
Measurement of Stratospheric Nitrogen Dioxide from the AES Stratospheric Balloon Program

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ABSTRACT

A spectrophotometer which is capable of measuring atmospheric nitrogen dioxide by remote sensing has been included on board the STRATOPROBE I and II balloon programs. The results obtained from the STRATO-

PROBE I flight from Churchill, Manitoba, on 22 July 1974, and preliminary results from the STRATOPROBE II flights from Yorkton, Saskatchewan on 17-18 August 1975, will be presented here.

1 Introduction

Nitrogen dioxide has strong absorption bands in the visible and near ultraviolet regions of the spectrum and for wavelengths between 430 and 450 nm the absorption varies rapidly with wavelength. This permits the measurement of atmospheric NO_2 by measuring its relative absorption of sunlight, using methods similar to those which are used to measure atmospheric ozone.

A program to measure atmospheric NO_2 was established in 1972 by Prof. A.W. Brewer at the University of Toronto. A spectrophotometer which was originally designed to measure ozone (Brewer, 1973) was adapted to measure NO_2 . The instrument is a modified 15-cm Ebert spectrophotometer which is capable of measuring simultaneously the light intensity at three wavelength intervals with a resolution of 0.5 nm. Earlier ground- and aircraft-based results have been formally reported (Brewer *et al.*, 1973, 1974). The program has been extended to be included in the AES stratospheric balloon projects during the summers of 1974 and 1975. Results from the 1974 program and some preliminary results from the 1975 program will be given here.

2 Method of measurement

The amount of NO_2 is determined by measuring the intensity of sunlight after it has been absorbed by atmospheric NO_2 . The intensity of sunlight at an isolated wavelength λ , after passing through the atmosphere, is given by:

$$\log_{10} I_{\lambda} = \log_{10} I_{0\lambda} - \alpha_{\lambda}X - \beta_{\lambda}m, \quad (1)$$

where $I_{0\lambda}$ is the intensity of sunlight outside the atmosphere at wavelength λ ,

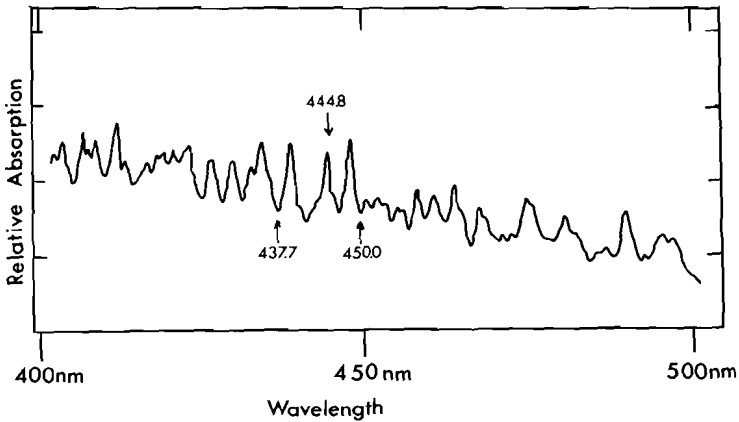


FIG. 1 The absorption spectrum of NO_2 (from Hall and Blacett, 1952) as measured at $25^\circ C$. The three wavelengths used in this work are indicated by arrows.

- α_λ is the decimal absorption coefficient of NO_2 (in cm^{-1}) at wavelength λ ,
- X is the optical depth (in cm at STP) of NO_2 in the path,
- β_λ is the Rayleigh scattering coefficient (per standard atmosphere) at wavelength λ , and
- m is the number of standard atmospheres in the optical path.

We measure light at three wavelengths in the NO_2 absorption spectrum with a resolution of 0.5 nm: $\lambda_1 = 437.7$ nm, $\lambda_2 = 444.8$ nm, and $\lambda_3 = 450.0$ nm. The NO_2 absorption at these three wavelengths, as indicated in Fig. 1, has a large variation with wavelength. The light intensity at each of the three wavelengths may be expressed in three equations similar to (1) with subscripts 1, 2, and 3 designating wavelengths λ_1 , λ_2 and λ_3 . It is now possible to form a combination of equations such as (1):

$$\log_{10} \frac{I_1}{I_2} - 1.46 \log_{10} \frac{I_2}{I_3} = \log_{10} \frac{I_{o1}}{I_{o2}} - 1.46 \log_{10} \frac{I_{o2}}{I_{o3}} - \Delta\Delta\alpha X$$

or
$$F = F_o - \Delta\Delta\alpha X \tag{2}$$

where
$$\Delta\Delta\alpha = (\alpha_1 - \alpha_2) - 1.46(\alpha_2 - \alpha_3) = -7 \text{ cm}^{-1}$$

and
$$1.46 = \frac{\beta_1 - \beta_2}{\beta_2 - \beta_3} = \text{weighting factor used to eliminate Rayleigh scattering.}$$

The weighting of light intensities given in (2) is such that F , our measured quantity, has maximum sensitivity to NO_2 and negligible sensitivity to Rayleigh scattering and all other effects which have slow monotonic wavelength dependence. Ozone absorbs at these wavelengths; however, its absorption is small and also nearly linear with wavelength. Using the absorption coefficients given by Vigroux (1953) and a typical ozone distribution, the effect of ozone on a measurement of F is about 4% that of NO_2 . This correction may be easily

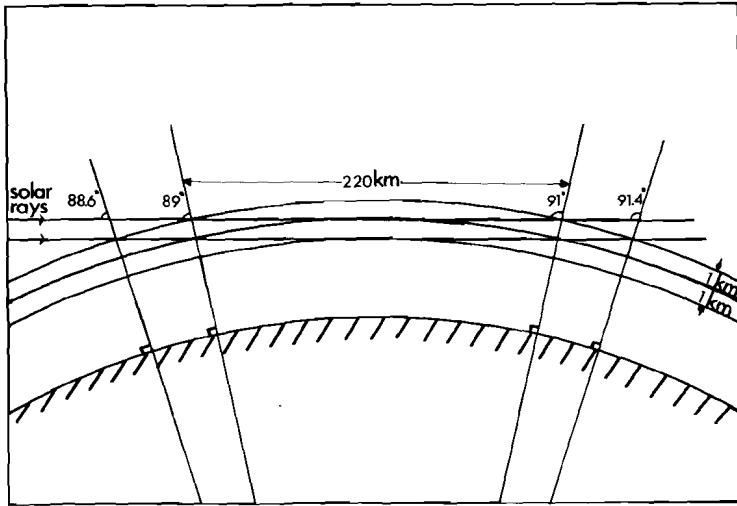


Fig. 2 The geometry of the tangent path technique. Tangent rays are approximately 220 km for 1-km-thick layers. A profile for NO_2 may be determined by comparing measurements at symmetric solar angles about 0° elevation. The effects of balloon-altitude changes during twilight may also be compensated.

applied to our measurements. We know of no other stratospheric constituent which absorbs light in such a way as to interfere with our measurements and we have carried out tests which indicate no interference caused by another stratospheric substance.

From our measurement of F we may deduce the amount of NO_2 in the solar path provided we know F_0 . From a balloon platform at 35 km it is possible to measure F_0 directly when the sun is higher than 20° elevation because the amount of NO_2 in the solar path is then negligible.

We have used our instrument to make laboratory measurements of $\Delta\alpha$ for NO_2 at room temperature and atmospheric pressure, and have found a value of -7.0 cm^{-1} . This value compares favourably with -5.91 cm^{-1} from Hall and Blacet (1952) and -8.17 cm^{-1} given by Johnston (1974). The absorption coefficient was found to be independent of pressure. Bass *et al.* (1976) have measured the effects of temperature on NO_2 absorption between 185 nm and 410 nm and for wavelengths at 410 nm they indicate about 10% less absorption at 235K than at room temperature. The effects of temperature on our $\Delta\alpha$ in the wavelength region between 430 nm and 450 nm have yet to be measured.

Vertical profiles of NO_2 may be measured quite accurately from a balloon during sunrise and sunset. This is accomplished by taking advantage of the very long tangential path lengths which result when the sunlight passes through the atmosphere below the balloon. For example, a ray tangent through a 1-km thick shell traverses a path of about 220 km through that shell. The geometry of this is shown in Fig. 2. The vertical profile is measured by first determining

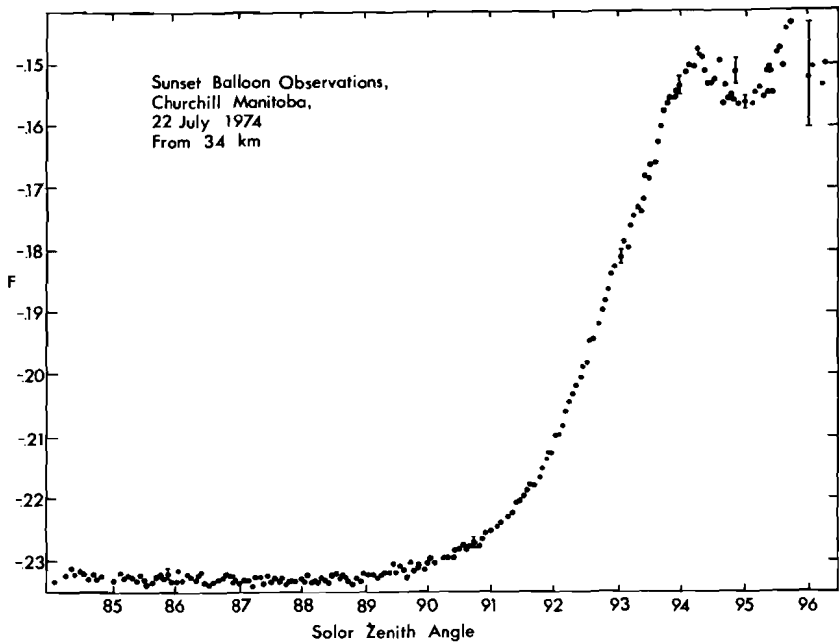


Fig. 3 The function F as a function of solar zenith angle as measured during sunset on July 22, 1974 from a height of 34 km. F increases during sunset because the sun's rays pass through atmospheric NO_2 . The shape of this curve is used to determine a unique vertical profile of NO_2 . Error bars indicate the error due to Poisson noise for an individual point.

the amount of NO_2 in the layer directly below the balloon and then proceeding to lower and lower layers.

3 Results

The usual timetable for the balloon flights allowed a late afternoon launch with the payload reaching float altitude about one hour before 0° solar elevation. Direct sun measurements were taken during sunset and during sunrise the next morning.

The evening measurements from the Churchill flight of 22 July 1974, are shown in Fig. 3. Meteorological conditions during the flight are given by Bain *et al.* (1976, this issue). The morning measurements of this flight are not available because of an instrument failure in the extreme cold overnight. This problem was rectified for subsequent flights. Fig. 3 shows the increase of F during sunset. This is caused by more and more NO_2 absorption as the sun's rays pass deeper and deeper through the earth's atmosphere. The error bars indicated in Fig. 3 are the single point errors which are estimated from the Poisson noise of photon counting.

The values of F in Fig. 3 were used to determine a unique vertical profile of NO_2 . Fig. 4 shows the reduced evening profile for the Churchill flight as

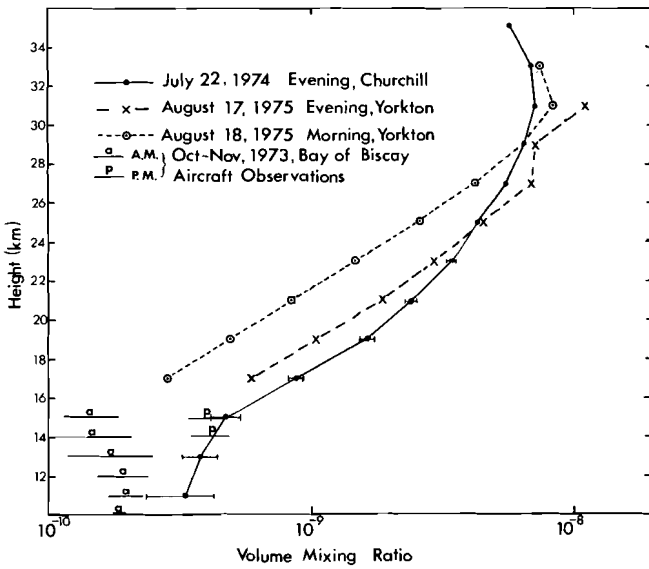


Fig. 4 Three measured profiles of NO_2 : sunset 22 July 1974; sunset 17 August 1975; and sunrise 18 August 1975. The range of aircraft measurements made with a different NO_2 instrument from a height of 15 km during October and November 1973 are also shown. The continuity between the aircraft measurements and the balloon measurements is quite consistent considering there is a spatial and time difference between the two sets of observations. This figure illustrates the difference between morning and evening NO_2 profiles. The estimated absolute error for all profiles is $\pm 20\%$. The error bars on the profile of 22 July indicate the estimated relative error due to Poisson noise.

well as the preliminary evening and morning profiles for the flight of 17–18 August 1975 from Yorkton, Saskatchewan. Also included in this diagram are previous measurements made from on board an aircraft at a height of 15 km during October and November 1973 (Brewer *et al.*, 1974).

In the reduction from the absorption as a function of zenith angle to NO_2 concentration as a function of height, corrections have been made to account for atmospheric refraction. The effect of refraction is to make the apparent position of the sun higher than its actual position. Consequently, the solar rays pass through the atmosphere at a higher tangent height than that which would be expected if refraction were neglected. Because the tangent rays are higher, the overall path length through the atmosphere is reduced. As a result, the concentration of NO_2 is corrected to larger values by about 5 to 10% between 10 and 15 km and less than that above 15 km.

The effects of the finite diameter of the sun have also been considered in the data reduction. As with refraction, the apparent position of the sun is raised. This is because the lower part of the sun is attenuated significantly more than the upper part. Incorporated into this correction is the fact that the limb of the sun is less bright than the centre of the solar disk. It was found that the

finite sun correction is about 15% of the correction due to atmospheric refraction.

The data in Fig. 4 illustrate one interesting feature. We have previously found that for lower altitudes there is usually a significant amount more NO_2 in the evening than in the morning, as indicated by the aircraft measurements. The results of the balloon measurements indicate that this diurnal variation is present but perhaps less pronounced at 30 km. The larger amounts of NO_2 at dusk may be explained by the slow dissociation of N_2O_5 into NO_2 and NO_3 during the day and the recombination of NO_2 and NO_3 to form N_2O_5 at night. A further discussion of this photochemical process is given by Evans *et al.* (1976, this issue).

In all, two morning and two evening profiles will be obtained from the 1975 program. It is hoped that these results and those of flights which are being planned for the future will contribute to a better understanding of the composition and photochemistry of our atmosphere.

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