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A Chemical Ozone Measuring Radio Sonde

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A CHEMICAL OZONE MEASURING RADIO SONDE - PETERSON

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by

Alan W. Peterson

A Thesis

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of Master of Science in Physics

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1957

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MASTER OF SCIENCE

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DATE

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A CHEMICAL OZONE MEASURING RADIO SONDE

Thesis committee

Victor H. Regener
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Jack Katzenstein

John R. Green

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CHAPTER I

THE INSTRUMENT

Introduction

The vertical distribution of atmospheric ozone has been determined spectroscopically either from surface observations or from balloon-borne spectrographs sent aloft. These spectrographic techniques have several disadvantages. Surface observations of the "Umkehr Effect" give only a rough distribution, four or five points for the entire atmosphere.[1] Balloon-borne spectrographs give an integral ozone curve which must be differentiated before the vertical distribution can be obtained. The differentiation process introduces considerable error, and all data are lost should the balloons fail to be recovered. Moreover, spectrographic observations must be made during daylight hours, thus precluding any night observations.

It is therefore desirable to obtain a more direct measurement of the vertical ozone distribution by some method which would permit better resolution than the spectrographic methods do, and which would at the same time not preclude the possibility of night observations. It would also be desirable to have the information obtained during a flight continuously telemetered to a ground station where it may be recorded in permanent form.

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1. S.K. Mitra, The Upper Atmosphere, Second Edition, (Calcutta, The Asiatic Society, 1952), Sec. 4-3

Introduction

The vertical distribution of [illegible] has been [illegible] mined spectroscopically [illegible] balloon-borne spectrographs [illegible]. [illegible] techniques have several [illegible]. [illegible] the "Umkehr-Effect" gives only a [illegible] points for the entire atmosphere.[1] [illegible] give an integral ozone [illegible] the vertical distribution can be obtained. [illegible] cess introduces considerable error, [illegible] the balloons fall [illegible] recovered. [illegible] servations must be made during [illegible] any night observations.

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1. S. K. Mitra, The Upper Atmosphere [illegible] The Asiatic Society, [illegible]

This thesis describes an attempt to develop a chemical ozone measuring radio sonde which would have the desired features.

General

The principle of the method used is that described by Bowen and Regener.[2] Ozone in an air sample is brought into intimate contact with an aqueous solution of potassium iodide and sodium thiosulphate. The ozone reacts with the Potassium iodide producing iodine which in turn reacts with the sodium thiosulphate. The solution is titrated electrolytically, the end-point being indicated by the depolarization of the cathode of a pair of sensing electrodes. The resulting current flow is then amplified and actuates a system to change the solution. A signal is transmitted to the receiving station by a radio sonde whenever the system cycles.

Reaction Chamber

The reaction chamber (Figure 1) is constructed by sealing two four-inch pyrex watch glasses together. The sensing electrodes are inserted at the bottom of the chamber through a ground glass joint. The air is admitted at the edge of the chamber through glass tubing 10 millimeters in diameter and it is exhausted through a thirty-millimeter tube sealed in the top center of the chamber. This tube serves to hold the air pump above the level of the water bath enclosure which holds

2. I. G. Bowen and V. H. Regener, Journal of Geophysical Research, 56, 3 (1951)

This thesis describes [illegible] measuring radio [illegible]

General

The principle of the [illegible] Regener.[2] Ozone in [illegible] with an aqueous solution of [illegible] The ozone reacts with the [illegible] turn reacts with the sodium [illegible] electrolytically, the [illegible] the cathode of a pair of [illegible] flow is then amplified and actuates [illegible] A signal is transmitted to the [illegible] ever the system cycles.

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2. I. G. Bowen and V. H. Regener, [illegible] 56, 3 (1951)

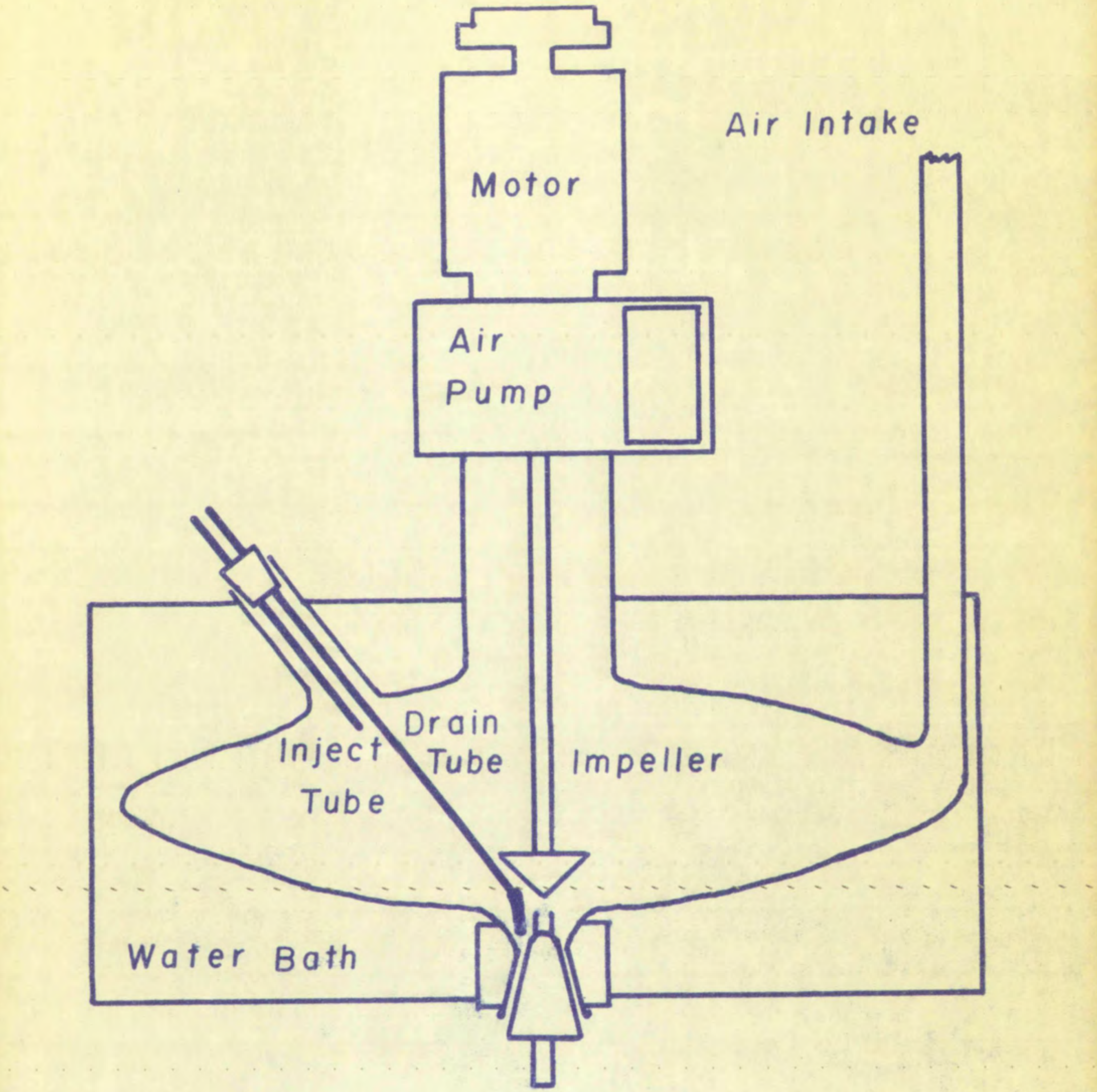

Figure 1

Reaction Chamber

about 800 cubic centimeters of warm water for the purpose of keeping the solution in the reaction chamber from freezing. Another tube, sealed at the proper angle on top of the chamber, allows two smaller tubes to enter for changing the solution.

The air pump is driven by a Delco model 5076135 governor-controlled 5000 r.p.m. 2 volt d.c. motor. The motor shaft is extended about four inches by a one-quarter inch lucite rod in order to rotate a pointed, cone-shaped impeller. The impeller picks up the solution from the bottom of the chamber and sprays small droplets outward to the upper surface of the chamber where it splashes and runs down the sides. This action facilitates the reaction of the ozone in the circulating air by exposing a large surface area of the solution.

Impellers one-half inch in diameter and one-quarter inch thick give good pumping action when they have a sharp point and four or eight small channels cut from the point to the upper edge. Blunt points serve only to churn the surface of the solution.

In an attempt to pre-heat the air before it entered the reaction chamber, it was found that glass heat exchangers of reasonable size were rather inefficient. Even with very thin walls the incoming air stream was heated to only about 60% of the temperature difference between the water bath and outside air.

Solution Injection and Drain Mechanism

The solution injection and drain system shown in Figure 2 consists of two medical hypodermic syringes driven by a lead screw. The

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Solution Injection and Flash [illegible]

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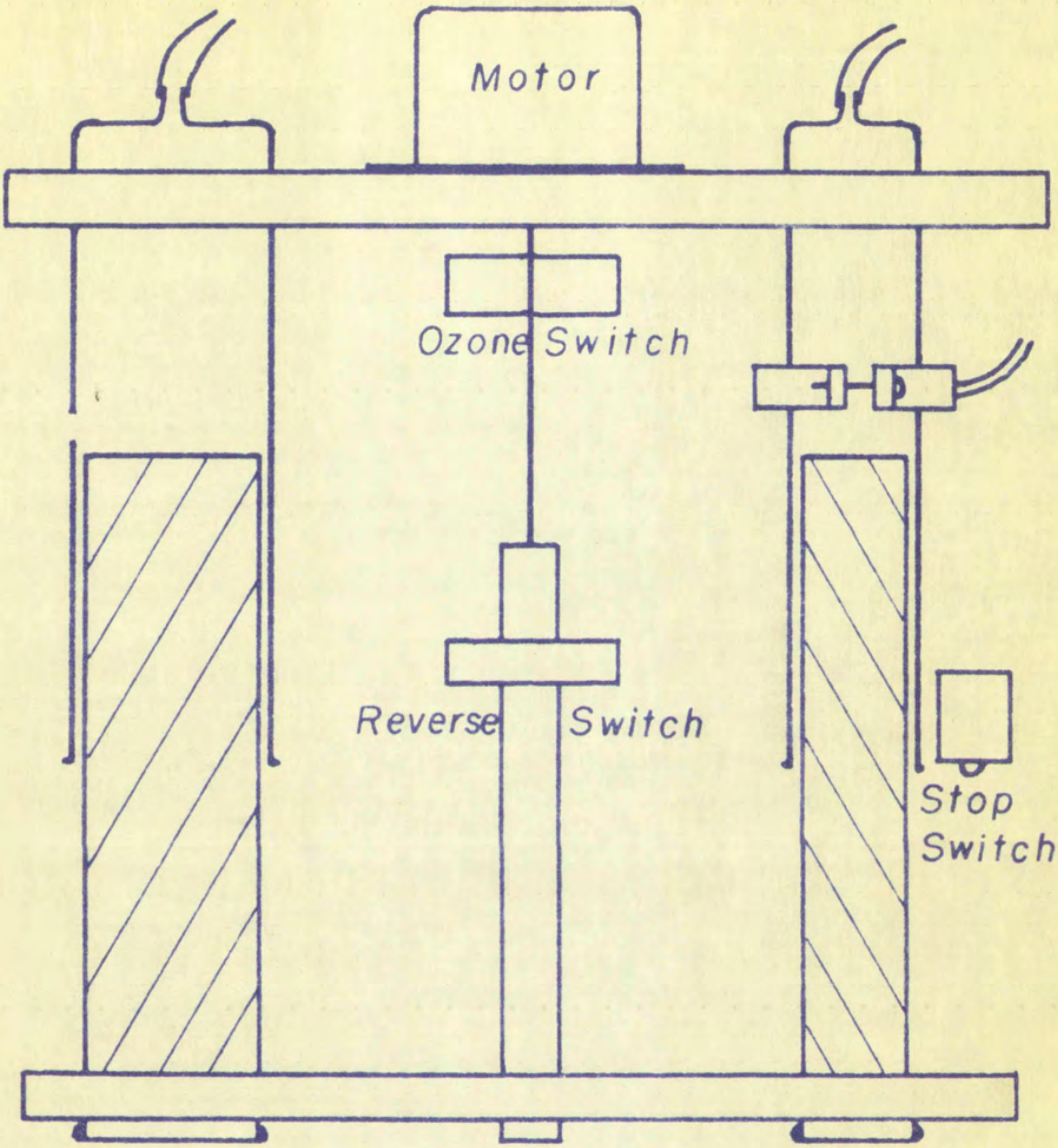

Figure 2

Injection – Drain System

draining operation is done by a 20 c. c. syringe. A hole is cut in the side of the barrel so that when 10 c. c. of travel has been accomplished the contents of the barrel discharge from the hole. The solution is picked up from the bottom of the chamber by a two millimeter plastic tip on the end of a thin glass tube which enters the chamber at such an angle as to miss the impeller and electrodes and yet pick up a maximum amount of solution. While only 5.2 c. c. of solution are injected, a larger drain volume is desirable to allow all of the circulating solution to reach the bottom of the chamber and be picked up. The 2:1 volume ratio works very well; all solution within reach of the pick-up tip is removed from the chamber.

Solution is injected with a 10 c. c. syringe. A split lucite ring surrounding the barrel at the 5 c. c. position allows connection of a plastic tube from the storage bottle. The barrel fills by gravity flow and injection takes place only after the plunger has risen above the cut in the barrel. The two millimeter plastic tubing which leads the solution from the syringe to the reaction chamber offers enough resistance to flow so that little solution will rise in it until such time as it is forced by the plunger. This keeps the injection volume essentially constant even though the solution bottle provides a varying head as its contents are used up. The solution is stored in a 300 c. c. flask.

The syringes are driven by a Haydon reversible d. c. clock motor turning a 6-32 lead screw. The motor is powered by a center-tapped

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The syringes are [illegible] turning a 8-32 lead [illegible].

45 volt battery as shown in Figure 3. The range of travel is adjustable by varying the position of the stop actuating the reversing switch.

A cycle of operation begins when the amplifier relay closes, thus starting the motor (Figure 3). The syringe plungers retract and the "stop" micro switch closes. This keeps the motor running even if the amplifier relay opens. The chamber is emptied by the drain syringe and its contents are dumped. The injection syringe fills, the reversing switch throws, and new solution is injected. Near the end of the syringe travel the stop switch opens, the reversing switch throws, and the syringes are brought to rest. The "ozone" switch (see Figure 2) closes at the start of the cycle and remains closed until the end of the cycle, thus applying the ozone signal to the radio sonde. This switch also serves as a stop to throw the reversing switch at the end of the operation.

This particular unit takes considerable power to operate and is also rather expensive to construct. It was thus desirable to look at alternative injection systems. Figure 4 shows a pilot model which was constructed using gravity flow and collapsible rubber tubing for valves. In this model a "Tiny Atom" toy motor operated by two R. C. A. Vs 232 1.5 volt batteries drives a gear chain to reduce its speed to about 10 r.p.m. A cycle of operation proceeds as follows. The motor starts pulling on the spring loaded wires. Valve V-1 is normally closed. Valve V-3 opens draining the chamber. Valve V-2 closes and the spring between the pivoted rods R-1 and R-2 delays the opening

45 volt battery is shown in Fig. [illegible] [illegible] able by varying the [illegible] [illegible]

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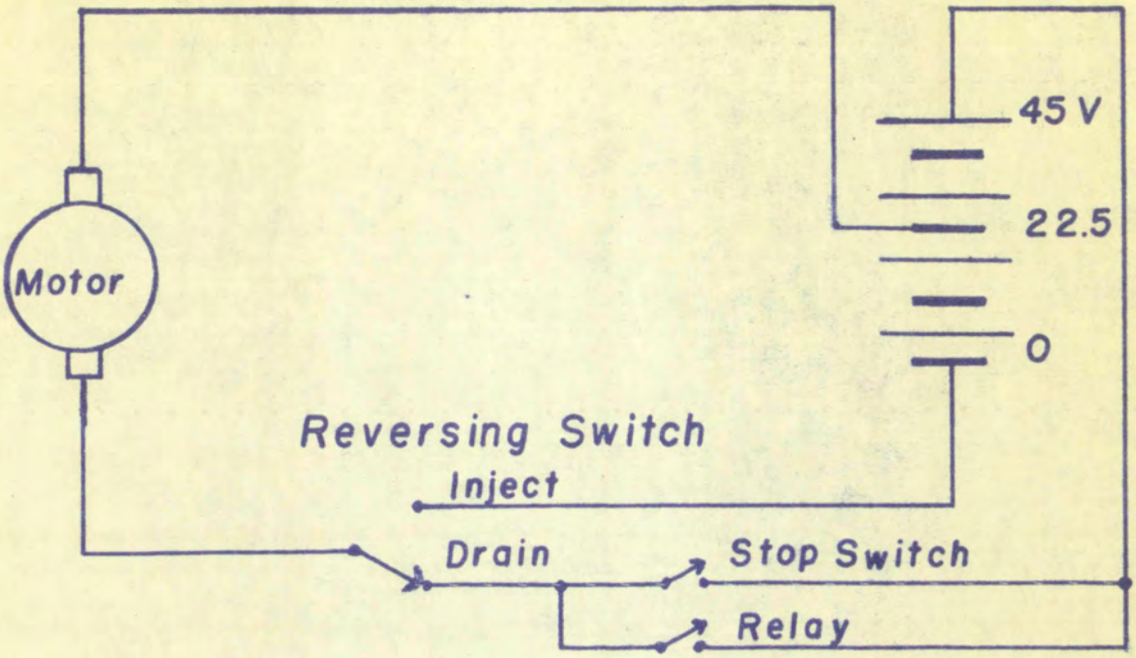
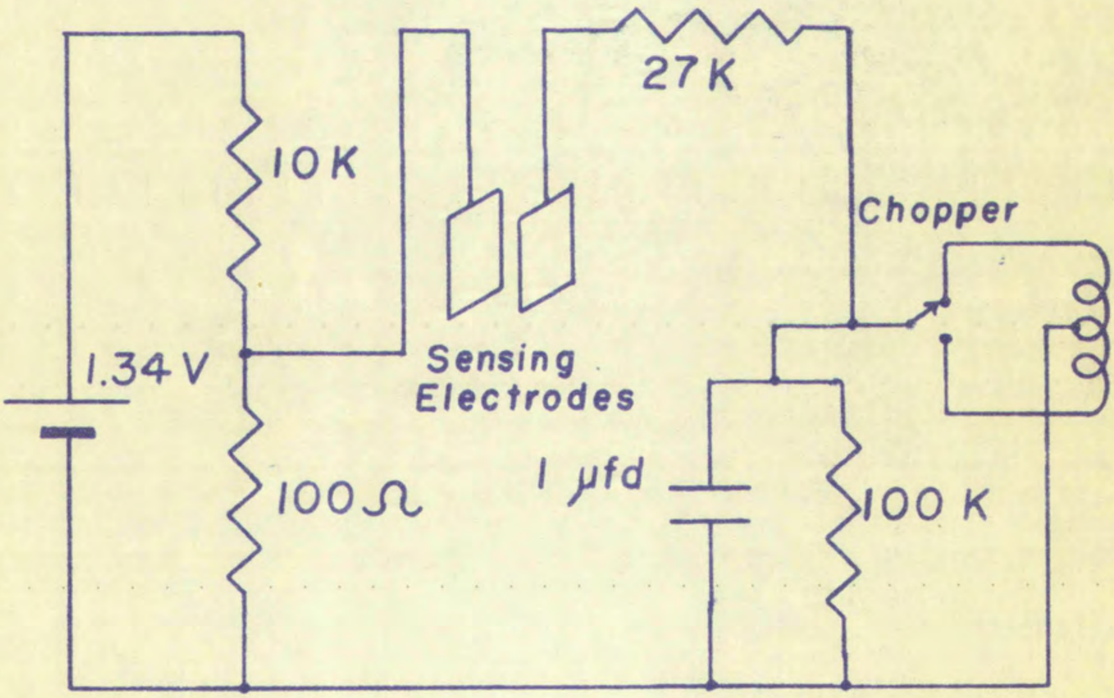


Injection and Drain Circuit



Sensing Circuit

Figure 3

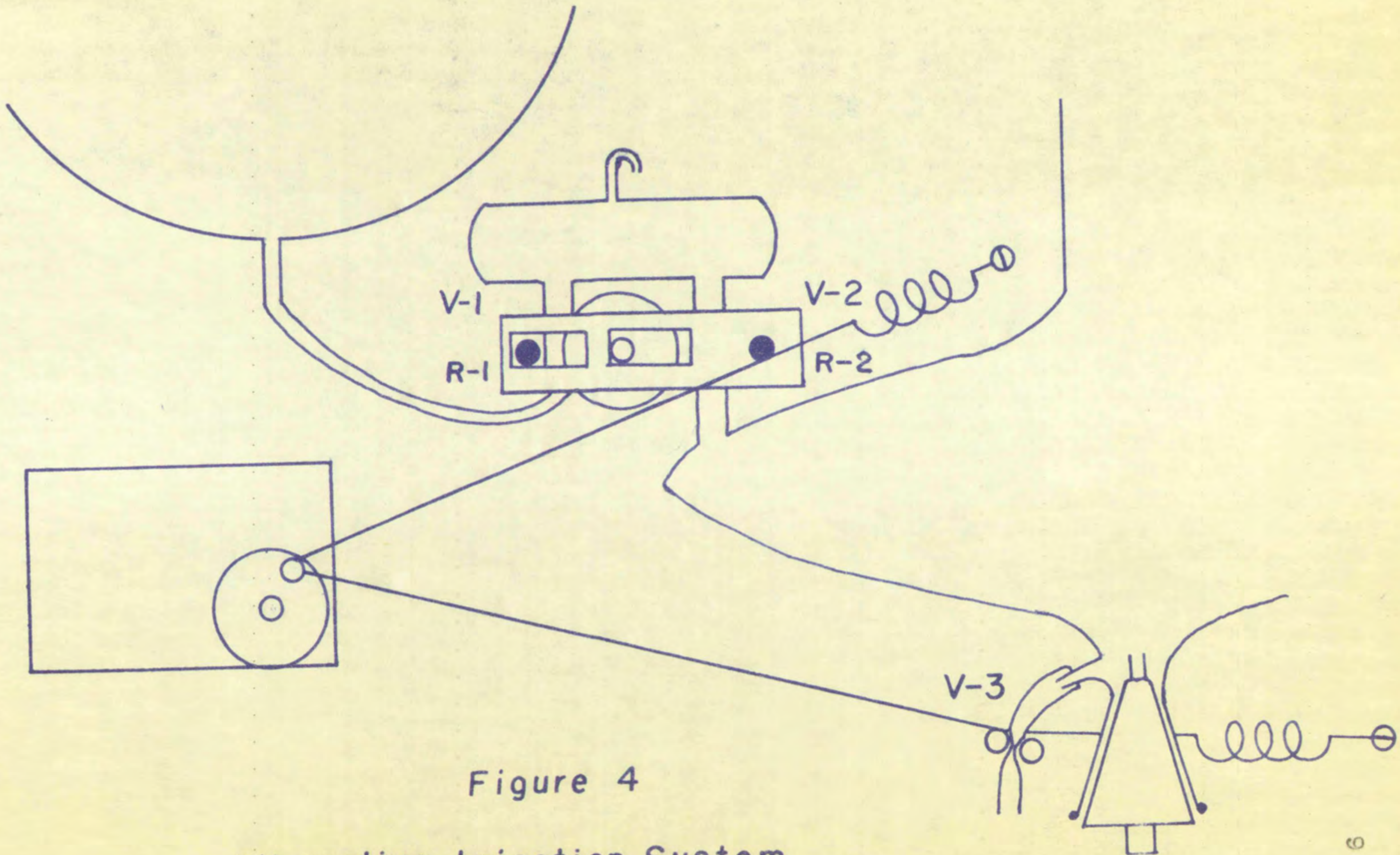


Figure 4

Alternative Injection System

of V-1 until V-2 is closed completely. This seals off the injection volume before it is filled with solution. Any excess solution runs out of a small neck on top of the injection chamber. With further rotation of the motor V-3 closes, then V-1 closes, and finally V-2 opens allowing the fresh solution to enter the reaction chamber.

Finding suitable tubing for use as valves appears to be the most trying problem here. It must be thick-walled and very flexible to permit complete closing with minimum pressure. Thin-walled surgical tubing is not suitable as it takes too much pressure to collapse the sharply curved edges.

This type of injection mechanism appears to be better than the syringes because of decreased weight, reduced time of operation, and ease of construction. A cycle of operation with this mechanism takes about five seconds as compared to nearly twenty seconds for the model used. At pressures below thirty millimeters of mercury the syringe fails to drain the chamber thus limiting the useful altitude of this device. Gravity flow would improve this situation.

Sensing Circuit, Chopper and Amplifier

The sensing circuit shown in Figure 3 is controlled by the sensing cell which consists of two platinum electrodes immersed in the circulating solution. A potential divider applies about 13 millivolts across the electrodes. This small potential polarizes the cathode preventing a flow of current between the electrodes until such time as free iodine

of V-1 until V-3 is closed completely. [illegible] volume before it is filled with solution. [illegible] of a small neck on top of [illegible] of the motor V-3 closes, [illegible] lowing the fresh solution to [illegible]

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<u>Sensing Circuit, Chopper and Amplifier</u>

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appears in the solution. The vibrating reed of the mechanical chopper connects the cell alternately to opposite halves of a center-tapped input transformer in the high-gain a. c. amplifier (Figure 5).

The chopper, a James Vibropower No. C-1142, less driving coil, operates by mechanical resonance. The vibrations are produced by mounting the chopper near the purposely unbalanced air pump motor. If no current flows between the electrodes, no signal appears at the output of the amplifier. However, when a small conduction current of about 10^{-8} ampere flows, it is converted into a 75 c. p. s. signal by the chopper. This is of sufficient amplitude to close the amplifier relay.

The amplifier proved to be very microphonic. It was necessary to isolate it mechanically from the vibrations caused by the pump motor. The isolation was accomplished by mounting the amplifier and the solution storage bottle on a balsa wood board and suspending this board with six short lengths of surgical tubing from the back of the panel carrying the remainder of the equipment.

When the ozone equipment was first tested with the radio sonde, it was found that the radio-frequency signal from the sonde jammed the ozone amplifier. In an attempt to remedy this situation capacitors were put across all leads entering the amplifier proper. In addition, radio-frequency chokes were inserted in series with the signal input leads and the filament power lead. The gain of the amplifier was also reduced by inserting a 3.3 megohm resistor between the coupling

appears in the switch. [illegible] connects the [illegible] put transformer [illegible]

The chopper [illegible] operated by [illegible] mounting the chopper [illegible] If no current [illegible] between the [illegible] output of the amplifier. However, [illegible] about 10^{-9} ampere flow, it is [illegible] the chopper. [illegible] relay.

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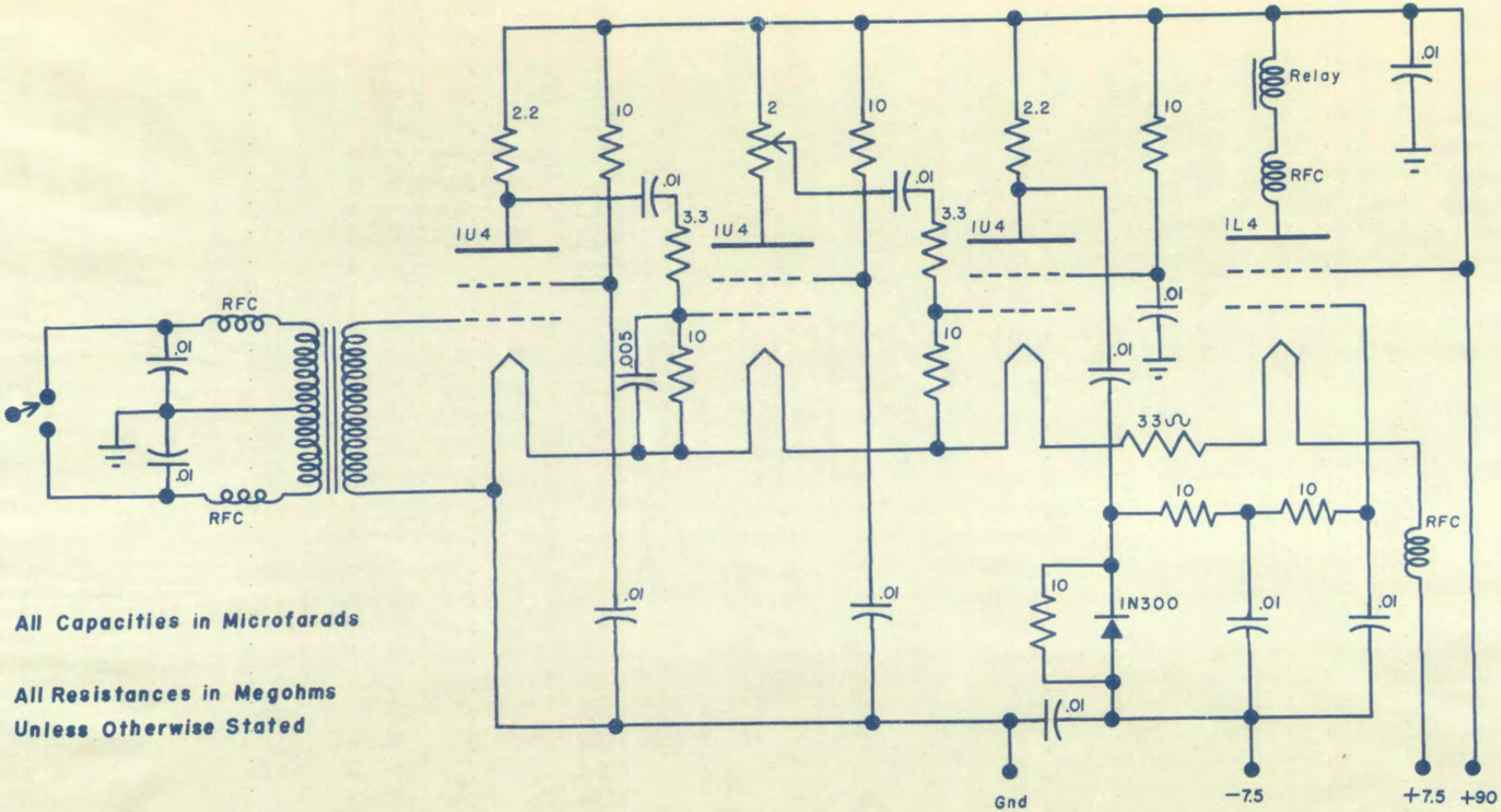

All Capacities in Microfarads

All Resistances in Megohms
Unless Otherwise Stated

Figure 5

Amplifier Circuit

capacitor and the grid of the second and third stages of amplification. This helped somewhat, but complete shielding of the entire unit with aluminum foil was necessary to allow the sonde to operate near the ozone unit without disturbing it.

Radio Sonde and Recording Equipment

A Weather Bureau radio sonde, suitably modified, is used to telemeter a signal to the ground whenever the ozone sonde changes solution. This signal is received and recorded by standard Weather Bureau equipment without disturbing the reception of meteorological information. The sonde normally transmits information on temperature, humidity, and air pressure along with two distinct reference signals. These data are in terms of audio modulation in the range from 0 to 200 c.p.s. Temperature and humidity signals lie in the region 0 to 160 c.p.s. The "low" reference signal is 190 c.p.s. and the "high" reference is at 194 c.p.s. Air pressure information is obtained by noting when the type of signal being sent changes. A calibration chart showing baroswitch contact versus air pressure is supplied with each radio sonde. Temperature is determined from the audio frequency by means of a slide-rule type calculator, and humidity is read from a set of calibration curves. The recording equipment plots these data on a graph with frequency as the ordinate and time as the abscissa.

The "high" reference frequency was chosen for the ozone signal since this signal, when switched in, will override any signal which is

capacitor and the grid of the second amplifier tube [illegible].
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aluminum foil was necessary. [illegible] the sonde [illegible] the
ozone unit will not disturb [illegible].

<u>Radio Sonde and Recording Equipment</u>

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tion. This signal is received and [illegible] by ground re-
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humidity, and [illegible].
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reference is at 19[illegible] c.p.s. [illegible]
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radio sonde. Temperature is determined [illegible] by
means of a slide-rule calculation, and humidity [illegible]
set of calibration curves. [illegible]
on a graph with [illegible].

The "high" reference frequency [illegible]
since this signal, when switched in, will [illegible]

being sent by a baroswitch contact. By adding a 3300 ohm resistor in series with the high-reference (red) lead to the baroswitch the regular "high" reference is still transmitted, but at 184 c.p.s. instead of 194 c.p.s. The ozone signal switch makes a short across this resistor, thus transmitting the original "high" reference signal at 194 c.p.s. and overriding the transmission of any other signal by the radio sonde. Instead of sending outside air temperature with the temperature contact, it was decided to send the temperature of the water bath surrounding the reaction chamber. The thermistor was removed from its position in the sonde and placed in a plastic tube inserted in the water bath. The humidity contact was then modified to send outside air temperature. This was done to give air temperature information up to the base of the stratosphere where the temperature becomes essentially constant.

Measurement of Pumping Rate at Various Pressures

Before one can convert the time interval of an ozone cycle to a corresponding quantity of ozone the volume of air passing through the equipment must be known. Since the equipment will operate at widely varying air pressures during a flight, it is necessary to determine the pumping rate for all pressures which may be encountered.

The apparatus for measuring pumping rates down to 35 millimeters of mercury is shown in Figure 6. The ozone equipment is placed inside the high-altitude test chamber. Its intake tube extends into the

being sent by a [illegible] contact. [illegible]

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"high" reference is [illegible]

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<u>Measurement of [illegible]</u>

Before one can [illegible]

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The apparatus for [illegible]

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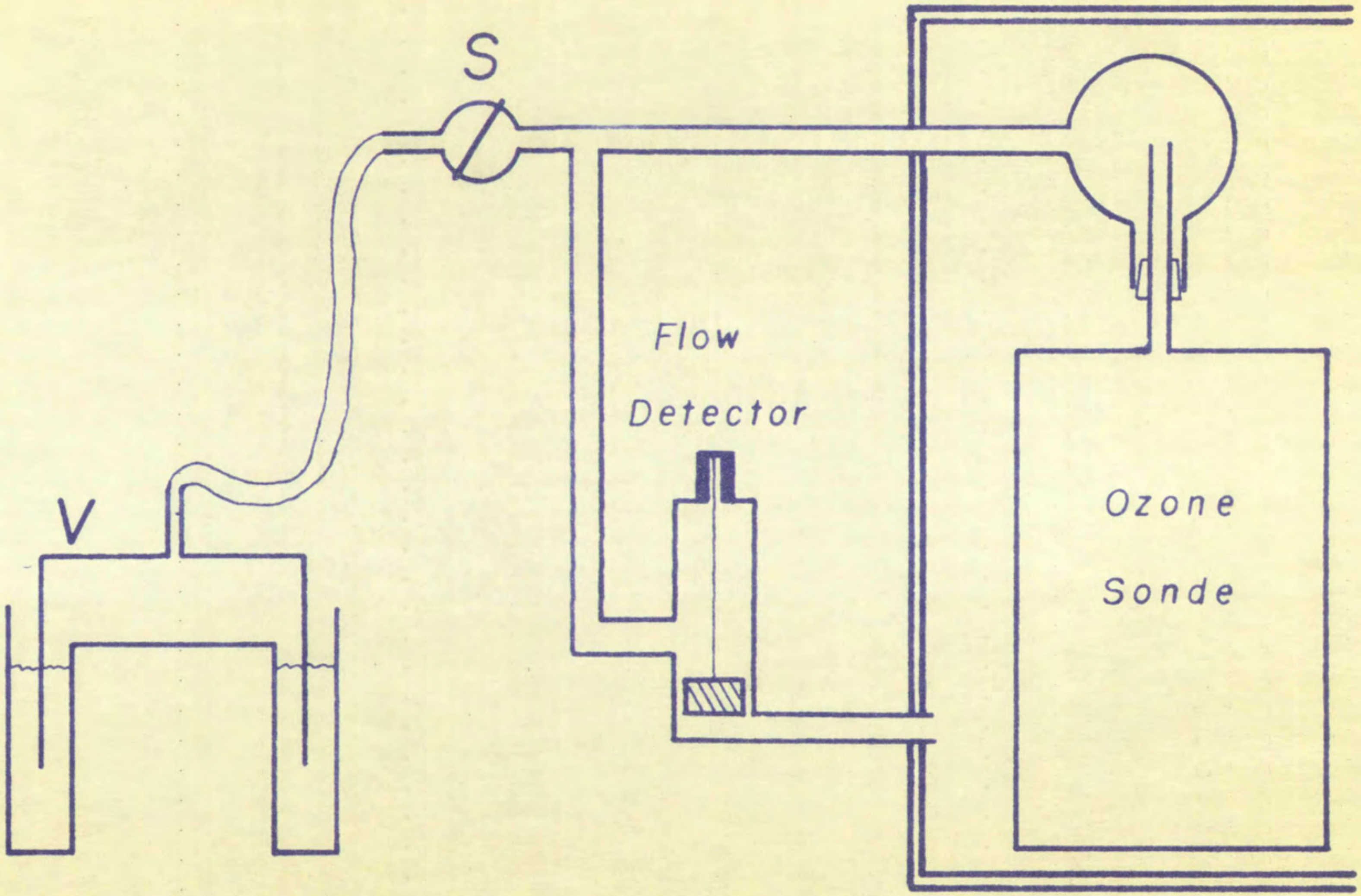

Figure 6

Apparatus for Measurement of Pumping Rate

center of a 500 c. c. flask. The purpose of the flask is to reproduce any possible "free space" end effect which may be present at the mouth of the intake tube. The neck of the flask connects with the inlet tube through which air is admitted from a gas meter V. The other arm of the inlet tube goes to a "wind mill" type air flow detector and then back into the tank. The flow detector's rotating vane is suspended from a galvanometer suspension and carries a small mica mirror. A light beam focused on the suspended mirror is reflected back to a calibrated scale. If no air flow occurs in the section of the loop containing the flow detector, there will be no deflection of the image. By proper adjustment of the stopcock S all air entering the system will be drawn through the air pump leaving the mirror undeflected. The cross-sectional area of the gas meter multiplied by the distance through which it descends per unit time gives the volume of air being pumped at the pressure inside the gas meter. This quantity multiplied by the ratio of the gas meter pressure to the tank pressure is the pumping rate for the pressure inside the high-altitude chamber.

Pumping rates were measured for all pressures down to 35 millimeters of mercury. Figure 7 shows the pumping rates measured with water being splashed in the reaction chamber for two different temperatures. Splashing water in the chamber decreases the pumping rate about 15% compared to the dry chamber rate. This difference appears to increase with decreasing pressure.

menter of a 500 c.c. flask. The [illegible] is [illegible] any possible "fore-[illegible]" [illegible] of the intake tube. [illegible], the flask [illegible] through which [illegible] the inlet tube [illegible] flow [illegible] back into the tube. The flow [illegible] from a galvanometer [illegible] light beam focused on [illegible] calibrated scale. [illegible] taining the flow detector, [illegible] proper adjustment of the [illegible] be drawn through the [illegible] cross-sectional [illegible] through which [illegible] pumped at the [illegible] by the ratio of the [illegible] ing rate for the [illegible].

Pumping rates were [illegible] meters of mercury. [illegible] with water being [illegible] temperatures. [illegible] water [illegible] rate about 15% [illegible] appears to increase [illegible].

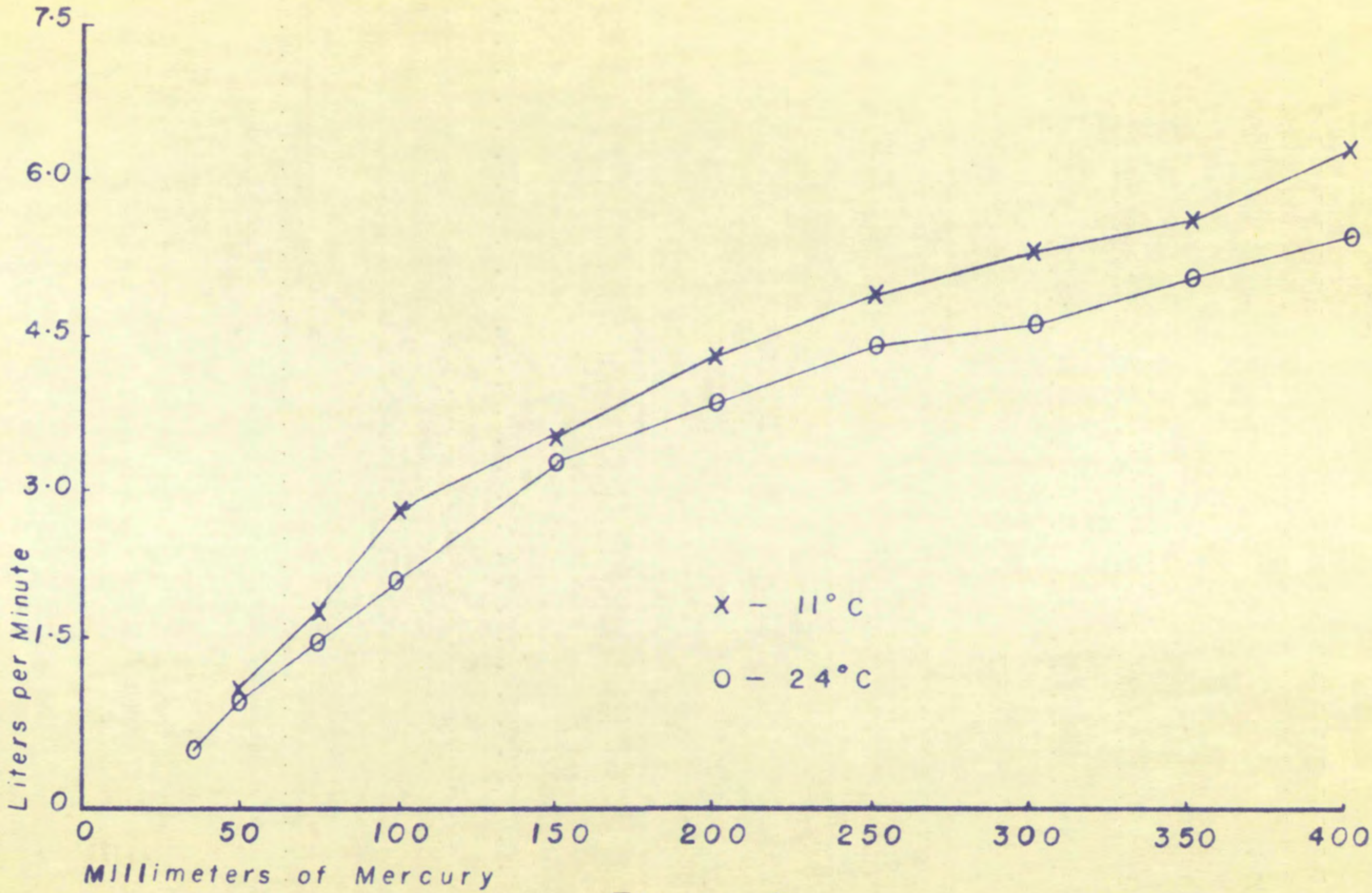

Figure 7

Pumping Rates

The decrease in pumping efficiency at low pressure is a desirable feature for this instrument. As the balloon ascends, the ozone concentration increases and the pumping rate decreases, thus the time of a titration cycle will tend to be constant.

CHAPTER II

ABSOLUTE OZONE MEASUREMENT

The following reactions take place in the chamber.

$$O_3 + 2KI + H_2O \text{ -- } 2KOH + I_2 + O_2$$

$$2Na_2S_2O_3 + I_2 \text{ -- } 2NaI + Na_2S_4O_6$$

These reactions occur in a solution containing 2% potassium iodide and 5×10^{-6}-normal sodium thiosulphate. Each injection of 5.2 c.c. of this solution contains 2.6×10^{-8} mol of sodium thiosulphate. One mol of ozone reacts with two mols of potassium iodide yielding one mol of iodine. The mol of iodine in turn reacts with two mols of sodium thiosulphate. Thus there is 1.3×10^{-8} mol or 0.624 microgram of ozone destroyed per injection. Therefore the concentration, C, will be given by $C = m/Qt$ in micrograms per cubic meter, where m is the mass of ozone destroyed per cycle, Q the pumping rate at the pressure of the measurement, and t the time of the cycle in minutes.

Surface ozone was measured on several occasions and the results were compared with measurements obtained from automatic ozone recorders of a different type (Figure 8). After correction for an error in the determination of the pumping rate at atmospheric pressure the measured concentrations compared well with those obtained by the recorders.

If the surface ozone concentration drops below about 10 micrograms per cubic meter, the time of a titration cycle increases to such an extent that a substantial amount of the water in the chamber

[illegible]

The following [illegible]

[illegible]

[illegible]

These reaction [illegible]

and 5×10^{-6} [illegible]

of this solution contains [illegible]

mol of ozone [illegible]

mol of iodide, [illegible]

dium thiosulphate. [illegible]

of ozone destroyed [illegible]

will be given by [illegible] grams per cubic meter [illegible]

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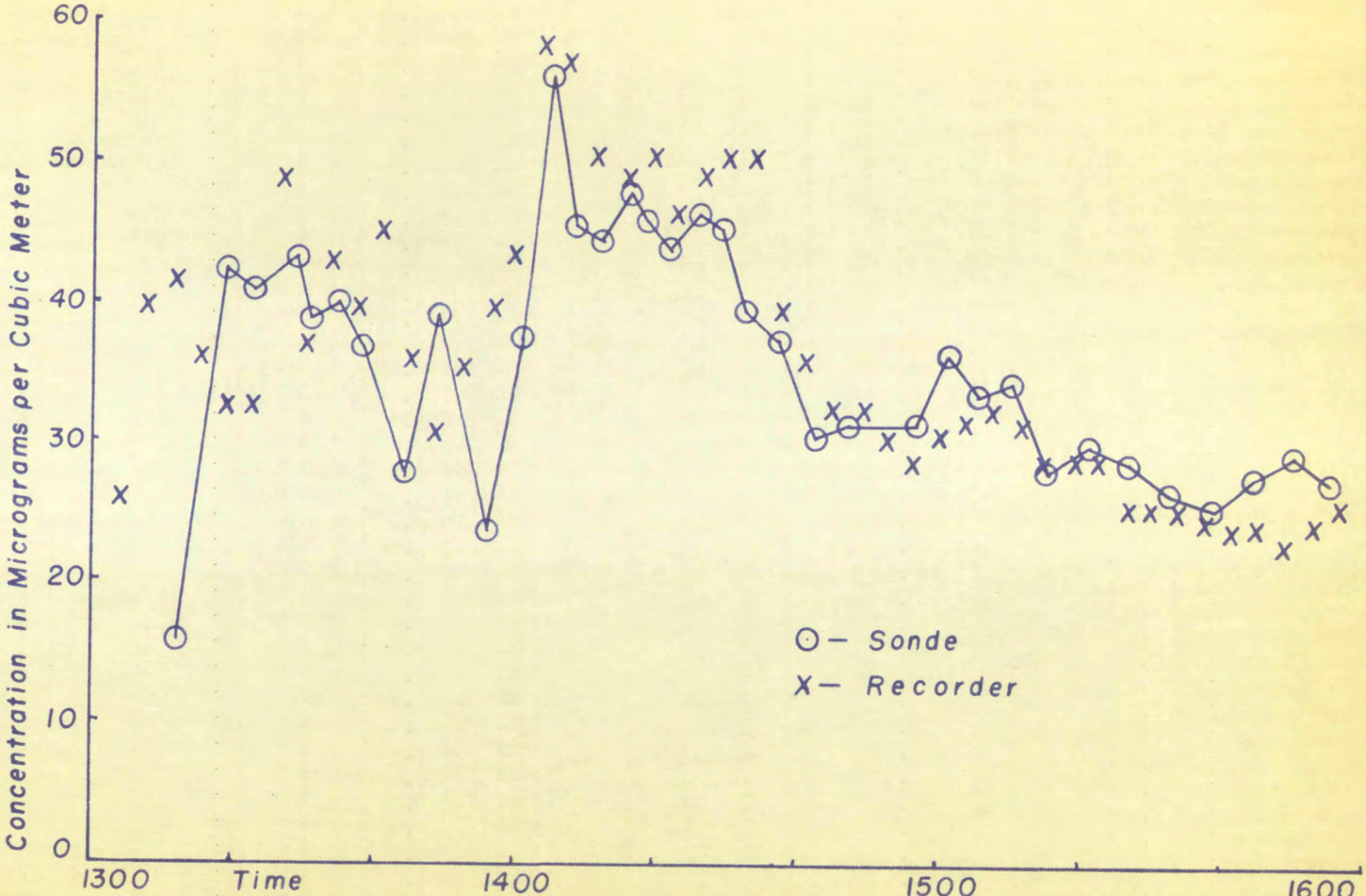

Figure 8
Comparison of Ozone Measurements

evaporates before the instrument cycles. This results in less splashing by the impeller and therefore in decreased efficiency of measurement. The effect was noted on several occasions while measurements were being carried out at sunset when the ozone concentration dropped drastically.

If the water bath is above about 30 degrees centigrade, it will increase the rate of evaporation of the solution and thereby cause the chamber to dry out rapidly.

A balloon flight was made but no information was obtained because of a failure in the electronic telemetering equipment.

I wish to thank Professor Victor H. Regener for his invaluable assistance in both the design and experimental phases of this project.

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[illegible]

Mitra, S. K., [illegible]

Asiatic Society, [illegible]

Bowen, I. S., [illegible]

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IMPORTANT!

Special care should be taken to prevent loss or damage of this volume. If lost or damaged, it must be paid for at the current rate of typing.