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PHYSICAL CHEMISTRY OF EXOTHERMIC GAS-AEROSOL  
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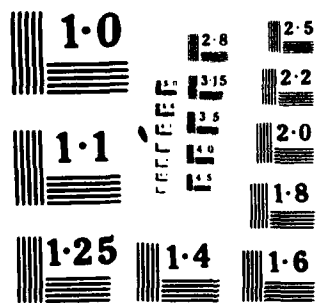
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| 19 ABSTRACT (Continue on reverse if necessary and identify by block number)<br>Infrared emission has been observed from exothermic gas-aerosol reactions. The principal system examined was liquid chlorosulfonic and aerosol reacting with ammonia and water vapor. The aerosols employed in this study have been polydisperse with mass medium diameters of a few microns. In order to develop methods to investigate the kinetics of rapid gas-aerosol reactions, a generator has been designed which produces monodisperse aerosol in the 0.5 - 1.5 $\mu$ m diameter range. This generator can be used with corrosive and reactive liquids. A flow reaction and sizing system has been designed and constructed. <i>Originator Suggested Keywords include:</i><br><br><i>Micrometer</i> |                                                    |                                                                                                 |                                                                                  |                                   |
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Spectral radiance

Infrared (IR)  
IR luminescence  
IR laser  
Thermal emission  
Volatile co-aerosol

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## PREFACE

The work described in this report was authorized by Contract DAAK11-80-C-0051, Physical Chemistry of Exothermic Gas-Aerosol Calorimetry. The work was performed from January 1983 to January 1984.

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## PHYSICAL CHEMISTRY OF EXOTHERMIC GAS-AEROSOL CALORIMETRY

### 1. INTRODUCTION

Infrared radiation in the atmosphere above normal background levels can be produced in a variety of ways. For example, combustion gases<sup>1</sup> can produce significant amounts of radiation in the infrared region (2-20  $\mu\text{m}$ ). However, the total mass of material, and thus the radiant emittance, is small. In addition, the gas cloud rapidly cools and disperses. In order to significantly increase the amount of airborne material, an aerosol must be employed.

At ambient temperatures (25°C) the maximum of the blackbody emission curve is at about  $1030\text{ cm}^{-1}$  (9.7  $\mu\text{m}$ ), which means that a few degrees increase in temperature will produce an increase in spectral radiance on the order of 5% at 5-10  $\mu\text{m}$ . A highly conducting and absorbing substance may approximate a blackbody, but most real aerosol particles will at best be "grey" bodies with perhaps some superimposed structure (selectivity). The (equilibrium) thermal emittance of an aerosol particle will therefore be less than that of a blackbody at the same temperature, according to Kirchoff's Law. A second and more selective method could involve the production of infrared fluorescence. This would have the advantage of being selective as to wavelength range and would thus also require much less total energy input.

In order to accomplish the desired goal, an exothermic chemical reaction must be employed to raise the temperature of the aerosol particle above ambient. This reaction must ultimately involve either the reaction of a gas with the aerosol or the simultaneous generation of a very highly disperse co-aerosol which will rapidly coagulate with the coarser aerosol and react. This is technically more difficult, and there would always be the problem of the

highly disperse aerosol coagulating with itself. In the former case, the gas could be generated as a volatile ex-aerosol.

A large number of chemical reaction studies have been performed on the upper end of the particle size spectrum with regard to the combustion of fuel sprays and dust clouds.<sup>2</sup> These involve particles in the super-micron range ( $10-100 \mu\text{m}$ ). Chemical reactions responsible for heterogeneous nucleation have also been investigated,<sup>3-5</sup> and the particle sizes here are below  $0.1 \mu\text{m}$ . However, once aerosols are produced either by nucleation and growth in the atmosphere or by nebulization followed by settling and coagulation, most of these achieve a relatively stable existence in the  $0.1-10 \mu\text{m}$  range as smokes, fogs etc.<sup>6-7</sup> These systems are polydisperse, with number densities generally less than  $10^7 \text{cm}^{-3}$ . Nonetheless, there have been relatively few studies of the reactions of gases with aerosol particles in this size regime.

In principle, the reaction rate may be controlled by gas phase diffusion of reactants and/or products in the particle, by the bulk chemical reaction, or by processes occurring in the droplet interface region. Cadle and Robbins<sup>8</sup> have developed equations for some limiting cases and applied them to the reaction of ammonia with sulfuric acid aerosols in the  $0.2-0.9 \mu\text{m}$  range and to the reaction of  $\text{NO}_2$  with a sodium chloride aerosol. In the former case, it was suggested that the rates in concentrated  $\text{H}_2\text{SO}_4$  droplets were controlled by diffusion of reaction product in the particle. In dilute  $\text{H}_2\text{SO}_4$  droplets, the rate was too fast to measure on their apparatus, and it was presumed that the rate was controlled by gas phase diffusion.<sup>8,9</sup>

There have also been a number of studies of the metal-catalyzed oxidation of  $\text{SO}_2$  in aqueous aerosols. Johnstone and Coughanour,<sup>10</sup> using a suspended  $500-1000 \mu\text{m}$  drop concluded that the reaction was liquid phase controlled with all of the reaction occurring in the outer shell at high manganese

concentration. At lower catalyst concentration, the  $\text{SO}_2$  penetrated to the center of the drop. The oxidation of  $\text{SO}_2$  in 100-1000  $\mu$  aqueous ammonia drops was also controlled by liquid phase diffusion.<sup>11</sup> However, extrapolation of the manganese catalyzed oxidation rates in the supermicron drop to an atmospheric fog of 20 $\mu$ m droplets predicted a rate 500 times than that observed.<sup>12</sup>

Because of the importance of atmospheric reactions,<sup>13</sup> studies have focused on water droplets and reactions involving  $\text{SO}_2$ ,  $\text{NO}_2$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{SO}_4$  and various metal salts. In these cases, the complex reactions are generally also accompanied by droplet growth. This is not the case in the well-controlled reaction of submicron sized 1-octadecene droplets with bromine gas.<sup>14</sup> Although, this reaction is slow and not highly exothermic. Nonetheless, these studies do indicate that it should be possible to produce thermal emission as a result of a gas-aerosol reaction.

The objective of this work was to investigate by means of exothermic reactions between aerosols and reactant gases the production of infrared radiation above normal background levels. The first stages of this investigation involved an examination of the feasibility of observing such infrared emission by examining a number of candidate (model) gas-aerosol systems. The reaction of a chlorosulfonic acid aerosol with ammonia/water vapor as the reactant gas was found to give reasonable emission levels, and was used for a confirmation of the feasibility studies. This work is described in the proceedings of the Chemical Systems Laboratory (CSL) Conference on Obscuration and Aerosol Research (1979 and 1980), and summarized in a final report to the US Army Research Office.<sup>15-17</sup>

In the second stage, a more quantitative study of gas-aerosol reactions was initiated, and experimental methods were further developed. Temperature-distance and radiant emittance-temperature profiles were obtained, and a new

monodisperse aerosol generator was designed. This is described and summarized in the proceedings of the 1981 CSL Conference on Obscuration and Aerosol Research,<sup>18</sup> a technical report,<sup>19</sup> and journal article.<sup>20</sup>

We report here on the operating characteristics of the monodisperse aerosol generator, the design of a flow system for kinetic studies, and the determination of the spectral distribution of the infrared radiation emitted from the reaction of chlorosulfonic acid aerosol with  $\text{NH}_3$  and water vapor.

## 2. AEROSOL GENERATOR

A schematic of the apparatus is shown in Figure 1. Helium carrier gas produces NaCl nuclei in the furnace (B), and this gas stream is then used to atomize the liquid in the nebulizer (E). The concentration of nuclei may be controlled by both the flow rate and the length of tubing between the furnace and nebulizer. The syringe pump is adjusted to maintain a constant level of liquid in the nebulizer to provide a constant output rate. The total amount of liquid in the nebulizer is about 10ml, and a syringe of any convenient size may be employed. Typically, 10ml of liquid will provide about two hours of continuous operation. The polydisperse aerosol entering the heated zone (H) is vaporized, and part of this vapor is recondensed on the salt nuclei in the air and water cooled chimney sections (J and K). The homogeneous (monodisperse) aerosol emerges from the outlet (L). Once the furnace and evaporator are at temperature, the colors of Higher Order Tyndall Spectra (HOTS) are observed within a few minutes of turning on the carrier gas supply (maintained at 20 psi gauge). The aerosol output stabilizes within ten minutes.

The entrance chamber (G) is 2 cm inside diameter (I.D.) and 14 cm long. The tube from the nebulizer enters about midpoint. This tube connects via a 24/40 standard taper to the evaporator (H) and air cooled chimney (J) which is

a single tube of 1.5 cm I.D. and 35 cm long. A length of 25 cm wrapped with heating tape is the evaporator section (H). The water cooled condensor (K) is 20 cm long with a 1.2 cm I.D., and connects to (J) via a 20/40 joint. The outlet (L) is a reduction fitting which necks down within 3 cm to a 0.5 cm I.D. tube from which the aerosol emerges.

The nebulizer output increases slightly with increasing flow rate ( $\sim 3-5$  L/min), although the mass concentration was approximately constant at  $2.5 \pm 0.01 \times 10^{-2}$  g/L (75% of this is lost in the entrance chamber). The polydisperse aerosol entering the heated zone is completely vaporized at  $125^{\circ}\text{C}$  as evidenced by the lack of both wall condensate and any visible aerosol for about 2-3 cm above the heating tape. Most of the remaining 25% represented by this vapor is lost by condensing on the walls of the cooling chimney, and only about 1% emerges as homogeneous aerosol. The evaporation temperature does not appear to be too critical as long as it is above some critical value. For example, at a flow rate and furnace temperature of 3.31/min and  $590^{\circ}\text{C}$ , respectively, essentially the same polarization ratio curves were obtained for evaporator temperatures of  $100^{\circ}$ ,  $125^{\circ}$ , and  $150^{\circ}\text{C}$ . However, at  $75^{\circ}\text{C}$ , appreciable polydispersity was evident.

A number of experiments were carried out under a fixed set of conditions in order to test the stability and reproducibility of the generator. By stability, we mean the uniformity of the particle radius as measured over a given period of steady operation of the generator, usually from several hours a day. The stability is illustrated by the the results in Table 1 obtained over a period of 3 hours. These have been selected from among scores of similar results as being typical of the performance of the generator. The mean radius is  $0.628 \mu\text{m}$  with a relative standard deviation of 0.4%. By reproducibility we mean uniformity of the particle size under the same operating conditions on different days or on the same day, with an intervening

period when the generator was either shut down or operated under different conditions. The data in Table 2, taken over a four month period, show a mean of 0.628  $\mu\text{m}$  and a relative standard deviation of 1.5%

Table 1. Aerosol Generator Stability Under Continuous Operation at a Furnace Temperature 590°C, Evaporator Temperature 125°C, and Helium Flow Rate of 3.3 Liters Per Minutes

| <u>Run</u> | <u>Time (min)</u> | <u>Radius (<math>\mu\text{m}</math>)</u> |
|------------|-------------------|------------------------------------------|
| 2          | 50                | 0.616                                    |
| 7          | 70                | 0.625                                    |
| 10         | 90                | 0.630                                    |
| 15         | 110               | 0.631                                    |
| 18         | 130               | 0.628                                    |
| 25         | 150               | 0.629                                    |

Note: The radii were determined from light scattering measurements by the polarization ratio method at two wavelengths.

Table 2. Aerosol Generator Reproducibility (Vide Text)

| <u>Run</u> | <u>Time</u> | <u>Radius</u> ( $\mu\text{m}$ ) |
|------------|-------------|---------------------------------|
| 5          | 30 min.     | 0.620                           |
| 9          | 3 hours     | 0.630                           |
| 16         | 6 hours     | 0.615                           |
| 25         | 10 hours    | 0.635                           |
| 26         |             | 0.640                           |
| 34         | 2 days      | 0.619                           |
| 35         |             | 0.628                           |
| 48         | 8 days      | 0.638                           |
| 49         |             | 0.630                           |
| 60         | 20 days     | 0.640                           |
| 61         |             | 0.630                           |
| 72         | 2 months    | 0.610                           |
| 73         |             | 0.619                           |
| 85         | 4 months    | 0.634                           |
| 86         |             | 0.628                           |

Note: Same conditions as in Table 1.

The effect of flow rate on radius number concentration is shown in figures 2 and 3. The radius decreases with increasing oven temperature and increasing flow rate due to an increase in nuclei concentration and possibly a bit less mass transfer in the evaporator and a bit more condensation loss in the chimney. This type of behavior has been observed in other generators.<sup>21</sup> Since the number concentration increases linearly with flow rate and the mass concentration does not vary greatly ( $1.5 + 2.5 \times 10^{-4}$  g/L) the nuclei concentration is roughly proportional to the flow rate.

That the particle radius in this generator does in fact depend on the external nuclei concentration is shown by the data in Table 3. Varying lengths of Tygon tubing were inserted between the furnace and the nebulizer to remove the nuclei by diffusion to the wall thus decreasing their concentration. As expected, the droplet radius increased.

Table 3. Effect of Decreasing Nuclei Concentration (Increasing Tubing Length) On Particle Radius at a Furnace Temperature 725 C, Evaporator Temperature 125 C, Helium Flow Rate 3.3 Liters Per Minute (Vide Text)

| <u>Run</u> | <u>Length</u> | <u>Radius of particle ( <math>\mu</math>m )</u> |
|------------|---------------|-------------------------------------------------|
| 120        | 2.00          | 0.504                                           |
| 121        | 2.00          | 0.500                                           |
| 122        | 2.00          | 0.506                                           |
| 123        | 2.00          | 0.501                                           |
| 130        | 7.50          | 0.547                                           |
| 131        | 7.50          | 0.545                                           |
| 132        | 7.50          | 0.540                                           |
| 135        | 15.00         | 0.630                                           |
| 136        | 15.00         | 0.636                                           |
| 137        | 15.00         | 0.628                                           |
| 140        | 30.00         | 0.704                                           |
| 141        | 30.00         | 0.710                                           |
| 142        | 30.00         | 0.707                                           |

It may also be mentioned that we have also successfully generated monodisperse aerosols of sulfuric acid and chlorosulfonic acid in this generator. All the components are glass, and the only change is the replacement of Tygon with flexible Teflon tubing.

## 3. LIGHT SCATTERING MEASUREMENTS

A Price-Phoenix series 2000 light scattering photometer was employed for measuring the scattered light intensity. The aerosol was flowed through a cell similar to that described by Matijevic, Vitani, and Kerker.<sup>22</sup> The only modification was the addition of a sheathing gas (nitrogen) flow of 2.1 l/min around the inlet tube to improve columnation and stability of the aerosol stream. The standard slit in front of the photomultiplier was replaced by a circular aperture of 1 mm diameter in order to minimize the solid angle subtended by the photomultiplier. The internal surfaces of the cell were painted black to reduce reflections and stray light. Signals corresponding to the intensities of the vertically and horizontally polarized components of the scattered light were measured at 2° intervals between 50° to 130°. The 436- and 546-nm lines of the mercury lamp were employed for all of the measurements. A background correction, taken with no aerosol flowing, was applied to the scattering measurements. After a set of background and sample intensities were obtained as a function of angle, the set was repeated to ensure constancy of the aerosol concentration and flow pattern. No polarization of the mercury light source was detected at any scattering angle.

## 4. MICROSCOPE MEASUREMENTS

The aerosol was diluted by a factor of about 8500 and allowed to impinge on a cleaned glass microscope slide from a tube of 0.7 cm I.D. The slide was examined under a REICHERT Light Microscope model number 324882 at a magnification of 1300X. A photograph is shown in Figure 4. The drops are somewhat distorted from collision with the slide. However, measuring both the major and minor axis of each drop yields a mean radius of 0.65  $\mu\text{m}$ . which, may be compared with a modal radius of 0.63  $\mu\text{m}$  from the light scattering measurements (vide infra).

## 5. MASS CONCENTRATIONS

The mass concentrations reported here were all obtained by allowing the aerosol stream to pass through 0.5- $\mu$ m millipore filters, 1 inch in diameter, in teflon holders. Aerosol was collected for 15 minutes, and the filter assemblies weighed on a five-place Mettler balance, model H18. The nebulizer rate was obtained by weighing the nebulizer operating by itself. The flow rates were measured by means of ACE Glass Incorporated, Vineland, NJ Model #7481 rotameters using #36 glass floats.

## 6. INFRARED EMISSION

The spectral distribution of the infrared (IR) emission from the gas-aerosol reaction has been determined employing the experimental apparatus shown in Figure 5. The reacting aerosol stream from the reaction tube passes in front of a remote chopper placed in front of the monochromator. Since only chopped radiation is detected by the pyroelectric radiometer, this eliminates emission from the monochromator itself, which has been found to constitute a significant background interference. Using this arrangement, a perfectly flat baseline is obtained over the wave length range examined to date (2-15  $\mu$ m). The function of the concave mirror is to focus as much of the emitted IR radiation as possible on the entrance slit of the monochromator. Low intensity, resulting in low signal to noise, is a significant problem. Operating with wide-open slits, the bandpass is 1.6  $\mu$ m. We have examined the effect of decreasing the slit width down to a bandpass of 0.32  $\mu$ m. The half width of the emission bands narrow, but the band maximum are unaffected. Therefore, in the present study all spectra were obtained at low resolution.

For reference purposes, spectra were also obtained by fixing a graphite rod in place of the aerosol stream. The rod was bored out, and a resistance heater inserted. The surface temperature of the rod was measured by means of

a flat thermistor. This arrangement was used in order to provide a heated (approximate) blackbody source of the same geometry as the aerosol stream. As a second reference, a flat plate target was positioned in place of the mirror. This was a blackened metal plate through which water was circulated to control the temperature.

A spectrum of the IR emission from the reaction of a chlorosulfonic acid aerosol with gaseous ammonia and water is shown in Figure 6. The two reference spectra are also shown. These spectra have not been corrected for the monochroator response (the grating is blazed at  $8\ \mu$ ). The reference spectra are blackbodies at least to the extent that the maxima obey the Wien displacement law. The emission spectrum from the gas-aerosol reaction is seen to consist of two principal bands centered at about 11 and  $13\ \mu$ . The nominal temperature of the reacting aerosol stream as measured by a thermistor is  $32^{\circ}\text{C}$ , the same as that of the reference targets. This 'nominal' temperature however is not necessarily either the drop or gas temperature. The total intensity emitted by the reaction is about 15% of that emitted by the graphite rod.

It is immediately evident that the aerosol is not emitting as a blackbody. It may also be noted that the emission should be coming from the aerosol particle since nitrogen does not emit here. There is of course some water vapor and ammonia gas also present at lower concentration. Water vapor does not have any major absorption bands in the 11-13  $\mu$  region, while  $\text{NH}_3$  does have a maximum at about 10.5  $\mu$ . Therefore, it seems unlikely that the observed  $1\ \mu$  emission is due to heat transferred to  $\text{NH}_3$  gas.

Aside from the carrier and reactant gases, what possible materials may be present during the course of the reaction? Some of the possibilities are listed below.

| <u>Substance</u>             | <u>Phase</u>                          |
|------------------------------|---------------------------------------|
| $\text{ClSO}_2\text{H}$      | liquid (unreacted aerosol)            |
| $\text{NH}_4\text{Cl}$       | solid (aerosol) or solution (aerosol) |
| $(\text{NH}_4)_2\text{SO}_4$ | solid (aerosol) or solution (aerosol) |
| $\text{NH}_4\text{HSO}_4$    | solid (aerosol) or solution (aerosol) |
| $\text{H}_2\text{SO}_4$      | liquid (aerosol)                      |
| $\text{SO}_2$                | gas or solution (aerosol)             |

It is also conceivable that species such as  $\text{NH}_4\text{ClSO}_3$  can exist for short periods in the aerosol particle. An important question that we then wish to answer is the source of the observed emission. In Figures 7 and 8 is shown the emission spectra of thermally heated samples of  $\text{NH}_4\text{Cl}$ ,  $(\text{NH}_4)_2\text{SO}_4$  and  $\text{ClSO}_2\text{H}$ . The solid salts were pressed into KBr discs and placed in a heated cell holder in front of the chopper. The liquid  $\text{ClSO}_2\text{H}$  was placed between quartz plates in the same cell holder. Appropriate background corrections for KBr and quartz were made, all at  $50^\circ\text{C}$ . In addition, a  $\text{ClSO}_2\text{H}$  aerosol was thermally heated to  $50^\circ\text{C}$  by passing it through a hot tube. As shown in Figure 8, both the heated bulk and aerosol  $\text{ClSO}_2\text{H}$  gave the same emission spectra. In all cases, the observed emission maxima correspond to the absorption maxima in the IR spectra of these substances. Of the three materials examined thus far, only  $\text{ClSO}_2\text{H}$  has a band at  $11\mu\text{m}$  and none have a band at  $13\mu\text{m}$ .

What is perhaps more important to note is that no other emission bands in the 8-15  $\mu\text{m}$  region are observed from the gas-aerosol reaction, while all bands are observed from thermally heated samples. Therefore, one possibility is that the 11 and 13  $\mu\text{m}$  bands are from a substance (or substances) which

have no other bands at wavelengths shorter than 11  $\mu\text{m}$ . A second and quite interesting possibility is that non-equilibrium emission is being observed. This means that some initial stage of the reaction leads to the population of a particular normal mode of a product, reactant or adduct, which then directly emits rather than distributing the vibrational excitation to other modes or to the lattice (i.e., in effect, IR chemiluminescence). At this point, chemiluminescence is still speculation and further studies will have to be performed to answer this question.

## 7. REACTION KINETICS

We are designing a system in which to examine the kinetics of the reaction between the gas and the aerosol. Monodisperse aerosols will be employed, and rate studies performed as a function of droplet diameter and reactant gas concentration. The first reaction which will be examined is that between gaseous  $\text{NH}_3$  and sulfuric acid aerosol. This system has been chosen since it has been previously examined.<sup>8</sup> In addition, it has also been shown to produce IR emission<sup>17</sup> and is chemically simpler than the  $\text{ClSO}_3\text{H}$  system. This apparatus will also be used subsequently to examine the  $\text{ClSO}_3\text{H}$  aerosol reaction. The basic idea is to react the aerosol and gas for specified lengths of time determined by the flow rate and reaction tube length and diameter. The gas is then separated from the aerosol using molecular sieves, and the aerosol collected and analyzed (Figure 9).

The generator used for producing monodispersed aerosol has already been discussed above. The aerosol generator employed in this study produces monodispersed aerosol at flow rates between  $237 \text{ cm}^3 \text{ sec}^{-1}$ . The mean diameter of the aerosol is about  $1.0 \mu\text{m}$ , which is determined on a Price-Phoenix light scattering photometer by measuring the polarization ratio. Using the above aerosol diameter, the number concentration is  $1.2 \times 10^5 \text{ cm}^{-3}$ .

The gas-aerosol mixer is constructed of glass (Figure 10). On opposite sides at the rounded end of a cylindrical cell, 10 mm in diameter and 30 mm long, are two orifices with 1.8-mm openings. At the outlet of the gas-aerosol mixer is a 14/20 ground glass female fitting to accommodate the 10 mm diameter reaction columns. Another mixer is also constructed with the same type of design and 1.8-mm orifices. However, the diameter of the latter design is increased to 20 mm and the ground glass fitting increased to 24/40 to couple with the 20-mm diameter reaction columns. The 1.8-mm orifices accelerates the incoming gas and aerosol to a velocity sufficient to achieve thorough mixing. The gas-aerosol becomes laminar immediately after leaving the mixing zone because of the relatively large cross sectional area of the cell cavity. This behavior is observed by employing a visible tracer. Hydrogen chloride gas is introduced through one orifice and ammonia gas through the other. Moreover, the Reynolds number for the 10-mm and 20-mm reaction columns are calculated to be 139 and 278 respectively. Both of these figures are well in the range for laminar flow.

The reaction columns are cylindrical glass tubes of various lengths. For short reaction times, 10-mm glass tubes with 14/20 ground glass male fittings at each end are used. In the interest of avoiding cumbersome lengths, the 20-mm glass tubes with 24/40 male fittings are employed at long reaction times.

Also, a system has been designed to monitor and control the reagent gas concentration. This system consists of a micro-flowmeter ranging from 0.0 to 15.0 ml/min and a micro-flow valve with a vernier scale to ensure reproducible flow settings.

The separation column is 80mm in diameter which effectively increases the residence time of the gas-aerosol mixture to increase the extraction efficiency of ammonia gas from the aerosol mixture. Moreover, the intake ends and

exhaust ends are tapered at 45 degrees to prevent sudden changes in volume which in turn eliminates turbulence. The overall lengths of the separation cavities are 10 cm with a 24/40 female fitting at the intake end for long reaction times and a 14/20 female fitting at the intake end for short reaction times. Both separation columns have 24/40 male fittings at the exhaust end.

At the exhaust end of the separation column is a 24/40 ground glass male fitting. A glass cap is placed in the exhaust end of the separation column which reduces to 1/4-inch teflon tubing. The reason for a nonhermetic separation system is because of molecular sieve replacement and cleaning ease. The collection device is a 47-mm filter holder. A 47-mm teflon filter with a 0.5- $\mu$  pore size is used for collecting the aerosol. The teflon filters after collection of aerosol are treated with 0.5 ml of ethanol to make the teflon wettable for aqueous extraction. The filters are then submerged in a glass titration beaker containing 50 ml of water. The glass titration beaker is then subjected to ultrasound to facilitate and ensure complete extraction.

Ion chromatography is used to analyze both the ammonium ion concentration and sulfate ion concentration. Ion chromatography has the advantage of determining the relative ammonium to sulfate ion concentration. It turns out that this feature is a necessity, on account of the lack of reproducibility in the sulfuric acid concentration. The lack of reproducibility stems from the loss of sulfuric acid on the molecular sieves. A calibration curve for the sulfate ion is very linear with a correlation coefficient of 0.9999%. On the other hand, the calibration curve for the ammonium ion is nonlinear. Since the detector in the Dionex ion chromatotron is a conductivity probe, the nonlinear behavior is expected for a weak electrolyte.

Before conducting the kinetic reactions an ambient flow rate of ammonia is determined. A value of 0.23 ml/min is sufficient for the gas-aerosol reaction without breaching the sieve column. Using the above ammonia flow

rate, in 0.0534 sec, 9 percent of the 1.0  $\mu\text{m}$  sulfuric acid aerosol has reacted with a total flow rate of 500  $\text{cm}^3/\text{sec}$  with a number concentration of  $1.2 \times 10^6 \text{ cm}^{-3}$ .

#### 5. SIZE DISTRIBUTION

When examining gas-aerosol reactions as a function of particle size one is interested, besides the kinetics, in knowing the particle size and the size distribution, i.e., monodispersity. Also, some information can be gained from determining the size distribution before and after a reaction. Sometimes it is necessary to see if the monodispersity changes as a function of time. To determine size distribution, techniques like monochromatic light scattering are employed to measure the polarization ratio and impactors which are time consuming and laborious. Using a monochromatic light source will afford the particle size but only gives some indication of their monodispersity. Furthermore, many parameters must be determined or known to calculate particle size, i.e., wavelength of incident light, detection angle of scattered light, and refractive index of the aerosol component. In other techniques, such as electron microscopy, preparatory steps must be taken to ensure the integrity of the droplet shape on the slide. The above techniques will not yield instantaneous or "on line" data.

By employing a computer based white light scattering instrument no previous knowledge of the aerosol composition is required. The polychromatic light source eliminates the dependence on incident light wavelength and detection angle. Additionally, no Mie scattering calculations have to be performed to generate scattering pattern graphs for comparison with Mie scattering data.

The design of a white light scattering instrument can best be described by dividing it up into four major components: optics, electronics, analog to digital convertor, and microprocessor.

The optical system consists of an optical cavity, tungsten filament lamp (2 volts, 0.15 amp), condenser lens, fixed slit relay lens, light trap parabolic mirror, focus lens, and photomultiplier tube (Figure 11). The light from the tungsten filament lamp passes through condensing lens and focused on the fixed slit, which defines the cross section of the beam. The light then passes through the relay lens and the image of the fixed slit is focused on the axis of the flow tube. If no particles are present all of the light from the beam is completely absorbed by the light trap. The light trap is placed at such a distance from the image focal point, as to capture all of the divergent source light and none of the scattered light. In the presence of aerosol particles some of the incident light is scattered and reflected off the parabolic mirror and directed towards the focus lens. At the focus lens the scattered light converges on a dinode in the photomultiplier tube. The electrical current given off by the photomultiplier tube is proportional to the intensity of the scattered light.

At the present time the electronic designs, i.e., amplifying and stabilizing circuits, have not been completed. However, a proposed general circuit system has been laid out (Figure 12). The line power is fed to a stepdown transformer and after this point it is rectified to D.C. voltage and smoothed. The power is then distributed to the tungsten filament lamp amplifier, and high voltage supply. To prevent voltage fluctuations there are independent voltage regulators supplying the tungsten filament lamp and the amplifier board along with the high power supply board. The photomultiplier tube is driven by the high power supply. The high power supply consist of a high voltage transformer followed by a high voltage D.C. filter and regulator. The signal coming off the photomultiplier tube is amplified and passed to a pulse height discriminator to determine if the signal is real. If the signal

is substantial it is sent to a sample and hold where the peak voltage is stored and later transferred to the analog to digital board. The analog signal is then converted to a digital signal and stored in the microprocessor (Figure 13).

The analog to digital (A/D) converter is a Tecmar AD-100 with a Data Translation DT2812 and resides in a C-100 Expansion Bus (Figure 14). The Tecmar A/D board is configured for an eight channel differential converter, plus or minus 10 volts input, and input/output (I/O) mapped. Zero volt input and +10 volt input corresponds to 0000H and 07FFH, respectively. Similarly, 10 volts is sectioned into 2048 division roughly five millivolts apart with 12 bit accuracy and linearity. The Tecmar A/D board is capable of 25 KHz data throughput rate with an absolute full scale accuracy of plus or minus the least significant bit (LSB) or 0.025 percent.<sup>23</sup>

The Exidy Sorcerer computer is a Z80 based microprocessor containing 48K of memory and a 4MHz clock cycle. There is actually only 32K of RAM less the CP/M operating system.<sup>24</sup> Peripherals consist of an Integral Data Systems printer, Amdex CRT, one single density and one double density Micropolis disk drive (16 hard sectored).

The printer is strapped to accept parallel data and the CP/M operating system is modified from a serial list driver to a parallel list driver making the two compatible. Parallel data transmission is chosen by virtue of its high data sending rate.

Individual pixel addressing for high resolution graphs is not possible with the Exidy Sorcerer computer. Rather the CRT is accessed in 8x8 pixel matrices because of the Exidy's screen RAM layout.<sup>24</sup>

In the following section the development of a software control system is discussed. Initially both the data acquisition and data manipulation programs are written in Microsoft BASIC (Appendix I). As somewhat expected, the data

acquisition program turned out to be extremely slow, about two seconds for each data point. On the basis of high speed data retrieval the data acquisition program is rewritten in assembly language with *WORD* opcode<sup>26</sup> (Appendix II). The data acquisition program basically utilizes the *286* microprocessor as a software controlled pulse high discriminator, sample and hold, and data retrieval system. Even with assembly language, the above software package proved to be taxing on the time domain required for high speed data acquisition. The main problem lies in the sample and hold portion of the program being synchronous, the time sampling intervals are too far apart to attain accurate peak heights. In other words, the time tolerance or precision is unacceptable in comparison with the 5 millivolt conversion limit on the A/D board. To increase the rate of data retrieval and to alleviate the time demands on the microprocessor, the sample and hold and pulse height discriminator are hardware controlled. The data acquisition program will eventually be changed to an interrupt driven subroutine to free up the microprocessor to perform the data manipulation program when no immediate data is present. For reasons of language flexibility, with respect to interrupt routines, the interrupt driven data acquisition program is written with *Z80* opcode (Appendix III).

#### 9. CONCLUSIONS

Initial studies have indicated that non-equilibrium infrared emission is observed from the  $\text{ClSO}_3\text{H}$  aerosol -  $\text{NH}_3/\text{H}_2\text{O}$  vapor reaction. However, due to the relatively low emission levels compared with high levels of background emission, these results need to be reexamined. The monodisperse aerosol generator should be useful in future studies where monodisperse high number density aerosols of reactive fluids are required. The flow system designed for the investigation of the kinetics of rapid gas-aerosol reactions should be adaptable to a variety of systems, but requires confirmatory testing.

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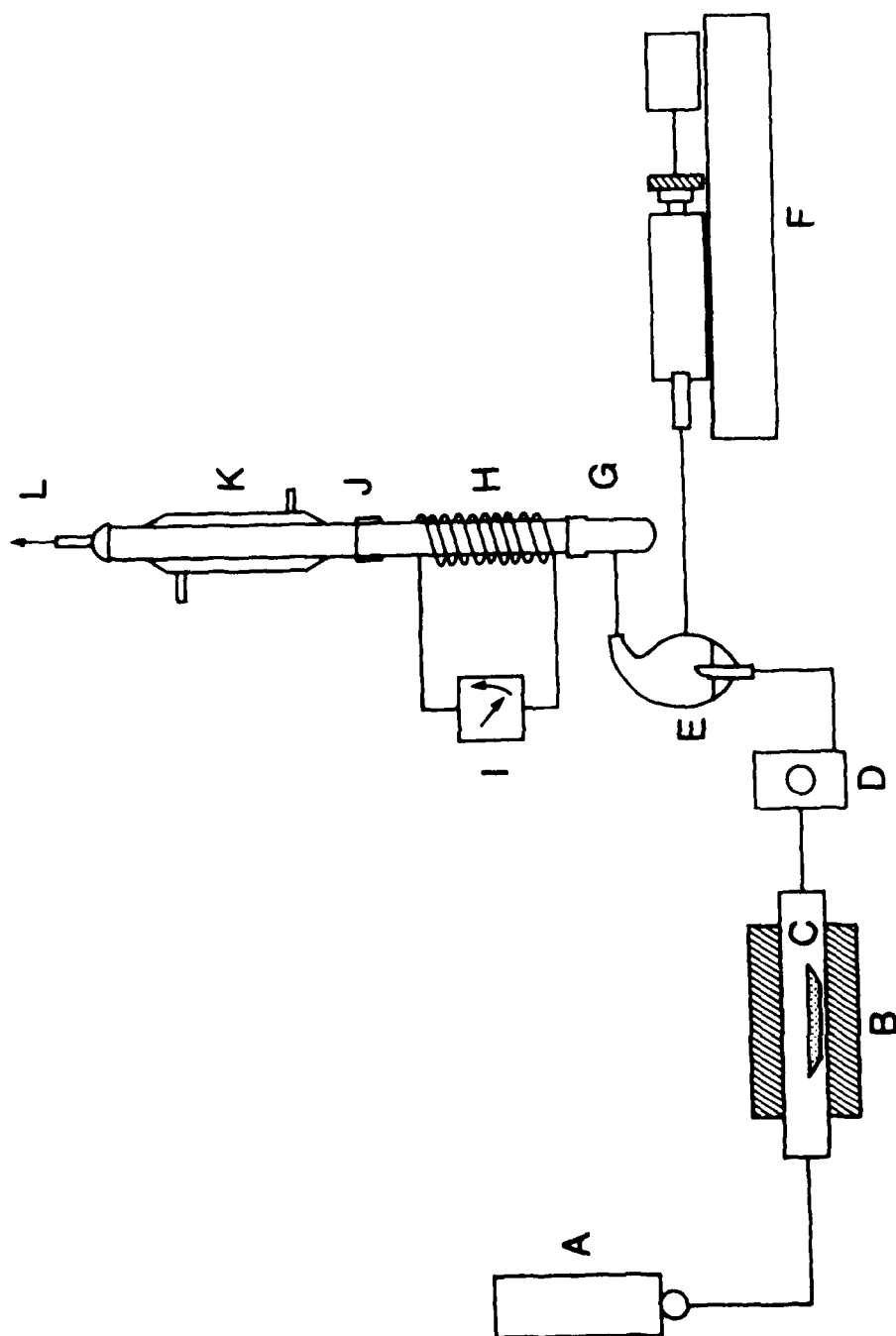


Figure 1. Schematic of Aerosol Generator.

(A) Gas supply, (B) Furnace, (C) Boat containing salt, (D) Flow meter, (E) Nebulizer, (F) Syringe and pump, (G) Entrance chamber, (H) Heating tape wrapped evaporator, (I) Voltage control, (J) Air cooled chimney, (K) Water cooled condenser, (L) Aerosol outlet.

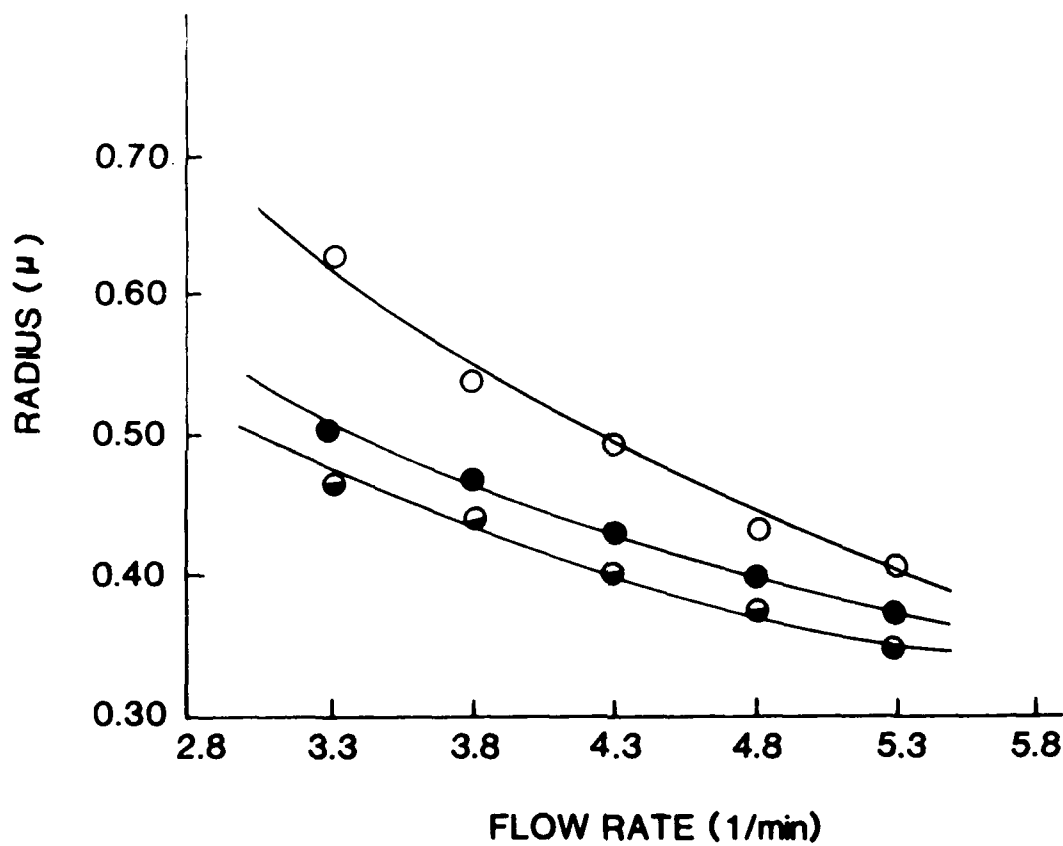


Figure 2. Radius as a Function of Flow Rate at Various Furnace Temperatures; 590°C (open), 725°C (closed), 790°C (half-filled)

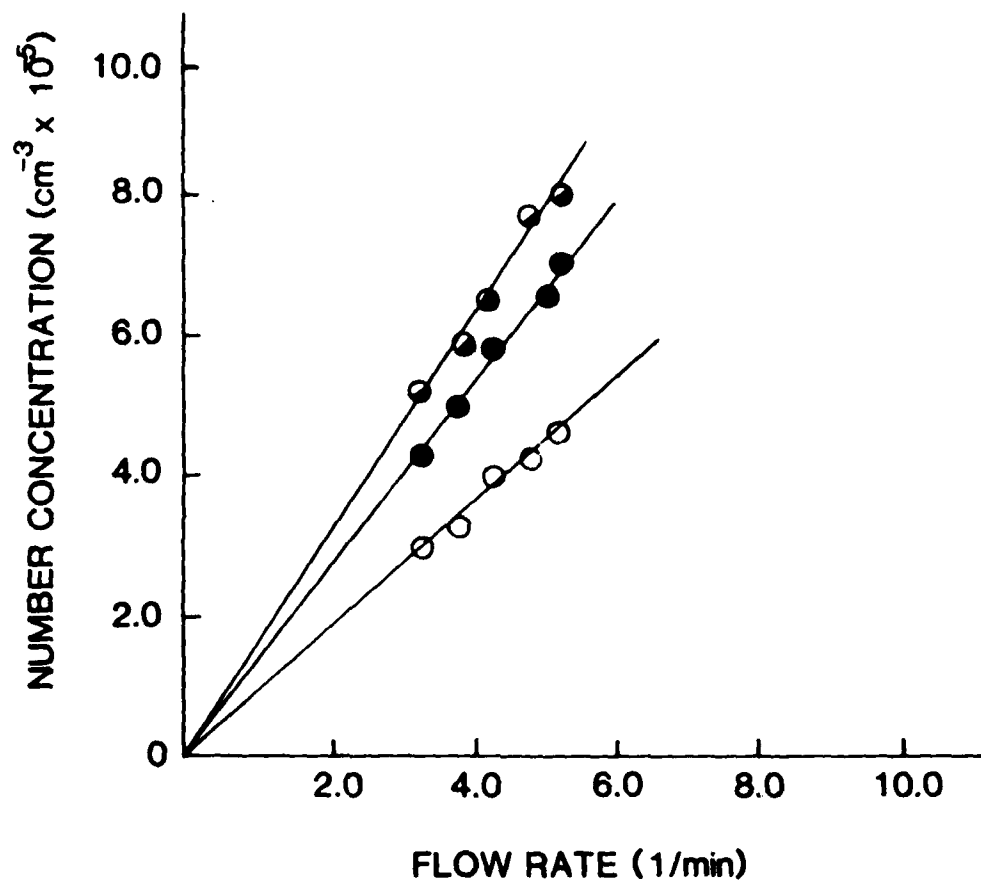


Figure 3. Number Concentration as a Function of Flow Rate at Various Furnace Temperatures; 590°C (open), 725°C (closed), 790°C (half-filled)

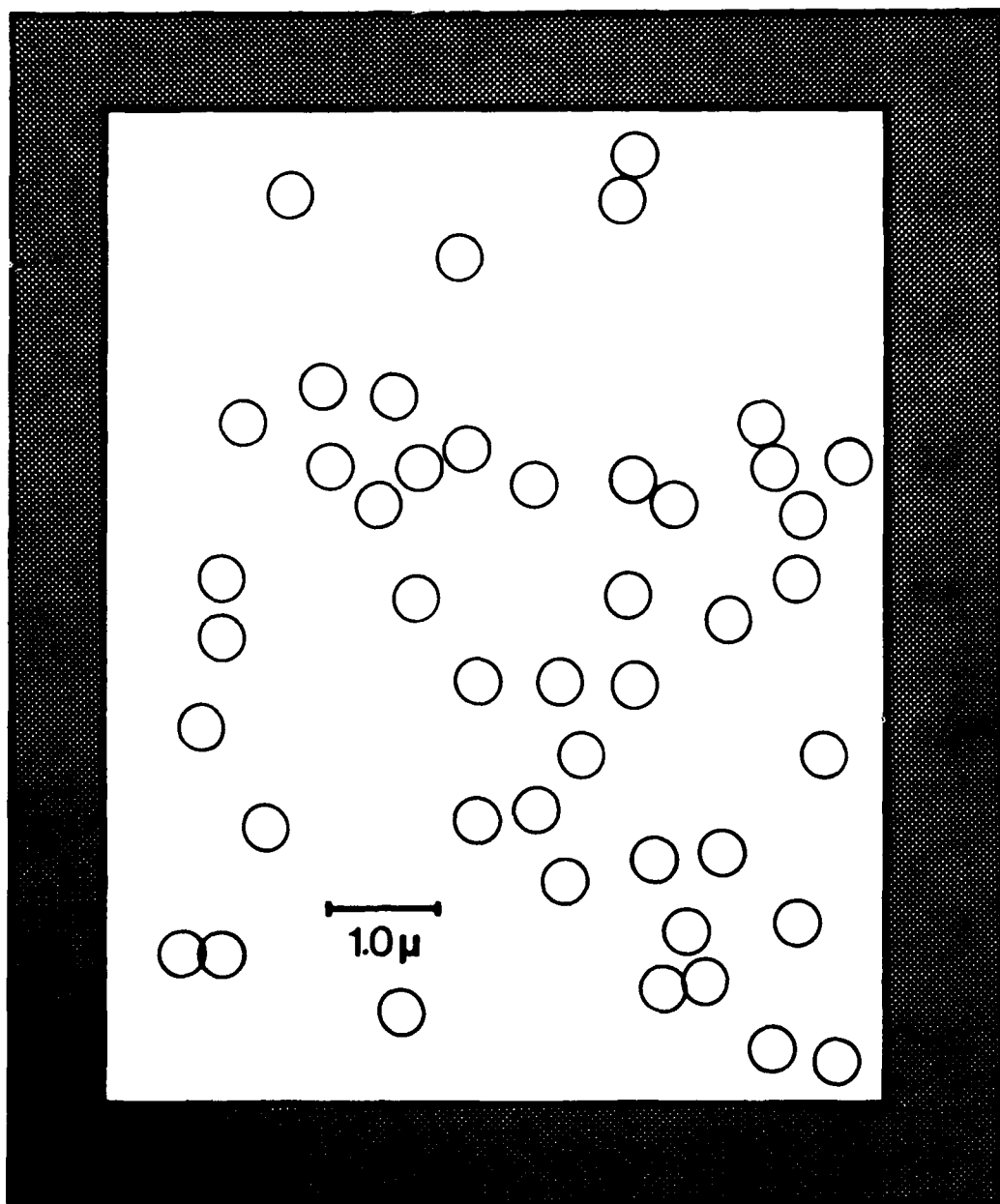


Figure 4. Photograph of Aerosol at 1300x Magnification

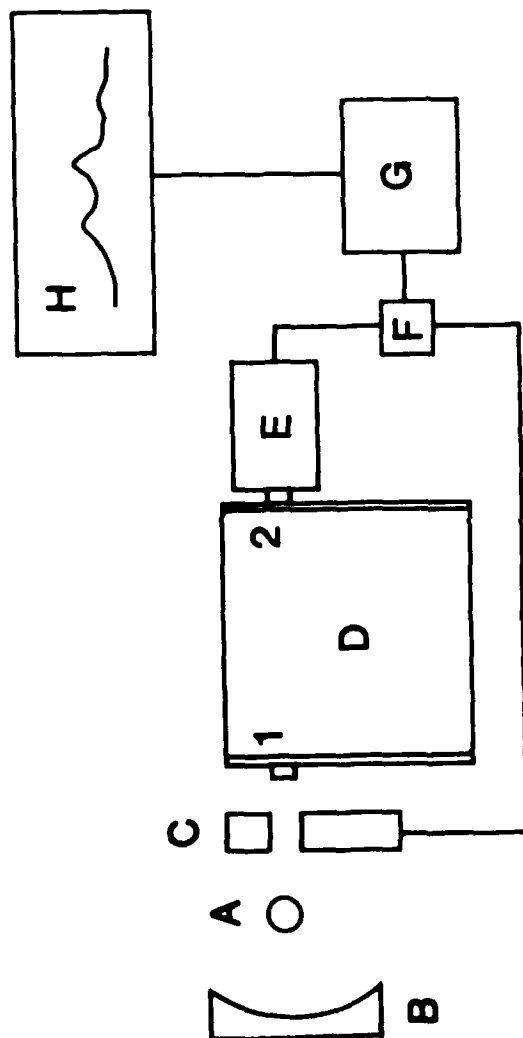


Figure 5. Block Diagram of Apparatus for Measuring IR Emission from Gas-Aerosol Reaction  
 (A) aerosol stream; (B) mirror; (C) chopper;  
 (D) monochromator with entrance (1) and exit (2) slits;  
 (E) radiometer detector head; (F) junction box;  
 (G) control unit; (H) recorder

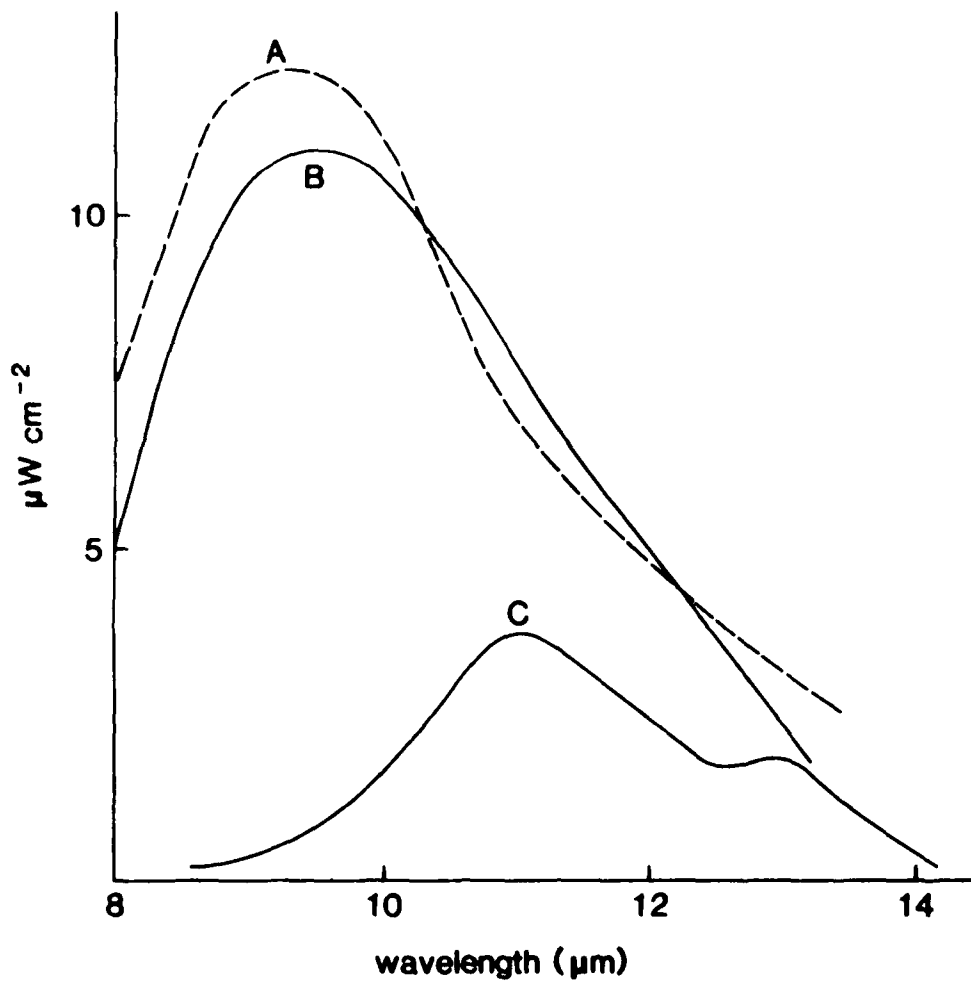


Figure 6. Emission Spectra at 32°C of (A) Flat Target;  
(B) Graphite Rod and (C)  $\text{ClSO}_3\text{H}$  Aerosol -  $\text{NH}_3/\text{H}_2\text{O}$  Gas  
Reaction (vide text)

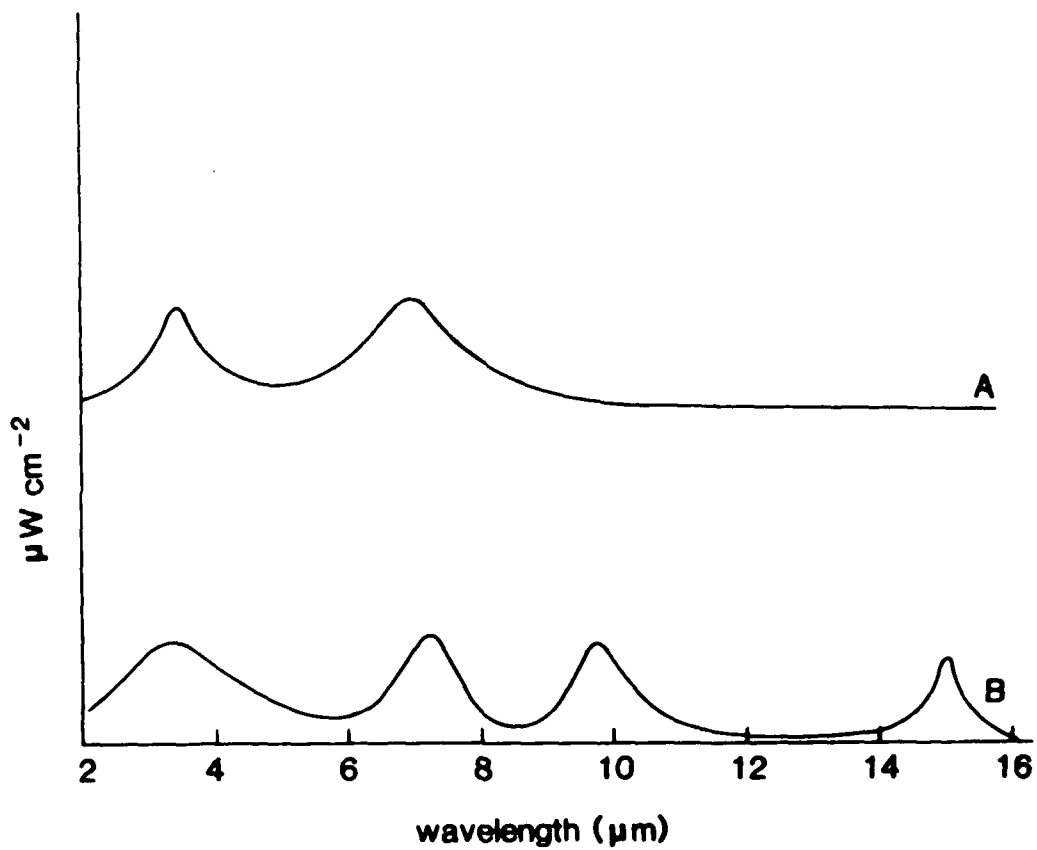


Figure 7. Emission Spectra of (A)  $\text{NH}_4\text{Cl}$  and (B)  $(\text{NH}_4)_2\text{SO}_4$  in KBr Pellets, Heated to 50% C

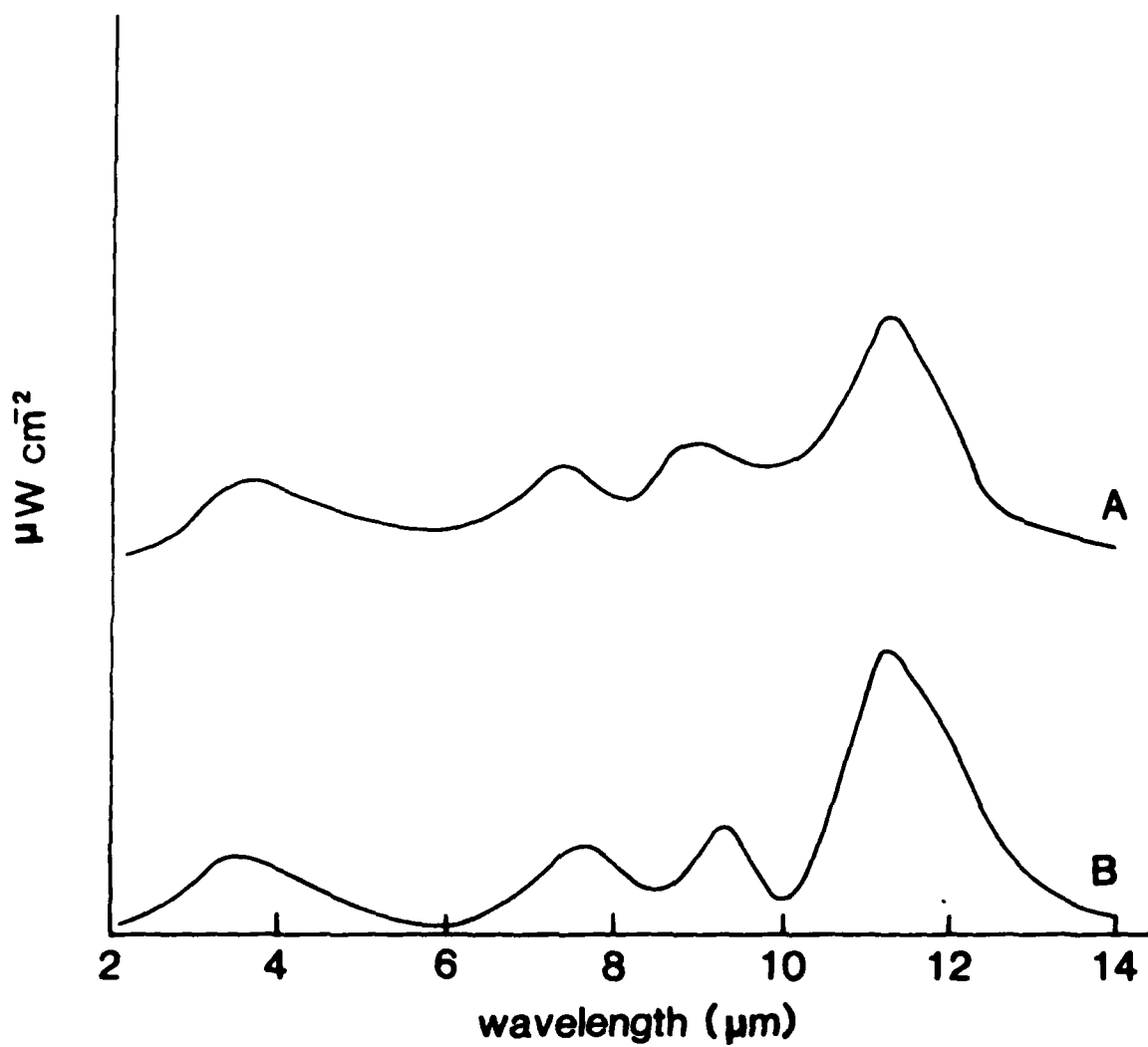


Figure 8. Emission Spectra of  $\text{ClSO}_3\text{H}$  Heated to  $50^\circ\text{C}$   
(A) Bulk; (B) Aerosol

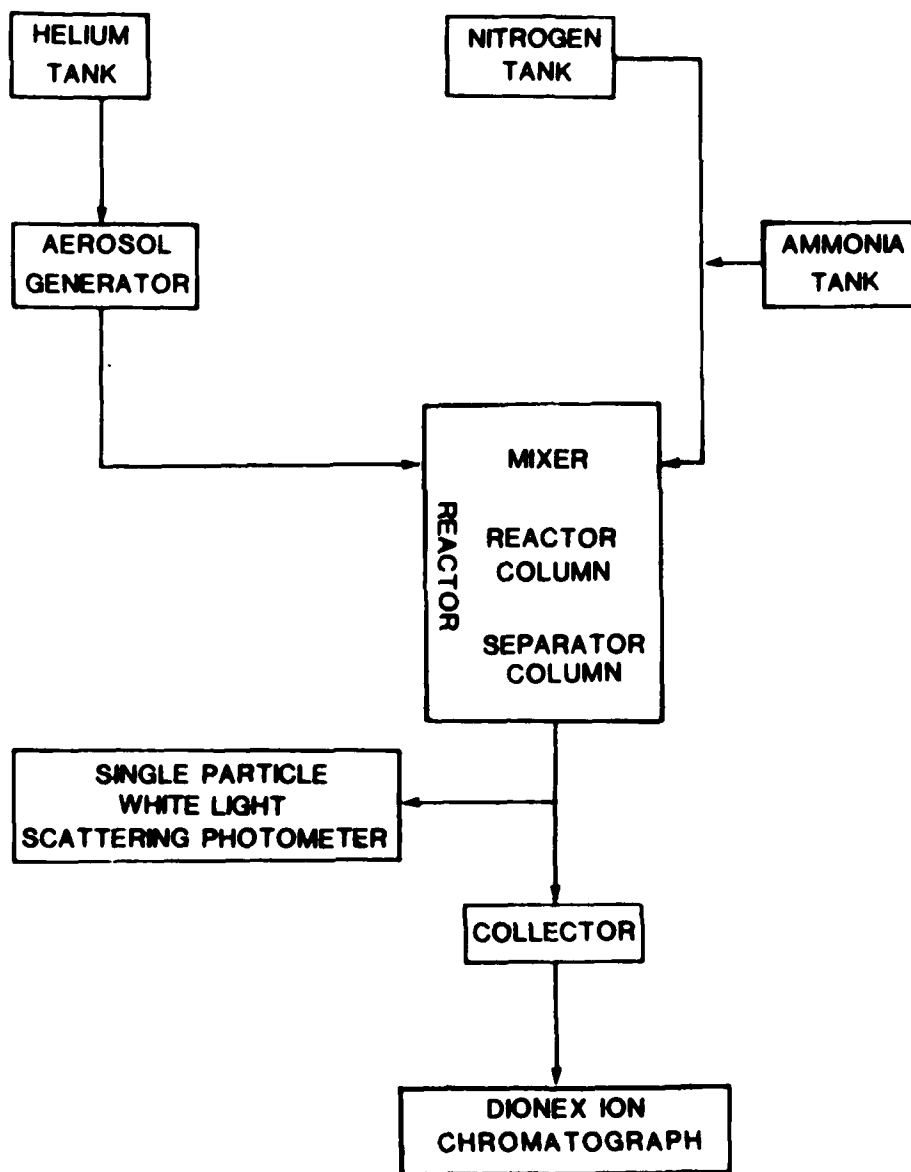


Figure 9. Schematic of Gas-Aerosol Reaction Experiment

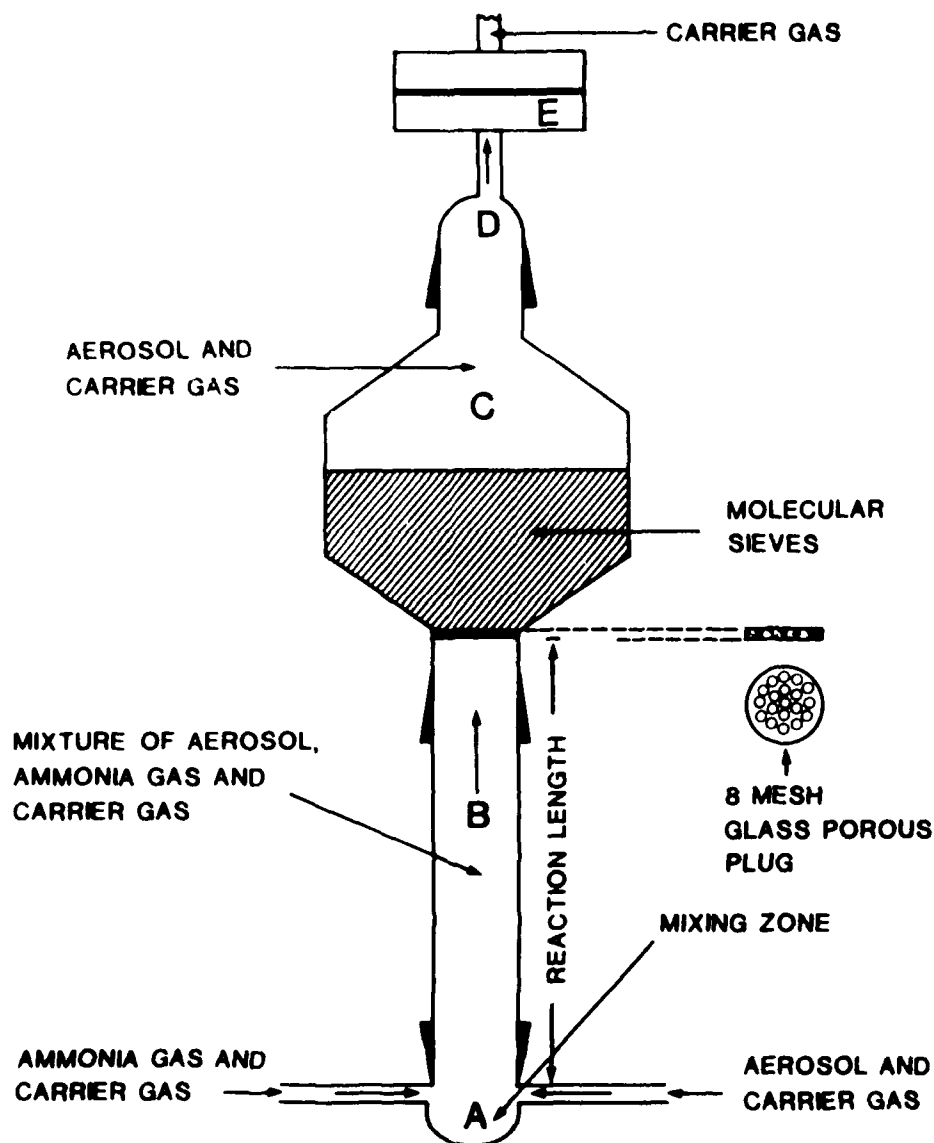


Figure 10. Schematic of Gas-Aerosol-Reaction System.  
 (A) Gas-aerosol Mixer (B) Reaction columns of various lengths  
 (C) Separation Column (D) Separation Reducer Cap  
 (E) Polycarbonate Filter Holder

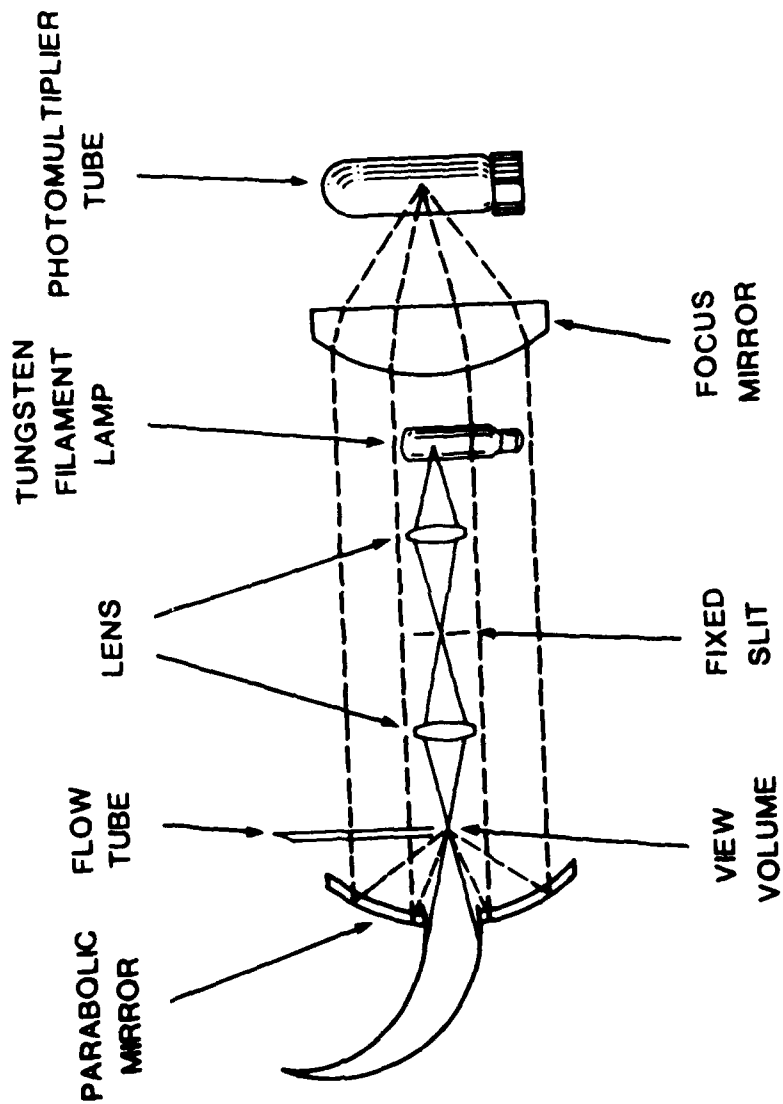


Figure 11. Optical System Schematic

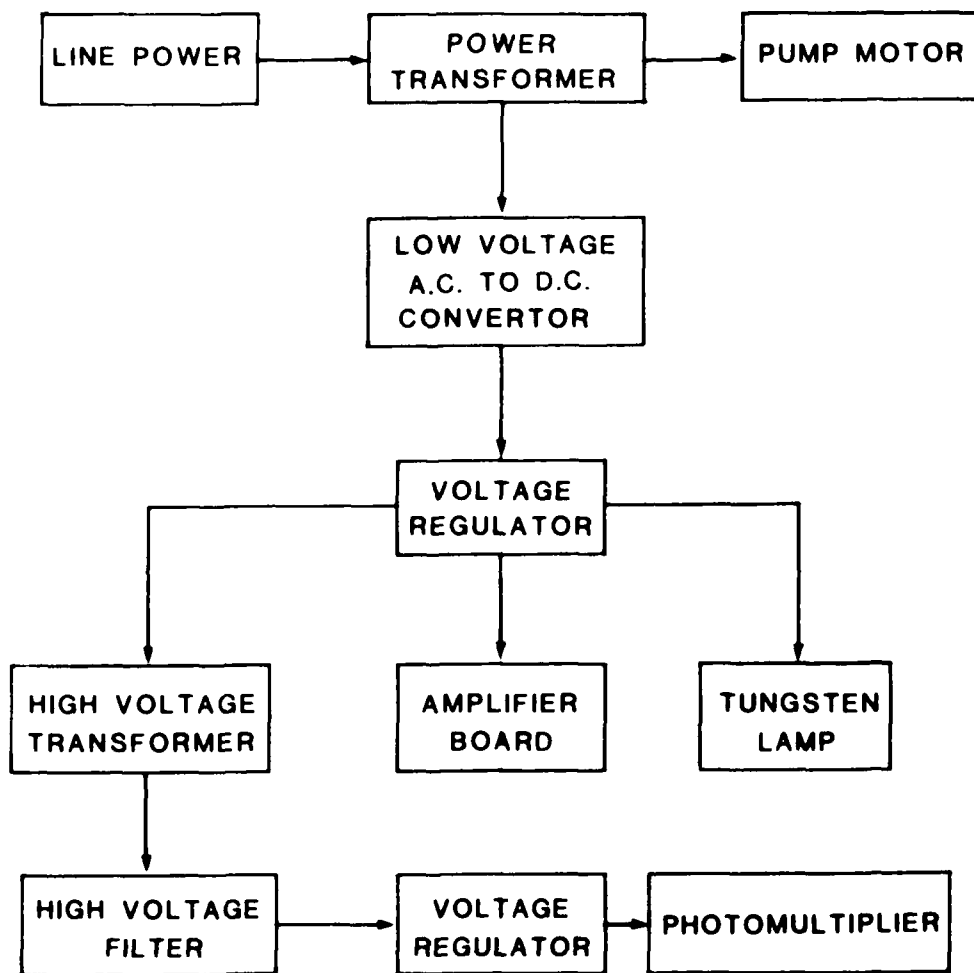


Figure 12. Power Supply Schematic

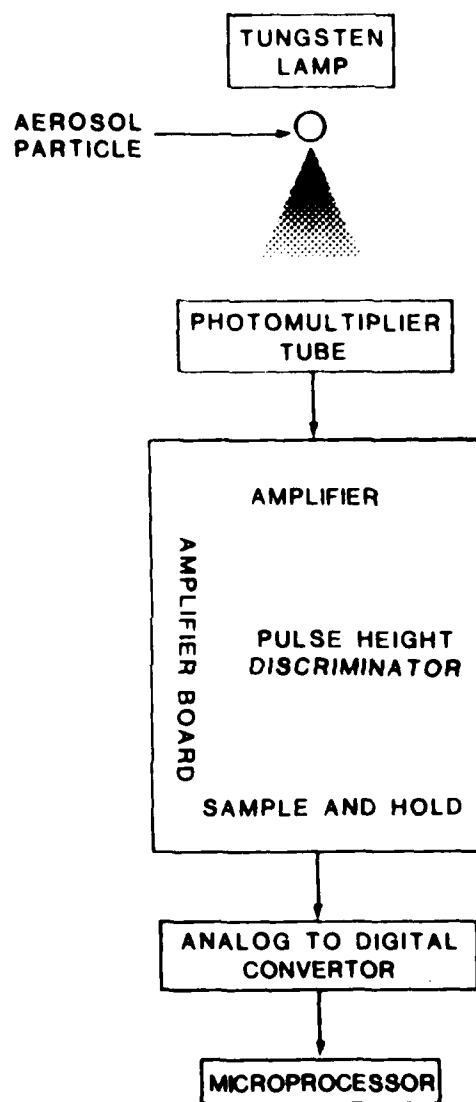
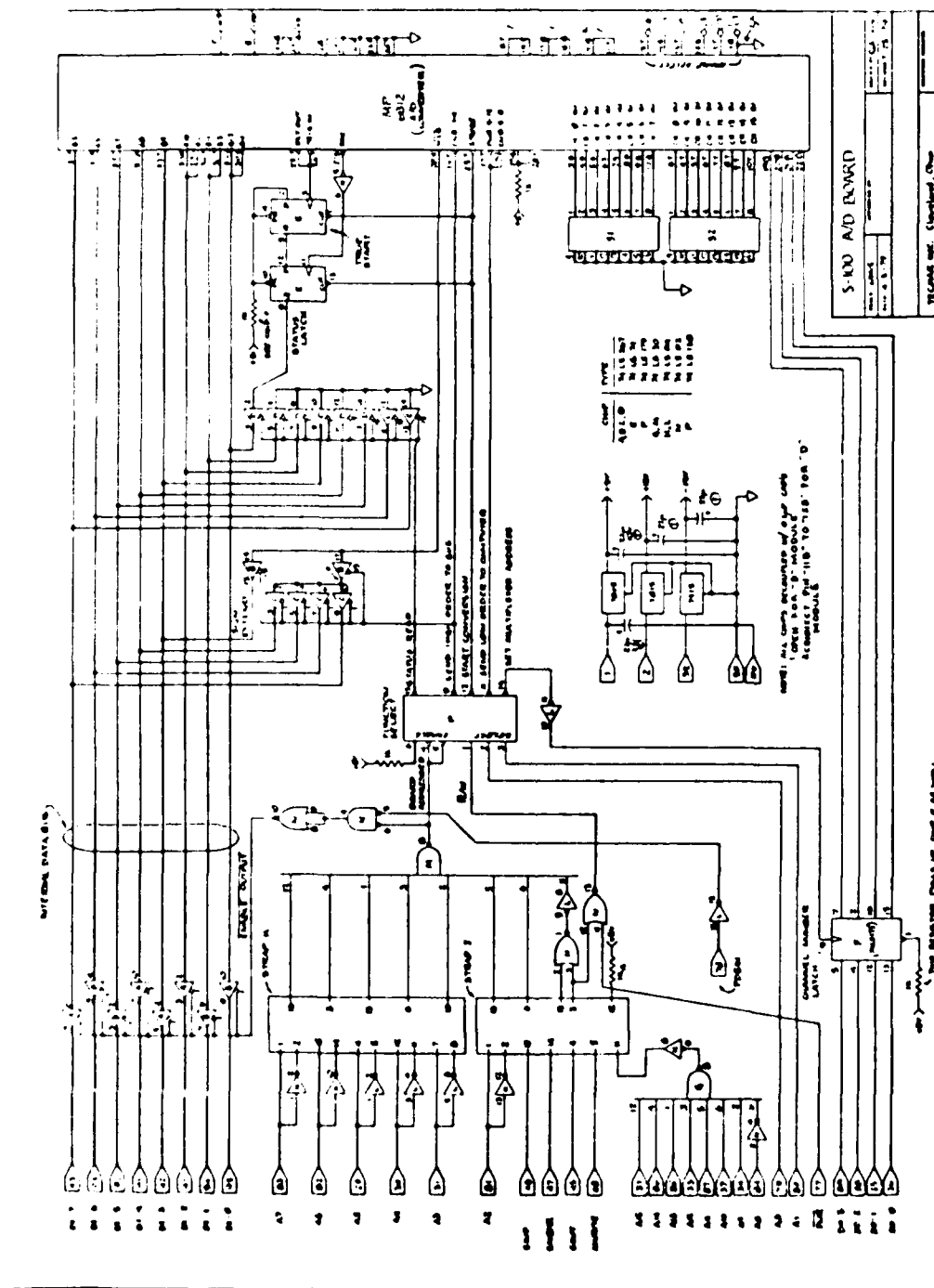


Figure 13. Schematic of Single Particle White-Light Scattering Photometer



**Figure 14. Schematic of Analog to Digital Converter**

# APPENDIX J

```

10 PRINT "ENTER FILE NUMBER "
20 INPUT F$
30 PRINT "ENTER NUMBER OR PARTICLES YOU WANT TO COUNT."
40 INPUT N
50 PRINT "ENTER NUMBER OF CHANNEL ON A/D CONVERSION BOARD "
60 INPUT Y
70 OUT 0,Y
80 DIM H(N),L(N),P(N),X(2048)
90 FOR I=1 TO N
100 OUT 1,0
110 S=INP(1)
120 IF S=0 GOTO 110
130 H(I)=INP(3)
140 L(I)=INP(2)
150 NEXT I
160 PRINT "PARTICLES HAVE BEEN COUNTED "
170 PRINT "DATA ACQUISITION OVER "
180 PRINT "DO YOU WANT TO SEE THE RAW DATA?"
190 PRINT "TYPE 1 FOR NO, 2 FOR YES "
200 INPUT D
210 IF D=1 THEN 280
220 PRINT "COUNTS", "SIGNAL"
230 FOR I=1 TO N
240 LET P(I)=H(I)*256+L(I)
250 IF P(I)>2048 THEN P(I)=0
260 PRINT I,P(I)
270 NEXT I
280 PRINT "WOULD YOU LIKE A HARD COPY?"
290 PRINT "TYPE 1 FOR NO, 2 FOR YES "
300 INPUT M
310 IF M=1 THEN 360
320 LPRINT "COUNTS", "SIGNAL"
330 FOR I=1 TO N
340 LPRINT I,P(I)
350 NEXT I
360 PRINT "DO YOU WANT TO SAVE RAW DATA?"
370 PRINT "TYPE 1 FOR NO, 2 FOR YES "
380 INPUT K
390 IF K=1 THEN 470
400 LET N$="DATA"+F$
410 OPEN "O",#1,N$
420 PRINT#1,N
430 FOR I=1 TO N
440 PRINT#1,P(I)
450 NEXT I
460 PRINT "RAW DATA HAS BEEN SAVED "
470 PRINT "WOULD YOU TO PROCESS DATA?"
480 PRINT "TYPE 1 FOR NO, 2 FOR YES "
490 INPUT B
500 IF B=1 THEN 1390
510 FOR I=1 TO N
520 A=P(I)
530 X(A)=X(A)+1
540 NEXT I
550 PRINT "WOULD YOU LIKE TO SEE PROCESSED DATA?"
560 PRINT "TYPE 1 FOR NO, 2 FOR YES "
570 INPUT T
580 IF T=1 THEN 640
590 PRINT "SIGNAL", " " OF SIGNALS"

```

```

10 IF X(A)=0 THEN 630
20 PRINT A,X(A)
30 NEXT A
40 PRINT "WOULD YOU LIKE A HARD COPY?"
50 PRINT "TYPE 1 FOR NO, 2 FOR YES "
60 INPUT V
70 IF V=1 THEN 730
80 LPRINT "SIGNAL", "# OF SIGNALS"
90 FOR A=0 TO 2048
100 IF X(A)=0 THEN 720
110 LPRINT A,X(A)
120 NEXT A
130 PRINT "WOULD YOU LIKE TO SAVE PROCESSED DATA?"
140 PRINT "TYPE 1 FOR NO, 2 FOR YES "
150 INPUT U
160 IF U=1 THEN 820
170 LET T$="PDATA"+F$
180 OPEN "O", #2, T$
190 FOR A=0 TO 2048
200 PRINT#2, A,X(A)
210 NEXT A
220 PRINT "YOU HAVE A MAX OF 2048 CHANNELS TO PLOT."
230 PRINT "ENTER STARTING CHANNEL NUMBER."
240 INPUT C
250 PRINT "ENTER FINAL CHANNEL NUMBER."
260 INPUT Z
270 PRINT "HOW OFTEN WOULD LIKE THE CHANNEL NUMBERS LABELED?"
280 PRINT "ENTER NUMBER OF SPACES."
290 INPUT L
300 PRINT"
310 PRINT"
320 FOR A=C TO Z
330 IF A<10 THEN E=3
340 IF A)=10 AND A<100 THEN E=2
350 IF A)=100 AND A<1000 THEN E=1
360 IF A)=1000 THEN E=0
370 LET Q=X(A)/N*50
380 LET G=CINT(Q)-1
390 IF A/L=INT(A/L) THEN 1030
1000 IF G<=0 THEN 1030
1010 PRINT"
1020 GOTO 1090
1030 PRINT"
1040 GOTO 1090
1050 IF G<=0 THEN 1080
1060 PRINT SPC(E)A)-" SPC(G)"*
1070 GOTO 1090
1080 PRINT SPC(E)A)-"
1090 NEXT A
1100 PRINT "DO YOU WANT TO REPLOT DATA?"
1110 PRINT "TYPE 1 FOR NO, 2 FOR YES"
1120 INPUT X
1130 IF X=1 THEN 1150
1140 GOTO 820
1150 PRINT "WOULD YOU LIKE A HARD COPY OF THE PLOT?"
1160 PRINT "TYPE 1 FOR NO, 2 FOR YES ."
1170 INPUT J
1180 IF J=1 THEN 1390
1190 LPRINT"
1200 LPRINT"

```

```

1210 FOR A=C TO Z
1220 IF A<10 THEN E=3
1230 IF A>=10 AND A<100 THEN E=2
1240 IF A>=100 AND A<1000 THEN E=1
1250 IF A>=1000 THEN E=0
1260 LET G=X(A)/N*50
1270 LET G=INT(G)-1
1280 IF A/L=INT(A/L) THEN 1340
1290 IF G<=0 THEN 1320
1300 LPRINT"      1" SPC(G)"*"
1310 GOTO 1380
1320 LPRINT"      1"
1330 GOTO 1380
1340 IF G<=0 THEN 1370
1350 LPRINT SPC(E)A"- " SPC(G)"*"
1360 GOTO 1380
1370 LPRINT SPC(E)A"- "
1380 NEXT A
1390 PRINT "WOULD YOU LIKE TO COLLECT MORE DATA?"
1400 PRINT "TYPE 1 FOR NO, 2 FOR YES."
1410 INPUT W
1420 IF W=1 THEN 1450
1430 ERASE H,L,P,X
1440 GOTO 10
1450 END

```

# APPENDIX 11

```

EXIT      EQU      0
START     LXI      SP,9000H ;START STACK AT 9000
          MVI      H,00H    ;INITIALIZING DATA STORAGE COUNTER
          MVI      L,04H    ;SETTING NUMBER OF RUNS TO 4
          PUSH     HL        ;STORE TOTAL NUMBER OF DATA POINTS AT
TOP OF MEMORY STACK
          MVI      D,00H    ;SETTING HIGH BYTE FOR DEAD BAND
          MVI      E,01H    ;SETTING LOW BYTE FOR DEAD BAND
READ1     MVI      A,0      ;READ CHANNEL 0
          OUT      0        ;SET MUX
          OUT      1        ;START CONVERSION
LOOP1     IN       1        ;READ STATUS
          RRC
          JNC      LOOP1    ;IF BUSY, WAIT LONGER
          IN       03       ;READ HIGH BYTE
          CMP      D        ;COMPARE HIGH BYTE WITH DEAD BAND
          JC       READ1    ;IF VALUE IS LOWER THAN HIGH BYTE THEN
READ CHANNEL 0
          JZ       COMP1    ;IF VALUE IS 0 THEN COMPARE LOW BYTE
          MOV      B,A      ;STORE VALUE IN REGISTER B
          IN       2        ;READ LOW BYTE
          MOV      C,A      ;STORE VALUE IN REGISTER C
          JMP      READ2    ;JUMP TO READ CHANNEL 1
COMP1     IN       2        ;READ LOW BYTE
          CMP      E        ;COMPARE LOW BYTE WITH DEAD BAND
          JC       READ1    ;JUMP TO READ CHANNEL 1
          MOV      C,A      ;STORE VALUE IN REGISTER C
READ2     MVI      A,0      ;READ CHANNEL 0
          OUT      0        ;SET MUX
          OUT      1        ;START CONVERSION
LOOP2     IN       1        ;READ STATUS
          RRC
          JNC      LOOP2    ;IF BUSY WAIT LONGER
          IN       3        ;READ HIGH BYTE
          CMP      D        ;COMPARE WITH HIGH BYTE OF DEAD BAND
          JNZ      LEAVE    ;IF NON-ZERO JUMP TO COMPARE WITH VALUE
ALREADY EXISTING
          CMP      B        ;COMPARE WITH VALUE ALREADY EXISTING
          JZ       COMP2    ;IF ZERO JUMP TO READ LOW BYTE
          IN       2        ;READ LOW BYTE
          CMP      E        ;COMPARE VALUE WITH DEAD BAND
          JC       SAVE     ;NEW VALUE MUST BE LOWER THAN DEAD BAND
SO JUMP TO THE SAVE ROUTINE
          JMP      READ2    ;JUMP TO READ CHANNEL 0
LEAVE     CMP      B        ;COMPARE VALUE WITH REGISTER B
          JC       READ2    ;IF VALUE IS LESS THAN EXISTING VALUE
JUMP TO READ CHANNEL 0
          MOV      B,A      ;STORE VALUE IN REGISTER B
          IN       2        ;READ LOW BYTE
          CMP      C        ;COMPARE VALUE WITH REGISTER C
          JC       READ2    ;IF VALUE IS LESS THAN EXISTING VALUE

```

```

THEN JUMP TO READ CHANNEL 0
      MOV      C,A      ;STORE VALUE IN REGISTER C
      JMP      READ2    ;JUMP TO READ CHANNEL 0
COMP2: IN      2        ;READ LOW BYTE
      CMP      E        ;COMPARE VALUE TO DEAD BAND
      JC       SAVE     ;IF LESS THAN DEAD BAND JUMP TO SAVE

ROUTINE
      CMP      C        ;IF VALUE WAS GREATER THAN DEAD BAND
COMPARE WITH REGISTER C
      JC       READ2    ;IF LESS THAN EXISTING VALUE, THEN JUMP
TO READ CHANNEL 0
      MOV      C,A      ;STORE LARGER VALUE IN REGISTER C
      JMP      READ2    ;JUMP TO READ CHANNEL 0
SAVE  PUSH     BC       ;MOVE MAX VALUE TO THE TOP OF MEMORY
STACK
      MVI      B,00H    ;CLEAR REGISTER B FOR NEW VALUE IN NEXT
RUN
      MVI      C,00H    ;CLEAR REGISTER C FOR NEW VALUE IN NEXT
RUN
      INR      H        ;INCREMENT VALUE IN REGISTER H TO
INDICATE ANOTHER PASS
      MOV      A,H      ;MOVE VALUE IN H REGISTER TO COMPARE
      CMP      L        ;COMPARE VALUE WITH L REGISTER WHICH
CONTAINS THE NUMBER PASSES TO BE RAN
      JNZ      READ1    ;IF VALUE DOESN'T EQUAL THE NUMBER OF
PASSES TO BE EXECUTED JUMP TO THE BEGINNING OF THE PROGRAM AND
READ CHANNEL 0
      JMP      EXIT     ;EXIT TO CPM SYSTEM

```

# APPENDIX III

```

EXIT    EQU    0
        LD     DE,0800H
LOOP1   IN     A,(01H)
        RRA
        RRA
        JP     NC,LOOP1
        LD     A,(00H)
        OUT    (00H),A
        OUT    (01H),A
LOOP2   IN     A,(01H)
        RRA
        JP     NC,LOOP2
        IN     A,(03H)
        LD     H,A
        IN     A,(02H)
        LD     L,A
        INC    HL
        INC    PC
        LD     A,B
        CP     D
        JP     NZ,LOOP1
        LD     A,C
        CP     E
        JP     NZ,LOOP1
        DEFS   07FFH,00H
        JP     EXIT

```

END  
DATE