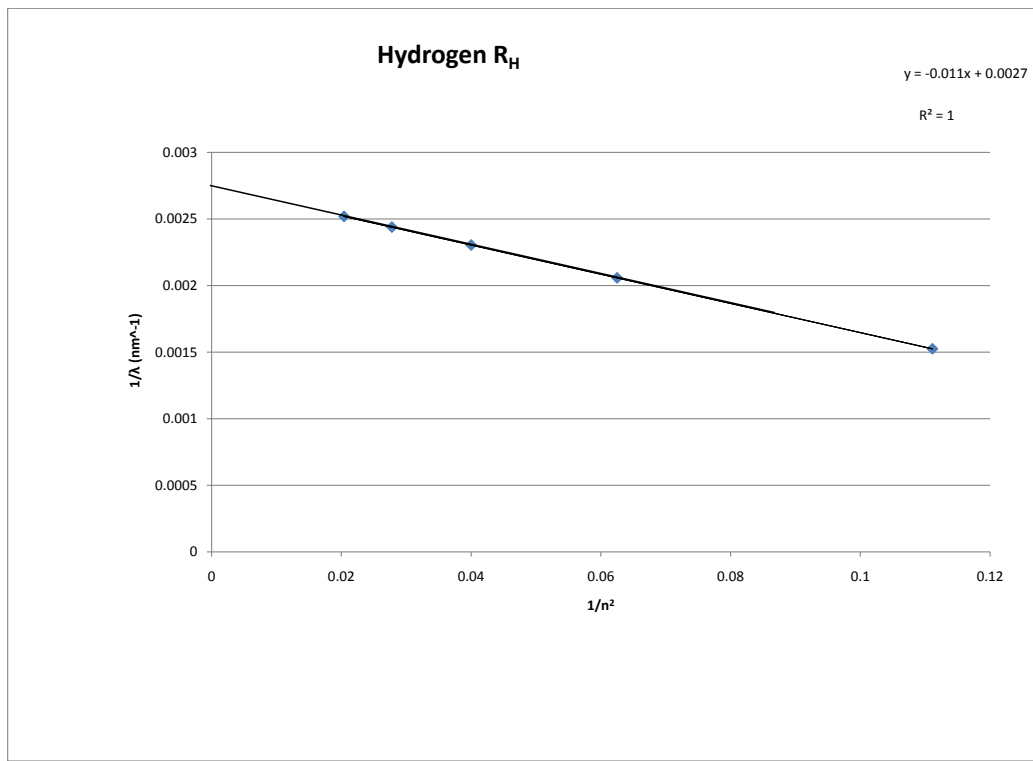


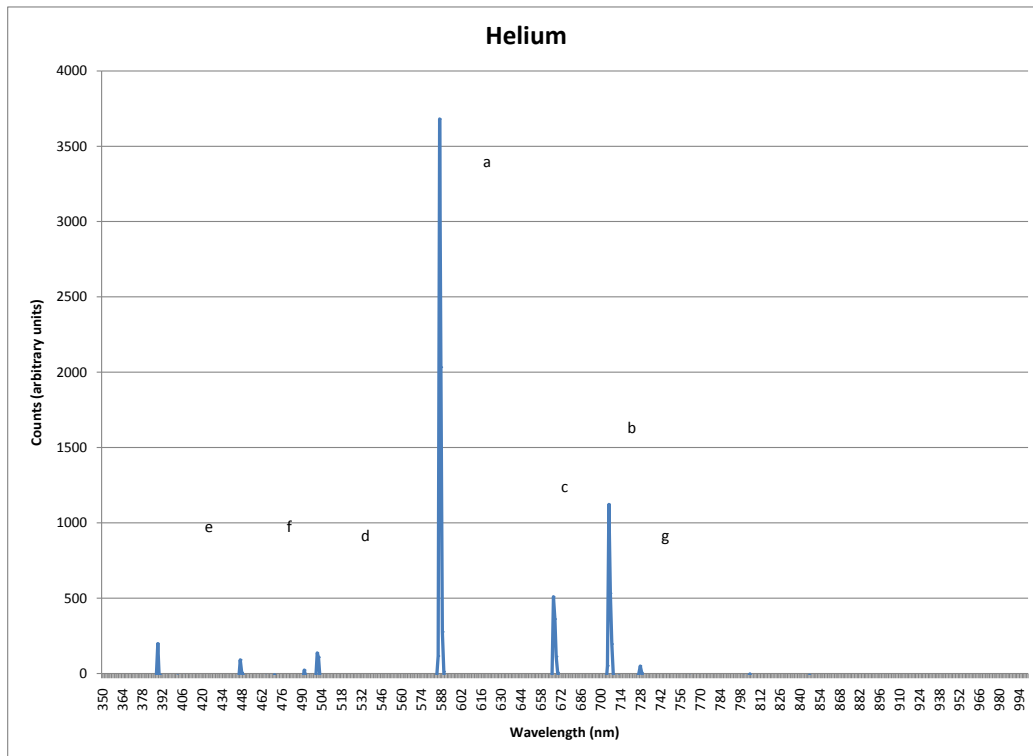
Table 1: Some relevant data for Hydrogen spectrum

Energy level (n)	Wavelength [nm]	Frequency [THz]	Energy [eV]
3	656	457	1.89
4	486	617	2.55
5	434	691	2.86
6	410	731	3.03
7	397	755	3.13

Figure 4: The graph yields a virtually perfectly straight line, as predicted. R_H is the negative of the slope.



5.2 Helium Spectrum



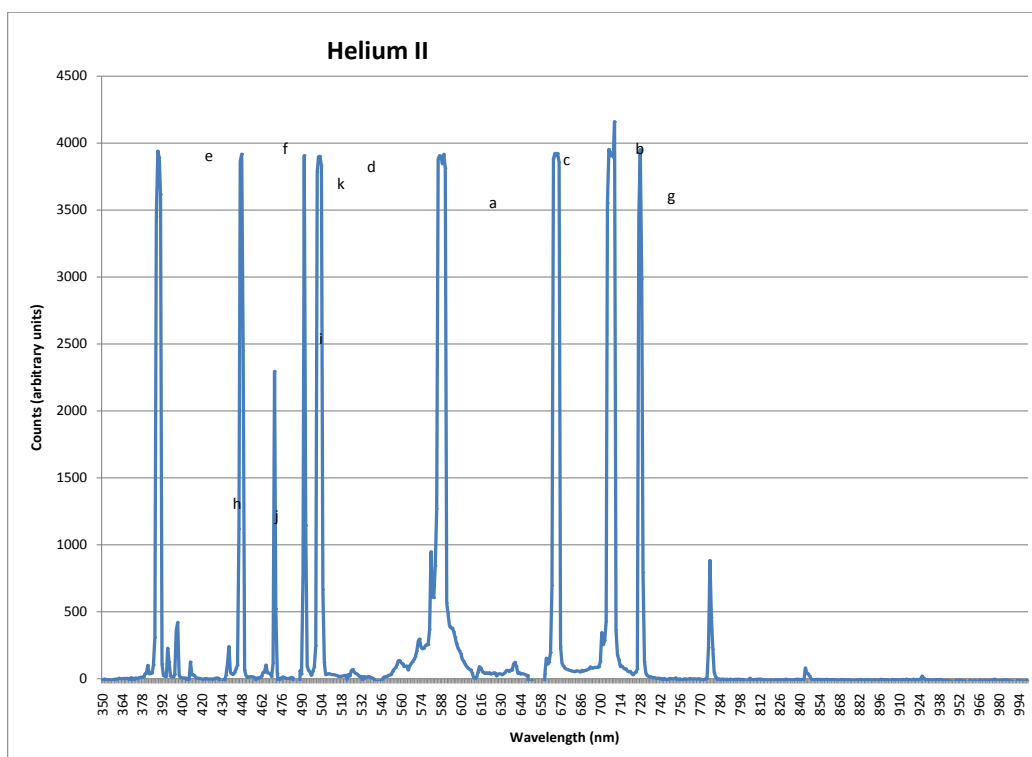
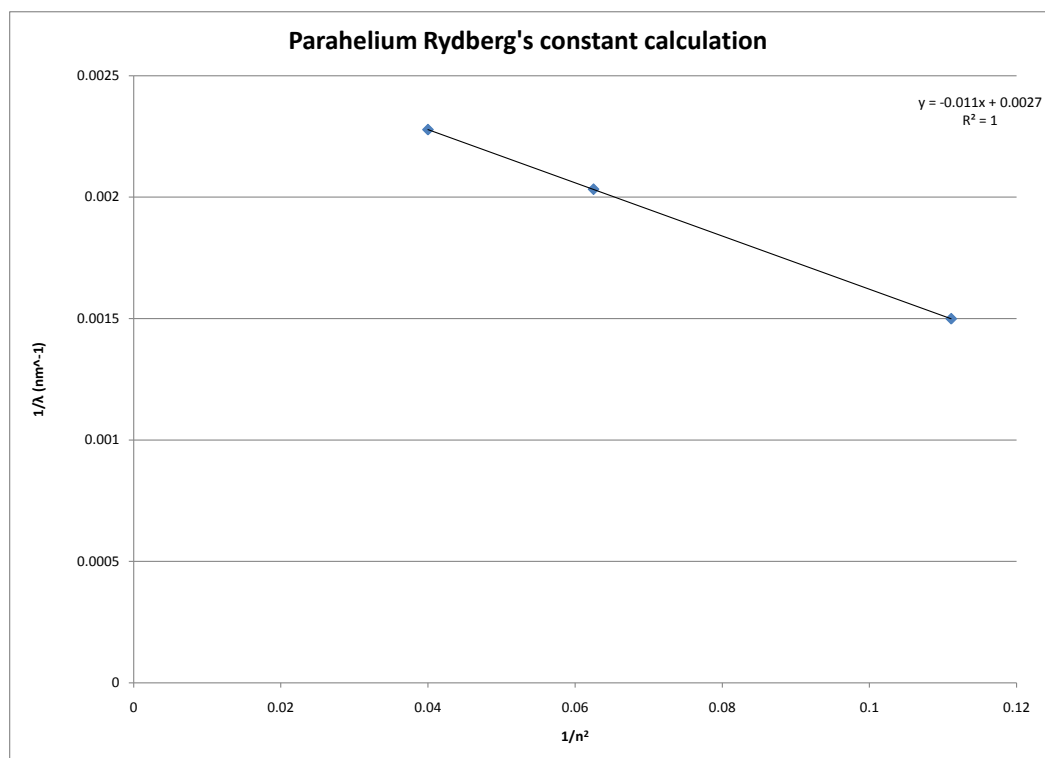
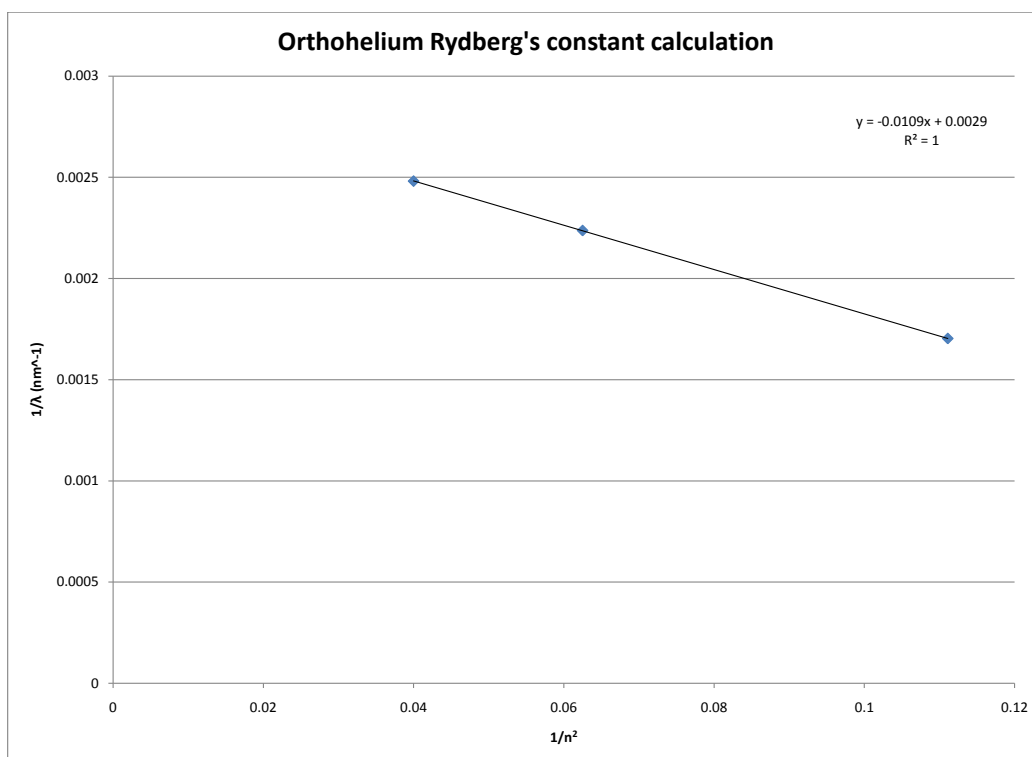


Table 2: Some relevant data for Helium spectrum

Emission line	Wavelength [nm]	Frequency [THz]	Energy [eV]
a	587	511	2.11
b	706	424	1.76
c	667	449	1.86
d	501	598	2.48
e	389	771	3.19
f	447	671	2.78
g	728	412	1.70
h	403	744	3.08
i	471	636	2.63
j	439	683	2.83
k	492	609	2.52

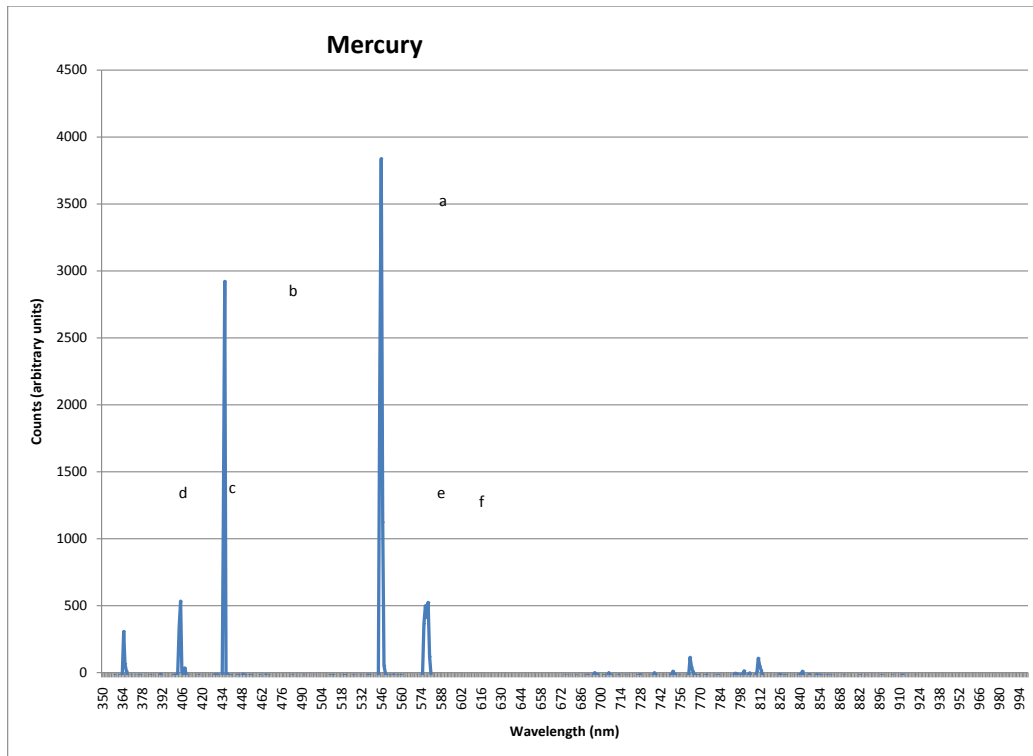
Figure 5: The lines are almost perfect, as predicted.





5.3 Mercury Spectrum

Figure 6: Mercury, with far more electrons than the first two elements, is far more complex. Nevertheless, it was still possible to identify some known spectral lines.



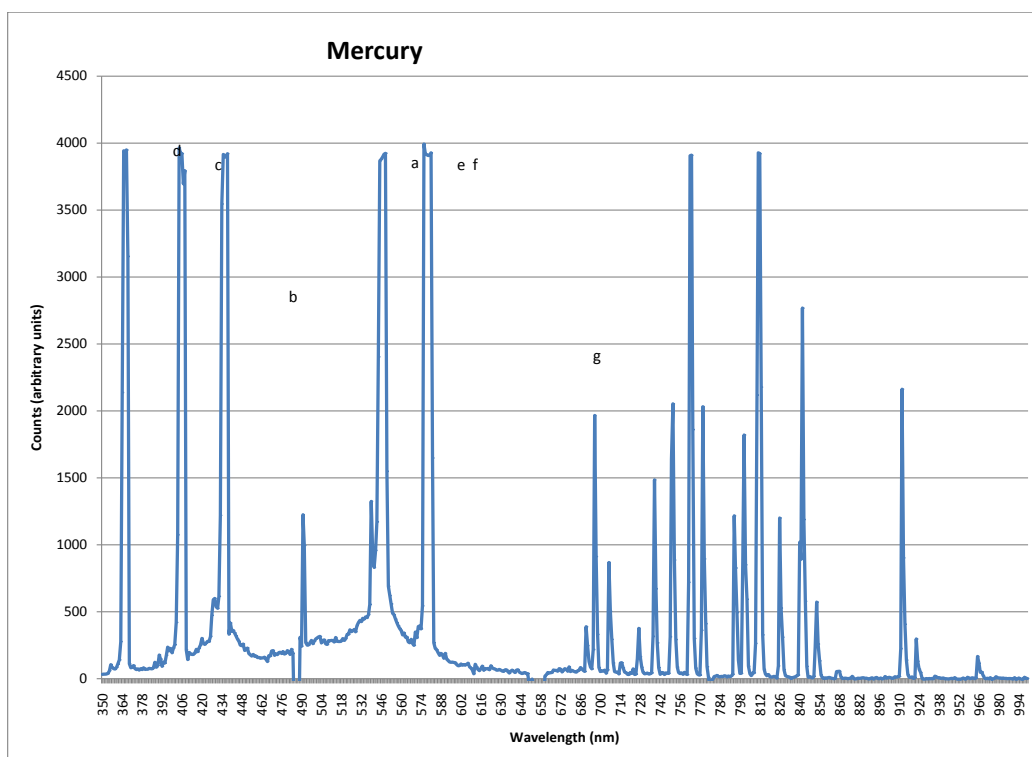
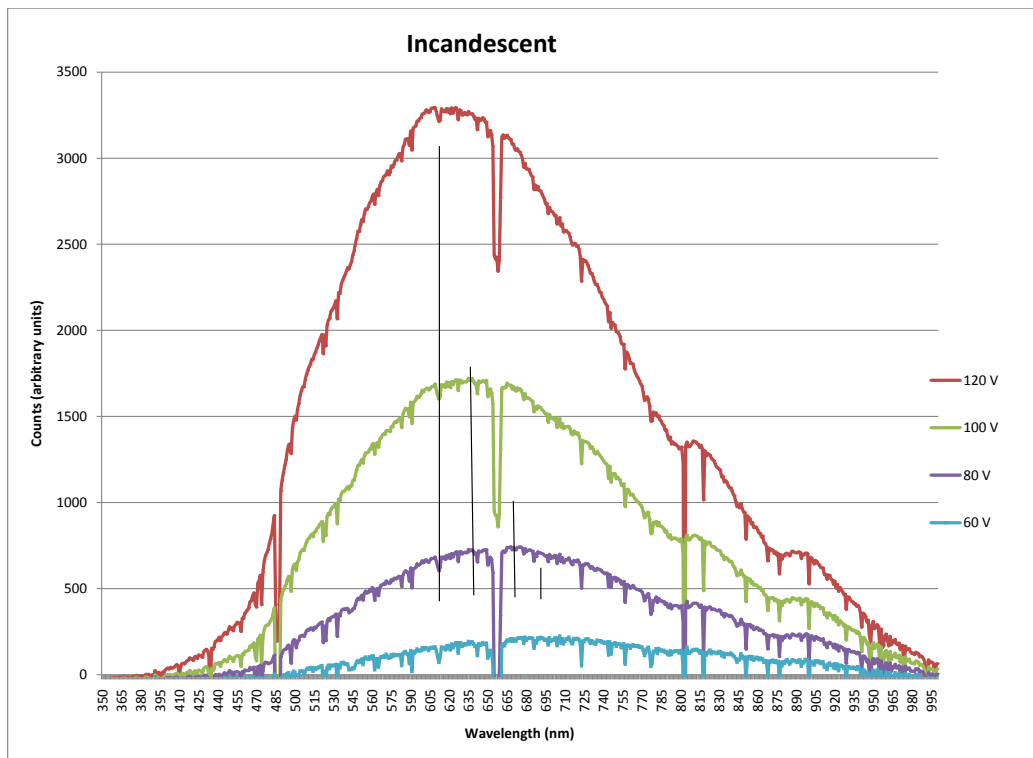


Table 3: Some relevant data for Mercury spectrum

Emission line	Wavelength [nm]	Frequency [THz]	Energy [eV]
a	546	549	2.27
b	436	688	2.85
c	405	740	3.06
d	365	821	3.40
e	577	519	2.15
f	579	518	2.14

5.4 Incandescent Bulb Spectra

The incandescent spectra closely approximate blackbody radiation. The curves widen and exhibit a longer peak wavelength at lower energies. Thus, a ‘color temperature’ can be used to describe these bulbs; ones that emit greater energy will have a shorter peak wavelength. These are sometimes more soothing to the eye; their mostly continuous distribution closely approximates the wavelength patterns emitted by the sun, in contrast to fluorescent bulbs, which have only a few peak wavelengths rather than a smooth curve. Higher voltages have much higher intensities.



Temperature shows an increasing linear dependence on voltage. Estimations of temperature were based on peak wavelength.

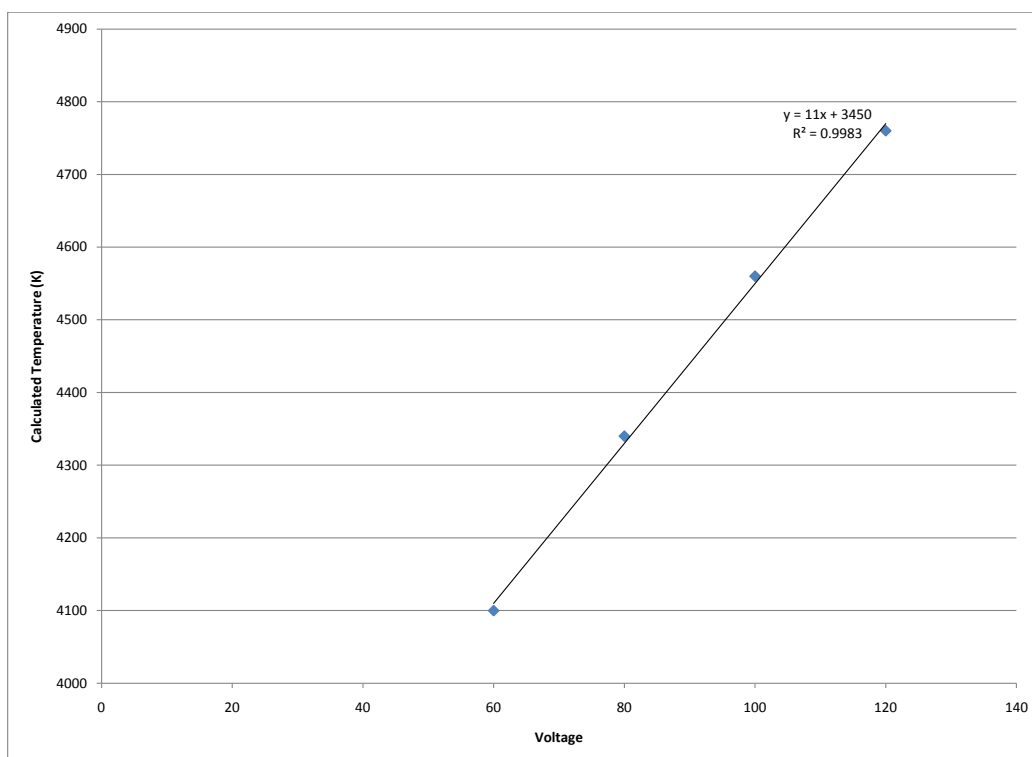


Table 4: Temperature v. Voltage

Voltage [V]	Temperature [K]
60	4100
80	4340
100	4560
120	4760