THE UNIVERSITY OF MICHIGAN

COLLEGE OF ENGINEERING

High Altitude Engineering Laboratory
Departments of
Aerospace Engineering
Meteorology and Oceanography

Quarterly Report

HIGH ALTITUDE RADIATION MEASUREMENTS

1 January 1970-31 March 1970

Fred L. Bartman

ORA Project 03635

under contract with:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
CONTRACT No. NSR 23-005-376
WASHINGTON, D. C.

administered through
OFFICE OF RESEARCH ADMINISTRATION ANN ARBOR

April 1970

Table of Contents

List of Illustrations

Abstract

This report summarizes project activity during the period 1 January 1970 to 31 March 1970. Experimental work discussed includes the high resolution measurements of the 15 μm band of CO_2 and the development of an ozone generating handling and measuring system. Theoretical analysis of the high resolution 15 μm CO_2 data and of the 9.0 μm O_3 band are in progress. A literature survey on the distribution of CO_2 in the earth's atmosphere is being made.

I. Introduction

This is the 2nd Quarterly Progress Report on Contract No. NSR 23-005-376, covering the period 1 January 1970 to 31 March 1970. Since the administrative decision to change this contract came after the Quarterly Progress Report for the period 1 October 1969 to 31 December 1969 had been distributed, that progress report has the number 05863-28-P instead of 03635-1-P.

The project effort during this time was divided among the following tasks.

1. High resolution measurements of the 15μm absorption band of CO_2 (L. W. Chaney).
2. Theoretical analysis of high resolution 15 μ m CO_2 measurements (S. R. Drayson).
3. Development of ozone generating, handling and measuring system (L.T. Loh and P. A. Titus).
4. Theoretical analysis of 9. 6 μm ozone band (W. R. Kuhn).
5. Literature survey on the distribution of CO_2 in the atmosphere.

II. High Resolution Measurements of the 15μ m Absorption Band of CO_2 (L. W. Chaney).

A. Status of the Jarrell Ash Spectrometer at the Beginning of the Reporting Period

1. Test spectra using the 8. 74 cm cell and the gas handling system had been made. The spectra indicated that a resolution better than . 08 cm^{-1} could be achieved. Also, the signal to noise ratio was satisfactory (see spectra in previous report).

2. The components required to interface the spectrometer and the IBM card punch were designed and complete, but not assembled or checked.

B. Tasks Completed During the Report Period

1. The spectrometer and the IBM card punch were connected.
2. A new interference filter was installed on the dewar helium station.
3. An investigation was made of the instrument resolution.
4. A wavelength calibration of the instrument was made.
5. Thermistors were installed to monitor the instrument temperature.
6. A nitrogen purge system was provided for the source area to reduce CO_2 background.

C. Detailed Discussion of Work Carried Out During the Reporting Period.

Originally it was planned to use a G. P. 2402 A integrating voltmeter ($\frac{1}{60}$ second integration time) and a H. P. 2547 A coupler to interface the spectrometer with the IBM summary punch. Since both items were available at the Willow Run Laboratory this was a very economical plan. However, further analysis showed that a better signal to noise ratio could be obtained with a system using the High Altitude Engineering Laboratory H. P 2410 C integrating voltmeter and an external oscillator to increase its integrating time from 1 second to 2.2 seconds. Since the output logic of the two voltmeters was different, two new cards were required for the coupler. They were purchased.

A new interference filter, used to isolate the first order of the grating was purchased from Optical Coating Laboratories Inc. The only available filter in stock was 1.5 inches in diameter. It was cut into two pieces. One piece was 0.75 inches diameter and the other 0.562 inches in diameter. The larger piece was mounted in a window holder with a KBR window. The purpose of placing the filter in the window was to reduce the thermal strain due to temperature cycling the detector. However, as a result of the increased background photons on the detector the sensitivity was reduced by 50%. The smaller piece was mounted on the helium station and the original sensitivity was restored. Thus far, there has been no discernible deterioration similar to that noted for the original filter. The fact that the new filter is more than twice as thick as the old one (0. 018 -.040 inches) may be significant. Also, less epoxy was used in cementing the filter to the helium station.

After completion of the card punch system and installation of the new filter, test spectra were run to check the entire system. The measured spectra were compared with calculated spectra in the region of 720 cm^{-1}. (see figures 1 and 2) and near 660 cm^{-1} The following conclusions were made as a result of these measurements.

1. The wavelength calibration was not linear.
2. The resolution varied between .055 and .07 cm^{-1}
3. The wavelength markers shifted with room temperature.
4. A method was needed to synchronize the initial card punch with a given wavelength marker.
5. Small amounts of CO_2 appeared in the background scans.

A very careful wavelength calibration of the anticipated spectral range was carried out. Several attempts were made to correct the non-linearity of the wavelength drive by adjusting the optical flat used in the sine bar drive. After several attempts to eliminate the non-linearity it became apparent that the maximum possible correction was inadequate. Hence, the sine bar was returned to the nominal position and a wavelength correction curve was generated.

The daily shift in the correction curve seems to be linear and dependent on room temperature. A single point will be used to re-check the calibration prior to recording a data set.

The individual lines in the Q-branch at 720 cm^{-1} vary in spacing from 0.15 to 0.01 cm^{-1}. Hence, a very small change in resolution can be detected in this region of the spectrum. A comparison between the measured spectrum and the theoretical spectrum reveals very clearly the instrument resolution.

Many spectra were taken of the same spectral region and it was determined that the change in resolution was related to the room temperature changes. A resolution less than 0.06 cm^{-1} can only be obtained when the variation in instrument temperature is less than 0.25^{o}C. The normal expected resolution will be between 0.06 and 0.07 cm^{-1}. The change in resolution with variation in temperature across the instrument is due to distortion of the optical mounts in such a way that the image of the slit rotates slightly.

Three thermistors were placed on the instrument to monitor temperature. The thermistor readings will be a part of the housekeeping data associated with each scan.

Synchronization of the card punch with wavelength markers is accomplished by aligning a pointer on the marker disk with a corresponding pointer on the photo cell housing using a large mirror which is placed behind the wavelength drive. The punch is started when the pointers are alined.

The entire area between the source and the input optics has been sealed with masking tape and purged with nitrogen gas. There is now no indication of CO_2 in the background spectrum.

The spectrometer is now completely ready for data recording. Instrument problems which have been postponed to a later date are: the stray light, fore pump vibration, and sealing of the main chamber. The instrument and associated apparatus are shown in figure 1.

III Theoretical Analysis of High Resolution 15μ m, CO_2 Measurements (S. R. Drayson)

The analysis of the data is still in a preliminary stage, but is expected to proceed more rapidly in the near future since most of the preliminary instrument work is now completed. A computer program was written to convert the spectrometer card output to absolute transmittances including computer produced plots of the spectra. At the same time existing programs were modified to calculate theoretically the absorption under the same conditions as the experimental spectra. Typical results are shown in figures 2 and 3. These comparisons are useful in estimating the resolution of the experimental data, as well as checking on frequency calibrations and making rough estimates of the accuracy of the input parameters used in the theoretically generated spectra.

IV Development of Ozone Generating, Handling and Measuring System (L. T. Loh and P. A. Titus)

A. Ozone Generating and Handling System.

Figure 4 is the schematic diagram of the ozone generating and handling system. The pipes which connect the oxygen and nitrogen tanks to the flowmeter, ozonizer and 40 meter cell "S" have been installed. The connection of the metal tubing to the glass tubulations of the ozonizer were critical. The metal tubing has been anchored to the ozonizer wooden box and connections to the glass tubulations were made by Tygon tubing with Teflon seals.

Pump out of the used sample has been arranged to be made directly into the pump or through a molecular sieve for destruction of O_3. Two pumps have been installed in parallel. The Welch pump is fast, but its oil is incompatible with O_2 or O_3. The small "Will" pump has a case of stainless steel and working mechanism of neoprene. It should be quite satisfactory for low concentrations of O_3 in O_2.

Pressure gauges suitable for use with O_3 have been ordered. A Datametrics Barocel Electric Manometer, Type 1023, with a 2000 mm Hg full scale maximum range and a 2 mm. Hg fullscale minimum range has been procured. A dial type pressure gauge made of 316 stainless steel will also be ordered.

A neon sign transformer which was on hand for use with the ozonizer was found to be defective. A new one was ordered, it is a special design with one side of the secondary winding grounded.

A pressure filter containing Linde 13-X molecular sieve material will be used to destroy ozone. Leaks in the O ring seals of the pressure must be eliminated before this device can be used.

The O rings on the 40 meter gas cells have been coated with Ascolube (Fluorositirone) grease so that they can be used with the O_3 mixture at low pressures. Eventually they will have to be replaced. A study of O ring materials and design has been made. Teflon and viton are materials best suited for use with O_3, however teflon has low resilience and viton is low in tear resistance. Both materials have a tendency to cold set. Teflon coated rubber O rings are also available. This combination combines the resilience of rubber with the excellent chemical resistance of teflon. This last type of O ring has been ordered for use with our system.

B. Quantitative Measurements of Ozone

A check of commercial instruments which can be used for quantitative measurements of ozone was made. The search indicated two instruments which would be quite suitable for this purpose, a Jarrell Ash 1/4 meter Ebert, model #82410 and a Heath Czerny Turner model EU-700. Although the Heath instrument had many intersting up to date design features deemed to be very desireable, delivery was uncertain. The Jarrell Ash Instrument has been ordered.

V. Theoretical Analysis of 9 μm Ozone Band (W. R. Kuhn).

For remote sensing purposes, it is necessary to know the spectroscopic band parameters (line strengths and positions) quite accurately. Recent work being done at the University of Michigan utilizing the 9μm spectral region of ozone indicates that there is need for more accurate parameters for this band. Russell (1970)[1] has found that uncertainties in these parameters in the band wings can lead to appreciable errors in ozone profiles and amounts. Also spectroscopic observations reveal discrepancies between transmission functions and theoretically calculated profiles (Drayson and Young, 1967)[2]. While our present knowledge of the 9μm region may be adequate for flux divergence calculations for climatological purposes, more accurate calculations are necessary for remote sensing investigations.

Although band parameters for the 9μm region have been determined by Clough and Kneizys (1965),[3] there are discrepancies between transmission profiles calculated using their data and experimental measurements; there is thus a need to repeat these calculations. To gain familiarity with the types of calculations involved, line positions for the ν_1 (1103 cm^{-1}) and ν_3 (1042 cm^{-1}) transitions are being calculated for a simple asymmetric rotor. The rotational constants used are from Clough and Kneizys (1965). The energy matrix is factored by the Wang transformation into the four submatrices and the roots (energy levels) of the characteristic equations of these submatrices and then evaluated. The type I^r representation was chosen since for nearly prolate asymmetric rotors ($K \approx -0.968$ for ozone), the energy matrix is nearly diagonal and leads to the most rapid solution. The roots are approximated by the continued fraction form of the submatrices (Allen and Cross, 1963)[4]. The importance of centrifugal distortion is demonstrated if one compares the rigid rotor model to the quantum mechanical results of

Clough and Kneizys (1965). For the rotational level $15_{4,\ 11}$ in the ν_3 vibrational state, we find an energy of 1193.36 cm^{-1} while the more precise treatment of Clough and Kneizys gives 1190.96 cm^{-1}. Differences in ground state energies for the two methods are much less, e.g. the rigid rotor energy for the $15_{4,\ 12}$ rotational level differs by only 0.28 cm^{-1} from the quantum mechanical result. The inclusion of centrifugal distortion and coriolis effect will be individually checked and the influence of each of these on the transmission functions will be systematically decuced. These calculations will make use of and be compared with ozone measurements which will soon be made at the High Altitude Engineering Laboratory. Improved band models will also be developed for use in atmospheric flux divergence calculations.

VI Literature Survey on the Distribution of CO_2 in the Earth's Atmosphere

The literature survey of CO_2 in the atmosphere has been continued. A large portion of the recent scientific activity is concerned with the seasonal variation of CO_2 near the earth's surface. The recent results on CO_2 in the upper atmosphere have been outlined in the last 2 quarterly reports, 05863-27-P and 05863-28-P.

Only one new brief note on CO_2 in the atmosphere away from the earth's surface is that by Cadle and Allen[5], "Present estimates of CO_2 concentrations near ground level average about 330 ppm. Although there is some evidence that it decreases by about 5 ppm above the tropopause, recent measurements made by Scholz, et al (33) in the vicinity of the stratospause indicate a CO_2 concentration of about 320 ppm."

A bibliography of references on CO_2 in the earth's atmosphere is being prepared.

VII Plans for Continued Work

Work during the period 1 April - 30 June, 1970 will include the following.

A. High Resolution CO_2 Measurements:

Spectra of the R branch of the fundamental (R6-R10, R36-R40,R54-R60) will be recorded using an 8.74 cm. cell and with pure CO_2 at eight pressures in the range of 5 mm. Hg. to normal atmospheric pressure. An investigation will also be made of the Q branch corresponding to the isotope $C_{12}O_{16}O_{18}$ near 662 cm^{-1}.

After the above spectra have been studied and analyzed, new regions yet to be selected will be studied. Other cells 10.5 cm, 2.5 cm and 5 cm) will be used in addition to the 8.74 cm cell.

If it should be decided that stray light in the instrument is intolerable, masking modifications will be made.

B. Ozone Generating, Handling and Measuring System

The work to be carried out on the construction of this system is listed in detail below. Estimated completion dates for each phase of the work, are given.

1.	Checkout Jarrell Ash Monochrometer mercury lamp and photomultiplier	May 1
2.	Complete ozonizer exhaust system	May 1
3.	Complete Barocel piping	May 8
4.	Complete molecular sieve piping	May 8
5.	Complete breadboard of U.V. transfer optics	May 8
6.	Leak check ozonizer system	May 15
7.	Test run Perkin-Elmer 221 Spectrophotometer and oxonizer	May 31
8.	Design adapter for transfer optics, fabricate adapter and install adapter	June 1
9.	Complete stirring device for sample cell	June 1
10.	Test run UV O_3 analyzer	June 16
11.	Take O_3 spectra	June 30

C. Theoretical Analysis

The analysis of the CO_2 R branch spectra will be carried out. Studies of the band parameters of 9μm O_3 will be continued.

D. Distribution of CO_2 in the Earth's Atmosphere

A report, containing a bibliography and summary comments on CO_2 in the earth's atmosphere, will be written.

VIII References

1. Russell, J. M., "Measurement of O_3 from Satellite Infrared Observations in the 96μm Band", PhD Dissertation to be published by summer 1970.

2. Private communication

3. Clough, S. A. and Kneizy's, F. Y. "Ozone absorption in the 9 Micron Region," Report, AFCRL 65-862, November 1965.

4. Allen, H. C., and Cross, P. C., "Molecular Vib-Roters," John Wiley and Sons, 1963, 323 pages.

5. R. D. Cable and Allen, E. R., "Atmospheric Chemistry," Science, vol. 167, no. 3916, 16 Jan. 1970, pp 243-249.

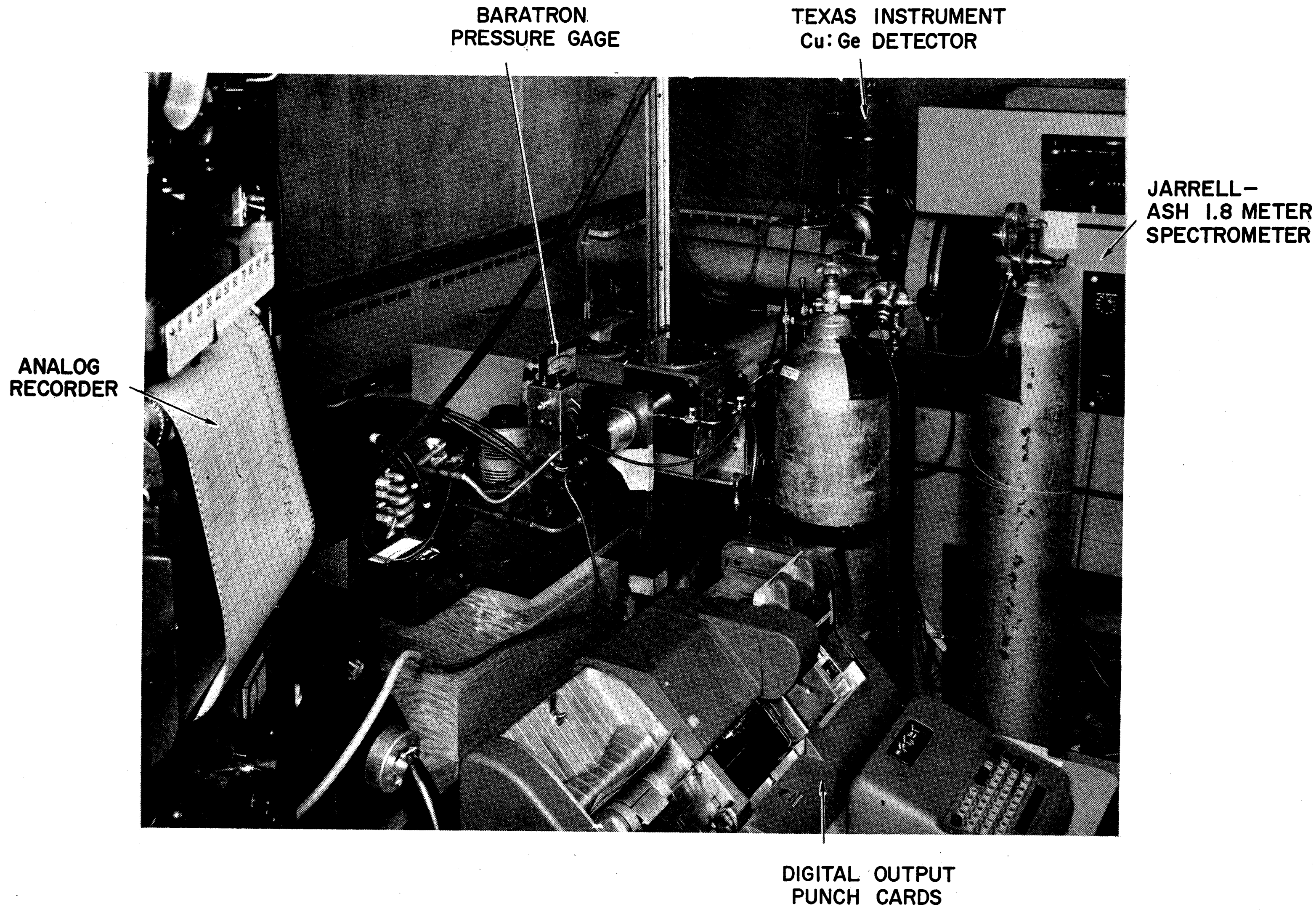

Figure 1. Jarrell Ash 1.8 meter spectrometer and associated experimental apparatus

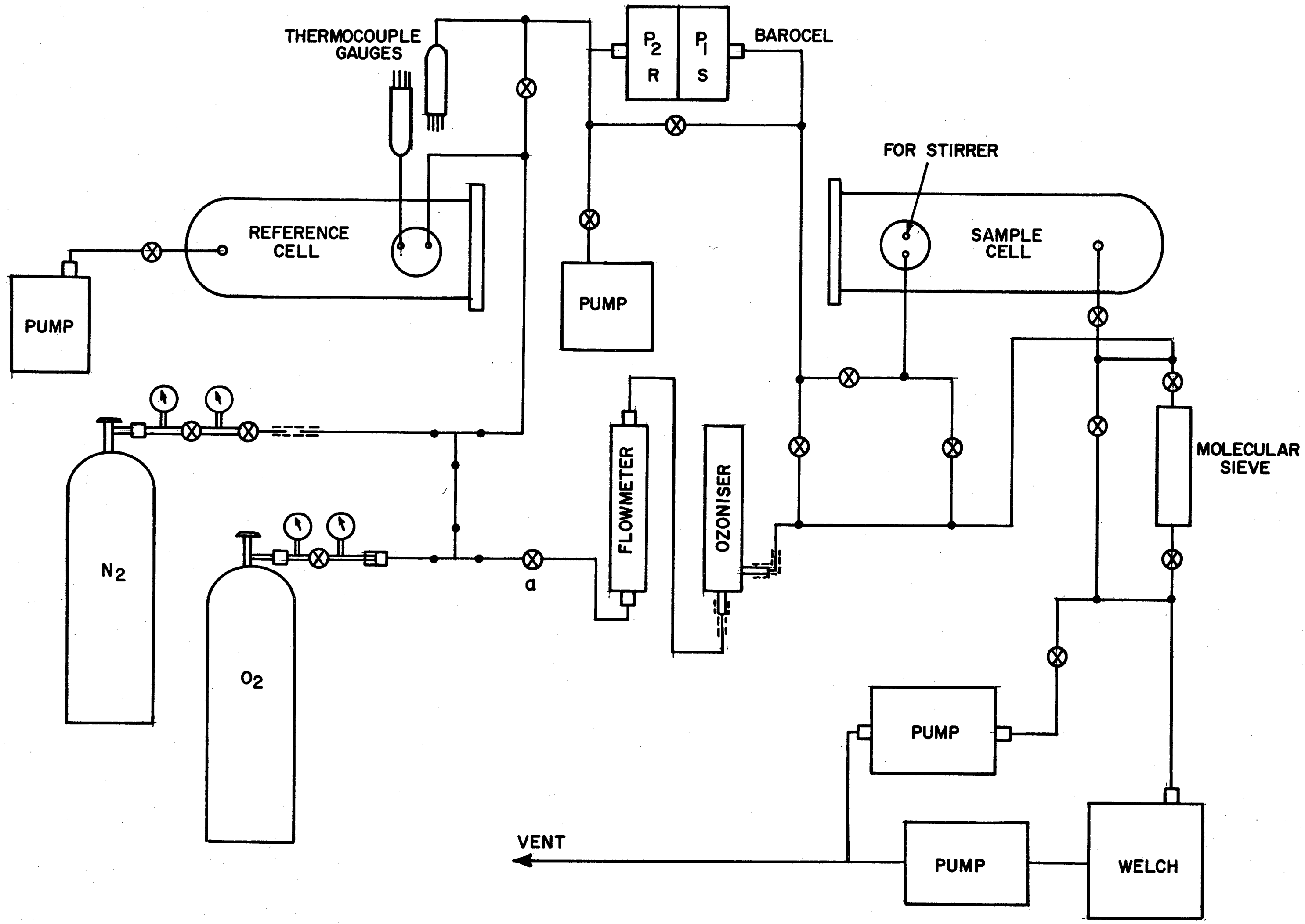

Figure 4. Schematic diagram of ozone generating and handling system.