

A SIMPLE SPECTROSCOPIC POLLUTION ANALYZER

by

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## ABSTRACT

The problems of the monitoring of gaseous, atmospheric pollutants, and the methods currently used for this, are surveyed. An apparatus for such analysis, using an automatically scanning spectrometer, (with a photomultiplier tube) to analyze the spectrum of a gas discharge through air, is discussed. Theoretical considerations about sensitivity are given. The apparatus which has been built is discussed in detail.

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## 1. INTRODUCTION

The aim of this experiment has been to design, build, and test an apparatus suitable for the detection of common gaseous atmospheric pollutants. (The problem of the detection of particulate pollutants was not included.) This apparatus was to be compact and light, so that, unlike the equipment commonly in use today, it could be used for quick analyses in remote areas, where one person could carry it and operate it by himself. The unit was to be simple, rugged, and inexpensive to produce. Furthermore, it was to be easy to operate and have readily interpretable output, so that a technician with a minimum of training could use it.

The method finally chosen was the following. Air samples are introduced into a small electrical discharge tube, and the resultant spectrum analyzed automatically with a photomultiplier tube. The output is on a small strip chart recorder, which plots intensity against wavelength. The intensity of several characteristic spectral lines and bands is used to indicate the concentration of significant pollutants in the air.

There are several advantages to this method. First, using transistorized circuitry, a very small, rugged, battery-powered unit can be built. Second, under proper conditions, concentrations of about 0.01 ppm (parts per million) can be measured. Third, this single method can be used to identify

many different pollutants. (Many detectors currently in use require the changing of reagents if they are to monitor different substances.<sup>1</sup>) Finally, the output can be in a form (with specially marked graph paper) which is easily interpreted.

The results to date have been somewhat mixed. The construction of a scanning spectrometer has proved complicated, since relatively high resolution is needed if the lines from the pollutants are not to be completely obscured by the many, intense lines of the nitrogen spectrum. Such resolution would be simpler to attain with a long light path, but since this unit is to be small, alternatives to this had to be found. The present apparatus gives resolution of about 10 Å, which may not be sufficient.



## 2. AIR POLLUTION MONITORING TECHNOLOGY

Many methods are currently in use for the analysis of air for gaseous pollutants (See Table I). This field can be broken into two major divisions -- source monitoring and ambient air monitoring. The latter requires high sensitivity and specificity; the former needs equipment that is durable and that can function without an operator near-by. While source monitors need only check for several specific pollutants, present in high concentrations, they must be placed in a severe environment where they are exposed to extremes of temperature and acidity. Ambient air monitors are not faced with these problems, but instead, they must detect a wider range of pollutants, present in far smaller concentrations.

The main requirements for an ambient air monitor are the following. It must take samples that are representative, and detect the presence of traces in concentrations as low as several parts per billion. It should give high reliability at minimum cost, and should require little service. It should be so simple to operate that someone with a minimum of training can use it.<sup>2</sup>

The most significant gaseous pollutants are listed in Table II, along with the highest concentrations considered safe. This table also lists the strongest lines emitted by these compounds in the region of sensitivity of the experimental apparatus. The line intensities listed are on a scale of 1 to 10, and are based on a visual inspection of the lines.<sup>3</sup>

TABLE I

COMMON METHODS OF AIR POLLUTION MONITORING -- AN EVALUATION<sup>4</sup>

| Method                | Sample Size                              | Sampling Time | Sensitivity                         | Cost    |
|-----------------------|--|---------------|-------------------------------------|---------|
| <b>Wet chemical:</b>  |  |               |                                     |         |
| SO <sub>2</sub>       | 1 liter                                  | 1 hr.         | 0.01 ppm                            | \$5000  |
| H <sub>2</sub> S      | 1000                                     | 2             | 0.001                               |         |
| N oxides              | 10                                       | 1             | 0.001                               |         |
| O <sub>3</sub>        | 50                                       | 1             | 0.010                               |         |
| Halogen compounds     | 100                                      | 7             | 10 <sup>-8</sup> gm/ft <sup>3</sup> |         |
| Combination of above  |  |               |                                     | 100,000 |
| <b>Spectroscopic:</b> |  |               |                                     |         |
| Flame                 | 1 cc                                     | 0 sec         | 1.0 ppm                             | 1000    |
| mass                  | 100                                      | 1000          | 1.0                                 | 10,000  |
| IR                    | 15,000                                   | 10            | 1.0                                 | 1000    |
| UV                    | 100/min                                  | 10            | 2.0                                 | 1000    |
| Visual                | -- useful for particulates only, to date |               |                                     |         |
| <b>Other:</b>         |  |               |                                     |         |
| Thermal conductivity  | 10,000 cc/min                            | 1 min         | 0.1%                                | 500     |
| VPC                   | 1 cc                                     | 20            | 0.001 ppm                           | 10,000  |

TABLE II

SIGNIFICANT AIR POLLUTANTS, DANGEROUS CONCENTRATION LEVELS,<sup>5,6</sup>  
AND MAJOR SPECTRAL LINES AND BANDS

| Pollutant                            | Upper Limit<br>of safe<br>Concentration | Prominent<br>Lines/<br>Bands           | Intensity    |
|--------------------------------------|---|--|--------------|
| CO                                   | 9 ppm                                   | 6080 A                                 | 9            |
|                                      |   | 5610                                   | 10           |
|                                      |   | 5198                                   | 10           |
|                                      |   | 4835                                   | 10           |
|                                      |   | 4510                                   | 10           |
|                                      |   | 4393                                   | 8            |
|                                      |   | 4123                                   | 7            |
|                                      |   | 4380                                   | 7            |
|                                      |   | 4124                                   | 7            |
|                                      |   | 3893                                   | 7            |
|                                      |   | 3134                                   | 8            |
|                                      |   | 3306                                   | 7            |
|                                      |   | 6804                                   | 8            |
|                                      |   | 6513                                   | 9            |
|                                      |   |  |              |
|                                      |   | 6433                                   | 10           |
|                                      |   | 6403                                   |              |
| CS <sub>2</sub>                      | 0.009                                   | 3275                                   | 8            |
|                                      |   | 3235                                   | 8            |
| Cl <sub>2</sub>                      | 0.033                                   | (bands 4871-3923)                      |              |
| HCl                                  | 1.0                                     | 3966                                   |              |
|                                      |   | 3599                                   |              |
|                                      |   | 3411                                   |              |
|                                      |   | 3251                                   |              |
|                                      |   | 3868                                   | (not listed) |
|                                      |   | 3518                                   |              |
|                                      |   | 3338                                   |              |
|                                      |   | 3184                                   |              |
| H <sub>2</sub> S                     | 0.005                                   | (no prominent lines in<br>this region) |              |
| HNO <sub>3</sub> (NO <sub>2</sub> ?) | 0.05                                    | 3681                                   | 9            |
|                                      |   | 3539                                   | 10           |
|                                      |   | 3416                                   | 8            |

TABLE II (CONTINUED)

|                 |                   |        |                              |
|-----------------|-------------------|--------|------------------------------|
| O <sub>3</sub>  | 0.5 ppm           | 4316 A | 5 (both are                  |
|                 |                   | 3358   | 6 masked by O <sub>2</sub> ) |
| SO <sub>2</sub> | 1.03              | 3691   | (strongest<br>heads)         |
|                 |                   | 3668   |                              |
|                 |                   | 3557   |                              |
|                 |                   | 4461   | (afterglow)                  |
|                 |                   | 4361   |                              |
|                 |                   | 4265   |                              |
|                 |                   | 4244   |                              |
|                 |                   | 4153   |                              |
|                 |                   | 3676   | 7                            |
|                 |                   | 3271   | 10                           |
|                 |                   | 3164   | 10                           |
| 3064            | 10                |        |                              |
| N <sub>2</sub>  | (for calibration) | 6545   | 10                           |
|                 |                   | 6469   | 10                           |
|                 |                   | 6395   | 9                            |
|                 |                   | 6323   | 7                            |
|                 |                   | 6070   | 7                            |
|                 |                   | 6014   | 7                            |
|                 |                   | 5959   | 8                            |
|                 |                   | 5906   | 8                            |
|                 |                   | 5854   | 8                            |
|                 |                   | 5804   | 7                            |
|                 |                   | 5755   | 7                            |
|                 |                   | 4059   | 8                            |
|                 |                   | 3998   | 9                            |
|                 |                   | 3943   | 8                            |
|                 |                   | 3894   | 7                            |
|                 |                   | 3804   | 10                           |
|                 |                   | 3755   | 10                           |
|                 |                   | 3710   | 8                            |
|                 |                   | 3577   | 10                           |
|                 |                   | 3537   | 8                            |
| 3371            | 10                |        |                              |

### 3. APPARATUS DEVELOPED

#### 3.1 REASONS FOR CHOICE OF METHOD

As can be seen from Table I, many diverse methods of air analysis are presently in use, yet most have obvious drawbacks. For convenience of sample size, speed of analysis, and specificity obtainable, only two methods -- vapour phase chromatography and flame spectrometry -- approach the proposed method. Of these, the latter is quite complicated, since it is usually used only to analyze the fractions obtained upon collecting samples in a chromatographic column.<sup>8</sup> Vapour phase chromatography has the drawback of requiring a massive, expensive piece of equipment, with a supply of gas (the carrier phase) and a power supply. However, VPC is the method most commonly used today for air pollution analysis, since it is fast, requires a very small sample, and presents easily interpretable output.

The choice of the proposed method seems obvious. Spectroscopic methods have been used for many years for the detection of trace quantities of the elements.<sup>9</sup> Methods somewhat similar to the one proposed are commonly used commercially to check metals for impurities.<sup>10</sup> The linear response of the photomultiplier tube to intensity,<sup>11</sup> and the direct proportionality of the incident light intensity of the appropriate wavelength to the concentration of the trace substance,<sup>12</sup> makes this method ideally suited to this

task. In most present applications of photomultiplier-equipped spectrometers, however, a small number of fixed slits is used to inspect just the few appropriate lines.<sup>13</sup> A scanning slit seems the logical approach to interpreting a spectrum as complex as the one emitted by air.

In theory, there are but several limitations to this approach. A pollutant must give off light in the region to which the photomultiplier is sensitive (3000 - 6000 Å), and these lines must be quite intense if they are to be observed when the pollutant is present in very small concentrations. Fortunately, only one major pollutant, H<sub>2</sub>S, does not have strong lines in this region.<sup>14</sup> However, it can be detected if the range of sensitivity is extended to 2000 Å.

### 3.2 DETAILS OF DESIGN CHOSEN

The apparatus is presently arranged in the following manner. (See Figure 1, and Appendix III for more detail.) A pyrex tube is capped at either end with brass compression fittings. The upper electrode is sealed with a solid brass plug; the lower one connects directly to an assembly including an inlet valve (rotating valve, adjustable) and a shut-off valve (toggle valve) connecting to the vacuum pump and a thermocouple vacuum gauge. At each end, a rubber O-ring forms a seal between the glass tube and the electrode. (This seal is tight enough to maintain a usable vacuum for 24 hours, so that continuous pumping is not necessary.)

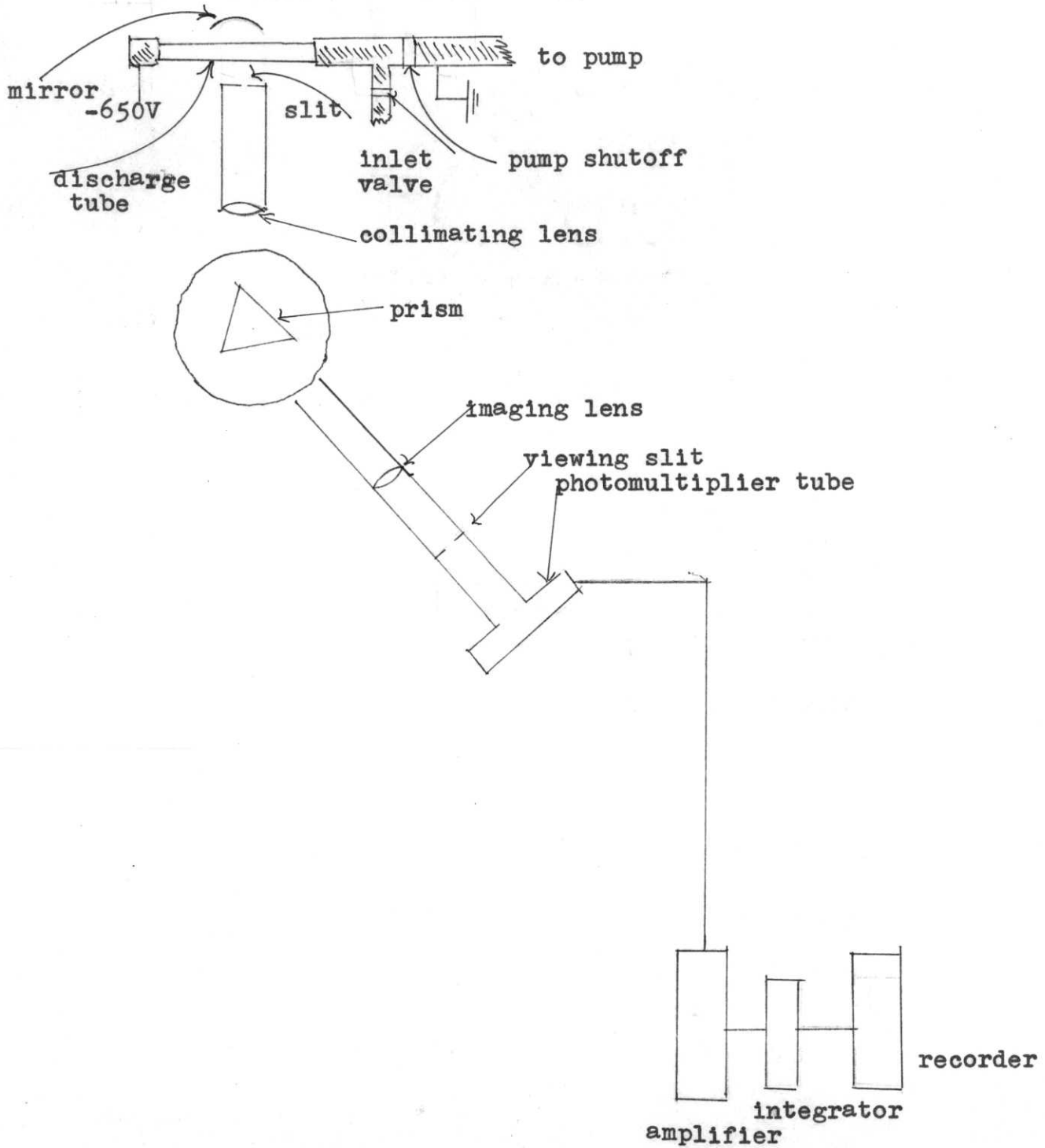


FIGURE 1. -- SKETCH OF POLLUTION ANALYZER

This tube is then pumped down to a pressure of about 0.7 mm Hg. and 650 volts is applied across the tube. (The exact pressure and voltage depend on the particular gas mixture being examined and the region of the discharge to be observed. A 1 megohm resistor is placed in series with the discharge tube to regulate the current drawn from the power supply. By adjusting the inlet valve, and thus the pressure in the tube, either the pink positive column or the blue negative glow may be inspected. (See Appendix II)

The tube is placed at the focal point of a small parabolic mirror, and the light emitted is aimed at the entrance slit of a small spectroscope. The slit width is adjusted to give as narrow a line as possible, without completely sacrificing intensity, and the slit position is adjusted so that it falls in the focal plane of the collimating lens. The light, parallel after passing through this lens, is refracted by a prism, and then focused by a second lens, onto a viewing slit approximately  $3/4$  mil wide. On the other side of this slit is positioned the photomultiplier tube. This entire latter assembly (photomultiplier tube, slit, and lens) is sealed in a rigid tube, which is rotated about an axis passing through the center of the prism, thus scanning the spectrum. This unit swings around the light-tight cylinder which contains the prism (meeting it in a light-sealed sliding bearing) at a rate of about three minutes of arc per second.

The photomultiplier is connected in the manner shown in Figure 2. The ten resistors between the stages divide the voltage,



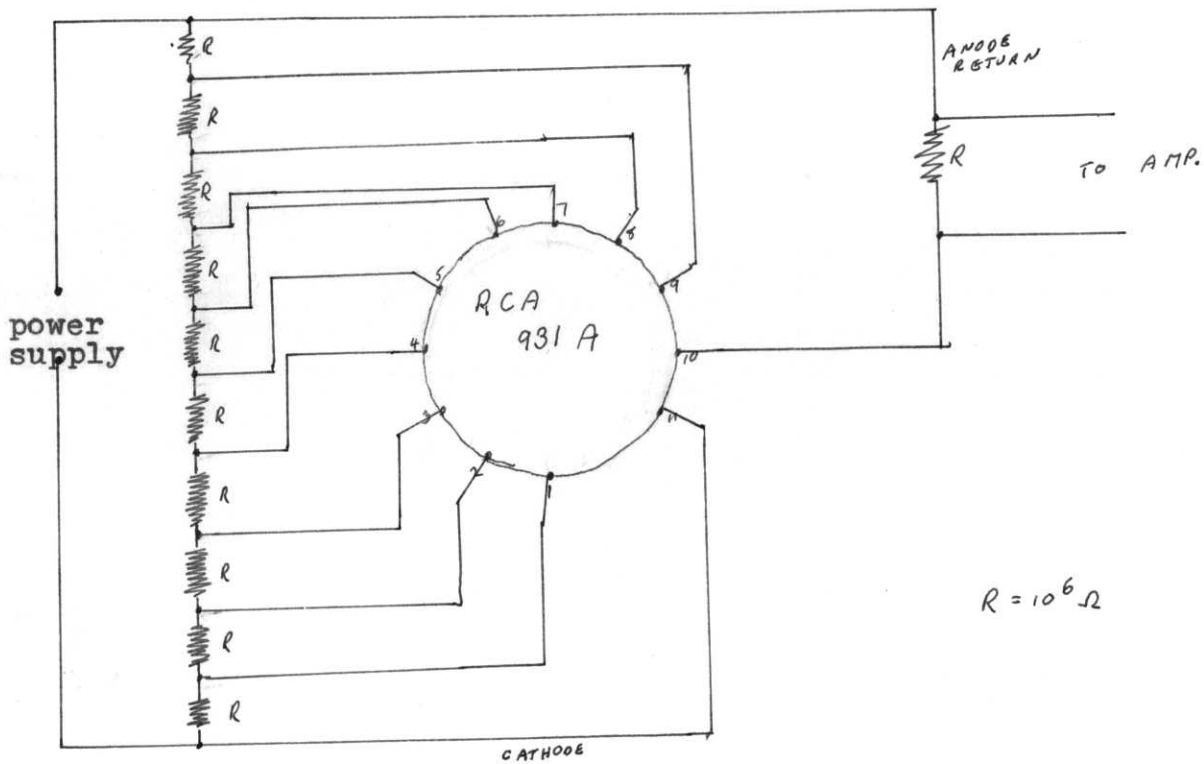


FIGURE 2. -- Photomultiplier circuit

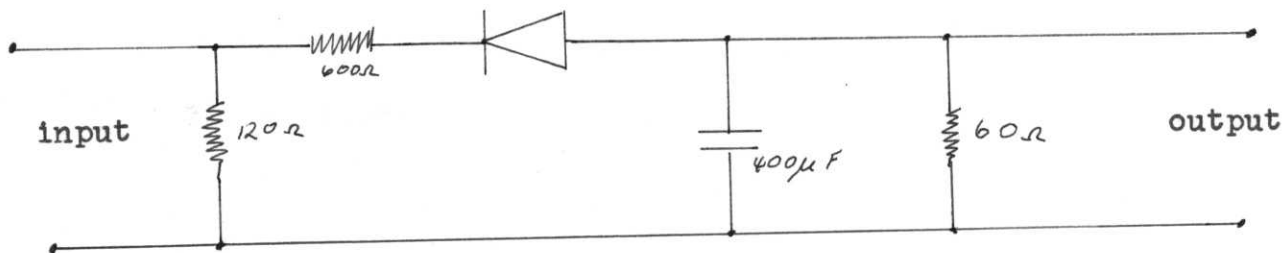


FIGURE 3. -- Integrator circuit

so that when 1000 volts is applied to the entire circuit, each stage in the tube is held at +100 volts relative to the preceding one. The anode current passes through a 1 megohm resistor, and it is the voltage drop across this resistor that is processed and recorded. This signal is taken to a pulse amplifier (by shielded coax) and from there, to an integrator.

The design of the integrator (see Figure 3) is chosen so that the output of the circuit indicates the rate of arrival of pulses at the input. Since, to a first approximation, each pulse represents the arrival of a certain number of photons at the photoemitter of the photomultiplier, more intense radiation (more photons per unit time) is indicated by a higher rate of arrival of pulses. The input time constant (0.25 seconds) is chosen to be long relative to the duration of each pulse (about two microseconds). The output time constant (0.025 seconds) is chosen to be long relative to the pulse length, but short relative to the time needed to scan across two resolvable lines. (See Appendix I) The ratio of the two is chosen so that the output signal is not excessively attenuated. The 120 ohm resistor is chosen to match the output impedance of the amplifier, and is needed to properly terminate the transmission line.

Thus, the capacitor builds up charge as a series of pulses arrives, and the voltage across it ( $V = (1/C)(\int idt)$ ) is approximately proportional to the intensity of the incident radiation, in the last short time period. This output voltage is then recorded on a strip chart recorder.

### 3.3 REASONS FOR CHOICE OF SCANNING METHOD

There were several reasons for choosing this particular method of scanning the spectrum. First, although it would seem obvious that rotating the prism would be far simpler than rotating the entire slit/photomultiplier assembly, this did not prove to be the case. The central part of the apparatus was a small spectroscope (borrowed from the Junior Lab), which presented a not convenient way of automatically rotating the prism table -- particularly, since it had to be enclosed in a light-tight cylinder.

Another possible arrangement was to use fixed slits at several appropriate positions, but this, too, had obvious drawbacks. First, such an approach would reduce the number of lines that could be monitored, and would make it virtually impossible to monitor lines that are close together. Second, a slight change in temperature, or a minor amount of vibration, could spoil the alignment of the slits, thus requiring a great deal of wasted time realigning the apparatus before each use.<sup>15</sup>

### 3.4 REASONS FOR CHOICE OF SPECTRAL ANALYZER

Spectroscopic analysis for trace quantities in a mixture suffers from two major difficulties, when the proposed approach is used. First, the very weak lines resulting from the excitation of trace substances must be found among the many, very intense lines of the nitrogen spectrum. Second, since the sensitivity is limited by the photomultiplier dark current, it is a function of the absolute intensity of the lines rather than their relative

intensities. Therefore, if the method is to succeed, an analyzer must be used which satisfies the following two criteria. It must give as high dispersion as possible, so that lines close together can be distinguished, and it must form as intense a spectrum as is possible.

The apparatus was first tried with a diffraction grating (15,000 lines per inch) but it was found that too much of the incident radiation was involved in higher order diffraction patterns, leaving the primary spectrum weak. Although the obvious next step was to try an echelon grating, this was dismissed as impractical considering the over-all qualities desired for the apparatus.

The solution finally chosen was to use a simple glass prism. Although a grating is preferable since it, unlike a prism, produces a normal spectrum,<sup>16</sup> the increase in intensity gained by using a prism, more than compensates for this difficulty. In addition, since the apparatus must be precisely calibrated anyway, this extra source of non-linearity is not particularly troublesome.

The prism finally used was a small one (in the form of an equilateral triangle, one inch on each side) with a refractive index of about 1.5. The resolution it can provide ranges from 1.1 Å at the blue end of the spectrum, to 7.4 Å at the red end. (See Appendix I for further details.)

## 4. SENSITIVITY

### 4.1 LINE INTENSITY

Molecular spectra are characteristic of the compounds which emit them. When gases are excited in a glow discharge, and the radiation emitted in the visual region is analyzed with a spectrometer of medium resolving power, band spectra are observed. These bands have their origin in the excitation of the vibrational and rotational states of the molecules.<sup>17</sup>

If a gaseous mixture of several compounds is excited, each substance present will emit light at wavelengths characteristic of it. In general, the relative intensities of the lines are proportional both to the concentration of the excited substances emitting them and to the transition probability for that particular line.<sup>18</sup> The latter theoretical variable underlies the empirical data on the relative intensities of lines, found in Table II. The former is the basis for this apparatus. Because of these effects, the spectrum produced by exciting a gas sample in a glow discharge, identifies the substances present and makes possible a good estimate of their relative concentrations.

#### 4.2 EFFECTS LIMITING SENSITIVITY

The sensitivity of the instrument is limited by imperfections in the optical components used, by the dark current of the photomultiplier, and by any stray light that enters the apparatus.

As described in Appendix I, the resolution available is limited by imperfections in the lenses, by the limited dispersion available with prisms, and by the difficulty in constructing a slit sufficiently narrow (or a light path sufficiently long in a compact apparatus) for the analysis of the resultant spectrum. Overall, these factors limit the resolution of the instrument so that no lines closer together than 10 Å can be distinguished as separate. (With excellent optics, and a long focal length imaging lens with folded optics, the resolution might be improved by a factor of 1,000.<sup>19)</sup>

The problem of the photomultiplier dark current is equally significant in the identification of trace quantities. This dark current is attributable to two main effects<sup>20</sup> -- thermionic emission and cold field emission. (The former is by far the more important of the two under normal operating conditions.)

Thermionic emission results as the electrodes warm up as the tube is used. Cold field emission results when surface irregularities and sharp edges are exposed to an electric field, creating a very intense local field. This field lowers the effective work function of the electrode material, and makes it

easier for charges to "tunnel" out.<sup>21</sup> The number of electrons released by this effect only becomes of interest when the more intense thermionic background current has been eliminated (by cooling).

Since any electron emitted by the electrodes gives rise to many more electrons at the anode collector, these effects can cause significant currents (typically,  $5 \times 10^{-8}$  amperes). Thermionic emission has been reduced in this experiment by packing the photomultiplier in dry ice, leaving only a small window ( $3/4$  inch diameter) for the incident light. The tube is designed to reduce cold emission as much as possible.<sup>22</sup> (The electrodes are made smooth and with rounded edges, but the residual effect remains.)

The problem of making the apparatus absolutely light-tight also is the cause of a residual background current, which limits the available sensitivity. To control this as much as possible, all joints are made tight-fitting, and are wrapped with opaque material. The problem is further complicated by the possibility of stray light entering the first slit, but by making this slit as narrow as possible, and enclosing the discharge tube, mirror, and slit in a blackened cardboard cylinder, this problem is limited. The level of current due to cold emission, and background light only becomes significant when the far more intense thermionic emission background has been minimized, and is found experimentally to be about 1% of the intensity.

## 4.3 CALCULATION OF THE SENSITIVITY LIMIT

First, if the dark current due to thermionic emission is reduced, the residual effect is found to be 1% of the former noise level. (See Table III for tube data values.)

$$\begin{aligned}(1\%)(5 \times 10^{-8} \text{ amp}) &= 5 \times 10^{-10} \text{ amp} \\ &= 3.1 \times 10^9 \text{ electrons/sec}\end{aligned}$$

Since the current gain of the tube is  $2 \times 10^6$ , and the quantum yield (number of electrons emitted for each incident photon) of the cathode is 13%, the equivalent incident radiation would be

$$\frac{(3.1 \times 10^9 \text{ electrons/sec})}{(2 \times 10^6)(0.13)} = 1.1 \times 10^4 \text{ photons/sec}$$

Now from the theory of collisions in gases, if

$$\begin{aligned}dN_c &= \text{number of collisions in distance } dx \\ n &= \text{number of gas molecules/unit volume} \\ N &= \text{number of incident electrons} \\ \sigma &= \text{effective collision cross section}\end{aligned}$$

it can be shown readily that<sup>23</sup>

$$dN_c = \sigma n N dx$$

Integrating this over the entire volume of the tube, assuming that  $n$ ,  $N$ , and  $\sigma$  are independent of position, gives the result

$$\begin{aligned}N_c &= \int dN_c \\ &= \int n N \sigma dx dy dz\end{aligned}$$

$$N_c = n N \sigma V$$

Now, the volume of the tube is 25cc and the current is 1 milli-amp ( $6.2 \times 10^{15}$  electrons/sec.)



TABLE III

## PHOTOMULTIPLIER CHARACTERISTICS 24,25

---

|   |                                      |
|---|--------------------------------------|
| Type  | RCA 931A                             |
| Spectral Response                           |                                      |
| photo-emitter                               | cesium treated antimony, nickel base |
| max. response range                         | 4000 A $\pm$ 500 A                   |
| short wavelength<br>cutoff (soda lime bulb) | 3000 A                               |
| long wavelength<br>threshold                | 6900 A                               |
| Current amplification<br>(at 100 V/stage)   | $2 \times 10^6$                      |
| Peak anode current                          | 10 mA                                |
| Max. anode dark current                     | $5 \times 10^{-8}$ amp               |
| Cathode quantum efficiency                  | 13%                                  |
| Ambient temperature                         | +75° C max                           |

---

To find  $n$ , the Ideal Gas Law ( $pV = nRT$ ) is used to give

$$n_{\text{tube}}/n_{\text{STP}} = (p_{\text{tube}}V_{\text{tube}}T_{\text{STP}})/(p_{\text{STP}}V_{\text{STP}}T_{\text{tube}})$$

Substituting  $p_{\text{tube}} = 0.7$  mm Hg,  $T_{\text{tube}} = 300$  K, and STP values,

$$n_{\text{tube}} = 2.1 \times 10^{15} \text{ molecules/cc}$$

Finally, if it is assumed that the radius, for collisions, of the molecules is about 5 Bohr radii (as a rough approximation)

$$\begin{aligned} \sigma &= \pi r^2 \\ &= 75 \times 10^{-18} \text{ cm}^2 \end{aligned}$$

Now  $N_c$  can be found

$$\begin{aligned} N_c &= (2.1 \times 10^{15})(6.2 \times 10^{15})(75 \times 10^{-18})(25) \\ &= 2.4 \times 10^{16} \text{ collisions/sec.} \end{aligned}$$

Therefore the radiation emitted by the discharge will be  $2.4 \times 10^{16}$  photons/sec. Now, if it is considered that only a volume of about 1 cc is exposed, and only about 1% of the radiation emitted by that volume falls on the slit

$$\text{Incident Light} = 1.1 \times 10^{13} \text{ photons/sec}$$

Consequently, if lines of equal intensity for equal concentration are considered, the dark current corresponds to a trace of concentration

$$\begin{aligned} 1.1 \times 10^4 / 1.1 \times 10^{13} &= 1.0 \times 10^{-9} \\ &= 0.001 \text{ ppm} \end{aligned}$$

Since this calculation is based on the averaged dark current, while the observed quantity is the sum of many randomly arriving charges in a capacitor, the actual effect of dark current is larger than this, and consists of many, randomly occurring spikes. To allow for a clear-cut decision, the sensitivity limit should probably not be considered to be less than 0.02 ppm.

## 5. EXPERIMENTATION

Once the apparatus was functional, the first step needed was the calibration of the output. This was accomplished by having the instrument scan the spectrum of a mercury discharge lamp several times, and, once a consistent pattern emerged, (Fig. 4) assigning appropriate wavelength values to the most intense lines observed. The relative intensities of these lines were found in tables<sup>26</sup>. As a final check, the spectrum was scanned visually -- through the slit -- and the colours of the spectral lines compared with a colour plate (calibrated) of the mercury spectrum.<sup>27</sup>

Two calibrations are necessary -- one for wavelength and one for intensity. For the first, the distance between the lines was measured, and the ratio of the difference in wavelength to the difference in position was plotted against wavelength. (See Table IV and Figure 5 for sample data,) Next the intensity response was calibrated, by plotting the ratio of the line height to the tabulated line intensity against wavelength. (See Table V and Figure 6 for sample data.)

Further tests were run, scanning the spectra of CO<sub>2</sub>, He, and N<sub>2</sub>. This last spectrum was essential, since these lines so dominate the spectrum of air, and are to be used for the calibration of the instrument. (The relative concentrations of pollutants are to be determined by direct comparison to the N<sub>2</sub> lines.)

Once this calibration had been performed, an air sample was taken and the spectrum scanned. (See Appendix IV for data.)

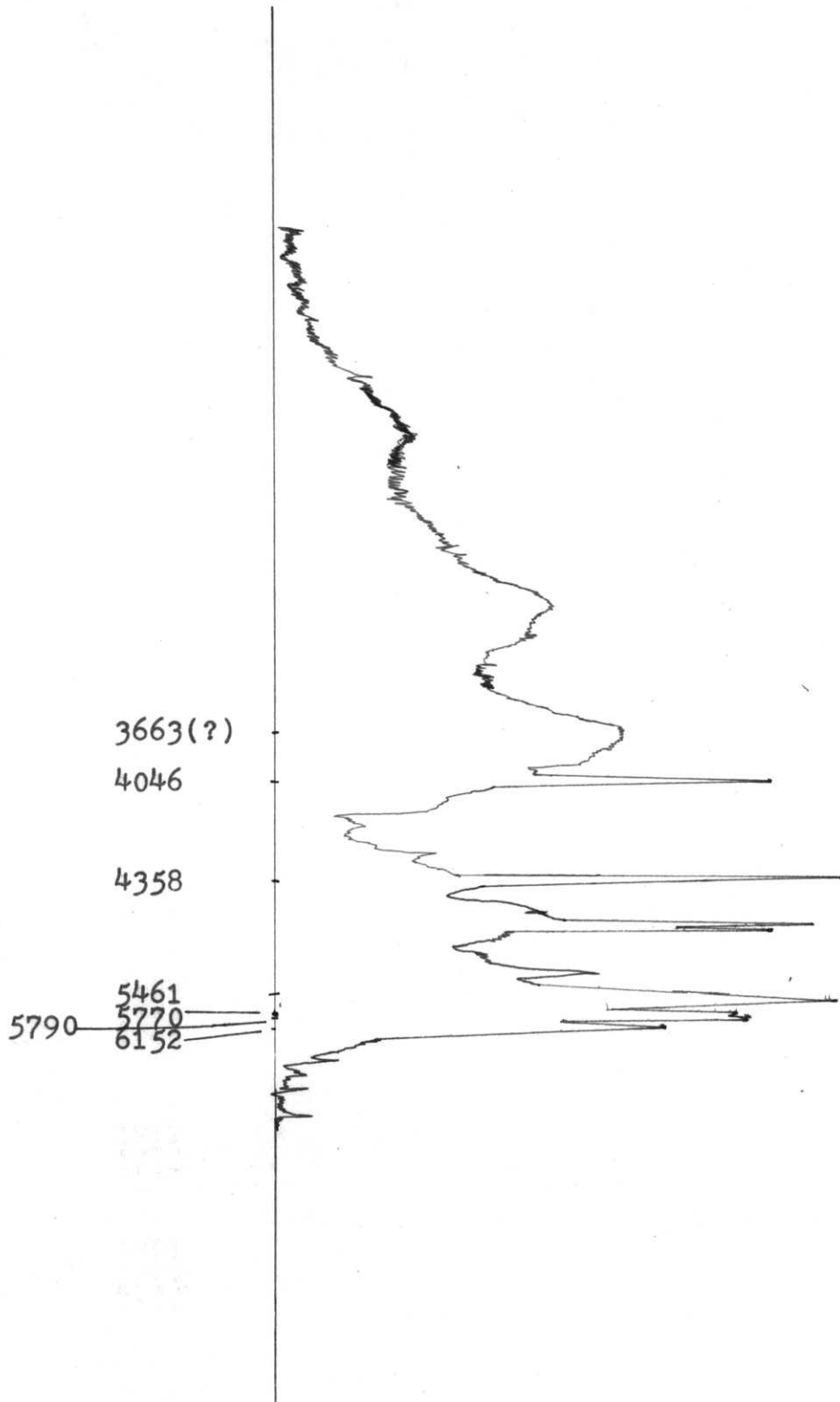


FIGURE 4. -- Scan of the spectrum of a mercury discharge tube

TABLE IV  
 WAVELENGTH CALIBRATION OF OUTPUT  
 (SAMPLE DATA)

| Wavelength <sup>28</sup> <sub><math>\lambda</math></sub> | Distance, $d$ , from<br>reference line | $\Delta \lambda$ | $\Delta d$ | $\Delta \lambda / \Delta d$ |
|--|--|------------------|------------|-----------------------------|
| 4046 A   | 0. cm                                  | 0 A              | 0. cm      | -                           |
| 4358   | 1.4                                    | 312              | 1.4        | 223                         |
| 5461   | 3.1                                    | 1103             | 1.7        | 655                         |
| 5770   | 3.3                                    | 309              | 0.2        | 1545                        |
| 5790 (values<br>approx.)                                 | 3.31                                   | 20               | 0.01       | 2000                        |
| 6152   | 3.46                                   | 362              | 0.15       | 2400                        |

TABLE V  
 INTENSITY CALIBRATION OF OUTPUT  
 (SAMPLE DATA)

| Wavelength <sup>29</sup> | Tabulated Intensity <sup>30</sup> | Output<br>Intensity | Output/Tabulated |
|--------------------------|-----------------------------------|---------------------|------------------|
| 3663 A                   | 500                               | 5.0 cm              | 0.01             |
| 4046                     | 200                               | 7.0                 | 0.035            |
| 4358                     | 3000                              | 8.2                 | 0.0033           |
| 5461                     | 2000                              | 8.0                 | 0.004            |

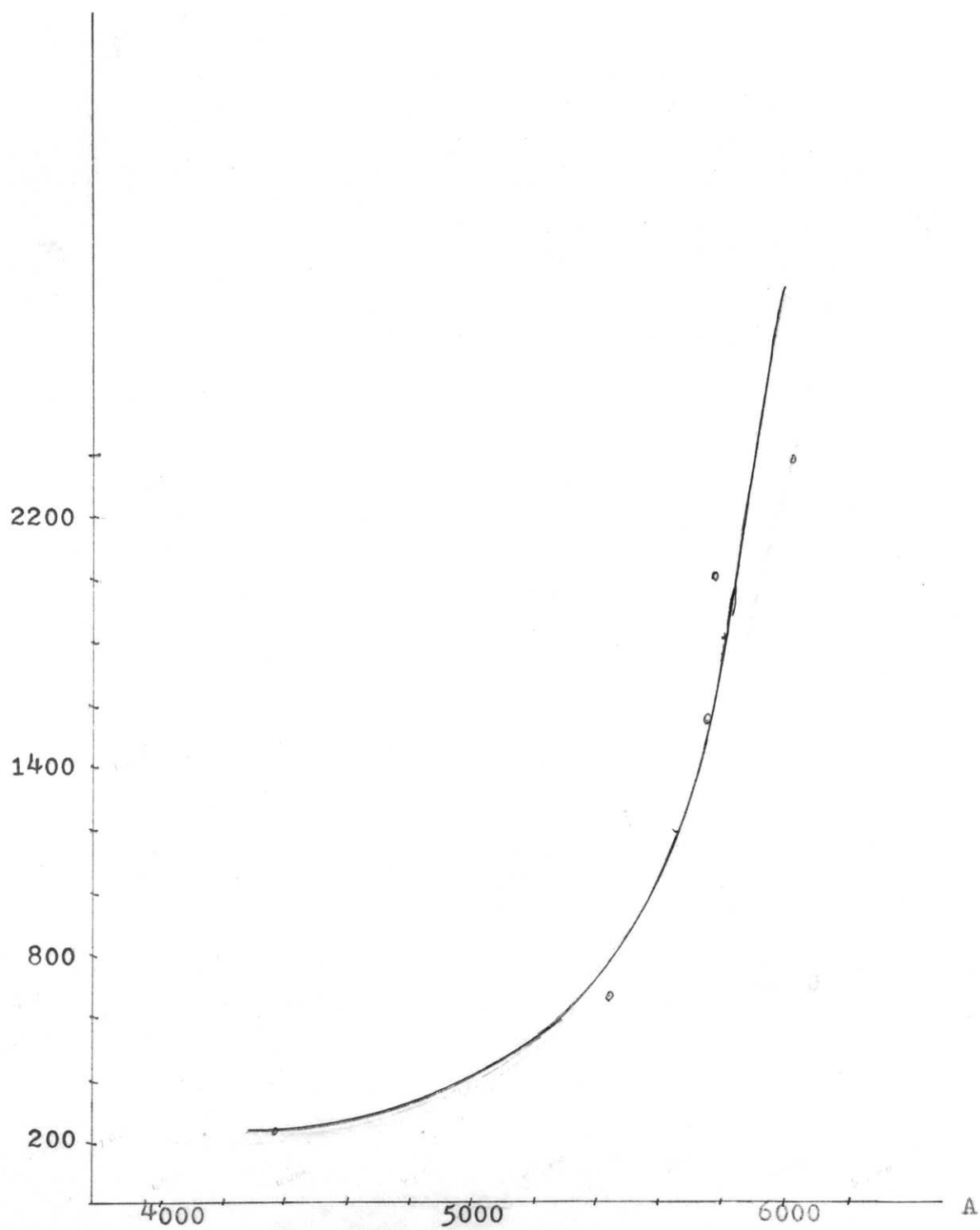


FIGURE 5. -- Wavelength calibration

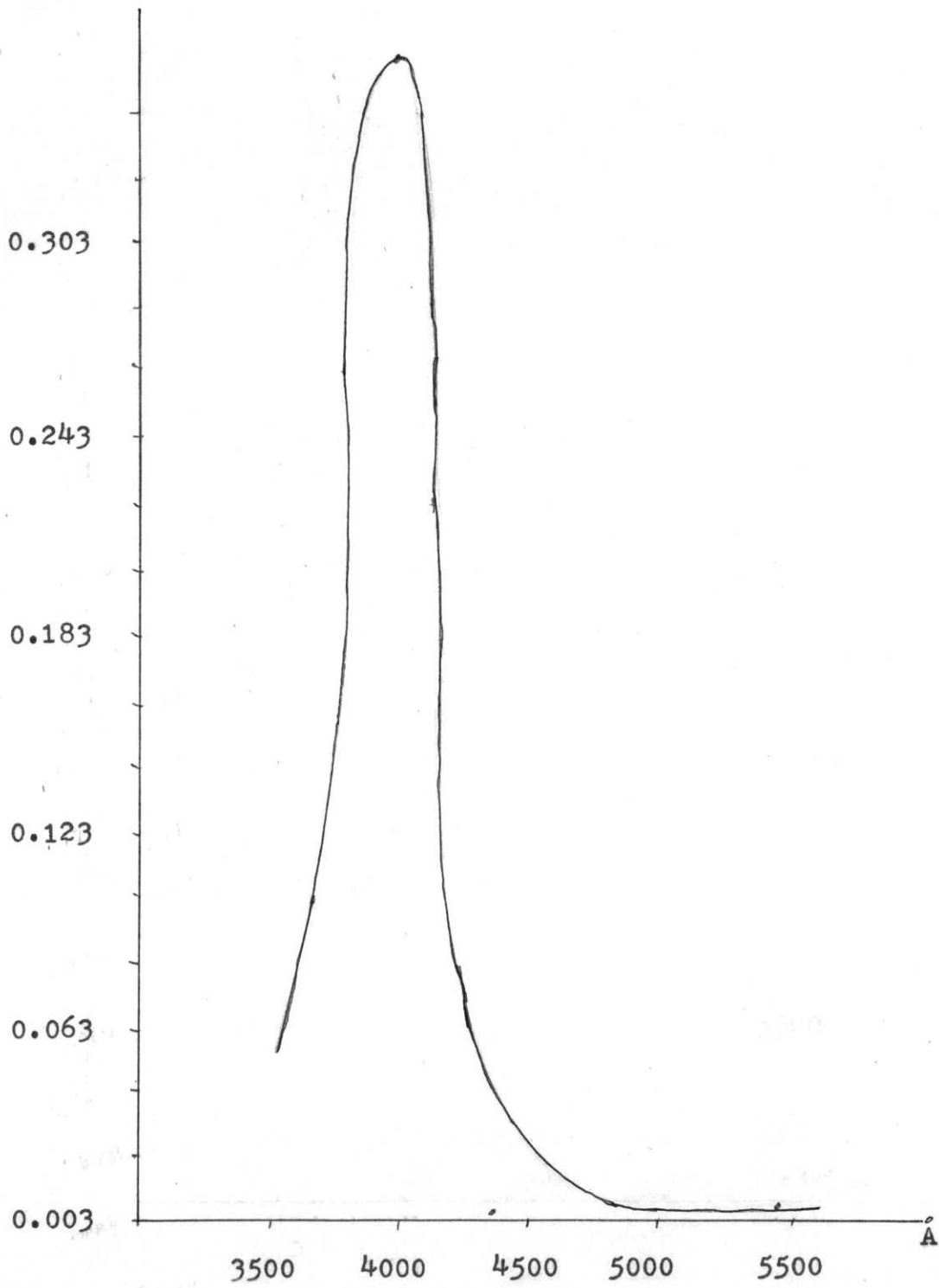


FIGURE 6. -- Intensity calibration

## 6. SOURCES OF ERROR

### 6.1 MACROSCOPIC

1) The resolution is not always adequate to clearly differentiate between lines close together, and so, confusion about the source of a given line may result.

2) The scanning arm does not always move perfectly smoothly. This can result in confusing misplaced lines, since the X - axis of the recorder (the independent variable is time) will no longer correspond to the position of the line. This might best be corrected by using position rather than time as the independent variable. A simple position detector might consist of a precision potentiometer (connected to the pivot point through a gear box (about 100/1)), and a battery across it. The voltage across the potentiometer would then indicate position.

3) Errors in calibration may cause a confused interpretation of the output. To accurately calibrate the apparatus, it should repeatedly scan an intense spectrum with many, well-known lines (such as iron).

4) Stray discharges (such as those found with improperly working fluorescent lights) and similar electrical noise can cause spurious traces resembling spectral lines in the output. Careful shielding reduces this effect, but does not eliminate it.



5) The deposition of dirt on the discharge tube can reduce sensitivity by reducing the amount of light transmitted by the walls. If the absolute intensity of lines were used to estimate concentrations, this could throw off the reading. This is best compensated for by using self standardization of the spectrum. The many strong nitrogen lines present in the air can be used for this purpose. Since the concentration of nitrogen in air is essentially constant, the intensities of other lines relative to the intensity of the nitrogen lines can be used to deduce concentrations. (This also provides a method of continually checking the wavelength calibration.)

6) The contamination of the electrodes may cause inaccurate readings, since the concentration of the contaminant in the tube will not be representative of its level in the ambient air.

7) Misalignment of the apparatus can lower the sensitivity, if the two slits become badly misaligned.

8) Fatigue in the photomultiplier tube will cause a loss of sensitivity after the tube has been operating for a while.<sup>31</sup> (The only way to compensate for this effect, is to turn the tube off for a while.)

## 6.2 MICROSCOPIC

- 1) Background dark current in the photomultiplier limits sensitivity, by producing spikes which can be of the same magnitude as a significant signal. Probably the best way to overcome this difficulty would be to modulate the light (a strobe disk would probably work) and then lock onto the output with a PAR.
- 2) Thermal noise in all electronic components can cause misleading signals.<sup>32</sup>
- 3) Statistical fluctuations in all signals measured in this experiment can give rise to random variations in signal intensity. Making several scans of the spectrum, rather than just one, can reduce the significance of these effects,
- 4) Irregularities in the discharge may be caused by the presence of trace quantities of compounds. Traces can have large effects on the nature of the discharge, and on the intensity of lines emitted by other compounds in the sample.<sup>33</sup>
- 5) Any lack of stability in the amplifier or power supplies can make the signal fluctuate.

## 7. SUMMARY

An apparatus has been designed and built to automatically analyze spectra. It requires only simple components (a photomultiplier, two power supplies, a pulse amplifier, one prism, two lenses, and two slits) and can be readily miniaturized with the aid of some transistorized circuitry. This apparatus has been used in conjunction with a gas discharge through a sample of ambient air, in an attempt to detect pollutants present in trace concentrations.

To date, the apparatus has been approximately calibrated and several trial runs on spectra of air have been made. It seems clear that the resolution of the instrument will have to be improved if it is to work properly, since the spectra of nitrogen and oxygen are extremely intense. Unless the resolution is improved, these lines will continue to obliterate all traces of the spectral lines from pollutants.

It seems clear, though, from the data gathered to date, that a small scanning spectrometer can be made. Theoretical estimates indicate that with high enough resolution, this instrument can be used to detect pollutants in minute concentrations.

## APPENDIX I

### OPTICS

Light emitted from the discharge tube is analyzed with a spectroscope. The intensity of the incident light is increased by having the tube pass through the focal point of a parabolic mirror. The position of the slit is adjusted so that it is in the focal plane of the collimating lens ( $f = 165$  mm) so that the light entering the prism is parallel,

The dispersion of the prism,  $dn/d\lambda$ , is the rate of change of the refractive index of the prism with wavelength.<sup>34</sup> For the prism used, the refractive index varies from 1.524 at 6563 Å to 1.542 at 3988 Å. Over the same range, the dispersion goes from  $-0.35 \times 10^{-5}$  /Å to  $-1.39 \times 10^{-5}$  /Å.<sup>35</sup>

The resolution of the spectroscope is limited by that of the prism. To determine how close together two spectral lines can be and still be resolvable, it is useful to use "Rayleigh's criterion".<sup>36</sup> This states, that for a rectangular aperture of width  $b$  (such as the side of a prism) two lines are resolvable when their angular separation,  $\alpha$ , is equal to  $\lambda/b$ .<sup>37</sup> This follows easily if lines are defined as being resolvable when the diffraction maximum of one falls precisely on the first minimum of the other.

For a prism, the minimum resolvable angle is again  $\lambda/b$

where  $b$  is now the width of the beam of light which emerges from the prism.<sup>38</sup> In this apparatus, this is about 1.2 cm., giving an average value of  $\alpha$  of about  $4 \times 10^{-5}$  radians.)

This value can now be used to determine the width needed for the viewing slit. The light emerging from the prism is focused by a small lens with a focal length of 6.5 inches. As can be seen from Figure 7, a simple ray diagram now gives the required slit width.<sup>39</sup>

(This construction is based on the consideration that when parallel light is incident on a thin lens, all the rays intersect in the focal plane of the lens. Thus, if a hypothetical ray parallel to the real ray, but passing through the center of the lens, intersects the focal plane at a given point, it follows that the real ray must also pass through that point.)

Now, it is clear from the diagram that

$$\begin{aligned} x &= f \tan \alpha \\ &\approx f \alpha \\ &\approx 0.27 \text{ mils} \end{aligned}$$

Unfortunately the narrowest slit that the experimenter could make was only about 0.75 mils wide (approximately) and no small lens of longer focal length could be found. Hence the resolving power was generally worsened, by as much as a factor of three.

It is also useful to estimate the smallest wavelength separation that can be resolved by the apparatus. From Figure 8 it can be seen that  $\Delta \lambda = \lambda / BD$ <sup>40</sup>, where  $D$  is the dispersion of the prism. This follows, since the optical path length is the same for all parts of the incident wave front, and hence,  $c + c' = nB$ ,<sup>41</sup>

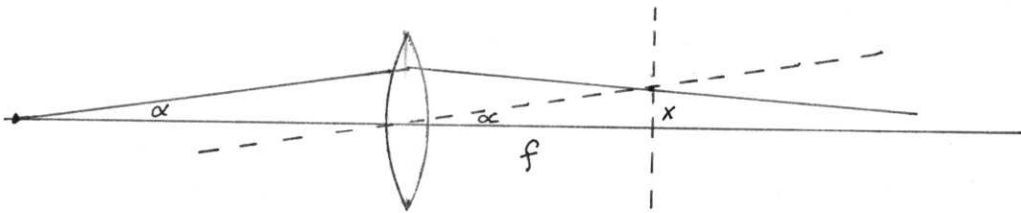


FIGURE 7. -- Slit width determination

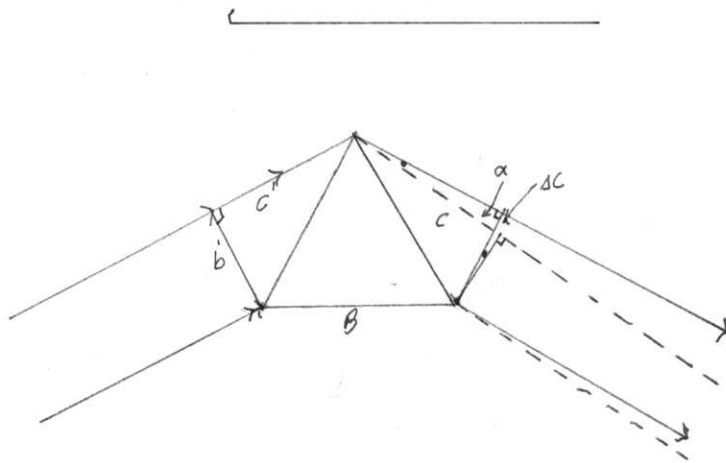


FIGURE 8. --Resolution determination

and for light of a slightly different wavelength,  $c + c' = (n + \Delta n)B$ . Subtracting one from the other gives the result  $\lambda = B\Delta n$ . Dividing both sides by  $\Delta\lambda$ , and making the assumption that for very small values of  $\Delta\lambda$ ,  $\Delta n/\Delta\lambda \approx dn/d\lambda = D$ , the desired result is obtained. Substituting in the appropriate data values gives a minimum separation of 7.4 Å at the red end of the spectrum and 1.1 Å at the blue end.

The time needed to scan between two minimally resolvable lines may now be calculated. Two lines that can just be resolved have been shown to have an angular separation of  $4 \times 10^{-5}$  radians. Since the scanning arm swings around the prism at a rate of about 0.05 radians/minute (0.0009 radians/second) the time needed is  $(4 \times 10^{-5} \text{ radians}) / (9 \times 10^{-4} \text{ radians/second}) = 0.044$  seconds. Therefore, as mentioned previously, the time constant of the integrator must be less than 0.04 seconds.

## APPENDIX II

### THE GAS DISCHARGE

#### II.1 GENERAL

Discharges in gases can be grouped into two classes -- self-sustaining and non-self-sustaining. In the latter, ions are produced primarily by external radiation or thermionic emission<sup>45</sup> (by means of an emitted electron ionizing a molecule), and once the source of the radiation is removed, the discharge stops. This discharge, which is of very low intensity, is the effect seen in ionization chambers. The discharge becomes self sustaining when the breakdown voltage is reached.<sup>46</sup>

#### II.2 BREAKDOWN<sup>47,48</sup>

To determine the criteria for breakdown of the discharge consider the following<sup>49</sup> In a discharge tube, a uniform electric field,  $E$ , is applied to a low pressure gas (pressure is between 0.1 and 1.0 mm Hg). External radiation can cause ionizations by directly hitting gas molecules, or by striking the cathode, (making it emit electrons, which, once accelerated by the field, can ionize molecules), (but not by striking the anode). Since far



less energy is needed to expel an electron from the cathode than to directly ionize a molecule, to a first approximation, cathode bombardment can be considered the cause of ionizations.

Now, as the field,  $E$ , is increased, the emitted electrons gain more energy, and can ionize more gas molecules. (Pressure effects are significant here, for if the pressure is too high, the mean free path is too short and the electrons cannot gain enough energy, between collisions, to ionize the gas; if the pressure is too low, they gain too much energy, greatly reducing the probability of collisions.) As each ion-electron pair is formed, the electron released is pulled towards the anode. If  $E$  is high enough, this electron will ionize another molecule, and the entire process will repeat itself.

The ion produced is accelerated towards the cathode. If the field is sufficiently intense, so that the ion can arrive at the cathode with energy equal to twice the work function, it will pull out one electron to neutralize itself, and expel a second one, which can be accelerated by  $E$ , to participate in more collisions.

Now, Townsend determined the following relationship. If  $dn$  is the increase in the number of electrons per second, travelling from position  $x$  to position  $x + dx$ , and  $\alpha$  is Townsend's first coefficient (a function of  $E$ , pressure, and the gas), then

$$dn = \alpha n dx$$

Integrating this equation from the cathode ( $x = 0$ ) to the anode,  $d$  units distant,  $n_a = n_0 e^{\alpha d}$  ( $n_0$  is the number of electrons leaving the cathode). Thus, for every electron leaving the cathode,  $e^{\alpha d}$

reach the anode, and so, it can be concluded, each electron has produced  $(e^{\alpha d} - 1)$  ion pairs.

Now, if the secondary electrons emitted by ion bombardment of the cathode are to be included, Townsend's second coefficient,  $\gamma$ , must be introduced. This term can be defined as the number of secondary electrons emitted from the cathode each time an ion strikes it. Thus, if  $(e^{\alpha d} - 1)$  ions reach the cathode,  $\gamma(e^{\alpha d} - 1)$  secondary electrons will be emitted. Since this effect will keep repeating itself, as secondary electrons ionize atoms, releasing electrons and more bombarding ions, the total number of electrons eventually arriving at the anode, due to the initial emission of a single electron, can be expressed as

$$\begin{aligned} n_a &= e^{\alpha d} + \gamma(e^{\alpha d} - 1)e^{\alpha d} + \gamma^2(e^{\alpha d} - 1)^2 e^{\alpha d} + \dots \\ &= e^{\alpha d} (1 + \gamma(e^{\alpha d} - 1) + \gamma^2(e^{\alpha d} - 1)^2 + \dots) \\ &= e^{\alpha d} / (1 - \gamma(e^{\alpha d} - 1)) \end{aligned}$$

The Townsend criterion for a self-sustaining discharge is now easily understood, for it states that  $\gamma(e^{\alpha d} - 1) = 1$ . Naturally, the theoretical infinite multiplication of electrons at this point is not attained, but the multiplication does become very large, and so many secondary electrons are produced that no further external radiation is needed to maintain the discharge. The discharge is now self-sustaining.

### II.3 NATURE OF THE DISCHARGE

Self-sustaining discharges are commonly grouped into three types, depending on the current-voltage relationship -- the Townsend discharge, the glow discharge, and the electric arc. The first is of very low intensity; the last requires a great deal of power and dissociates the molecules present. Consequently, these two are of little interest for this experiment.

The glow discharge normally divides itself into a number of light and dark bands.<sup>51</sup> (See Figure 9) In the Aston dark space, immediately adjacent to the cathode, little light is emitted, since the electrons have not yet gained enough energy to excite gas molecules, while the incoming ions are travelling so fast that their collision cross section is quite small. In the next region, the cathode glow, some of the excited gas molecules return to their ground state, after having been excited by the electrons. Next, in the Crookes dark space, those electrons which were not involved in collisions in the cathode glow region now have enough energy to ionize gas molecules, producing secondary electrons without sufficient energy to excite other molecules. In this region, a large, positive space charge builds up. The large voltage gradient thus produced accounts for most of the voltage drop across the tube. Electrons crossing this region are rapidly accelerated. At the junction of this region with the negative glow, the electron density becomes so great that the space charge becomes negative and the electrons are no longer accelerated. These electrons then

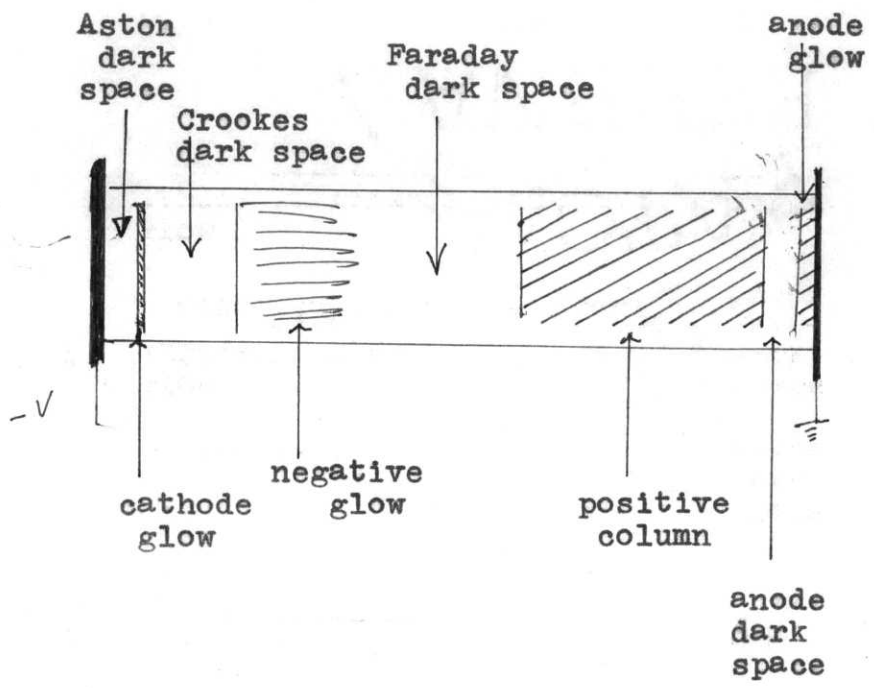


FIGURE 9. -- The gas discharge<sup>52</sup>

proceed through this region, ionizing gas molecules until all their kinetic energy is lost. Gradually, as the electrons lose their energy, this region fades into the Faraday dark space. As the slow-moving electrons are lost by recombination and diffusion in this region, the space charge returns to zero, and the field regains a value of several volts per centimeter. This leads to the formation of the last major region, the positive column, in which gas molecules are excited by the accelerated electrons.

The positive column is not characteristic of the discharge and, in fact, can be made to disappear under appropriate conditions of pressure and geometry. An arc line spectrum is emitted by this region.

## APPENDIX III

### DETAILS OF CONSTRUCTION

The discharge tube is made of Pyrex tubing,  $5/16$  inches in diameter (inside), and 3 inches long. (Tygon tubing was tried as a substitute for the glass, since it is far less fragile, but it was found to collapse when evacuated, and to melt, when the discharge was running.)

At each end of the tube is a brass compression fitting, as an electrode. The upper electrode is plugged with brass, (one end of which is made smooth, and projects into the discharge tube; the other is forced into a nylon insulator, which is firmly clamped to the supporting rod).

The prism table is enclosed in a brass cylinder, 4 inches in diameter, and  $3 \frac{1}{2}$  inches high. It has one opening, connected to the spectroscope collimator (by means of a short brass sleeve and a rubber light seal) and another, in the form of a slit  $1 \frac{1}{4}$  inches high and 3 inches long, at the height of the prism. At this level, a depression  $1/16$  inch deep and 2 inches wide is machined all the way around the cylinder. A sheet of thin brass, 2 inches wide and  $5 \frac{1}{2}$  inches long is formed to a 2 inch radius of curvature, and a  $3/4$  inch hole is machined in it (at prism level). Thin black felt is cemented to the inside of this sheet. On the outside, a tapered connector is soldered, to connect to

the scanning arm. This sheet swings around the cylinder in the depression. It is held in place, in a light-tight sliding bearing, by stretched 1/8 inch black foam rubber.

A cardboard tube, 7 1/2 inches long, is clamped firmly to the tapered fitting with a vacuum hose clamp. The other end is clamped, in like manner, to a brass assembly holding the imaging lens ( $f = 6 \frac{1}{2}$  inches), the viewing slit (in the focal plane of the imaging lens), and 3 inches further out, the photomultiplier. This entire assembly is enclosed in brass. All connections are made with long, tightly fitting, brass sleeves, and the joints that are not soldered are wrapped in black rubber. The inside of the entire apparatus is painted with three coats of ultra-flat black paint, to reduce glare and reflections. The inside of the cylinder containing the photomultiplier is wrapped with heavy, dark-coloured construction paper. This acts as thermal insulation, so that the dry ice packed around the photomultiplier does not have to cool the entire apparatus, too.

The assembly comprising the photomultiplier, the slit, the lens, and the curved sheet of brass, is firmly mounted on a brass rod, which rotates around a pivot directly under the prism. This arm is driven, through a worm gear drive and 1000/1 gear box, by a 300 RPM synchronous motor (connected to the gear box and worm gear through a flexible potentiometer coupler). (A slower, 60 RPM, motor can also be used, to reduce the jerkiness of the movement; however, this has not proved necessary.) The arm is mounted on two 3/4 inch ball bearings as wheels, and can swing quite freely. (It is driven at a rate of about  $0.05^{\circ}$ /second.)

The most critical part of the apparatus that had to be built was the  $3/4$  mil viewing slit, which was made in the following manner.

First, a brass tube 3 inches long and  $1\ 1/4$  inches in diameter, was machined to fit snugly inside the brass tube which holds the lens. Then two pieces of 6 mil copper stock,  $2$  inches square, were cut. One edge of each was filed straight. One of these pieces was then gently soldered to the supporting tube, so that its filed edge lay on a diameter of the circle. The second piece was then placed on the supporting tube, with its filed edge facing that of the first. Placing a piece of 1 mil copper stock between the two pieces, as a wedge, the two were pressed together, and the second soldered into place. This method was used to make both a 1 mil wide slit and a  $3/4$  mil slit. (The latter happened somewhat fortuitously, as the second piece of copper slipped at the critical moment, and overlapped the wedge slightly. In this manner, a perfectly good  $3/4$  mil slit was made.)



## APPENDIX IV

### ADDITIONAL DATA

The next two diagrams are typical of the data now being obtained. Both have the blue end of the spectrum at the top of the page. The strongest lines of helium have been marked, based on calibrated photos of the helium spectrum.<sup>53</sup> The wavelengths indicated correlate reasonably with those that would be estimated by superimposing the spectrum on page 28 onto this trace. For these two scans, the recorder is on a scale twice as sensitive as the one on page 28. These were made immediately after repacking the photomultiplier in dry ice.

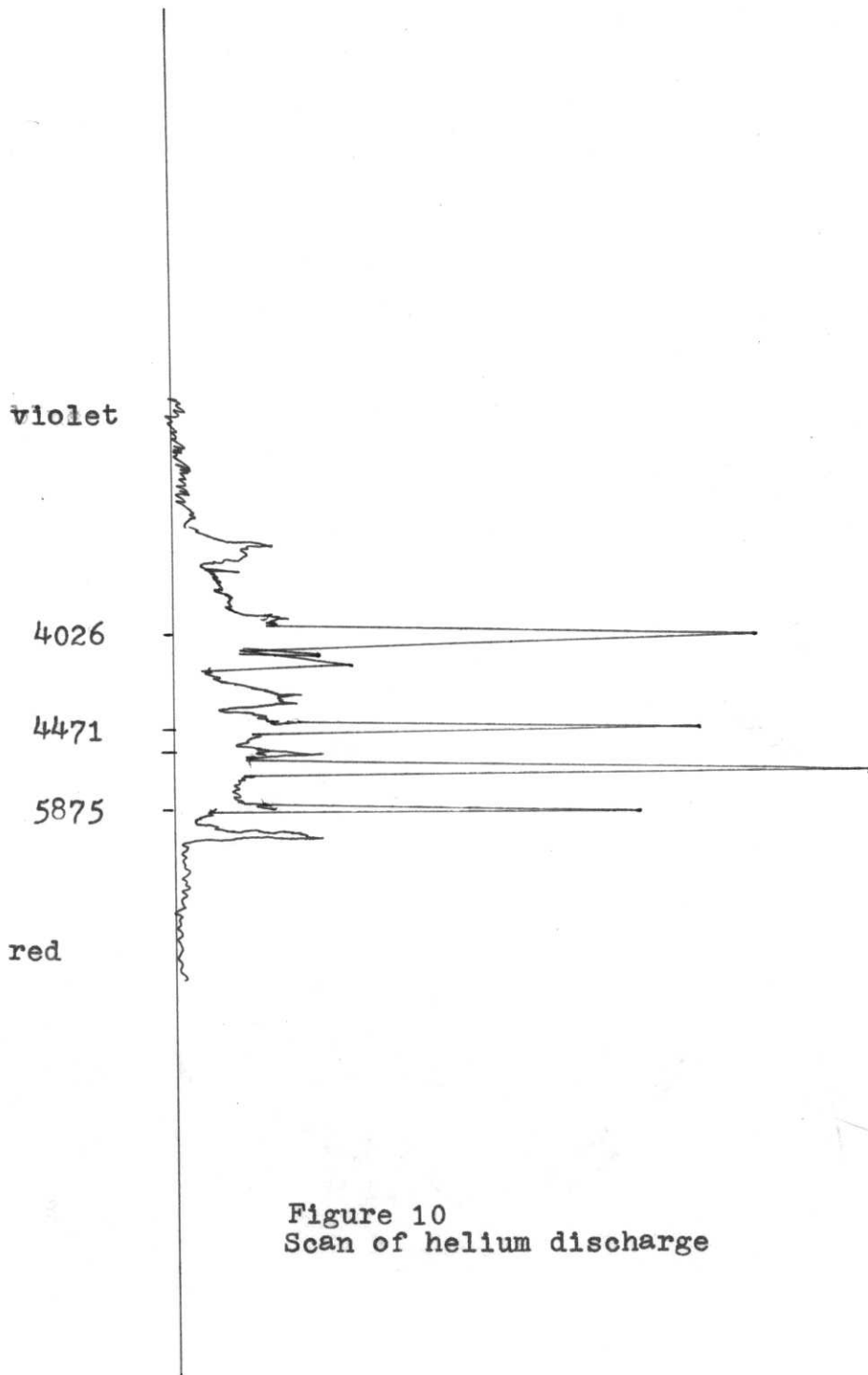


Figure 10  
Scan of helium discharge

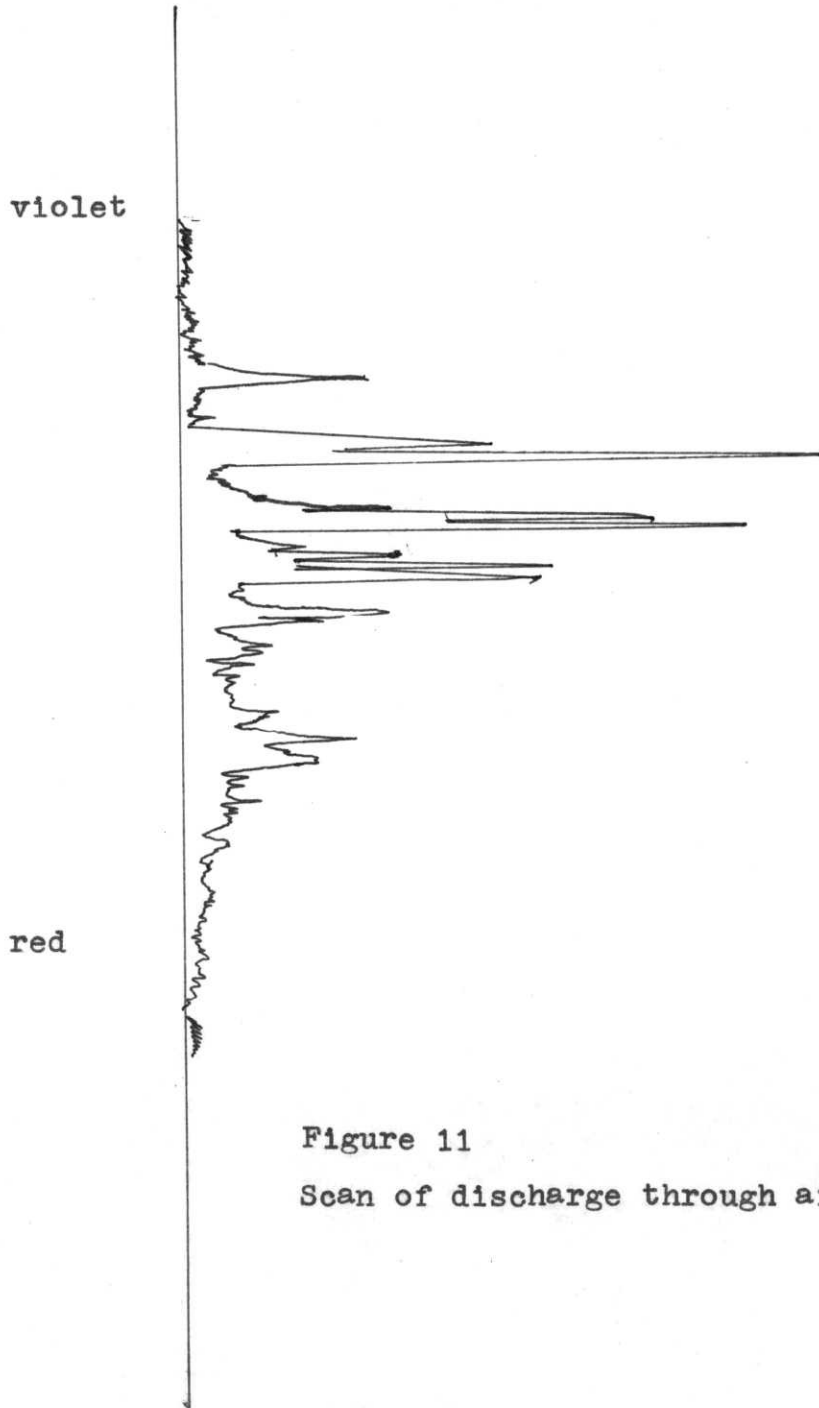


Figure 11  
Scan of discharge through air

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