

UNIVERSITY OF SOUTHAMPTON

ELECTRODELESS DISCHARGE BULBS

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ABSTRACT

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ELECTRODELESS DISCHARGE BULBS

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This project is concerned with the discovery of new spectral outputs for electrodeless discharge bulbs.

The possibilities of new electrodeless discharge bulbs have been examined in the literature and sulfur has been extensively studied as a new light emission source.

The process of using H_2S as a source of sulfur in the electrodeless discharge bulbs has been examined and used in the production of mixed gas bulbs.

The recording of spectra has also been used in a brief investigation of spectral intensity vs power output.

Table of contents

Chapter 1 Introduction	1
1.1 Basics of electrodeless discharge bulbs	2
1.2 Advantages of electrodeless discharge bulbs	3
1.3 Aims of the current project	4
1.4 Previous work done at Southampton	4
1.5 Spectral output recording	6
1.6 Research on new fillings	8
1.6.1 Xenon	8
1.6.2 Deuterium	8
1.6.3 Excimers	9
1.6.4 Sulfur	12
1.6.5 Selenium	13
1.6.6 Boron	14
1.6.7 Fluorine	15
1.7 Phosphor chemistry	16
1.7.1 Definition of a phosphor	16
1.7.2 Effect of phosphor on mercury consumption	16
1.7.3 Reason for interest in phosphors	17
1.7.4 Lanthanide chemistry	18
1.7.5 Commercially available phosphors	21
1.7.6 Thin film phosphors	22
Chapter 2 Experimental	23
2.1 General procedure	24
2.2 Experiments carried out on the vacuum line	25
2.2.1 Mercury/argon testing of the vacuum line	25
2.2.2 Sulfur/argon bulb	25
2.2.3 Sulfur dioxide bulb	25
2.2.4 H ₂ S bulb	25
2.2.5 H ₂ S/Ar bulb	25
2.2.6 Selenium dioxide/argon bulb	25
2.2.7 On going experiment	26
2.3 Photo-diode experiments	27
2.3.1 Mercury/argon bulb test	27
2.3.2 H ₂ S	28
2.3.3 Purification of H ₂ S	29
2.4 Production of silica electrodeless discharge bulbs	30
2.4.1 First silica H ₂ S/Ar bulb	30
2.4.2 Second silica H ₂ S/Ar bulb	31
2.4.3 Production of the third H ₂ S/Ar bulb	31
2.4.4 Production of the fourth H ₂ S/Ar bulb	32
2.5 Recording of the spectra	33
2.6 Phosphor sheath	34

<i>Chapter 3 Results and discussion on sulfur</i>	35
3.1 Sulfur/Argon bulbs	36
3.1.1 Sulfur/Argon bulb	36
3.1.2 Why does this "Flashing" occur?	36
3.2 H₂S/Ar bulb testing	38
3.3 H₂S sealed bulbs	39
3.3.1 First silica H ₂ S/Ar bulb	39
3.3.2 Second silica H ₂ S/Ar bulb	39
3.3.3 Why are the bulbs unstable?	39
3.3.4 Stability and discharge characteristics of the third and fourth H ₂ S/Ar bulbs	40
3.3.5 Spectra of the sulfur bulbs	40
3.4 Investigation of power input Vs spectral intensity	44
3.6 Conclusions about the H₂S/Ar bulb	45
<i>Chapter 4 Other work</i>	46
4.1 Testing of the vacuum line	47
4.2 Selenium/argon bulb	49
4.3 Mercury/argon testing of the photo-diode	49
4.4 Phosphor sheath	49
<i>Chapter 5 Further work</i>	53
5.1 Further work	54
<i>Appendix 1 Spectrum of selenium</i>	55
<i>Appendix 2</i>	60
<i>References</i>	64
References	65

Table of diagrams and tables

Diagram/Table	Page
Figure 1: Schematic of an electrodeless discharge bulb	2
Table 1: Comparison of electrodeless discharge bulbs and normal light sources	3
Figure 2: Diagram of the vacuum line	4
Figure 3: A typical emission spectrum from a Hg/Ar bulb	6
Figure 4: Emission spectrum of KrCl	11
Figure 5: Emission spectrum of XeCl	11
Figure 6: Emission spectrum of S ₂	12
Figure 7: Emission spectrum of Fluorine lamp	15
Figure 8: Mercury concentration in glass Vs. depth	16
Figure 9: Schematic of a fluorescent lighting tube	17
Table 2: Colours obtained from f-configurations	18
Figure 10: Fluorescence spectra of BaFCl:Eu ²⁺	19
Figure 11: Photoluminescence spectrum of LaOCl:Sm ³⁺	20
Table 3: Phosphors available from Photek	21
Table 4: Emission peaks for some thin films	22
Figure 12: Diagram of vacuum line	24
Figure 13: Vacuum line set up for the testing of the photo-diode	27
Figure 14: Bulb used for H ₂ S collection	29
Figure 15: Diagram of the vacuum line when filling the bulb	30
Figure 16: Diagram of the vacuum line	31
Figure 17: Diagram of the new bulb design	32
Figure 18: Diagram of the vacuum line	32
Figure 19: Diagram of the phosphor sheath	34
Figure 20: Flow chart of the cyclic flashing	36
Figure 21: Absorption of UV by Pyrex	37
Figure 22: Literature emission spectrum of sulfur	41
Figure 23: Emission spectrum of the third H ₂ S/Ar bulb	42
Figure 24: Emission spectrum of the fourth H ₂ S/Ar bulb	43
Figure 25: Power setting 3	44

Diagram/Table	Page
Figure 26: Power setting 4	44
Figure 27: Sample spectrum of Hg/Ar bulb at 70 % power	47
Figure 28: Graph of Intensity at 254 nm (arbitrary units)vs. Pressure (mbar)	48
Figure 29: An emission spectrum of a Hg/Ar bulb	50
Figure 30: Spectrum from the phosphor sheath prototype	51
Table 5: Spectrum of selenium	56
Table 6: Comparison of literature and experimental peak positions of sulfur spectra	61

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Chapter 1

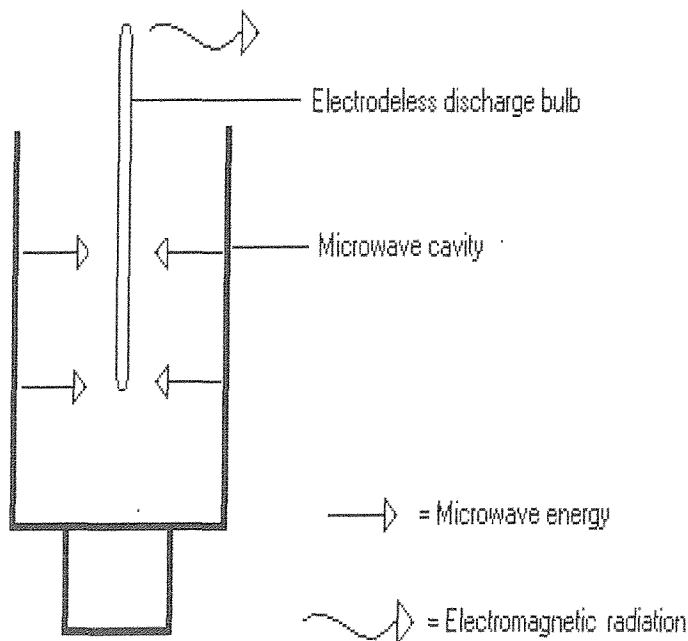
Introduction

Introduction

1.1 Basics of electrodeless discharge bulbs

The basics of electrodeless discharge bulbs are shown in a schematic in figure 1, and are discussed by Dakin¹.

Figure 1: Schematic of an electrodeless discharge bulb



The molecules inside the electrodeless discharge bulb, e.g. mercury and argon, absorb the microwave radiation shown in figure 1. The molecules are now in an excited electronic state and are able to relax back to the ground state by emission of electromagnetic radiation. The emission is dependent mainly upon the molecules within the discharge bulb.

1.2 Advantages of electrodeless discharge bulbs

The advantages of electrodeless discharge bulbs are summarised in table 1.

Table 1: Comparison of electrodeless discharge bulbs and normal light sources¹

Quality	Normal light source	Electrodeless bulb
Lifetime	Finite due to the corrosion of the electrodes, or lifetime of the filament	As there are no electrodes to corrode, the electrodeless system offers a much longer lifetime
Homogeneous light source?	No, Bulbs with electrodes contain areas which are brighter than others due to the fact that the electrons do not freely leave the cathode, therefore areas of charge build up.	Yes, the saturation of the bulb with microwave radiation means that a symmetrical output is achieved
Intensity of light source	Less intense bands	More intense at specific wavelength leading to specific applications
Easy to activate?	Extremely, as all that is needed is a DC power source	Once a microwave source is obtained, yes.

As can be seen the electrodeless discharge bulb has a distinct advantage over the normal light source as it has a much longer lifetime, has a homogeneous distribution of light within the bulb and a more intense spectrum, once activated. These factors make the electrodeless discharge bulb an area that is well worth developing.

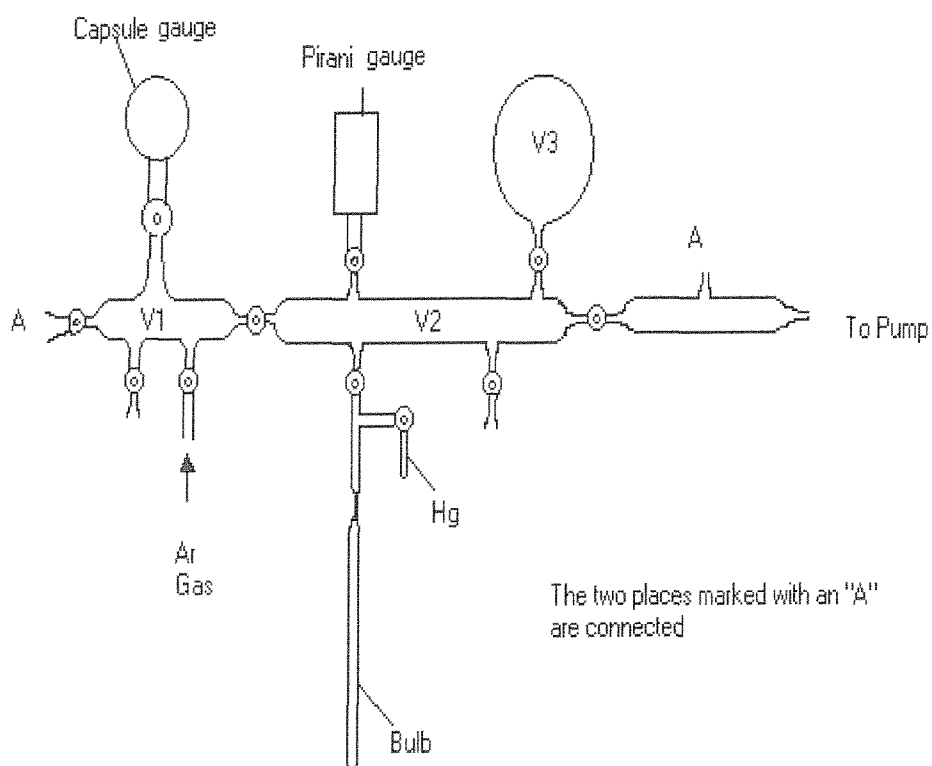
1.3 Aims of the current project

The aim of the current project is to change the spectral output that is obtained from the electrodeless discharge bulbs. This will be done, as is described later, either by changing the molecules within the bulbs or by selective use of phosphors.

1.4 Previous work done at Southampton

The work that has already been done at Southampton involves the production and optimisation of mercury and argon electrodeless discharge bulbs. The electrodeless discharge bulbs are prepared using a vacuum line. The vacuum line that was constructed for the laboratory is capable of handling pressures $<10^{-6}$ mbar. This vacuum line is shown diagrammatically in figure 2.

Figure 2: Diagram of the vacuum line²



Bulbs that are prepared using the vacuum line are first heated *in vacuo* to a temperature of *ca.* 800 K using an external tube furnace, for 2-3 hours. This is done to ensure that all adsorbed gases such as water are removed prior to filling. The bulbs are then filled after cooling. As an example fill Hg/Ar shall be used from reference two.

Firstly mercury is added to the bulb. This is done by cooling the bulb to 77 K using liquid nitrogen under vacuum, this causes the volatile mercury to collect in the bulb.

The sublimation rate of mercury was found to be *ca.* 6 mg/hr. The sublimation time could then be used as a guide for how much mercury had been placed within the bulbs. Direct weighing of the bulbs was also used to double-check the mass.

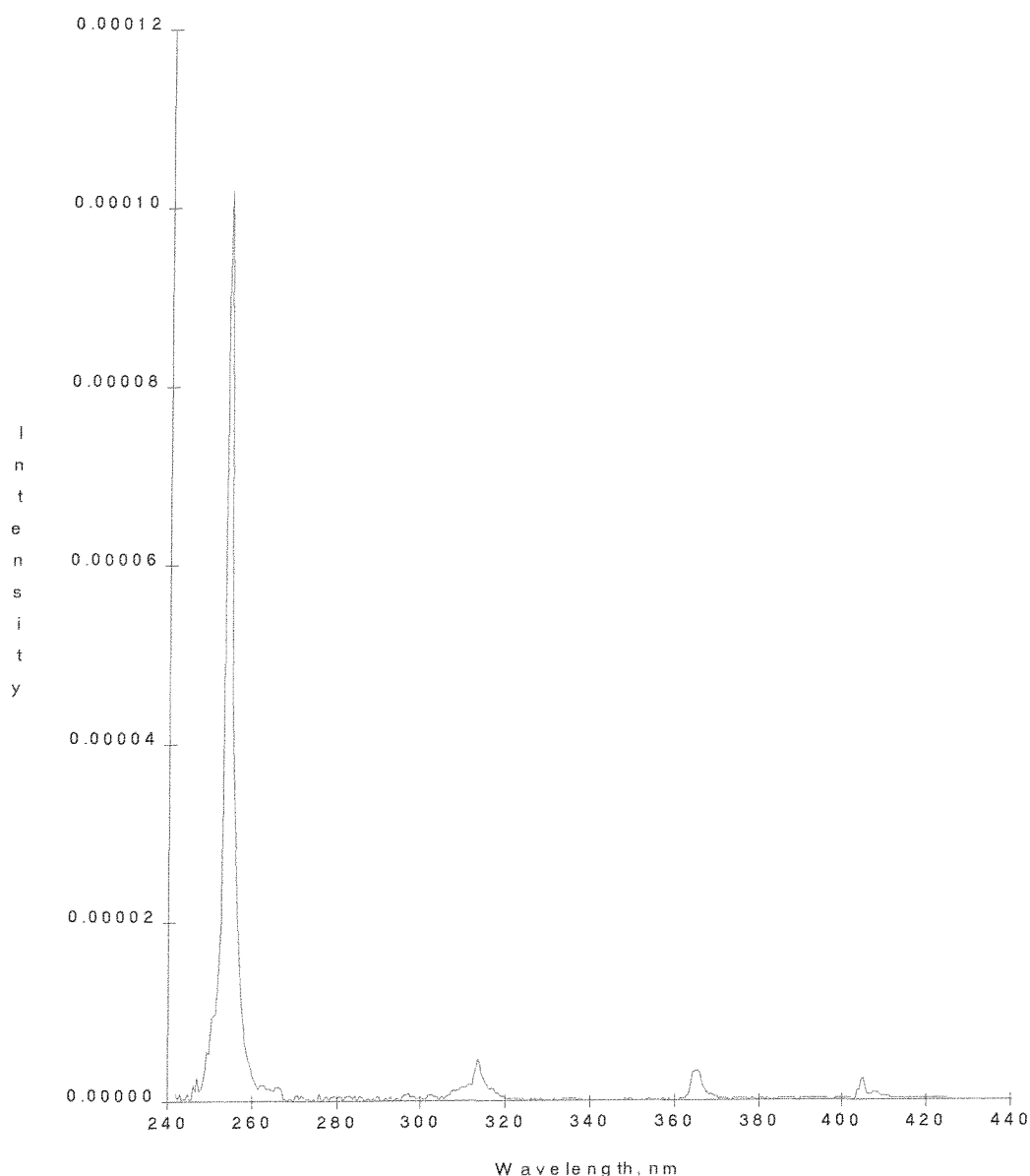
Argon is added to the bulb in accurate amounts by volume expansion. The vacuum line has been calibrated by use of the volumes marked as V1, V2 and V3. The result of this is that, for an initial pressure in V1, the amount of argon that is admitted into the bulb is known.

Once the bulbs have been filled they may be sealed off and then the spectra recorded.

1.5 Spectral output recording

The spectral output of the discharge bulbs is recorded by the Solascope, which is a small UV/visible emission spectrometer. The Solascope has a range from 240 – 425 nm with a collection time of 300 ms.² When a good spectrum from an emission has been recorded it is transferred to a PC using the software package “Solaterm” which can then be analysed using “Microsoft Works”. Regular spectra can be obtained from “Microsoft Works” by creating an X-Y scatter graph from the data points. A typical spectrum obtained in this manner is shown in figure 3.

Figure 3: A typical emission spectrum from a Hg/Ar bulb



As can be seen the Hg/Ar bulb has an intense emission at 254 nm and small features at *ca.* 315, 365 and 410 nm. As was explained earlier the position of these bands is because mercury and argon were used in the bulb, if other molecules had been used then another spectrum would have been obtained. For this reason a literature search was carried out to find materials that could be used as new fillings for electrodeless discharge bulbs.

1.6 Research on new fillings

The references that were used in this section were provided by Dr. Howard's bibliography³ and from library searches utilising chemical abstracts. Many of the references were of little use in the context of finding new fillings, but did have theory that may be of use at a later date.

1.6.1 Xenon

Xenon may be used as mercury is in fluorescent lighting tubes, in conjunction with phosphors. Xenon has an emission at 147 nm, which is the lowest of the noble gases and makes it suitable for this purpose. The phosphor in a fluorescent tube absorbs this 147 nm light and then re-emits it as visible light⁴.

1.6.2 Deuterium

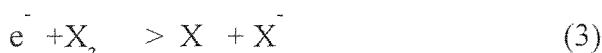
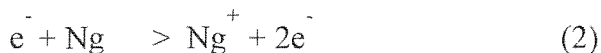
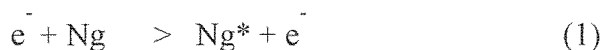
Deuterium lamps have long been used in industry, research, and medicine for transmission, absorption, and fluorescence measurements. Deuterium emits in a line-free dissociate continuum from 160 nm to 350 nm. The deuterium plasma in lamps is usually intensified by a molybdenum constriction. However the content of the plasma in commercial deuterium lamps is unknown for the most part; this is due to the fact that special techniques are required as the plasma has small dimensions (< 1mm), impurities, and nonequilibrium conditions (filling pressure < 15mbar)⁵.

1.6.3 Excimers

Efficient lighting may also be obtained from excimers of halogen and noble gases.⁶ The reaction mechanism for the formation of these excimers is rather complex, however several key steps can be identified.

A. Ionisation and excitation of noble gas and halogen

High-energy electrons ionise and excite the noble gas and halogen.

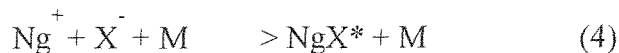


Ng stands for noble gas and X is a halogen species.

While the high energy electrons would not be present in the electrodeless discharge system, a way past this can be found, as can be seen from the reactions above the electrons in fact cancel out when the system is summed, so a small source of electrons, stimulated by the microwaves could be used to initiate the reaction, also Zhang⁶ refers to excimer bulbs powered by microwaves.

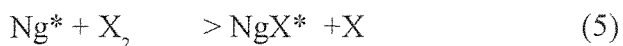
B. Formation of noble gas halide excimers

The excimers may be formed from a three-body recombination of the positive noble gas ions from equation 2 with the negative halide ions, formed in equation 3.



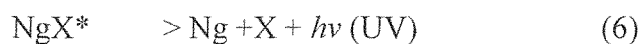
M is a collisional third body that in many cases can be an atom or molecule of the active species or of the buffer gas.

The other reaction for the formation of the excimer is the Harpooning reaction (5) in which the excited noble gas atom transfers its loosely bound electron to the halogen molecule or halogen-containing compound to form the electronically excited excimer.



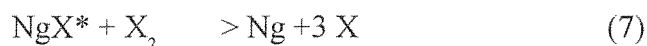
C. Emission of radiation

The excimer that is formed is very unstable and rapidly breaks down to its component atoms, giving rise to ultraviolet radiation.

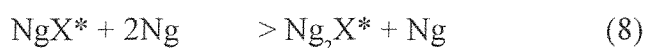


D. The quenching process

There are several quenching processes; however, two distinct processes are dominant. At low pressures quenching by the halogen species is dominant.



At higher pressures a three-body reaction involving noble gas atoms is dominant.



These quenching mechanisms are in competition with the radiative process.

There are two specific examples of this excimer light source, the KrCl^* excimer, which has an intense emission at 222 nm and two less intense emissions at 235 nm and 325 nm; and the XeCl^* excimer, which also has three emissions, the more intense at 308 nm with two weaker emissions at 236 nm and 345 nm.⁶ The spectra of these excimers are shown overleaf in figures 4 and 5.

Figure 4: Emission spectrum of KrCl^6

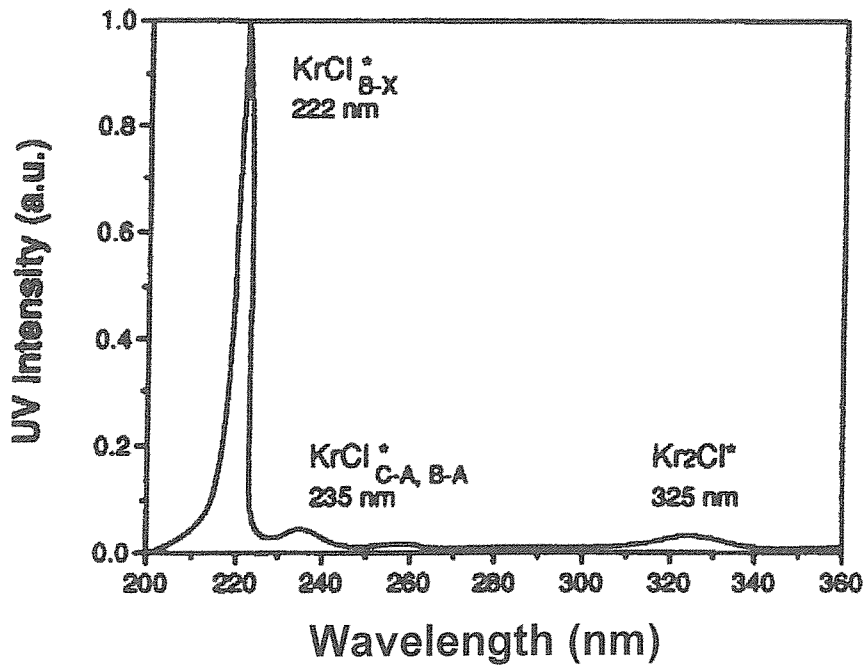
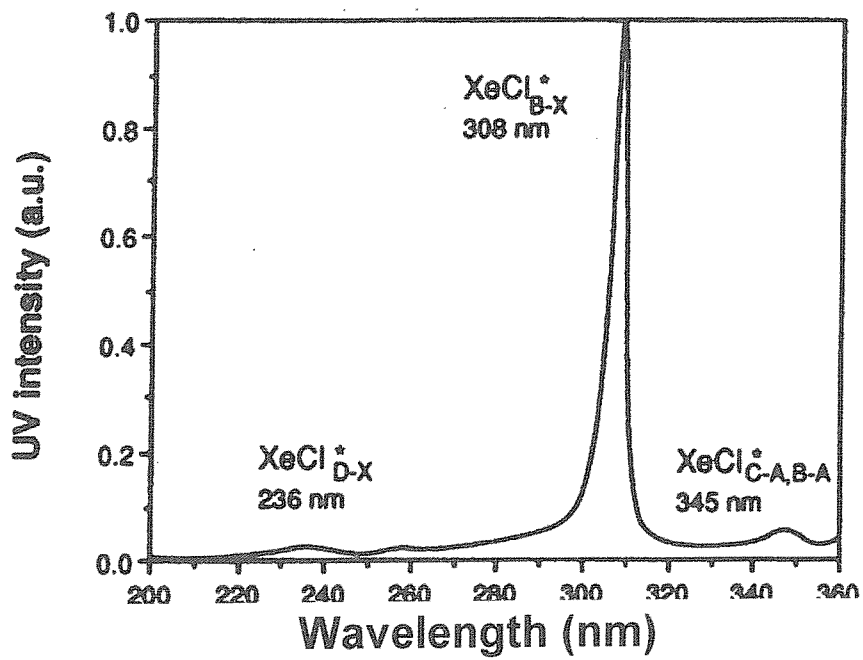


Figure 5: Emission spectrum of XeCl^6

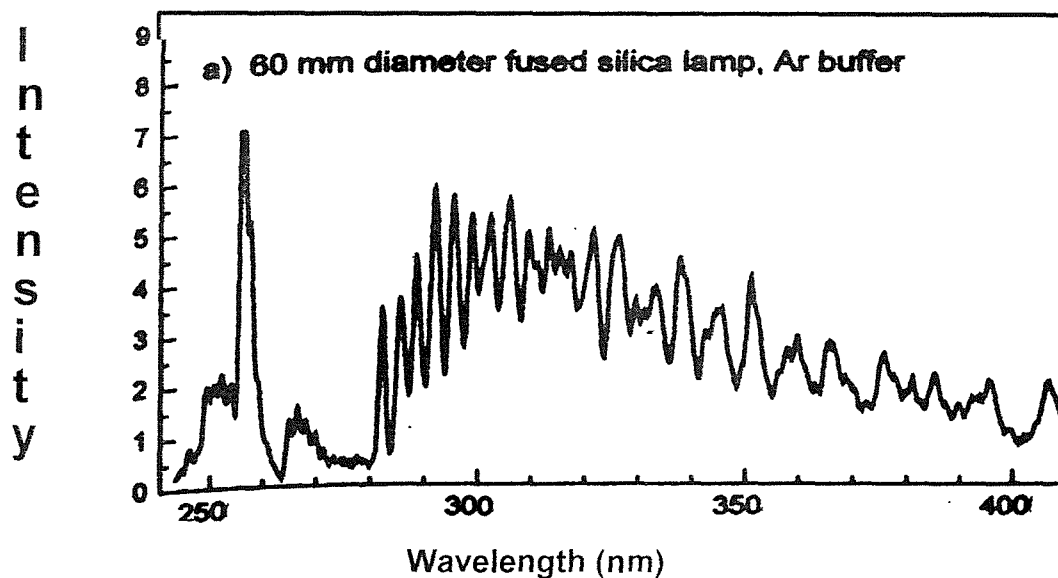


1.6.4 Sulfur

Solid sulfur is in the form of S_8 rings. At higher temperatures, in the vapour phase, these rings open and break up to give simpler species. As a vapour sulfur is known to exist of a mixture of S_8 , S_7 , S_6 , S_5 , S_4 , S_3 and S_2 molecules.⁷ At 600 °C and at low pressure the vapour will be predominantly S_2 .⁷ The species that the interest is in, is the S_2 species that has a quasi continuum, as shown in figure 6. Sulfur is very corrosive on electrodes⁸ so an electrodeless system is ideal.

Sulfur in the form of S_2 has a vapour pressure similar to that of mercury at room temperature and also has an emission spectrum. The emission recorded has a strong band at *ca.* 260 nm and a quasi-continuum from 270 to over 400 nm⁸; this is shown in figure 6.

Figure 6: Emission spectrum of S_2 ⁸



The electrodeless system has been investigated for sulfur/argon systems.^{8a} Turner^{8a} has investigated the differences between electrodeless discharge bulbs and ordinary lighting.

1.6.5 Selenium

Selenium is the element beneath sulfur in the periodic table and has a similar vapour pressure, which makes it an obvious subject for study. Selenium is an allotropic species, with a “metallic” grey hexagonal form which is very stable, red selenium which is monoclinic and thought to be comprised of Se_8 molecules. Finally an amorphous system is thought to exist as a black or red solid⁹. In the vapour state the Se_8 molecule breaks down to Se_6 and Se_2 as with sulfur.

A search has been carried out for the emission spectrum of selenium (Se_2). The emission spectrum found¹⁰ showed that the spectrum consisted of a large number of lines, such as the sulfur spectrum, in the visible and near ultra-violet region between 370 nm and 588 nm. The spectrum that has been observed was captured on photographic film as a number of bands of differing intensities. The data has been tabulated in appendix one.

Rosen¹¹ was the first to propose a vibrational quantum analysis for selenium, which definitely showed that the bands observed came from the Se_2 diatomic molecule. All bands were included in one electronic system as shown in the equation:

$$\nu = 27307 + (247.2 \nu' - 2.3\nu'^2) - (397.5 \nu'' - 1.32\nu''^2) \quad (9)$$

Nevin¹² later qualified Rosen's theory in a short note to *Nature* but had emission bands at higher wavelengths, and these bands could be arranged into two different excited levels, but a single final state which is identical to the ground state. According to Nevin there are three band systems, the main alpha system which is observed in emission and absorption, the beta blue emission and the gamma yellow-green bands, both of which are solely emission bands. The following equations were derived for the band systems.

$$\text{Alpha: } \nu = 27371 + (254.7 u' - 2.42 u'^2) - (387.8 u'' - 0.63 u''^2) \quad (10)$$

$$\text{Beta: } \nu = 21945 + (431.1 u' - 0.83 u'^2) - (373.5 u'' - 0.66 u''^2) \quad (11)$$

$$\text{Gamma: } \nu = 18342 + (336.3 u' - 0.19 u'^2) - (386.5 u'' - 0.59 u''^2) \quad (12)$$

There have been various revisions of this scheme^{13,14}, to include such things as isotopic effects and discovery of new band systems. The theory that was outlined by Asundi and Parti¹⁰ was based around seven such band systems which make up most of the band structure of the emission spectrum.

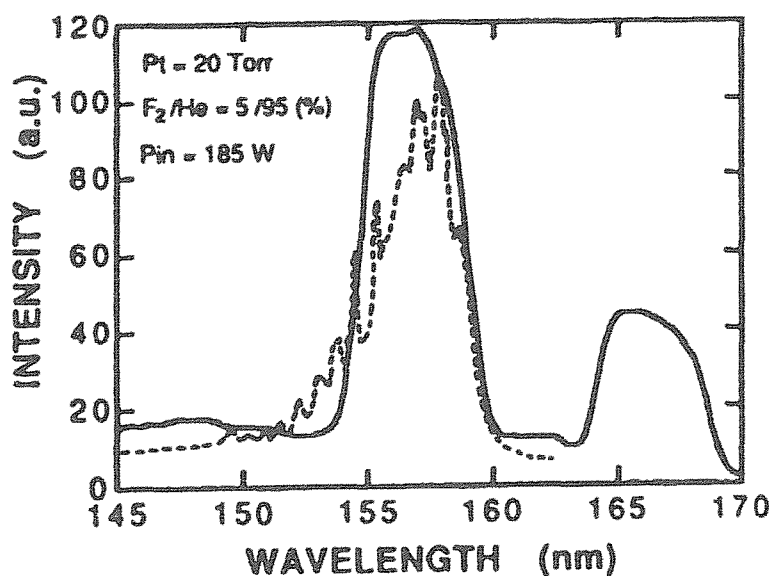
1.6.6 Boron

The emission of boron may be of use as it is a well known emission and boron may be easily placed in a bulb in the form of gaseous BH_3 . The emission spectrum of boron has been well documented¹⁵ as spark spectra recorded on photographic film over a period of several hours. Crookes¹⁵ stated that boron has three major lines that appear at 345 nm, 249 nm and 249 nm. The values obtained by Crookes compared favourably to previous results of other researchers, if to a higher degree of accuracy.

1.6.7 Fluorine

A vacuum ultraviolet bulb was developed due to the lack of an efficient bulb that emits in this region¹⁶. Fluorine was used in this bulb and two bands were observed, one at 155 nm and one at 166 nm, the 155 nm line being 5 nm wide. The spectrum is shown in figure 7.

Figure 7: Emission spectrum of Fluorine lamp¹⁶



The dashed line shows a comparison to a fluorine laser, demonstrating that the 166 nm line has not been observed before. The composition of the lamp was 1 Torr F_2 and 19 Torr He. The bulb was excited by microwave radiation at 185 W.¹⁶

During the literature research it became apparent that phosphors have the ability to change an emission to another wavelength. As this would be useful to the research the possibilities were explored.

1.7 Phosphor chemistry

1.7.1 Definition of a phosphor

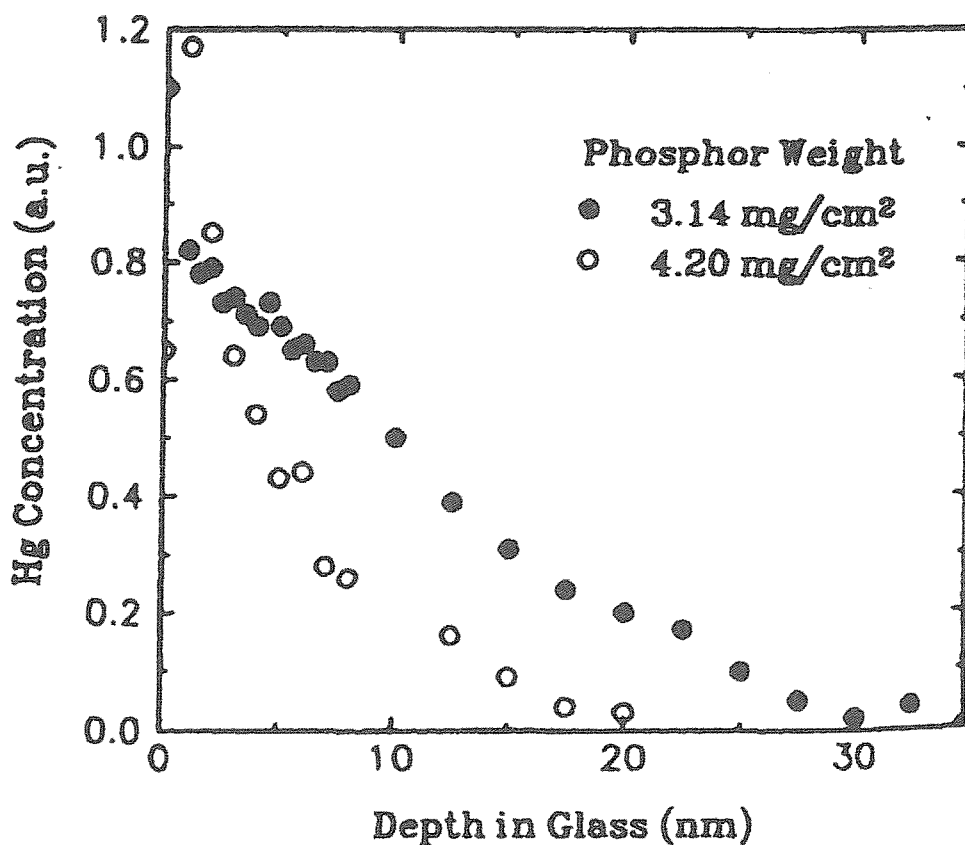
A phosphor is defined as an inorganic material which luminesces. In materials in which the luminescence depends on impurities or defects in structure the imperfections responsible for the spectral output are termed as activators. Other imperfections are termed as coactivators if they are essential to luminescence but have no or little effect upon the spectral distribution of the emission.¹⁷

1.7.2 Effect of phosphor on mercury consumption

Phosphors also slow the rate at which mercury is consumed by glass. Figure 8 shows a graph which shows this to be true, as the sample with more phosphor has less mercury.

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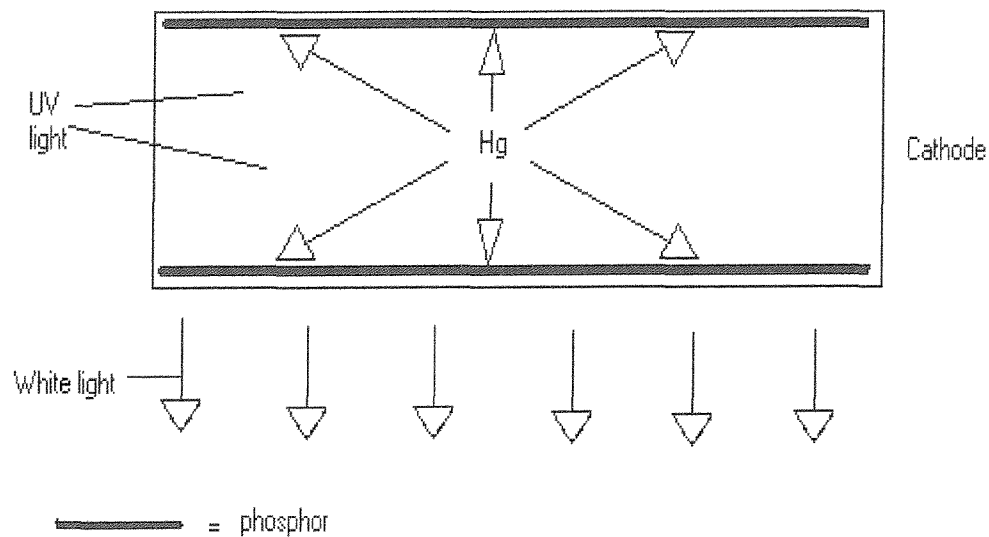
Figure 8: Mercury concentration in glass vs. depth¹⁸



1.7.3 Reason for interest in phosphors

The interest in phosphors for this project has come from the fact that phosphors may absorb ultra-violet radiation and then emit visible light. This is the manner in which household fluorescent lighting operates. The household fluorescent lighting tube has some problems in that it has several distinct bands that are not as bright as others and the short life span of the bulb due to corrosion of the electrodes¹. In these fluorescent tubes a mixture of lanthanides (Eu^{3+} , Ce^{3+} and Eu^{2+}) combine their emission to give a white light¹⁹. Figure 9 shows a schematic of an electronically excited fluorescent lamp.

Figure 9: Schematic of a fluorescent lighting tube¹⁹



1.7.4 Lanthanide chemistry

Lanthanides need a host crystal structure, such as BaFCl, doped with the lanthanide and sometimes also a sensitiser.¹⁹ The colour that is emitted from a lanthanide ion depends upon the number of f-electrons. Table 2 shows the f-configuration and the likely colour that is obtained in from absorption spectroscopy.²⁰

Table 2: Colours obtained from f-configurations²⁰

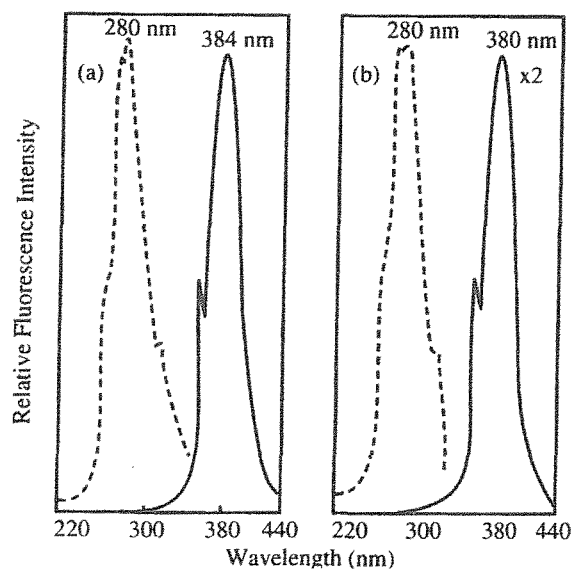
f-electrons	colour	f-electrons
0	colourless	14
1	colourless	13
2	green	12
3	red	11
4	pink	10
5	yellow	9
6	pink	8
7	colourless	7

The colours that would be obtained from emissions would be at lower energy light e.g. the green would be seen as a blue or possibly a red light. As can be seen from table 2 after the number of f-electrons reaches seven then the colours repeat in reverse order.

If certain types of phosphor with specific emission were then used with the electrodeless discharge bulbs, fine-tuning of the wavelength would become possible; the correct phosphor need only be selected.

The phosphors may either be synthesised or bought. The synthesis of a phosphor requires the reacting of specific quantities of inorganic material at high temperatures; for example in the production of BaFCl:Eu^{2+} appropriate quantities of BaF_2 , BaCl_2 and EuF_3 were reacted together at about $700\text{ }^\circ\text{C}$ for an hour²¹. Figure 10 shows spectra from the emission of these phosphors, with the photoluminescence shown in the solid line and the excitation studies in a dotted line. The matrix in which the Eu^{2+} is located balances the charge.

Figure 10: Fluorescence spectra of BaFCl:Eu^{2+} ²¹.



A

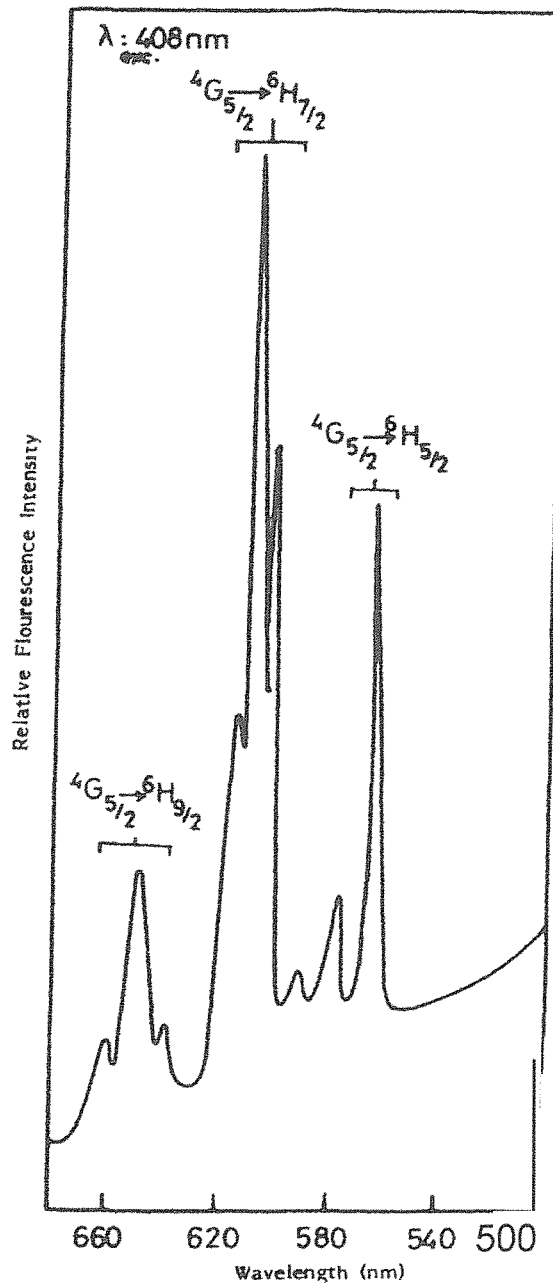
B

The spectrum A is of a phosphor produced under reducing conditions, whereas B is of a phosphor produced under neutral conditions. The phosphor B shows twice the intensity of phosphor A, at the 380 nm line produced by photoluminescence.

Phosphors doped with Sm^{3+} have been produced in a similar manner; these phosphors have an emission in the region of 500-680 nm.²²

This is shown in figure 11.

Figure 11: Photoluminescence spectrum of LaOCl: Sm^{3+} .



Few papers have been written on the subject of synthesis of phosphors however there is also the practical problem of attaching the phosphors to the tube of an electrodeless discharge bulb. It would seem best at the moment to consider the purchase of a pre-made phosphor tube.

1.7.5 Commercially available phosphors

The company Photek has a wide range of phosphors in stock and these can be bought in, as they are needed (in a tube). Table 3 below shows a range of phosphors that can be purchased from Photek²³.

Table 3: Phosphors available from Photek²³

Type	Colour	Peak emission (nm)	Persistence Decay to 10%	Efficiency Lumens/Watt	Efficiency W/W
P11	Blue	446	50 ms	10	15
P20	Yellow/Green	540	50µs-10 ms	30	13.5
P43	Green	548	1.2 ms	60	25
P46	Yellow/Green	530	160 ns	7	2.5
P47	Blue	410	80 ns	2.3	3.2

1.7.6 Thin film phosphors

Phosphors may also be made in the form of thin films. These films may be formed through vacuum deposition. In this method a vacuum is established in a working chamber containing source material and a substrate, energy is applied to the source material for vaporisation, and condensation occurs on the substrate (sides of a tube) until the desired thickness is achieved. Table 4 shows some of the emission peaks available, the values quoted arise from cathodoluminescent data.²⁴

Table 4: Emission peaks for some thin films²⁴

Compound	Measured emission (nm)
ZnS (5%Mn), fired	585
ZnS, unfired	590
CaF ₂ (pure)	425
CaF ₂ (5% Mn)	490
CaF ₂ (10% Mn)	500
Alpha Zn ₂ (PO ₃) ₃ (3% Mn)	640
Beta Zn ₂ (PO ₄) ₄ (3% Mn)	545
CaWO ₄ (W)	430
ZnSiO ₄	525

Chapter 2

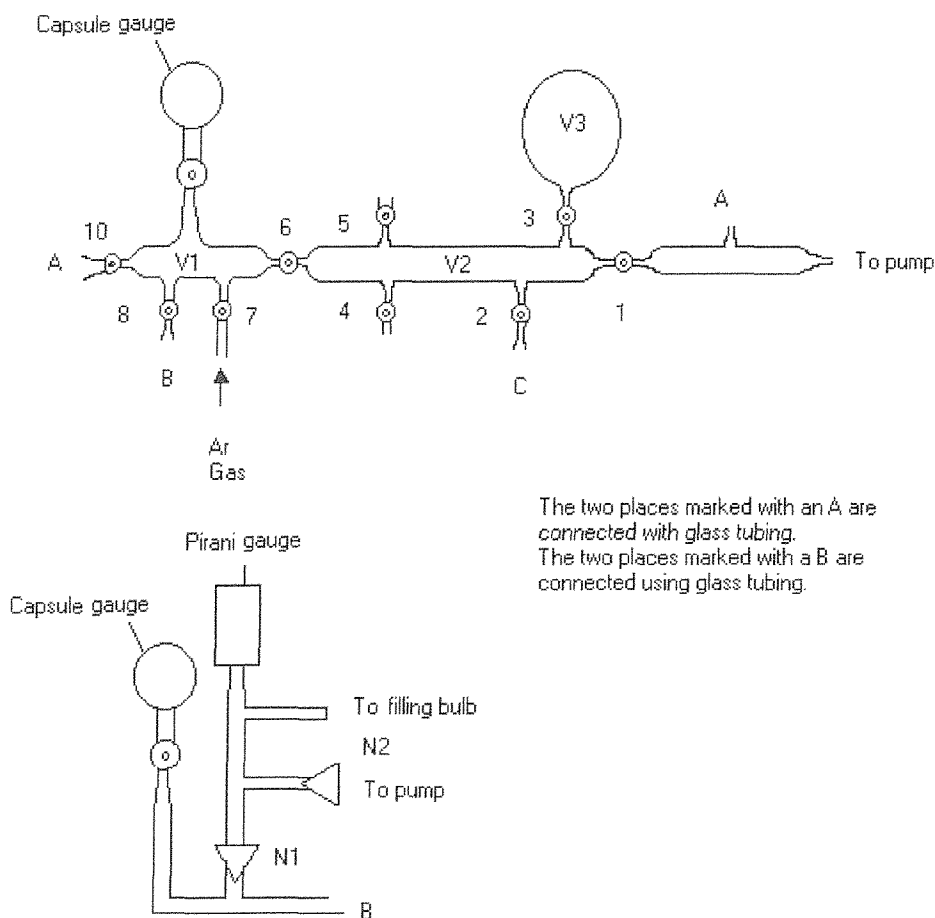
Experimental

Experimental

2.1 General procedure

The apparatus that was used for experimentation was the high quality vacuum line that is shown as a diagram below.

Figure 12: Diagram of vacuum line



The valves are numbered one to ten with needle valves labelled N1 and N2.

In preparation the vacuum line was evacuated totally and checked for leaks by monitoring for increases in pressure by the capsule and pirani gauges. As the bulb is prepared with the element being studied gas was then admitted to the vacuum line. When the gas in question was argon, valves 1, 2, 3, 4, 5, 6 and 10 are closed. When another gas was admitted *via* point C the valves 1, 3, 4, 5, and 10 were closed. This meant that gas was in the system up until the needle valve N1.

The pressure in the bulb could then be altered as desired using N1 to admit more gas and N2 to remove it.

2.2 Experiments carried out on the vacuum line

2.2.1 Mercury/argon testing of the vacuum line

The vacuum line was tested first using a familiar system. The bulb to be used was a silica bulb which had been prepared with a small amount of mercury. The bulb was filled with various pressures of argon and the spectra taken. The intensity of the 254 nm line was used to analyse the spectra taken, the aim of the experiment being to find the optimum amount of argon for the highest spectral output.

2.2.2 Sulfur/argon bulb

A small amount of sulfur was added to a Pyrex bulb. As a Pyrex bulb was used no spectra were obtained due to the limited range of the Solascope spectrometer. A discharge occurred as an intense blue light, the discharge was not stable.

2.2.3 Sulfur dioxide bulb

A clean Pyrex bulb was utilised for the experiment, as the aim was to get a small known amount of sulfur in the bulb *via* the breakup of sulfur dioxide. Unfortunately no discharge occurred.

2.2.4 H₂S bulb

The aim of this experiment was the same as the last, to provide a small amount of sulfur within the bulb *via* decomposition of H₂S. No discharge was observed.

2.2.5 H₂S/Ar bulb

When H₂S failed to work by itself argon was added to the mixture. This was achieved by treating V1 and V2 as a single volume and making a rough mixture of argon and H₂S. It was found that only a small amount of argon was required to make a sulfur discharge possible.

2.2.6 Selenium dioxide/argon bulb

Selenium dioxide was used as a way to handle the selenium for the bulb in a safer manner. The selenium dioxide decomposed nicely to give selenium in two of its allotropic forms, grey and red. Red selenium seems to emit under argon in a purple colour. Grey selenium does not emit.

2.2.7 On going experiment

The sulfur and selenium systems both showed a tendency to “flash” on and off. As the effect was believed to be heat related, cooling in the form of oxygen being passed over the bulb was applied.

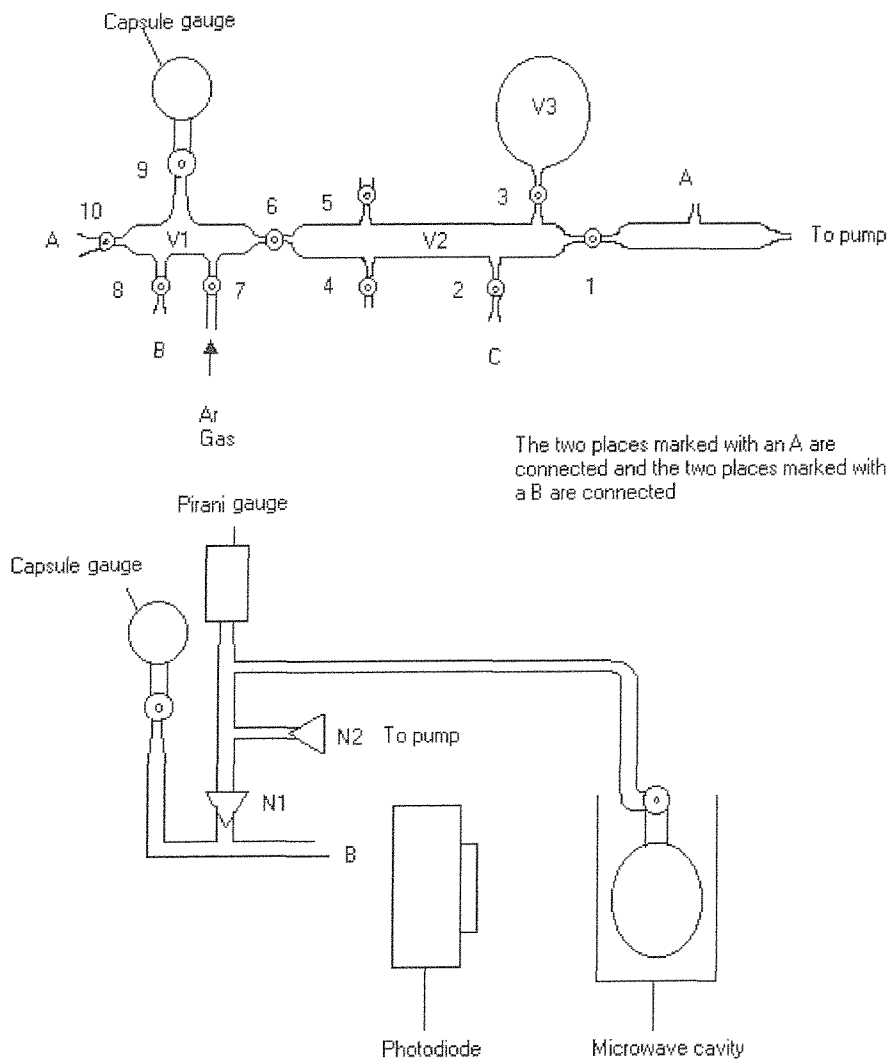
2.3 Photo-diode experiments

2.3.1 Mercury/argon bulb test

The photo-diode was used to collect the total light that was emitted from the electrodeless discharge bulbs. It was used in conjunction with the vacuum line configuration that enables the pressure of gas to be altered in a bulb that is discharging.

The photo-diode was first tested using the mercury and argon bulbs. A small amount of mercury was used to prime the bulb and then the bulb was attached to the vacuum line as shown below in figure 13.

Figure 13: Vacuum line set up for the testing of the photo-diode



The advantage of this vacuum line arrangement as previously stated is that the pressure of the gas, in this case argon, may be changed whilst the discharge is running. The pressure was changed with needle valve 1 (N1), which increased the pressure of argon in the bulb and needle valve 2 (N2), which removed argon from the system. The results were recorded on the plotter. The experiment carried out was to let the pressure of gas increase at a steady rate and observe the discharge with the photo-diode.

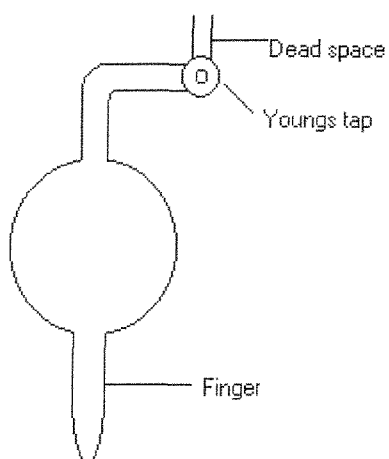
2.3.2 H₂S

Light output readings from the H₂S/Ar bulb were then taken using the photo-diode. The apparatus was as shown in figure 13, with a clean Pyrex tube that was used for the bulb, and the pressure altered as for the mercury/argon bulb. In the end it was found that the bulb had to be sealed to get good results, with less “noise”. Different mixtures of argon and H₂S were also used in an attempt to make a better mixture of gases. As no cylinder of H₂S was available the H₂S had to be collected and purified.

2.3.3 Purification of H₂S

The H₂S was collected in an evacuated bulb as shown in figure 2.

Figure 14: Bulb used for H₂S collection



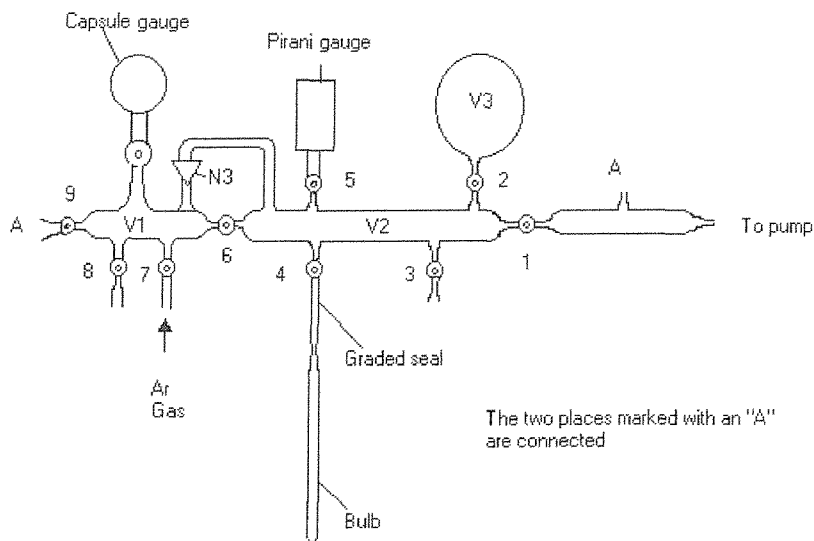
The bulb was connected to the vacuum line and the dead space evacuated. The finger on the bottom of the bulb was then placed in a dewar of liquid nitrogen and left until the H₂S had frozen. The tap on the bulb was then opened and any air inside the bulb pumped out. The tap was then closed and the bulb allowed to warm to room temperature.

2.4 Production of silica electrodeless discharge bulbs

2.4.1 First silica H₂S/Ar bulb

The optimisation of H₂S/Ar mixture for the production of silica bulbs has been the aim of the previous experiments. From the previous experiments the pressure of H₂S/Ar mixture was known. A quartz bulb with a graded seal was attached to the vacuum line as shown below in figure 15.

Figure 15: Diagram of the vacuum line when filling the bulb



The bulb was filled to a pressure of 0.6 mbar of the H₂S/Ar mixture which is a ratio of H₂S:Ar 30:1.

The procedure for filling the bulb is as follows:

- 1) Evacuate the entire system.
- 2) Close the tap 4.
- 3) Make up the mixture of H₂S/Ar by treating the V1 and V2 as one vessel, filling the vacuum line up to a pressure of 0.6 bar on the capsule gauge. Argon is then added to increase the pressure by 0.02 bar.
- 4) Tap 6 is then closed and V2 was pumped out (the diffusion pump must be off for this step).
- 5) When V2 is evacuated tap 4 is opened and needle valve N3 is used to fill V2 and the bulb to the pressure of 0.6 mbar, using the Pirani gauge to monitor the pressure.
- 6) The bulb is then sealed off.

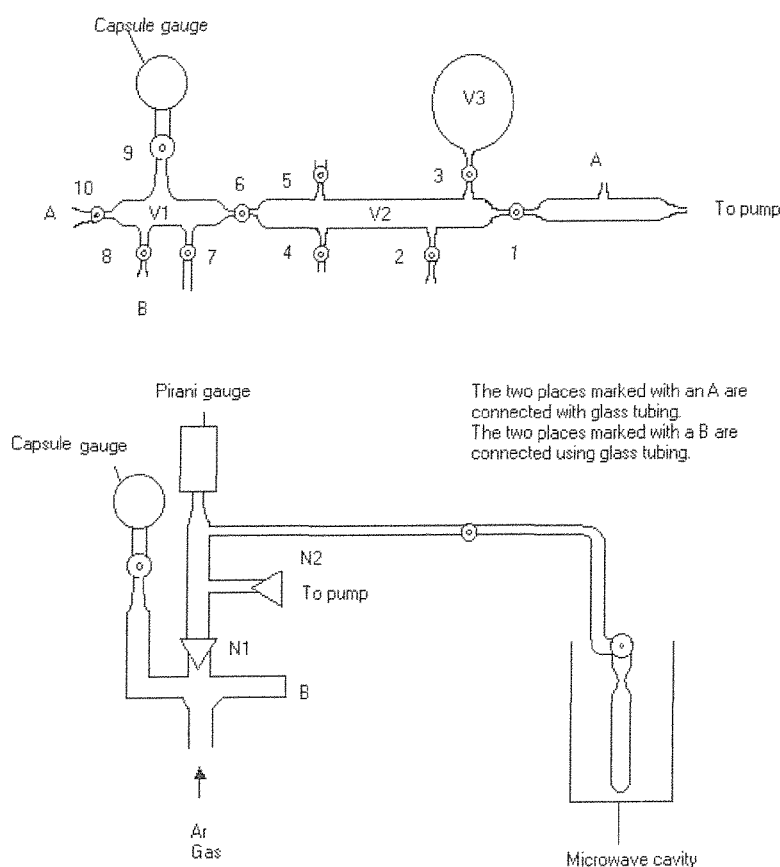
2.4.2 Second silica H₂S/Ar bulb

A second bulb was constructed and attached to the vacuum line. This bulb was then evacuated for a long period of time using a diffusion pump. The bulb was also heated whilst under vacuum to desorb any gases on the silica surface. The mixture of H₂S/Ar that was made contained a slightly higher partial pressure of argon (0.06 bar), as this should allow easier striking. As before the bulb was filled with a pressure of 0.6 mbar of the H₂S/Ar mixture by using N3 and the procedure as set out above. The bulb was then sealed off from the vacuum line and tested in the microwave oven.

2.4.3 Production of the third H₂S/Ar bulb

The mixture of H₂S and argon (0.6 bar H₂S, 0.06 bar Argon) as used previously for the unsuccessful bulbs was used in the production of this bulb. The vacuum line was set up as shown below.

Figure 16: Diagram of the vacuum line

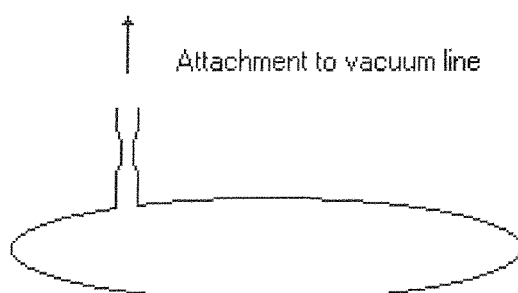


After the bulb had been thoroughly evacuated the mixture was admitted into the bulb via the needle valve N1 to a pressure of 0.5 mbar. The microwave cavity was then used to check that discharge would occur, after this had been verified the bulb was sealed off.

2.4.4 Production of the fourth H₂S/Ar bulb

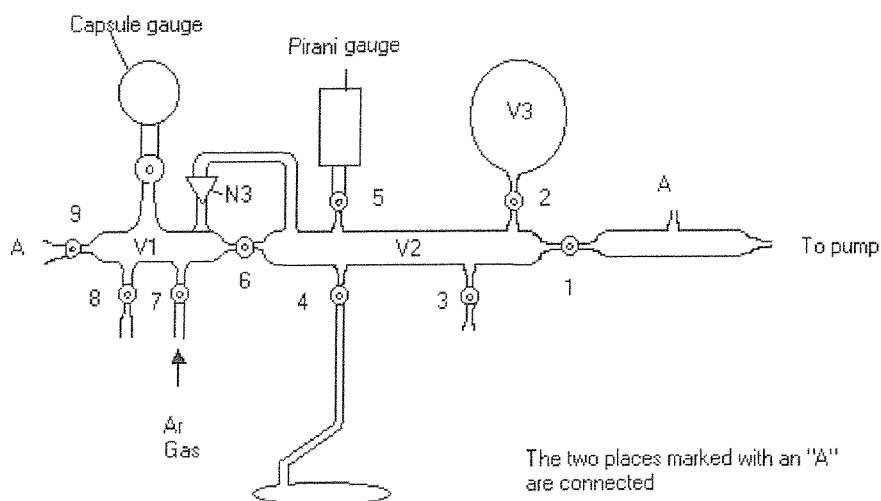
In the production of the fourth sulfur bulb the H₂S was purified more than once with the method outlined in 2.3.3. As little radiation is emitted in the UV region the bulb was made of Pyrex, to reduce cost and was of a new design shown below.

Figure 17: Diagram of new bulb design



The bulb was connected to the vacuum line as shown below:

Figure 18: Diagram of the vacuum line



The bulb was thoroughly evacuated and filled, using needle valve N3 to a pressure of 0.5 mbar with the argon and H₂S mixture. The bulb was then sealed off.

2.5 Recording of the spectra

The emission of the bulbs was recorded on an atomic absorption spectrometer, provided by Dr. Howard.

Accurate peak recording was hampered by the need for the blacked out fume cupboard. The procedure used to record the spectrum takes this in to account.

- 1) With the bulb in the microwave cavity a spectrum is recorded (with the fume cupboard closed) over a large number of wavelengths using a fast scanning speed (100 nm per second), this gives an idea where the peak positions are.
- 2) The wavelength is set to a value below the area with peak intensity.
- 3) The spectrometer is then started at the same time as the spectrum plotter and the starting value noted.
- 4) The fume cupboard is then closed and the discharge started
- 5) The spectrum is recorded at a slower scanning speed (4 - 10 nm per second).
- 6) When the spectrum has been recorded the discharge is stopped, the fume cupboard opened and the final wavelength is noted and the plotter stopped.
- 7) The peak position is then found by using the scale as set out by the final and initial values of the spectrum.

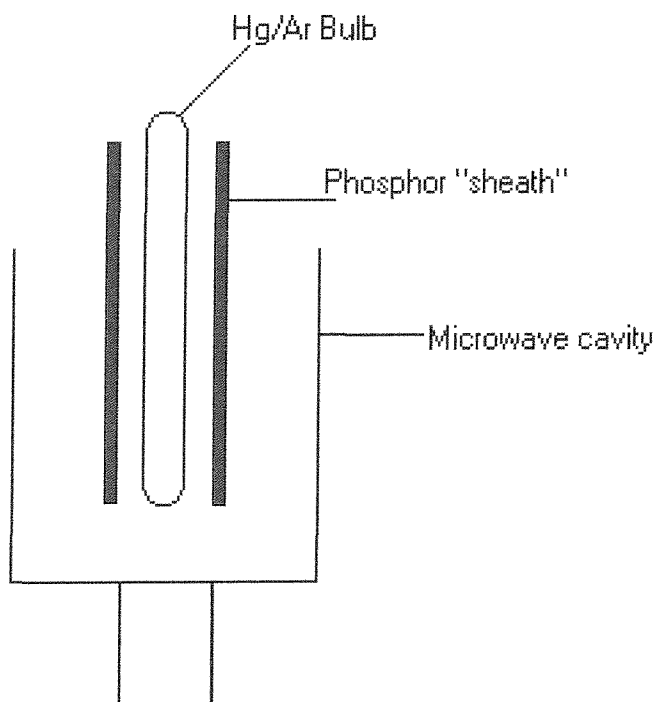
The spectra of the third and fourth H₂S/Ar bulbs have been taken as well as the spectrum of a typical mercury bulb.

An investigation of spectral intensity vs power output has also been made using this spectrometer.

2.6 Phosphor sheath

A phosphor sheath surrounded an ordinary mercury/argon electrodeless discharge bulb. This sheath was created by taking a fluorescent tube which was no longer working and taking a 10 cm section from it by a hot spotting technique. This sheath was placed around the electrodeless discharge bulb as shown in figure 19.

Figure 19: Diagram of the phosphor sheath



Chapter 3

Results and discussion on sulfur

Results and discussion on sulfur

3.1 Sulfur/Argon bulbs

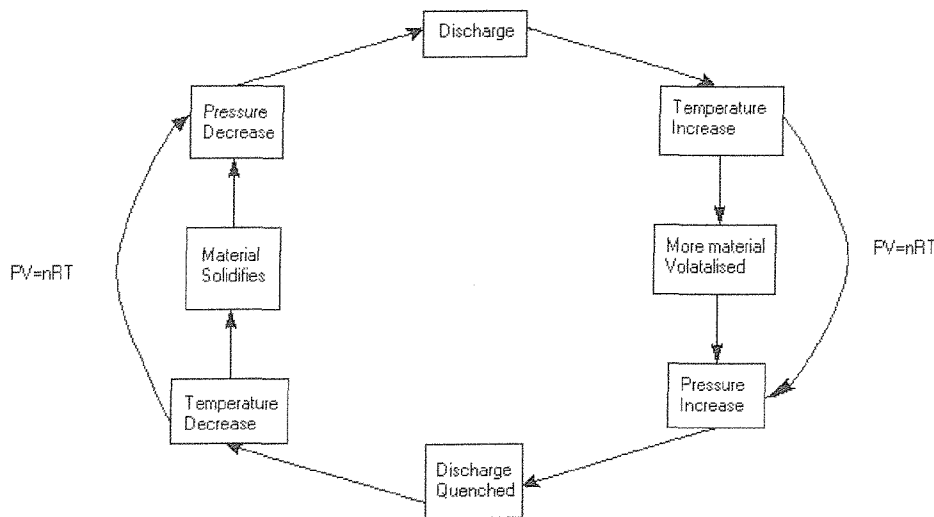
3.1.1 Sulfur/Argon bulb

The sulfur bulb was constructed using a small amount of solid sulfur in the Pyrex tube shown earlier. The pressures of argon that produced a discharge varied from 0.4 mbar to 1 mbar at 70% power. However the discharge was not stable. The sulfur argon bulb showed a tendency to flash on and off.

3.1.2 Why does this “Flashing” occur?

Experiments that cooled the bulb by passing a flow of pure oxygen showed that the cooling did improve the bulb’s stability and the flashing must be related to temperature. From experimental observation it is also known that an excess of pressure may quench a discharge. From these observations a theory as to why this flashing occurs was formulated and is shown diagrammatically in figure 20.

Figure 20: Flow chart of cyclic flashing



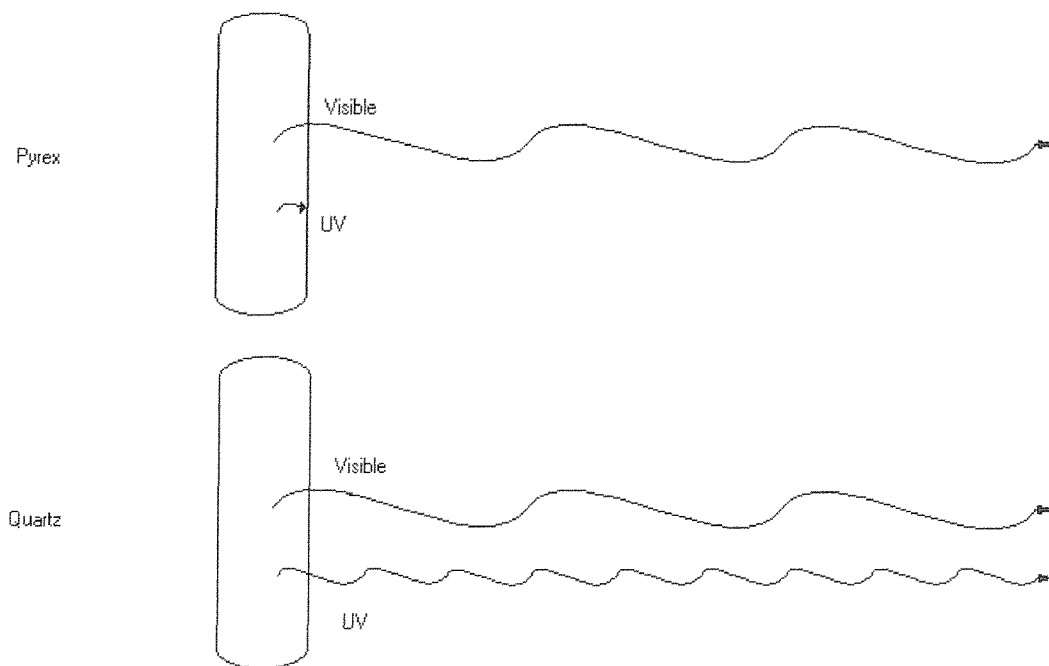
When the discharge is on, as shown at the top of the diagram, a rise in temperature occurs. This in turn leads to a rise in pressure, both directly, as $PV=nRT$, and by making more sulfur or selenium vapour. As stated above after a certain pressure the discharge is quenched and this is what happens. Now that the discharge has been quenched the temperature drops and then the pressure will also drop, which means that the discharge may start again.

As the real problem with the cyclic quenching of discharge is the abnormal rise in pressure, there are two practical solutions to them.

1) Use less material in the bulbs. This measure means that there will be less material to volatilise and therefore not such a dramatic increase in pressure. This is the reasoning behind the use of H_2S .

2) The use of silica as the construction material of the bulbs. This measure is due to the fact that Pyrex absorbs UV radiation, as is shown below in figure 21.

Figure 21: Absorption of UV by Pyrex



As Pyrex absorbs the UV light, the energy must go somewhere. A likely sink for this energy would be as heat. This would provide extra heating to the bulb and hence an extra increase in pressure that the quartz or silica bulb would not experience because quartz does not absorb UV radiation.

3.2 H₂S/Ar bulb testing

The H₂S bulb showed an increased stability with regard to the sulfur bulb. The testing of the H₂S/Ar bulb showed that a stable discharge was possible between 0.6 mbar and 0.8 mbar.

The photo-diode provided us with the information that the greatest light output was at the lower pressures of gas mixture.

Addition of increasing the amount of argon in the H₂S/Ar mixture showed that higher partial pressures of argon induces an easier strike, at lower pressures of gas mixture in the test bulb, but less intense colouration, until at a mixture of 1:1 H₂S:Ar no colour is evident.

However the discharge was not a homogeneous colour, the blue of the sulfur discharge seemed to be contaminated with a pink discharge. At first this was assumed to be an air leak in the system. After an extensive check this possibility was discounted as no significant leaks were discovered. The H₂S had been purified before use and it is standard practice to purge the argon line before use, so air is not a likely contaminant.

A likely possibility is that the H₂S decomposes under the conditions of discharge into sulfur and hydrogen. The sulfur would produce the blue colour and the hydrogen the pink. As the H₂S bulb is stable it was decided to make a bulb in silica so that the spectrum could be taken. The spectrum that would likely be exhibited is the sulfur spectra with hydrogen lines also present.

3.3 H₂S sealed bulbs

3.3.1 First silica H₂S/Ar bulb

The bulb did not strike by itself, but in the presence of a mercury argon bulb then discharge occurred. The discharge was not stable and showed bright red flashes not previously observed in the test bulb. The bulb had not been purged of surface adsorptates and this was a possible reason for the instability of the bulb.

3.3.2 Second silica H₂S/Ar bulb

This bulb was evacuated by a diffusion pump and heated to remove surface adsorptates. The bulb also discharged with assistance from a mercury argon bulb, but was no more stable.

3.3.3 Why are the bulbs unstable?

The bulbs that have been sealed are not stable. The repeat bulb production shows that the adsorbed molecules on the surface of the silica are not to blame as no significant increase in stability occurred in the second bulb.

There are two possible reasons why these bulbs did not have a stable discharge:

- 1) The volume of the bulb was less than that of the test bulb and the discharge occurs more readily with a larger volume.
- 2) The filling of the bulb was inaccurate. The portion of the vacuum line used for the testing of the bulbs has less volume than that of V2. Therefore V2 is less sensitive to changes in pressure than the test area.

If these reasons are correct then the filling procedure needs to be changed and the design of bulbs also needs to be altered.

3.3.4 Stability and discharge characteristics of the third and fourth H₂S/Ar bulbs

The sulfur bulbs produced a stable discharge when placed within the microwave cavity. The discharge was predominately blue in colour, with a pink tinge. The third bulb seemed to have a greater amount of the pink colouration than the fourth bulb. This could be the result of the fourth bulb having more rigorously purified H₂S than the gas placed in the first bulb. The implication of this would be that the pink colour observed is in fact an impurity that is not completely removed in the first purification of the H₂S.

The sulfur bulb gets hot very quickly and this will lead to an increase in pressure inside the bulb. As stated earlier a high pressure leads to a quenching of the discharge. This does occur in the sulfur bulbs produced, a flicker in the discharge can be observed after the bulb has been operating for a time (typically 1-2 hours, depending upon the efficiency of the cooling).

3.3.5 Spectra of the sulfur bulbs

The spectra were recorded on the atomic absorption spectrometer. The results are shown in Appendix 2, and have been compared to a spectrum recorded by Gibson and Lawler²⁵.

The comparison of the spectra shows that the fourth sulfur bulb matches the emission of sulfur as stated by the literature²⁵. The third sulfur bulb has many peaks which are missing when compared to the literature. This is fairly indicative that the third sulfur bulb contains impurities that have altered the spectrum. This can be concluded as the only differences between this bulb and this fourth bulb are the shape of the bulb and the purity of the H₂S. It is likely that side products are absorbing parts of the sulfur spectrum as the most likely contaminant is air, which absorbs energy at lower wavelengths than are being investigated here. It is unclear however whether the impurities or the side products that are formed within the conditions of discharge produce the extra peaks that may be observed in the spectrum of the third bulb. The spectra are shown below in figures 22, 23 and 24.

Figure 22: Literature emission spectrum of sulfur²⁵

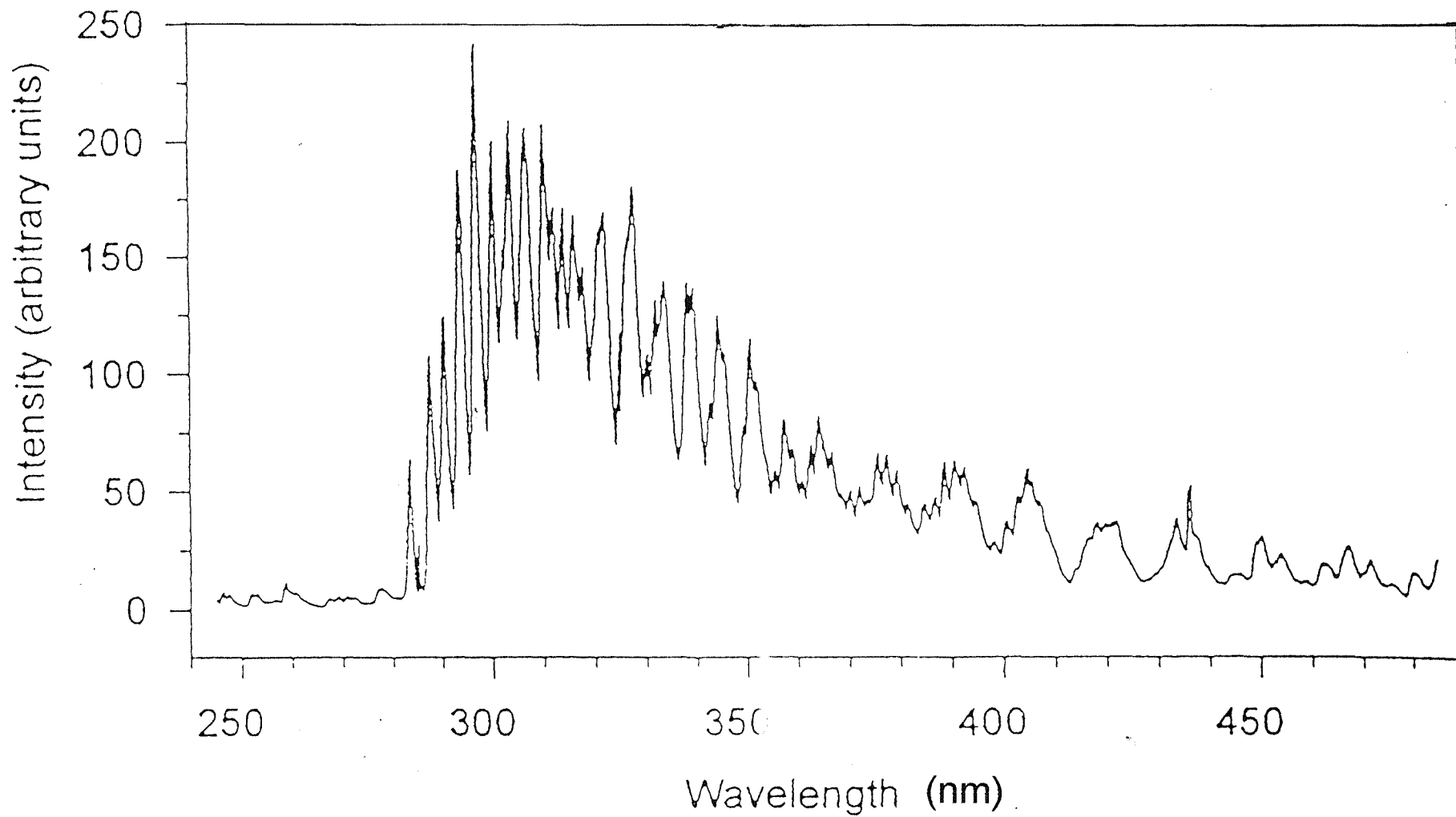


Figure 23: Emission spectrum of the third H₂S/Ar bulb

* = Peak attributed to impurity
= Peak attributed to sulfur below the Pyrex absorption point

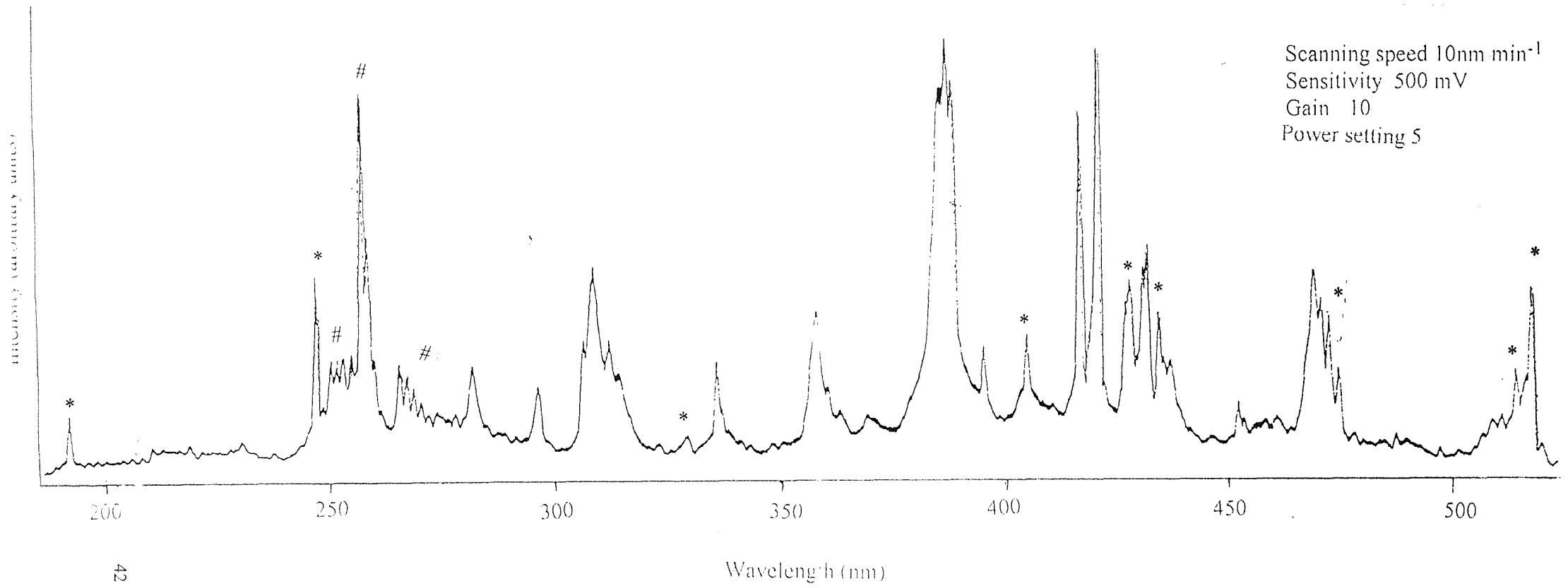
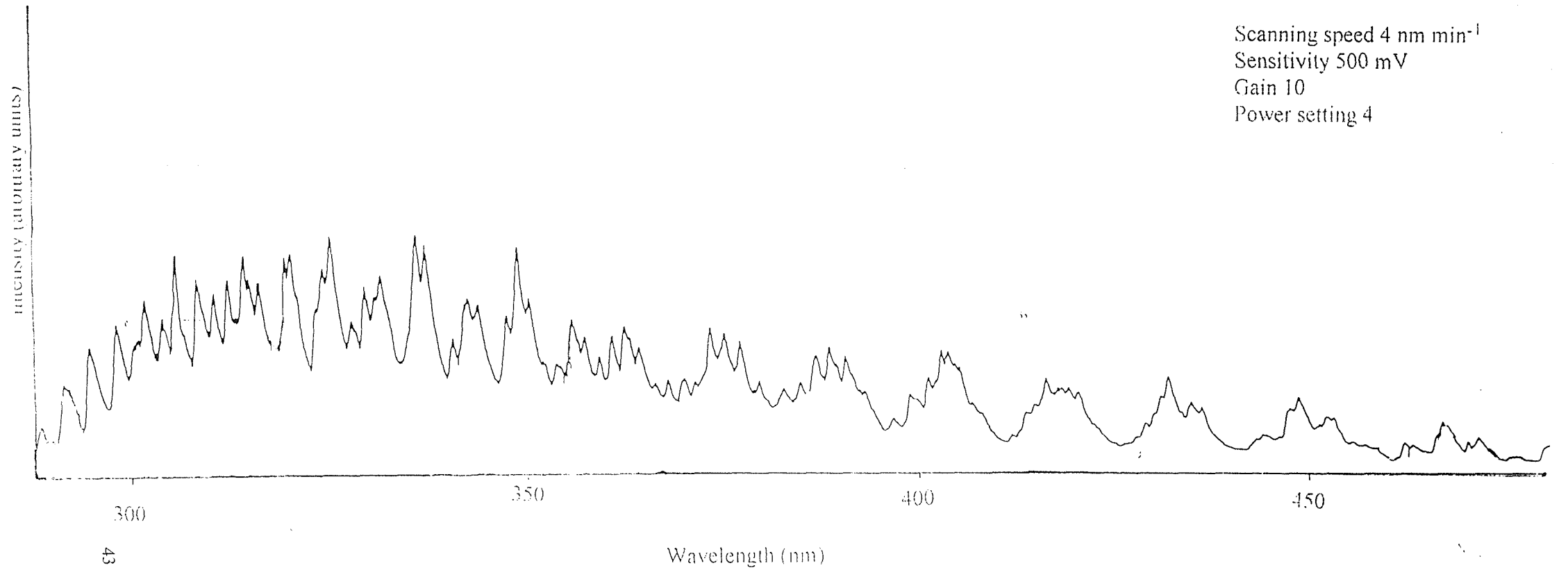


Figure 24: Emission spectrum of the fourth H₂S/Ar bulb



3.4 Investigation of power input Vs spectral intensity

The spectra of the fourth sulfur bulb were recorded on different power settings on the microwave generator in order to see the difference between them. The spectra are shown below in figures 25 and 26.

Figure 25: Power setting 3

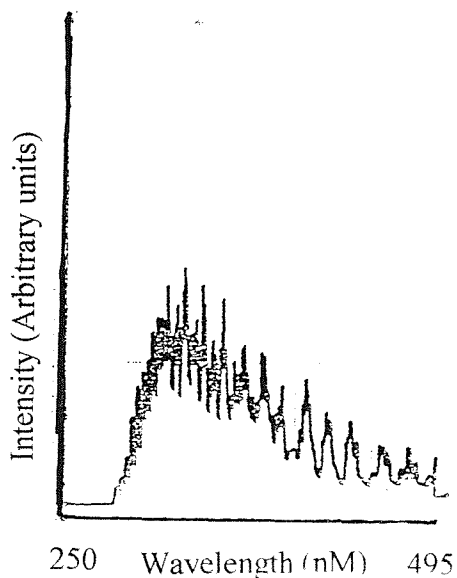
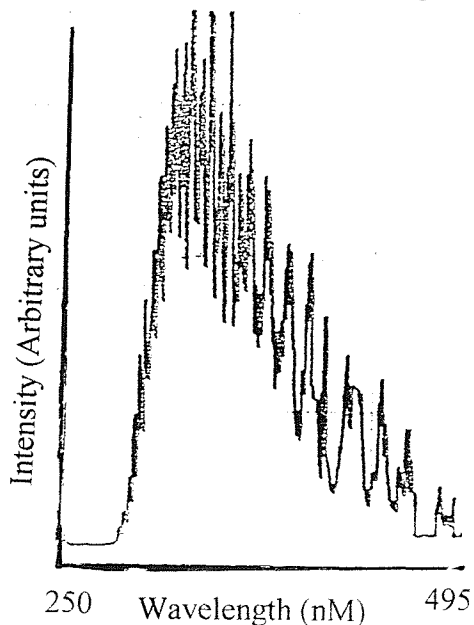


Figure 26: Power setting 4



Spectra recorded at 40 nm min^{-1} and a sensitivity of 500 mV

The spectra were recorded under identical conditions and hence can be compared. It can be seen that the increase of one power setting on the microwave generator has had the effect of more than doubling the spectral intensity. Further studies at higher power settings would have been made but too much flickering occurred at power level 5.

3.6 Conclusions about the H₂S/Ar bulb

In conclusion it is possible to say that using a mixture of the gases H₂S and argon has made a stable sulfur bulb. The discharge is blue in colouration to the naked eye and has a UV/visible emission spectrum, which is reproducible, and that is the same as the sulfur spectrum that has been found in the literature²⁵. It has also been seen that the sulfur bulb is very sensitive to impurities such as air as the third bulb has a drastically altered spectrum with a small amount of impurity.

The intensities of the peaks are dependent upon the level of power of microwaves that is applied to the bulb, estimating an increase of twice the peak height in an increase of one power setting.

The material that the bulb is made of makes no difference in terms of stability and the spectrum shows no departure from the literature. The volume of the bulb should be large as this stops a rapid increase of pressure that led to the first and second bulbs being unstable.

Chapter 4

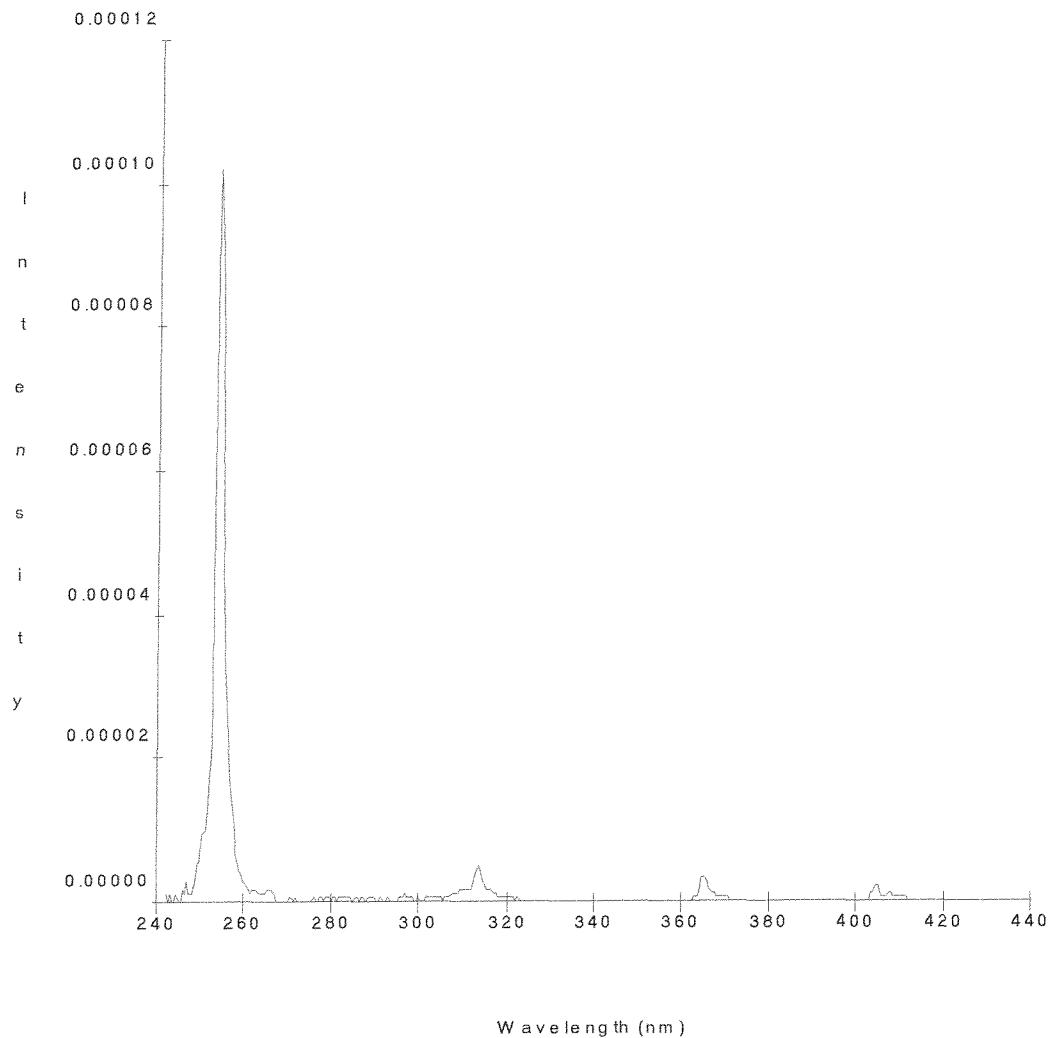
Other work

Discussion of other work

4.1 Testing of the vacuum line

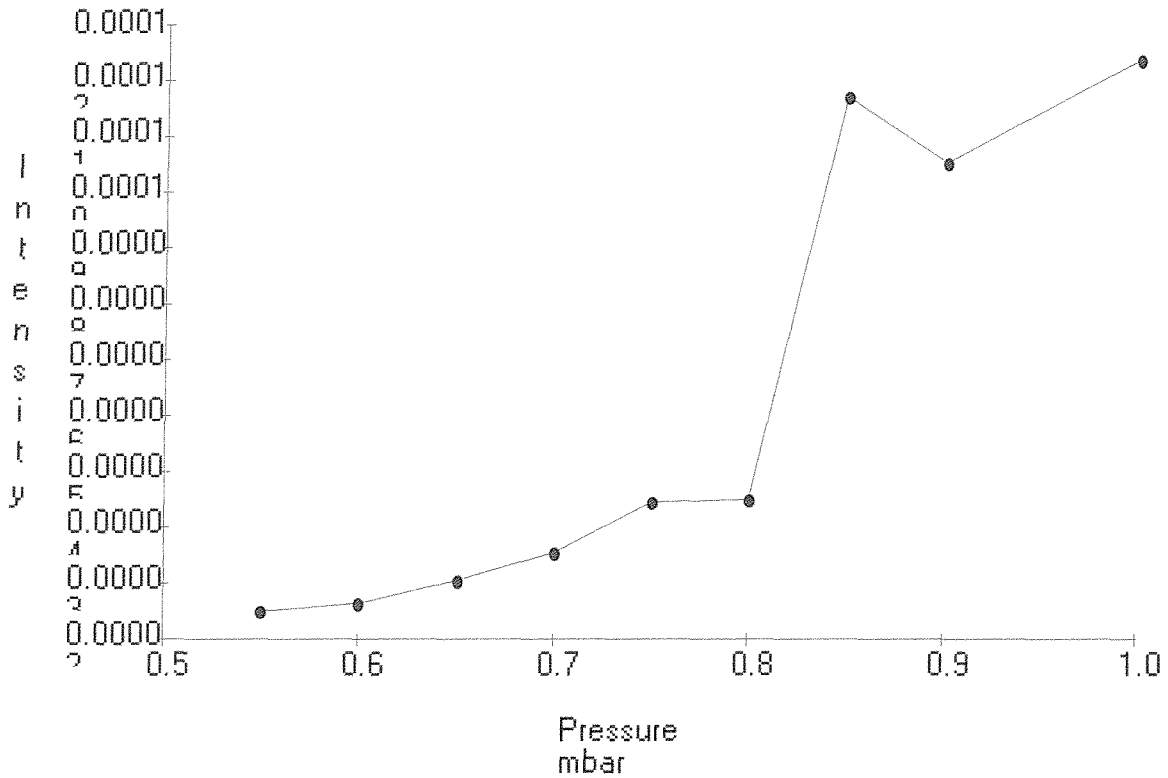
The tests that were performed using mercury and argon gave spectra that were identical to results previously obtained, shown in figure 27.

Figure 27: Sample emission spectrum of mercury and argon bulb
At 70% power



The spectra were taken at many different pressures and the intensities of the 254 nm line recorded. These intensities were made into a graph plotting the intensity of the 254 nm line Vs pressure of argon. This is shown in figure 28.

Figure 28: Graph of Intensity at 254 nm (arbitrary units) vs Pressure (mbar)
 at 70% power



The trend seems to state that higher intensities are reached at higher pressures, however from the report² that was written for Jenton International the opposite trend was noted. This can be explained simply from experimental observation. The first pressures to be recorded were the higher pressures, as the experiment proceeded mercury could be seen in the vacuum line. As the bulb is open to the system this is the source of the mercury. Therefore the heat that is generated in the discharge has caused the mercury vapour to condense further up the vacuum line, where the temperature is cooler. This means that as time goes on less and less mercury is within the discharge bulb and intensities are reduced. This has the implication that the data produced by the new way is less reliable than the procedure used in the Jenton report.

4.2 Selenium/argon bulb

The selenium and argon bulb has a rich purple discharge. The bulb is also subject to the flashing that is seen in the sulfur argon bulb. The range of pressures of argon that allow discharge are 0.6 mbar to 1.5 mbar at 73% power.

4.3 Mercury/argon testing of the photo-diode

The greatest output of light occurred with a low pressure of argon within the bulb, ca. 0.4 mbar of argon. This concurs with the report² that was prepared for Jenton International, and so proves that the photo-diode can be useful. With this information the photo-diode was then used with the H₂S/Ar bulb.

4.4 Phosphor sheath

A spectrum of the Hg/Ar bulb is shown overleaf (figure 29), as can be seen an intense signal may be seen at 254 nm with less intense features at 315, 360, and 400 nm.

The spectra that resulted from the prototype was much less intense than is ordinarily seen from the Hg/Ar bulbs and did not contain the 254 nm line, it did however contain the 315, 360, and 400 nm lines. It is also very likely that other emission bands are present, however due to the limited range of the Solascope they were not observed.

The spectrum of the prototype is also shown overleaf.

Figure 29: An emission spectrum from a Hg/Ar electrodeless discharge bulb

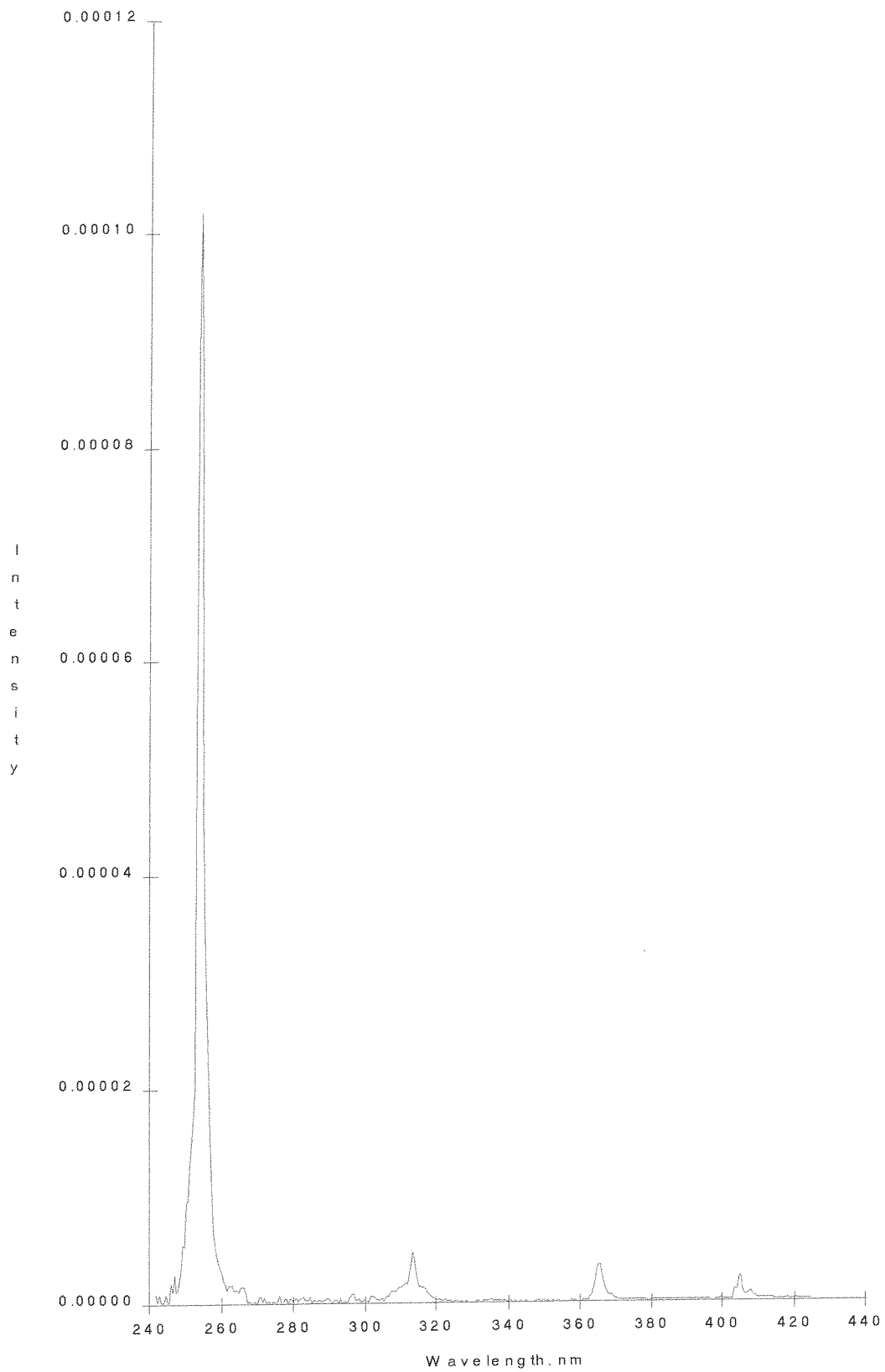
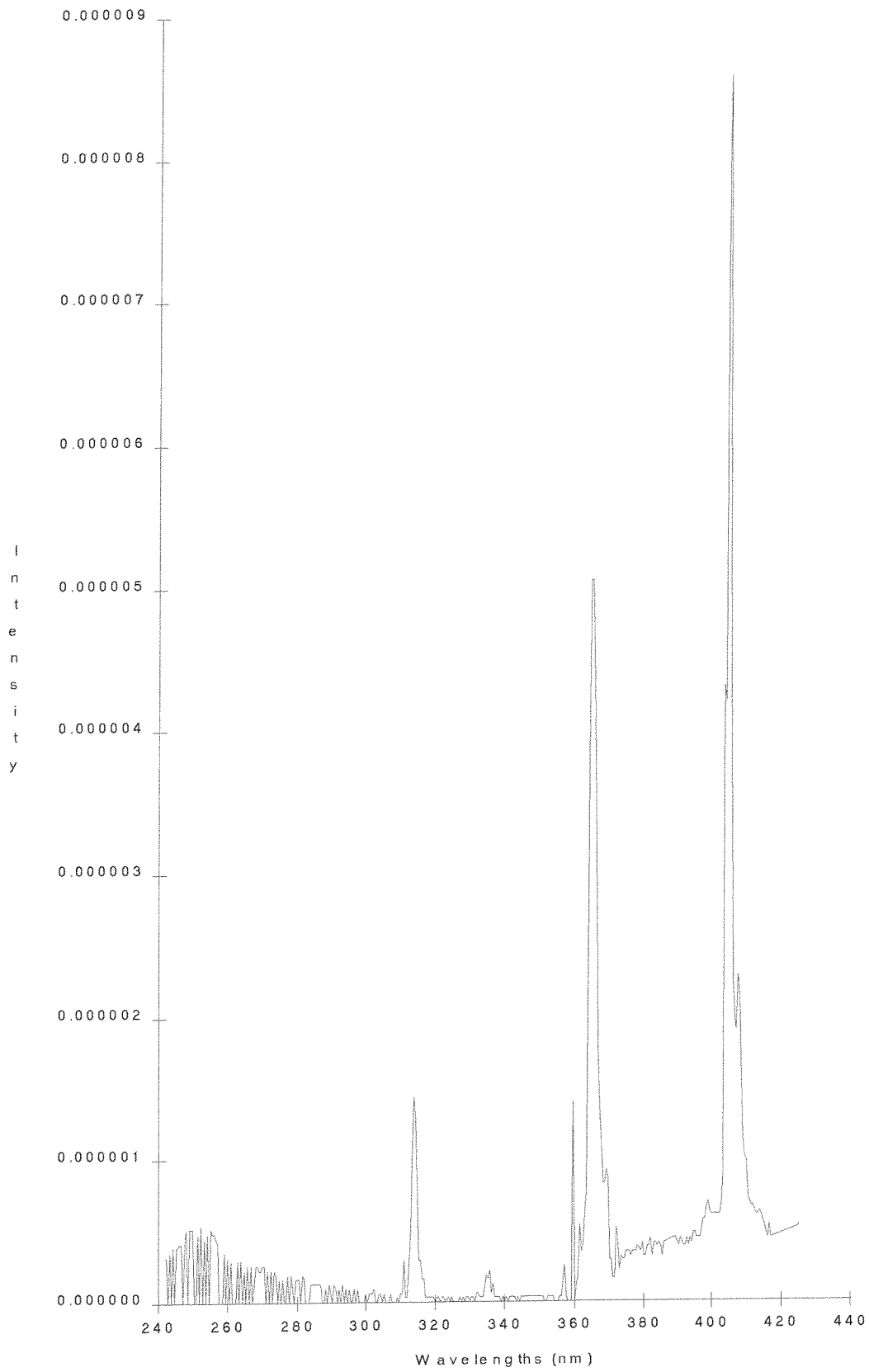


Figure 30: Emission spectrum from the sheath prototype



The phosphor sheath has completely removed the emission at 254 nm. The fact that no new bands were seen doesn't mean that they are not there, as the Solascope has a limited range and the phosphor sheath obviously performed as intended because the 254 nm line was removed. During the experiment white light was also observed coming from the electrodeless discharge bulb which, though qualitative, is further evidence of the phosphor absorbing the UV radiation and emitting visible light. The phosphor has altered the emission that is seen in figure 30 as expected.

Chapter 5

Further work

5.1 Further work

In continuation of this project other sources of microwave light sources should be investigated. The first source that should be investigated is selenium as it has shown that it has potential for microwave discharge and a similar spectrum to sulfur. Also selenium seems not to have been developed in this manner before and so makes a prime target for discharge.

Boron also would seem to be a prime target as using the mixed gas experience that was developed in the H₂S bulb a discharge bulb should be quickly stabilised.

The exploration of the excimer system could yield an appreciation of how the electrodeless discharge bulbs actually work. This can be stated as free electrons initiate excimer discharge. If a discharge were to occur with the emission spectrum of an excimer system without the presence of an electron source then it would be free electrons that would be the cause of discharge, if not then some other manner of excitation would be in action.

The application of phosphors also has not been fully explored. Phosphors do possess considerable ability to tune the output of a bulb and this should be fully looked into, by finding a system of electrodeless discharge bulb that will be compatible with a phosphor in the system.

Appendix 1

Spectrum of selenium

Table 5: Spectrum of selenium¹⁰

Int.	Wavelength nm	Int.	Wavelength nm
3	381.5	2	482.7
2	382.8	0	483.6
5	384.8	1	485.7
2	387.2	0	487.6
4	388.5	0	488.3
6	390.7	0	488.5
d3	392.1	db2	490.2
7	394.3	db0	491
1	395.9	0	491.2
8	398	0	491.8
d5	400.2	0	492.5
2	401.4	0	493.9
2	401.9	0	494.3
d2	403.2	0	494.8
4	404.1	0	496.5
3	404.9	0	497.1
2	406.4	1	499.3
2	408.2	0	499.8
2	408.8	0	500.3
2	409.3	0	501.7
4	410.3	2	502.3
4	414.8	1	502.8
4	416.8	d2	503.2

Int.	Wavelength nm	Int.	Wavelength nm
5	421.6	b1	503.7
7	425.5	b1	504.2
4	425.8	0	505.2
2	429	0	505.9
7	430.3	1	511.2
3	430.6	d2	511.4
1	438.9	d2	512.4
2	439.3	3	513.1
1	439.6	4	513.4
1	440.5	4	514.1
2	442	5	514.4
1	442.4	d1	515
2	443.8	d0	515.5
1	444.1	2	516.2
1	444.5	d2	517.3
2	446	d1	518
2	446.7	d1	518.4
1	447.8	d1	51934
d2	451.2	d1	520.5
d2	451.7	d0	501
d3	453.4	d0	521.5
0	455.6	d2	522.5
0	457.5	d2	523.4

Int.	Wavelength nm	Int.	Wavelength nm
d4	458.3	d1	523.9
4	459.1	d2	524.5
3	461	d2	525
0	461.6	d2	526.2
2	463	d3	526.6
0	463.9	d1	527.1
2	464.1	d0	528
1	465.3	d1	529.2
1	465.7	d1	530.3
0	467.3	d0	530.9
1	468.9	db2	531.8
0	471.3	d0	532.1
1	471.9	d2	532.9
1	474.7	d1	533.2
0	475	d0	533.8
0	475.4	d2	534.2
0	477.1	d2	535
0	477.6	0	535.8
3	479.4	2	538.1
0	480.3	4	538.8
d4	481.9	1	539.3
4	540	5	562.2
2	541.4	4	563.8

Int.	Wavelength nm	Int.	Wavelength nm
3	542	d3	565.3
d2	542.6	d3	566.7
d1	544.5	d2	567.4
3	545.2	d2	568.3
2	545.8	2	569.8
1	546.4	3	571.4
5	547.1	4	571.9
2	548.5	4	573
3	548.8	3	574.5
3	549.6	3	576.1
5	550.2	5	577.9
4	551.8	3	579.2
d1	553.3	0	580.8
d1	554.7	0	582.5
db2	555.9	1	583.3
d4	557.6	1	583.9
4	559.1	3	585.8
4	560.6	2	587.3

Intensity explained

The numbers associated with a particular band are firstly given a numerical value, which starts at 0 for the weakest band intensity and increases for successively stronger bands. The symbol d represents a band that is diffuse and the symbol db indicates a band that is both diffuse and broad.

Appendix 2

Table of sulfur spectra

Table 6: Comparison of literature²⁵ and experimental peak positions of sulfur spectra

Literature value of sulfur peaks (nm)	Experimental value of sulfur bulb 3 (nm)	Experimental value of sulfur bulb 4 (nm)
283	282	284
287	-	287
290	-	290
294	-	294
297	296	297
300	-	300
304	305	304
307	308	308
311	312	310
313	314	313
315	-	314
317	-	317
319	-	318
-	-	321
323	-	322
-	-	327
328	-	328
-	-	330
333	-	332
335	336	334

Literature value of sulfur peaks (nm)	Experimental value of sulfur bulb 3 (nm)	Experimental value of sulfur bulb 4 (nm)
338	-	338
340	-	339
344	-	343
346	-	344
347	-	346
350	-	350
351	-	351
352	-	353
356	-	356
358	358	358
360	361	360
362	-	361
364	-	364
365	-	366
368	-	368
371	370	370
372	-	372
376	-	375
378	379	377
380	380	379
382	381	382

Literature value of sulfur peaks (nm)	Experimental value of sulfur bulb 3 (nm)	Experimental value of sulfur bulb 4 (nm)
386	-	385
388	-	387
390	-	389
391	-	391
394	-	393
396	395	395
399	-	399
401	-	401
403	-	403
405	-	405
407	415	406
420	420	420
434	432	434
437	436	438
445	-	446
450	451	451
454	-	454
463	-	463
467	466	467
472	472	472
481	-	480

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