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HIGH ALTITUDE RADIATION MEASUREMENTS

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## Abstract

This report summarizes project activity during the period 1 October 1969 to 31 December 1969. Adjustments, tests and modifications of the Jarrell Ash 1.8 meter spectrometer, which are being made prior to measurements of the 15  $\mu$ m band of CO<sub>2</sub>, are reported and plans for systematic analysis of the data are described. The considerations leading up to the construction of a simplified ozone generating, handling and measuring system are discussed. Results of the survey of the literature on the distribution of CO<sub>2</sub> in the earth's atmosphere are indicated.

## I. Introduction

This is the 28th Quarterly Progress Report on Contract No. NASr-54(03) covering the period 1 October 1969 to 31 December 1969. The project effort during this time was divided among the following tasks.

1. High Resolution Measurements of the  $15\mu\text{m}$ . Absorption Band of  $\text{CO}_2$  (L. W. Chaney)
2. Development of Ozone Generating, Handling and Measuring System
3. Survey of the Literature Regarding the Distribution of  $\text{CO}_2$  in the Earth's Atmosphere.
4. Report Writing

## II. High Resolution Measurements of the $15\mu\text{m}$ Absorption Band of $\text{CO}_2$ (L. W. Chaney)

### A. Status of Jarrell Ash Spectrometer at the Beginning of this Work Period.

1. The optical alignment procedure had been carried out.
2. The instrument was essentially vacuum tight.
3. A test spectrum had been run.
4. The cooled detector could not be properly tightened into position without causing excessive boiling of the liquid helium.

### B. Work on Detector and Exit Optics

The boiling of liquid helium could be corrected by loosening the detector very slightly being careful to maintain a vacuum in the spectrometer. This indicated that a careful inspection of the detector assembly be made .

When the detector Dewar was completely disassembled, it was discovered that the entrance window, mounted between two "O" rings, touched the helium cooled aperture if the "O" rings were completely compressed.

The window and the aperture were modified to prevent this "touching" and, at the same time, the IRTRAN-6 window was replaced by a KBr window.

The order filter mounted on the helium cooled aperture, was cracked during the modification. Fortunately the remaining piece was just large enough to cover the opening. However, it is suspected that the filter was gradually deteriorating. Background scans made during subsequent data runs indicate that interference ripples associated with the filter were increasing in magnitude. This might be due to cracking the filter as noted above or deterioration due to temperature stress. A new filter has been ordered from OCLI. It will be mounted on the window even though this means that more unmodulated energy will fall on the detector. However, temperature stressing of the filter will be eliminated.

While an instrument was shut down for modifications of the detector, it was decided to correct the alignment of the exit optics. This required the re-soldering of the mounting flange. Re-alignment permitted all the mirrors to be completely filled with light. The resoldered flange leaked slightly, but was repaired with epoxy cement.

### C. Instrument Check Out:

The following checks were made:

1. Signal to Noise. A 10 cm cell was borrowed and filled with CO<sub>2</sub>. Scans were made of the spectrum from 800 to 650 cm<sup>-1</sup>. The noise was about 1% of full scale for a 3 second integration time. This was comparable to the performance previously reported for the instrument.

2. Slit Widths. The proper slit widths were determined by finding a well separated single line and scanning the line using a succession of slit openings. The resolution improves as the slits are narrowed up to the basic

instrument resolution. Narrowing the slits beyond this point reduces the signal.

After the slit widths were picked by the above test, the pressure in the cell was varied to make sure that the line width was due to the instrument rather than pressure broadening.

Lines were checked at both ends of the spectrum and the resolution varied from .072 to .085  $\text{cm}^{-1}$ . This will be more thoroughly investigated when more accurate spectra are generated.

3. Output linearity. During a previous study of  $\text{CO}_2$  by H. G. Reichle, a set of variable width chopper blades were used for linearity checks. The available blades have: 90%, 80%, 60%, 40%, 20%, 10% and 5% transmission. The instrument was linear within 1% of full scale as measured with these blades.

#### 4. Preliminary Spectra and Stray Light:

Preliminary spectra with both a background scan and a 100% absorption trace were run at various cell pressures in order to present typical data. The stray light was found to be 5% of full scale. This amount is undesirable, but tolerable.

#### D. Instrument modifications:

In order to set the instrument up for accurate data recording the following modifications were made.

1. The chopper was modified so that the chopping was done in front of the source rather than in front of the gas cell, also the chopper and the source were physically made an integral unit.

2. A gas handling manifold was designed, built and tested. It provides means for putting measured amounts of gas into the cell and means



for broadening the CO<sub>2</sub> with either nitrogen, oxygen or other gases.

3. Three gas cells, originally built by Reichle were modified and a new cell constructed. The cells now available are: 8.74cm, 5.0 cm, 2.5 cm and 0.5 cm. The 8.74 cm cell was checked for leaks and mounted in the spectrometer. Test spectra using this cell and the gas handling system have been made.

4. An index wheel with lamps and photo cells was designed and built for the wavelength drive. This equipment will permit the spectrometer to be interfaced with an IBM card punch. The parts are now complete, but the system has not yet been checked out.

#### E. Analysis of the results.

The high resolution spectra from the Jarrell Ash spectrometer will be used to deduce line intensities and half-widths of CO<sub>2</sub> lines near 15  $\mu$ m, and later some information on line shapes. These parameters will then be used in atmospheric applications, particularly in the remote sensing of temperature from satellites.

The instrument has already been shown to produce less noisy, higher resolution spectra than any previously reported measurements of CO<sub>2</sub> absorption near 15  $\mu$ m. This will yield significantly better estimates of band parameters, particularly for weaker overtone bands whose lines are often overlapped by lines of more intense bands, or are lost in noisy data. Some care has been given to choosing small spectral regions (about 5 cm<sup>-1</sup>) which will be intensively studied. Criteria include avoiding overlapping lines as much as possible, including lines of low, intermediate and high rotational quantum numbers, verifying existing values of parameters and measuring those that are uncertain. In particular, vibrational-rotational interactions for high J-numbers will be studied.

#### F. Plans for the Next Quarter's Work.

1. Compute the index wheel-card punch modifications.
2. Install the new order filter in the detector window.
3. Start taking data (should begin about 2-1-70) and continue taking data through the balance of the next reporting period.
4. Begin Analysis of data.

### III. Development of Ozone Generating, Handling and Measuring System. (L. T. Loh)

#### A. Ozone Generating and Handling System.

A program of medium resolution and high resolution measurements of the  $9.6\ \mu\text{m}$  and  $14.2\ \mu\text{m}$  bands of  $\text{O}_3$  is being started in the High Altitude Engineering Laboratory. This work, which will be similar in scope to that already underway on the  $15\ \mu\text{m}$  band of  $\text{CO}_2$ , will follow along behind the  $\text{CO}_2$  measurements. It is estimated that there will be a time lag of 6-12 months between similar phases of the  $\text{O}_3$  and  $\text{CO}_2$  work.

The initial phase of the  $\text{O}_3$  measurements program is to construct the  $\text{O}_3$  generating, handling and measuring system. Systems for this purpose have been built by other researchers. The one used at Ohio State University<sup>1</sup> will serve as an example of such a system. Figure 1 is a schematic diagram of their system, which used oxygen containing a small amount of methane. The methane was removed from the oxygen by being oxidized to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  by platinum black. The  $\text{CO}_2$  and  $\text{H}_2\text{O}$  were then trapped in the Ascerite drying column. The ozonizer was a gaseous discharge tube using a 15000 volt neon sign transformer. A mixture of 2%  $\text{O}_3$  to 98%  $\text{O}_2$  was produced at room temperature with a flow rate of 10 liters per hour.

The ozone concentration was monitored with a U. V. spectrophotometer which measured emission lines of Hg. produced by a low pressure lamp. The transmission of the ozone-oxygen sample for this U. V. radiation was measured. Since the absorption coefficients at these wavelengths were known, the ozone concentration could be calculated.

Several members of our staff visited Ohio State University in October to discuss the ozone infrared measurements and the ozone generating and handling system. After this a literature search was carried out for additional information and possible new techniques. The American Chemical Society Monograph<sup>2</sup> "Ozone Chemistry and Technology" was found to be very useful.

The design of the ozonizer initially proposed for use in our laboratory is shown in figure 2. It is similar to the Ohio State system, however an additional feature, the capability of storing O<sub>3</sub> in cooled Si O<sub>2</sub>, has been added. This system would use 0.2 of silica gel, dry ice cooling, commercial O<sub>2</sub> with Platinum black oxidizer and Ascarite dryer for the removal of H<sub>2</sub>O.

Typical operating procedures are as follows. Starting with all valves closed.

1. Pump out gas cell.

Open valve #11, pump (B), read pressure (D), close valve 11.

2. Pump out sodalime.

Open valve 9, pump (A), with fan on, close #9.

3. Pump out ozonizer section.

Start pump (A) and fan, open 5, 6, 3, 2, 1 & 7 in order mentioned, read pressure (C), close 5.

4. Charge with  $O_2$ , and making of  $O_3$ . #6, 3, 2 & 7 open.  
Heat up Pt black. Cool down heat exchangers and silica gel, using dry ice.  
Meter  $O_2$  from tank by valve 1 at 10 liter/hr. Watch pressure gage C. Start ozonizer when C gets to 1 psi. Watch C going up. Close 1 when C reaches 10-15 psi. Start circulator. Add more  $O_2$  as needed (after closing #2 & 7). Close 1. Judging the amount of  $O_3$  formed from the total operating time of ozonizer, or from change in pressure on C.  
Close valves 1, 2, 3, 6 & 7.
5. Pump out unused  $O_2$ .  
By opening of valves 6 & 5 briefly, close 6 & 5.
6. Transfer  $O_3$  into gas cell.  
By opening valves 6 & 10. Watch pressure. Heat may be applied through the heating coil. Close #6 & 10.
7. Add broadening gas.  
Use valve #4. Watch pressure. Close #4.
8. More  $O_3$  and/or broadening gas may be added.
9. Make IR & UV runs
10. Pump out gas cell.  
Open valves 9, 8 & 10, watch pressure D, close 10, 8 & 9.
11. Pump out ozonizer.  
Open valves 9, 8, 6, 3, 2 & 7. Watch pressure on C. When vac is OK, close 7, 2, 3, 6, 8 & 9.  
Remove dry ice if necessary.
12. The system is now ready for another cycle.

Although the complete system described above will probably be built eventually, a simplified system will be used at the start. Starting with a more pure grade of  $O_2$  and using only  $O_2$  as a broadening gas will give us a much more simple system, and it will still be possible to cover a reasonable range of  $O_3$  concentrations in  $O_2$  by controlling the time duration of the ozonizer operation.

The simplified system is shown in fig. 3. The Platinum black purifier and Ascarite dryer, heating and cooling devices, silica gel  $O_3$  absorber,  $O_2$  recirculating device, regulators, gauges, and several valves have been removed. The  $O_2$  used is ultra pure  $O_2$ , Airco grade 4<sup>TM</sup>, of 99.99% purity, dew point  $-97^\circ\text{F}$ .

Operating procedures for this system, starting with all valves in a closed position are:

1. Pump out gas cell

Start pump A and fan, open 5 & 7. Watch pressure on D.

Close 7 and 5.

2. Pump out Sodalime.

With pump and fan on, open #9. Close #9.

3. Pump out ozonizer.

With pump and fan on, open 5, 6, and 1. Watch pressure.

Close 1, 6 & 5.

4. Charge gas cell with  $O_2 + O_3$ .

Open  $O_2$  tank, and set low pressure gage to 15 psi. Open

7. Open 1 & 6 very slightly and adjust flowmeter to 10 liters

per hour. The time to start and to stop ozonizer depends on the

amount of  $O_3$  needed. Operate the ozonizer with pressure 1 psi. Stop the ozonizer. Sweep all  $O_3$  into gas cell, then close #1. Close #6 and #7. Check pressure on D all the time. Check  $O_3$  in gas cell with UV.

5. Make UV and IR run on  $O_3 + O_2$  in gas cell.

Stir up the  $O_3 + O_2$  in gas cell. Watch UV absorption and total pressure. Run the  $O_3$  IR spectra.

6. Pump out gas cell.

With pump and fan on, open 9, 8, & 7. Watch pressure and UV absorption. Close 7, 8, & 9.

7. Pump out ozonizer.

Open 5 and 6 with pump and fan on. Watch pressure on C. Close 6 and 5.

8. Flush pump with air.

Open 12 slightly for a minute. Turn off pump and fan.

Close #12.

9. Close  $O_2$  tank.

Construction of the simplified system has been started. The glass ozonizer was constructed in the University's Chemistry Department according to the Ohio State design, see fig. 4. Unfortunately the double seal at the top of the ozonizer was faulty as indicated in the figure. The double seal cracked twice and so the design was changed. A standard taper glass joint was fused onto the necked down outside jacket of the glass cell, providing a gas tight joint without the use of a double seal, see fig. 5. Also a teflon spacer was added to eliminate the vibration of the central long glass electrode. The

assembled ozonizer was operated and tested for production of  $O_3$  with KI-starch paper.

### B. Quantitative Measurements of Ozone

Another problem that has been considered is the quantitative measurement of  $O_3$  in the sample cell. It will be also be necessary to monitor the concentration of  $O_3$  in the room air and to provide a warning to personnel whenever the concentration exceeds a maximum allowable amount. Three methods are available for this purpose.

#### 1. Measurement of U. V. absorption.

Knowledge of UV absorption coefficients allows one to convert measured UV transmissivities into total ozone amounts.

#### 2. Ozone thermal decomposition

The measurement of the heat of decomposition of  $O_3$  on the catalyst coated surface of a thermistor can be related to  $O_3$  concentrations.

#### 3. Ozone "wet chemistry".

The oxidation of KI by  $O_3$  in  $H_2O$  can also be related to  $O_3$  concentrations.

The first of these three techniques appears to be best suited for measurement of  $O_3$  amounts in the sample cell. McCaa and Shaw used a 26 cm path length in their sample cells for UV measurements. The absorption of the 2536, 2893, 2967, 3021, 3131 and 3341 Angstrom lines of Hg in this path were measured with a Perkin-Elmer 12-C spectrophotometer. The source of radiation was a low pressure Hg lamp.

Instruments now in our laboratory which might be adapted for this purpose are:

1. The Perkin-Elmer 13-U spectrophotometer.
2. The Perkin-Elmer SG-4 spectrophotometer.

The 13-U instrument is very large. It would appear to be difficult to adopt portions of it for use in these measurements. Use of the entire instrument would involve undesirably long pipe lines to take the gas mixture from the infrared sample cell to an ultraviolet sample cell.

The Perkin Elmer SG-4 instrument was originally designed for remote sensing in the near infrared range. Modifications would have to be made in order to use it in the ultraviolet. A new grating and a new detector would have to be installed. Suitable gratings may be available from Bausch and Lomb. The new detector would probably be a 1P28 photomultiplier which may be difficult to adapt to the instrument. The modification of this instrument will be considered in detail and a check will be made to see what other instruments are available commercially for this purpose.

#### IV. Survey of the Literature Regarding the Distribution of CO<sub>2</sub> in the Earth's Atmosphere.

The literature survey to locate information available regarding the distribution of CO<sub>2</sub> in the atmosphere has been continued. Recent measurements of atmospheric CO<sub>2</sub> have been reported by Kelley<sup>2</sup> and Keeling, et al<sup>3</sup>.

Kelley's measurements were made in April 1967, using infrared absorption techniques on aircraft flights at 500 mb. altitudes between the west coast and Denver, Colorado. Results include:



1. A 2p. p. m difference in CO<sub>2</sub> in the air between the west coast and interior areas of the United States. Air over the west coast contains a higher concentration of CO<sub>2</sub> (as much as 323.3 ppm) than does air in inland areas (321.5 ppm over the Denver to Grand Junction Area).
2. A vertical carbon dioxide gradient over the Los Angeles area indicates a source of CO<sub>2</sub> at the surface. Concentrations of CO<sub>2</sub> vary from 326 ppm at the surface to 321.2 ppm at 4 km.
3. The results obtained agree with monthly averages reported by Bolin and Keeling<sup>4</sup> for the region 125°-155° W. Longitude and 25°-70° N latitude. The value obtained by Bolin and Keeling for April 1960 is 317.3. Allowing for a rate of increase of 0.68 ppm per year, the adjusted value for 1967 is 322.3 ppm.

Keeling and his associates reported measurements made by sampling on aircraft at the 500 and 700 mb levels above the North Pacific and Arctic Oceans from April 1958 to December 1961. Results indicate:

"The concentration (mixing ratio) of CO<sub>2</sub> oscillates seasonally. . . . . Variations with altitude are slight. Typical monthly mean values referred to a 1960 datum are: south of 20°N, maximum of 316 ppm in June, minimum of 311 ppm in October; north of 70°N, maximum of 317 ppm in May, Minimum of 308 ppm in August. Significant horizontal variations in CO<sub>2</sub> concentration are observed on the scale of the weather patterns during summer, when photosynthesis by land plants produces an intense sink for CO<sub>2</sub>. During other seasons the concentration is uniform over great distances. "

Conversations with E. A. Martell of NCAR indicates that reports of the results obtained by their rocket-borne sampler will be published soon in the Journal literature.

#### V. Report Writing

The technical report 05863-19-T, "An Experimental Fourier Transform Asymmetrical Interferometer for Atmospheric Radiation Measurements" by L. W. Chaney was re-written. At the end of this work period it was ready for publication.

#### VI. References

1. McCaa, D. J., and J. H. Shaw "The Infrared Absorption Bands of Ozone", Scientific Report No. 2., The Ohio State University Research Foundation, Columbus, Ohio, Contract No. AF 19(628)-3806, Air Force Cambridge Research Laboratories Report No. AFCRL-67-0237, February 1967.
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4. Bolin, B., and C. D. Keeling, "Large Scale Atmospheric Mixing As Deduced from the Seasonal and Meridional Variations of Carbon Dioxide," J. Geophys. Res. 68, No. 13, 1 July 1963.

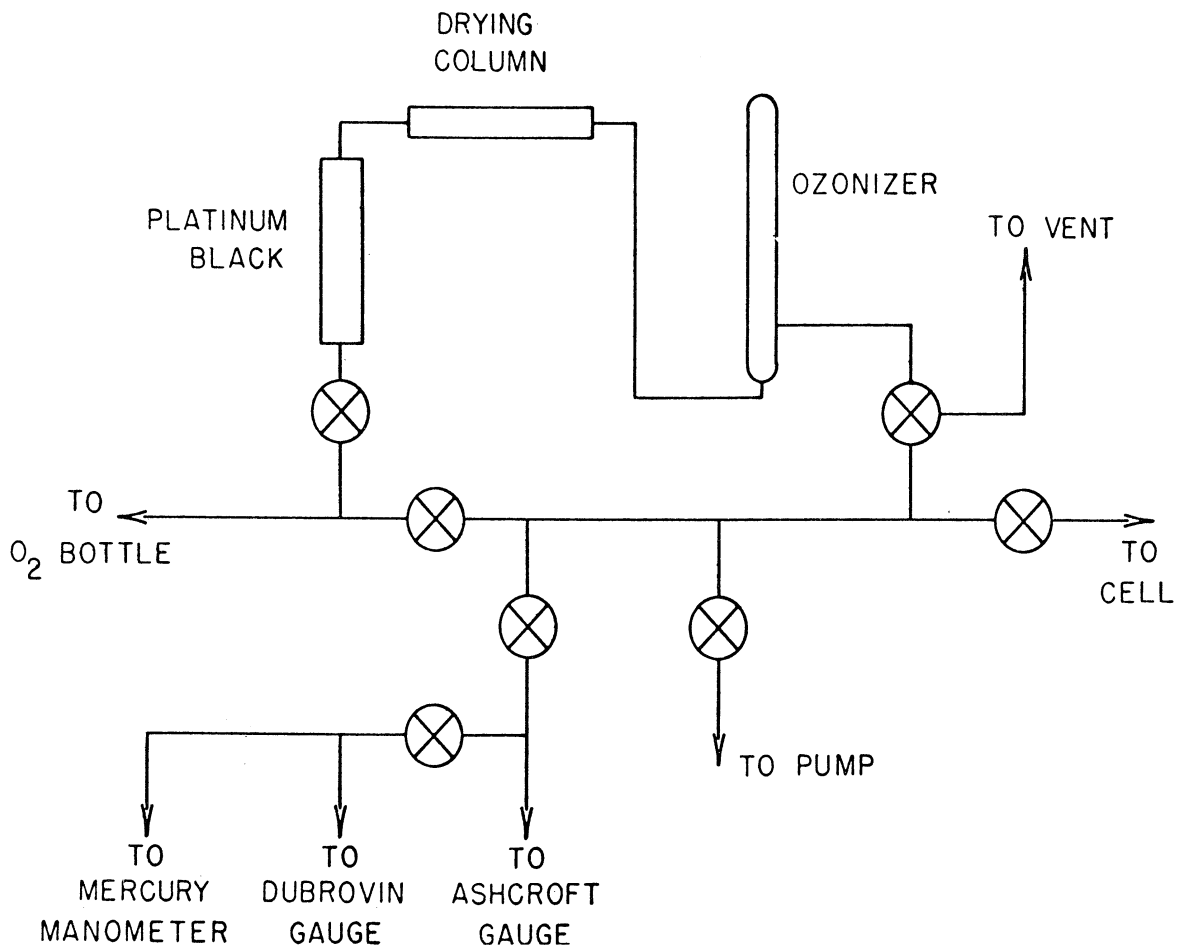


Figure 1. Schematic diagram of ozone generating and handling system used by McCaa and Shaw<sup>1</sup>

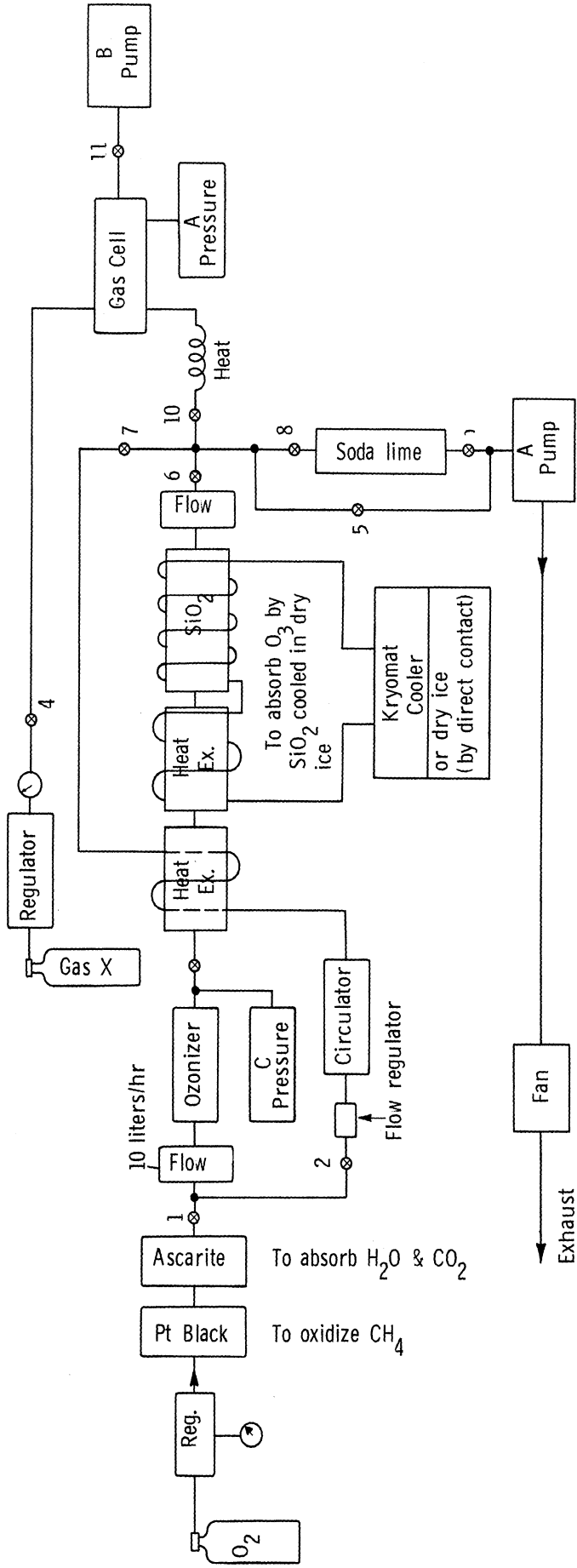


Figure 2 Schematic diagram of ozone generating and handling system initially considered for use in the High Altitude Engineering Laboratory

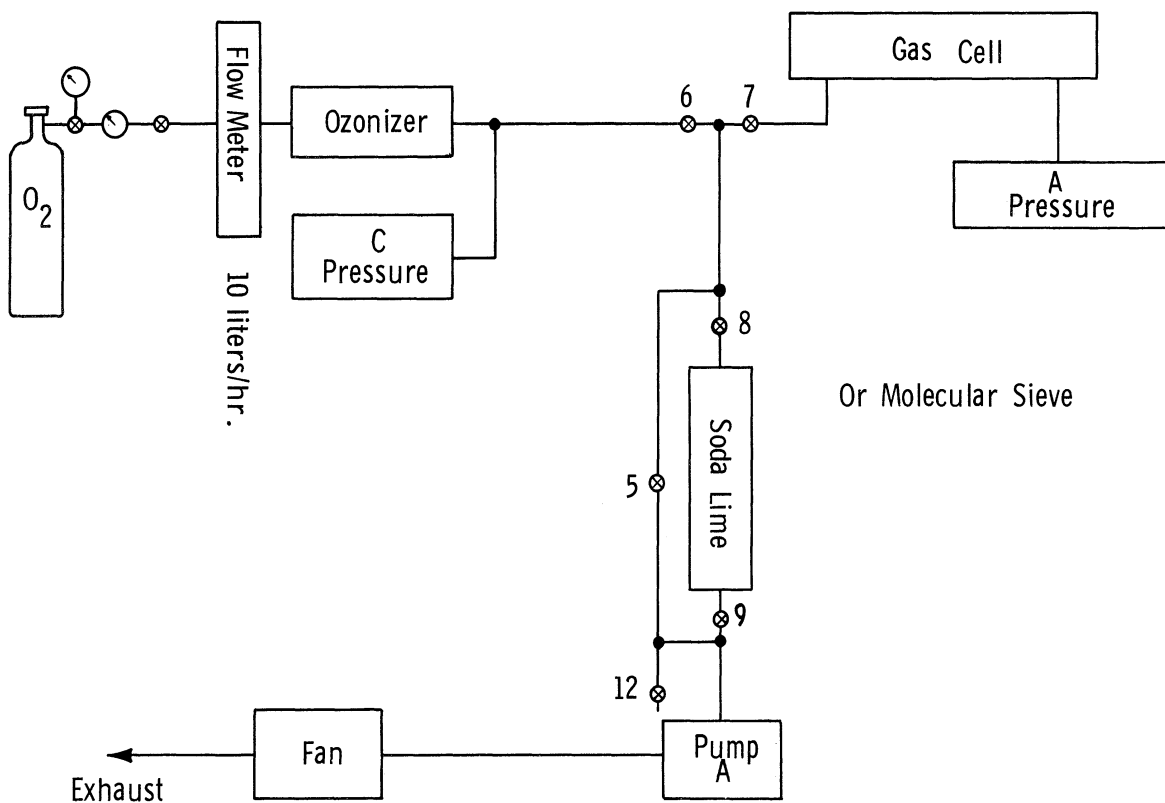


Figure 3 Schematic diagram of simplified ozone generating and handling system now being built in the High Altitude Engineering Laboratory

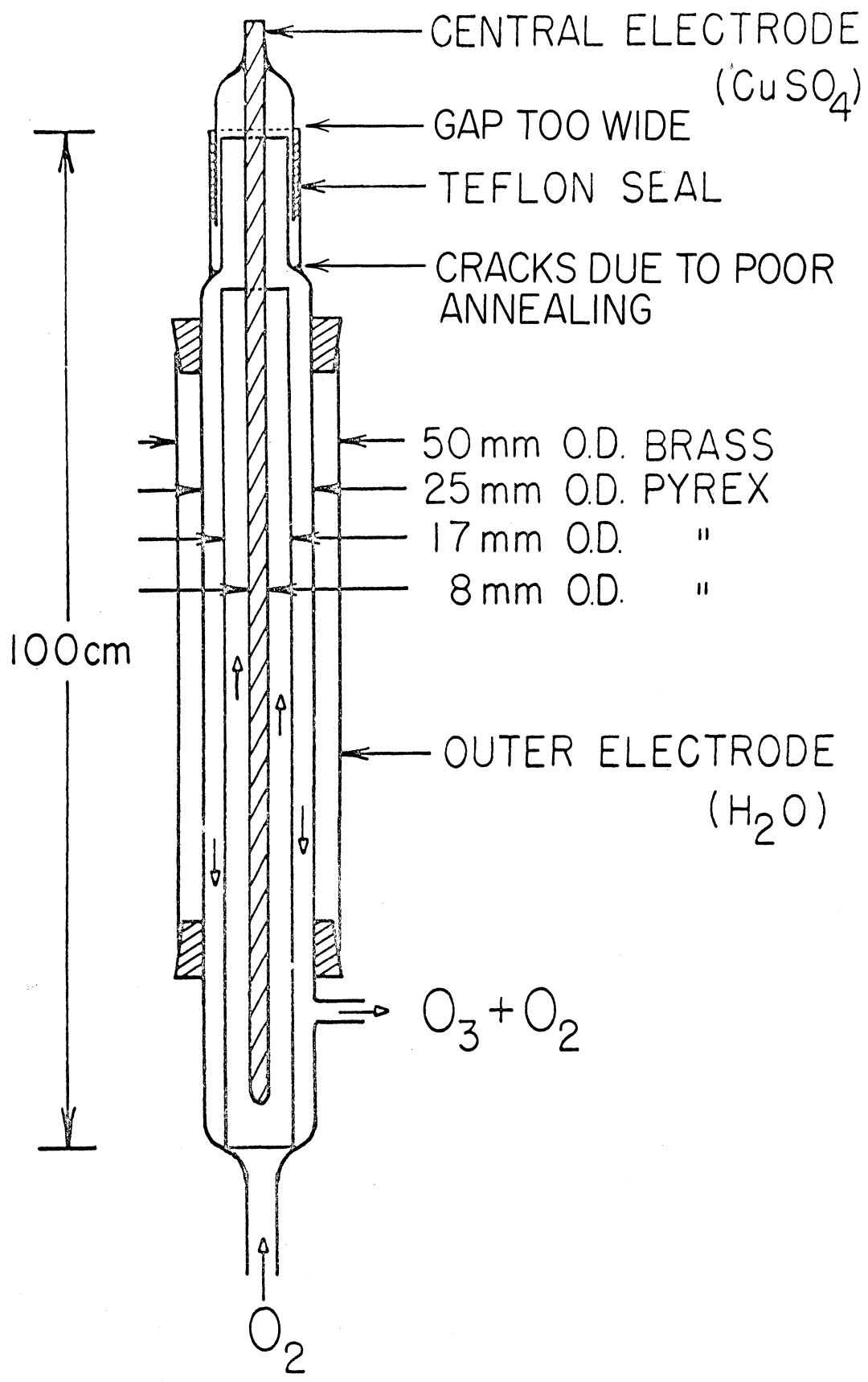


Figure 4 Ozonizer used by McCaa and Shaw<sup>1</sup>

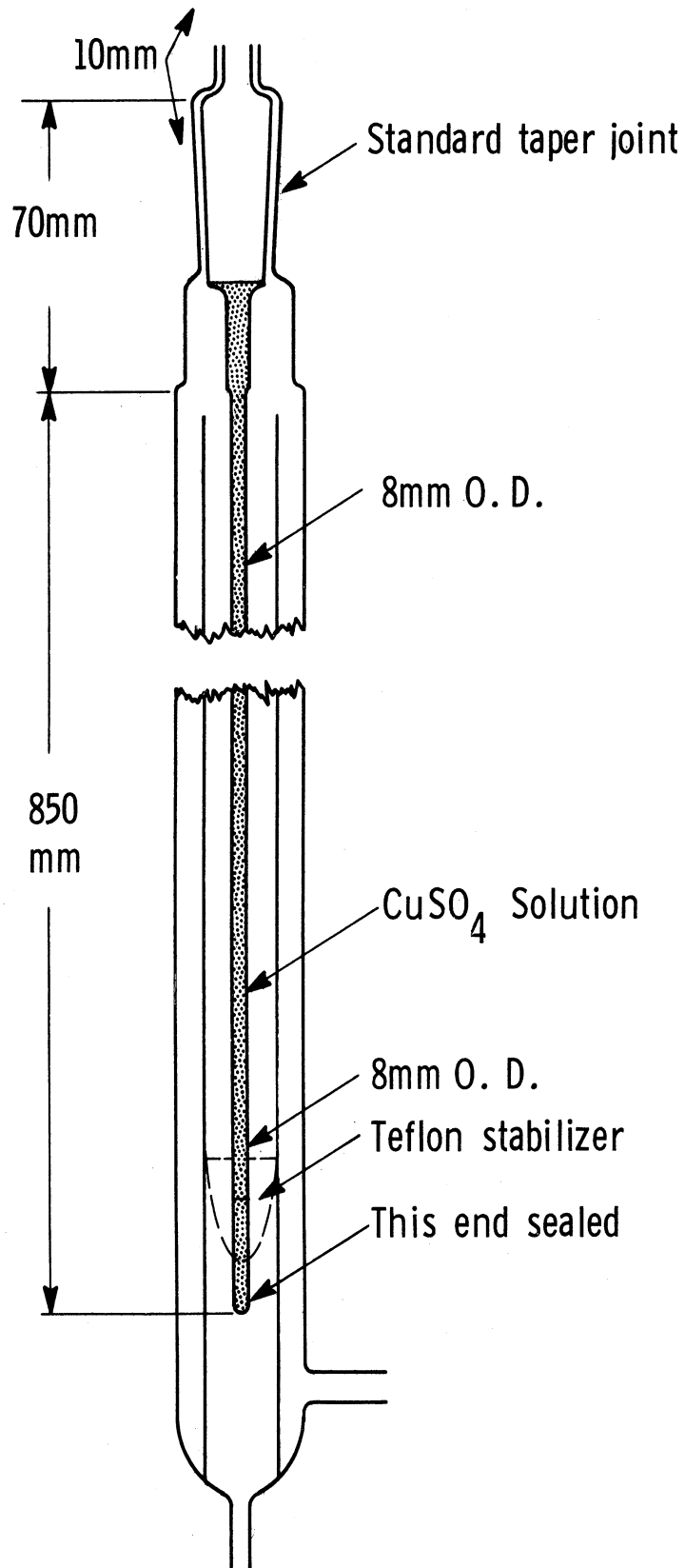


Figure 5 Ozonizer which will be used in the High Altitude Engineering Laboratory

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