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## The Altitude Distribution of Nitric Acid at Churchill

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### ABSTRACT

The altitude distribution of nitric acid vapour was measured from observations of atmospheric thermal emission in the  $11.3\text{-}\mu\text{m}$  band during a balloon ascent launched at 2317 GMT on 22 July 1974 from Churchill, Manitoba (latitude  $58.7^\circ\text{N}$ ). The total amount of nitric acid above the tropopause was  $0.32$  matmcm. The nitric acid

layer was peaked at  $24$  km with a maximum mixing ratio of  $5.5$  ppbv. This measurement is similar to other available measurements of nitric acid in terms of layer shape and peak concentrations. The total amount of  $0.32$  matmcm is consistent with aircraft measurements of the latitudinal variation of nitric acid.

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### 1 Introduction

As part of Project STRATOPROBE, which had the objective of making coordinated measurements of key nitrogen constituents in the ozone layer chemistry, it was necessary to develop a technique to measure the altitude distribution of nitric acid from the same balloon payload as instrumentation designed to measure nitric oxide, nitrogen dioxide and ozone. The thermal-emission technique employed by Murcray *et al.* (1973) was chosen and an instrument was designed to make nitric acid profile measurements based on the same principle. Measurements of the atmospheric thermal-emission spectrum from Murcray *et al.* (1973) over the spectral region from  $9$  to  $14\ \mu\text{m}$  are shown in Fig. 1. The nitric acid band is located in the atmospheric window at  $11.3\ \mu\text{m}$  and is relatively free from interference by other atmospheric constituents. Five interference filters were used to cover this spectral region; the band-passes of these filters are also indicated in Fig. 1 in relation to the nitric acid emission feature at  $11.3\ \mu\text{m}$ . Note the broad band pass of filter B ( $11.0$  to  $11.6\ \mu\text{m}$ ) and the narrow band pass of filter D ( $11.23$  to  $11.39\ \mu\text{m}$ ); these filters were used to measure the nitric acid emission feature. Filters A, C and E provide supplementary information on the atmospheric thermal-emission spectrum which has not been analyzed in this paper.

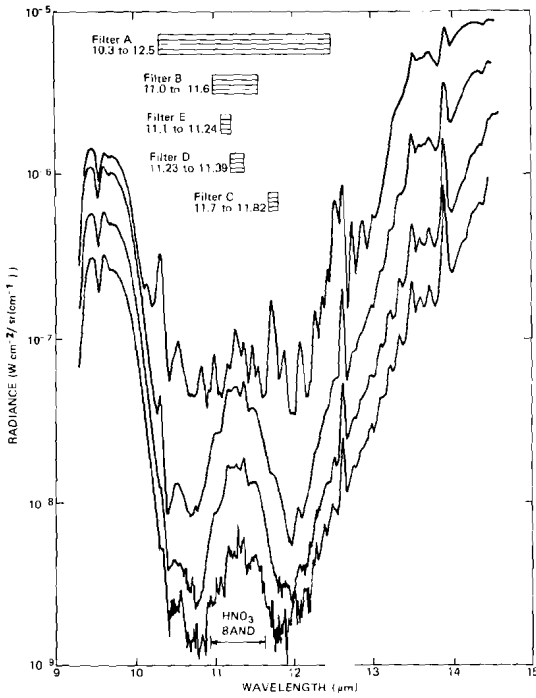


Fig. 1 The wavelength position of the bandpasses of the infrared interference filters in relation to the thermal-emission spectrum of nitric acid observed in the atmosphere by Murcay *et al.* (1973) at 3.4, 10.0, 20.1 and 24.7 km.

## 2 Theory of thermal emission measurements

Consider a layer  $i$  with:

$T_i$  = temperature of layer  $i$ ,

$P_i$  = mean pressure of layer  $i$  (expressed in atmospheres),

$R_i$  = radiance at top of layer  $i$ ,

$B(T_i)$  = black body emission of layer  $i$ ,

$\Delta R_i$  = change in radiance across layer  $i$ ,

$h_i$  = altitude of layer  $i$ ,

$\Delta h_i$  = thickness of layer  $i$ ,

$\tau_i$  = transmission of layer  $i$ ,

$\epsilon_i$  = emissivity of layer  $i = 1 - \tau_i$ ,

$U_i$  = amount of nitric acid (atmosphere-cm),

$Q_i$  = volume mixing ratio of nitric acid,

$(S^\circ/\delta)$  = effective continuum absorption coefficient of the nitric acid band.

$$\frac{\downarrow R_i}{\text{layer } i \begin{matrix} T_i, P_i, U_i, Q_i, \Delta h_i \\ \epsilon_i, \tau_i \end{matrix}} = \frac{\downarrow R_i + \Delta R_i}{h_i}$$

The appropriate radiative transfer equation is:

$$(R_i \tau_i + \Delta R_i) - R_i = \epsilon_i B(T_i) \quad (1)$$

or  $\Delta R_i = \epsilon_i B(T_i)$  since  $\tau_i \approx 1.0$  for an optically thin layer. (2)

Thus  $\epsilon_i = \Delta R_i / B(T_i)$ . (3)

Now for weak absorption,  $\epsilon_i = (S^0/\delta) U_i$ . Here, the observed thermal emission of the layer is treated as the ideal black body radiation multiplied by the emissivity due to absorption by the amount of nitric acid in the layer.

$$\text{Inverting, } U_i = \Delta R_i/B(T_i) (S^0/\delta) \quad (4)$$

$$\text{and the volume mixing ratio } Q_i = U_i/(P_i \Delta h_i \cdot 273/T_i). \quad (5)$$

The effective band absorption coefficient was derived from the measurements at laboratory pressure and temperature by Goldman *et al.* (1971) with the expression

$$(S^0/\delta) = (S^1/\delta) (T^1/T_i)^{3/2}.$$

The appropriate room-temperature values of the band absorption coefficient,  $(S^1/\delta)$  were  $8.4 \text{ cm}^{-1}$  and  $11.3 \text{ cm}^{-1}$  for the filter B measurements and filter D measurements, respectively.

The nitric acid band is located in a spectral region relatively free from interference by other atmospheric gases. Scattered solar radiation is negligible due to the long wavelength, and contributions from the water vapour continuum will be insignificant above the tropopause at 11 km due to the low mixing ratio of water vapour in the stratosphere.

### 3 Instrumentation

The five infrared interference filters were mounted on a continuously rotating wheel with one revolution every two minutes. A cross section diagram of the instrument is shown in Fig. 2. The total optical system is enclosed in a liquid nitrogen jacket with a capacity of 7 l. Extreme attention was paid to insulation design in order to obtain a long "hold time"; as a result, operation of the instrument is possible for more than 12 h under flight conditions.

Incident radiation enters the narrow aperture at the bottom of the cone of the copper jacket and is modulated by a 200-Hz Bulova tuning fork chopper. The radiation then passes through the filter wheel with the five interference filters mounted on it. The rotating filter wheel is driven by a set of gears from a fibreglass shaft attached to a d.c. Globe motor in the warm electronics section. The filtered radiation is then focussed onto a mercury cadmium telluride detector by a concave and flat mirror combination. The detector is operated with a 1 k $\Omega$  load resistor and a 4-volt bias. The signal is amplified by a low noise, low input impedance preamplifier. This is followed by two parallel linear and logarithmic amplifiers with a phase sensitive detector in each channel. The output filters have a 0.5-s time constant and the total instrument has a noise equivalent brightness of  $10^{-8} \text{ W cm}^{-2} \text{ sr}^{-1} \mu\text{m}^{-1}$ , which permits a signal to noise of  $\sim 30$  on a typical observation of the total nitric acid layer.

The entire instrument is enclosed in a 30 cm  $\times$  30 cm  $\times$  60 cm block of foamed polyurethane with a 1.6-mm fibreglass shell. The instrument was mounted on the antisolar side of the STRATOPROBE 1 gondola with the optical axis at a zenith angle of  $62.5^\circ$ . Flight data were sampled at 7 samples/second by the pulse-code modulation telemetry system.

The instrument was calibrated radiometrically before and after flights with

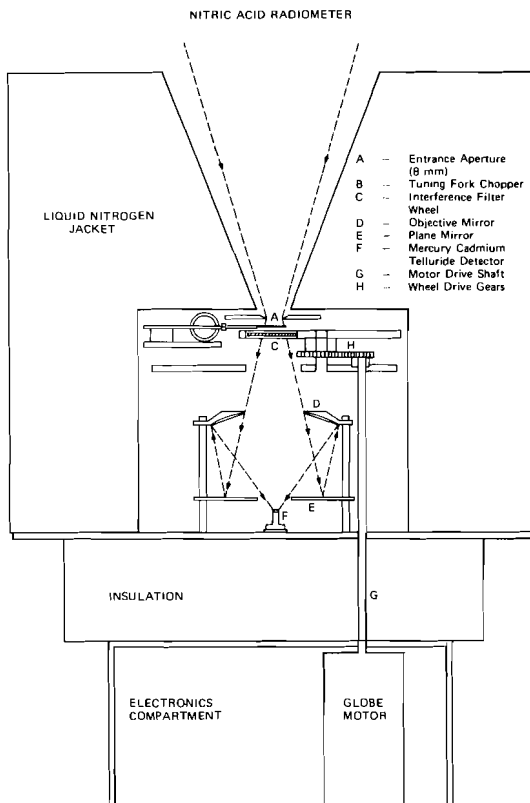


Fig. 2 A cross section view of the nitric acid radiometer.

a liquid nitrogen cooled “cold target” black body, the temperature of which could be varied from about 90 to 300 K in order to provide a range of radiance levels similar to those encountered in a balloon flight. The liquid nitrogen jacket is pressurized to maintain a constant detector sensitivity. The variation of detector sensitivity with pressure was measured in a high altitude simulation chamber; a small measured increase in instrumental sensitivity of 25% was corrected for in the data analysis.

#### 4 Flight data

The present measurements were obtained from the ascent of the second STRATOPROBE I flight launched on 22 July 1974 at 2317 GMT from the airstrip at Churchill, Manitoba (latitude 58.7°N, longitude 94.3°W). The ascent to 34.5 km took approximately 120 min. The radiance data measured on this flight are shown in Fig. 3. A measurement by Murcay *et al.* (1973) from September 1970, at 33°N (small circles), is included for comparison. The radiance data measured by the 11.0 to 11.6  $\mu\text{m}$  filter are indicated by the large open circles and the radiance data measured by the 11.2 to 11.4  $\mu\text{m}$  filter are indicated by the solid triangular symbols.

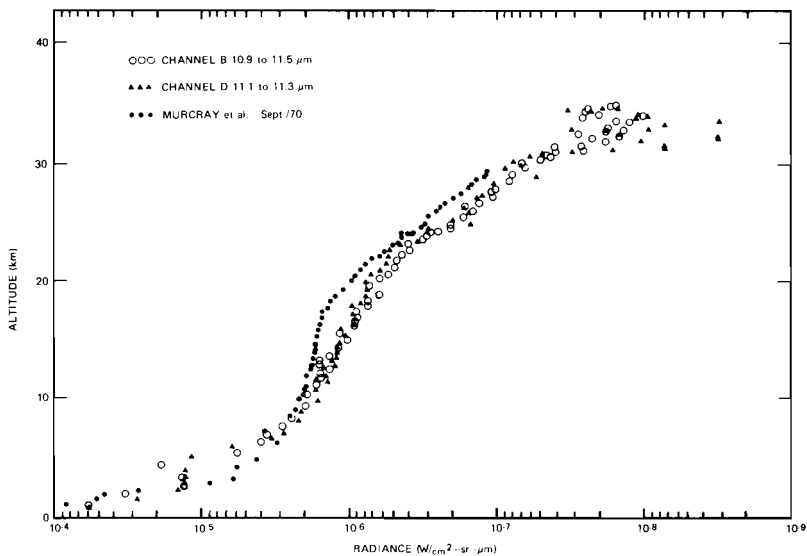


Fig. 3 The observed radiance profiles as a function of altitude for 22 July 1974 at Churchill.

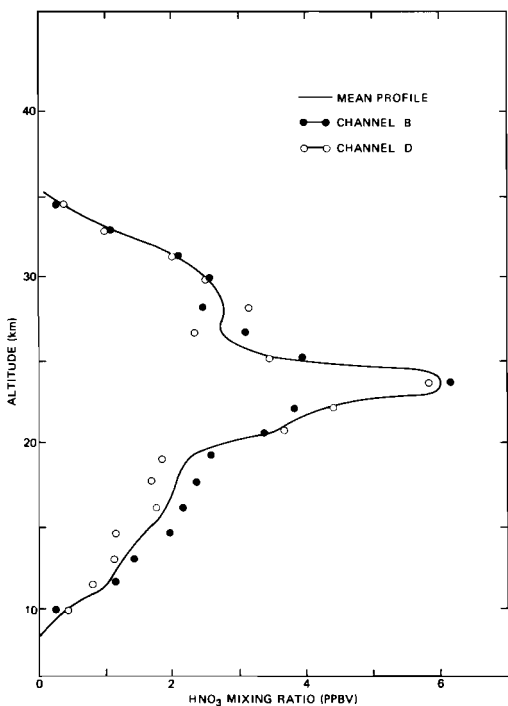


Fig. 4 The altitude distribution of nitric acid derived from the measured radiance profiles.

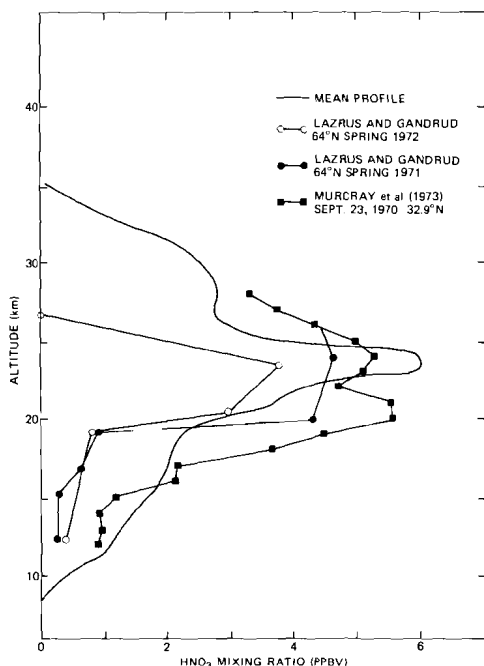


Fig. 5 A comparison of the nitric acid distribution measured at Churchill in July with other measurements of nitric acid distributions by Lazrus and Gandrud (1974) and Murcraey *et al.* (1973).

The tropopause was located at 11 km and is readily apparent in the radiance profiles as an inflexion at this altitude. The detailed temperature structure is given in Bain *et al.* (1976).

The observed radiance profiles were processed according to the expression in (5) to obtain the altitude distribution shown in Fig. 4. The radiosonde temperature profile data used to invert the radiance profile are given in Bain *et al.* (1976). The data from filter B yielded the profiles denoted by the closed circles while the analysis of the filter D data yielded the profile indicated by the open circles. The difference between the two profiles gives some indication of the relative error of the measurement, since the profiles were measured by two interference filter channels. An estimate of the relative error in the shape of the profile due to instrumental errors, such as detector noise, is  $\pm 0.5$  ppbv, roughly constant as a function of altitude. The absolute accuracy of the mixing-ratio profile due to uncertainty in the absolute radiometric calibration is estimated to be  $\pm 30\%$ . It should be noted that the layer peak is located at 24 km with a peak mixing ratio of 5.5 ppbv.

### 5 Comparison with other observations

A comparison of the nitric acid profile obtained at Churchill ( $58.7^\circ\text{N}$ ) on 22 July 1974 with measurements of the altitude distributions of nitric acid at high

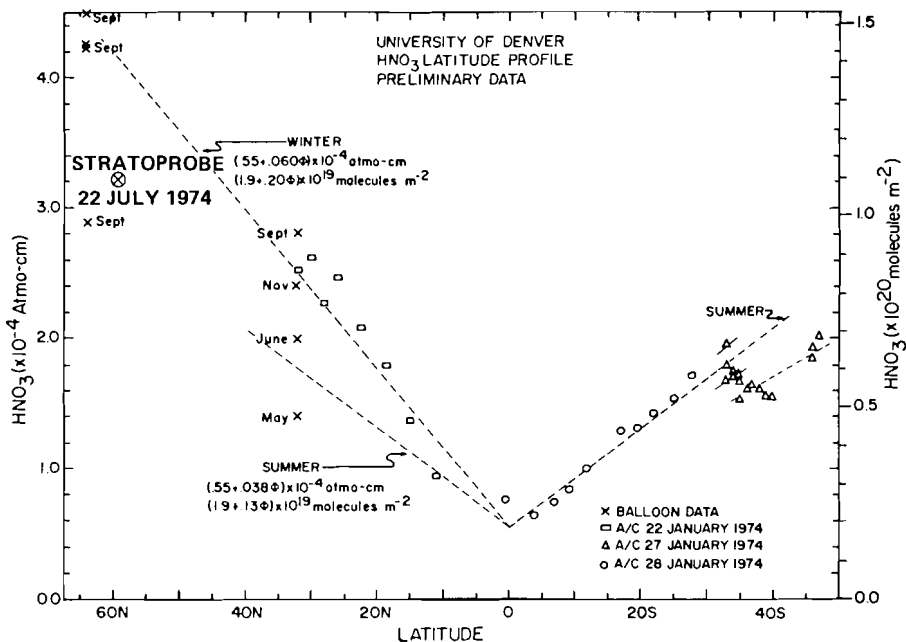


Fig. 6 The total column amount of nitric acid in relation to measurements of the latitudinal variation by Murcray *et al.* (1975).

latitudes in spring by Lazrus and Gandrud (1974) is shown in Fig. 5. A profile measured by Murcray *et al.* (1973) at 33°N in September, 1970 is also shown. It should be noted that the Lazrus and Gandrud (1974) measurements were made with an *in situ* sampling filter technique and generally indicate nitric acid concentrations a factor of two smaller than those measured by Murcray *et al.* (1973) with the thermal-emission technique. In any case, the altitude distribution observed in this paper appears to have the same general shape, similar peak altitude and peak concentrations as other measurements of nitric acid profiles. Vertical profile measurements taken exactly at 60°N in mid-summer by other experimenters are not available for comparison.

The total overhead amount of nitric acid measured was 0.32 matmcm; this is compared with recent results on the latitudinal dependence of total nitric acid from Murcray *et al.* (1975) in Fig. 6. The measured amount increases with latitude from 0.1 matmcm at the equator to more than 0.35 matmcm at 60°N. The measurement from this paper at 58.7°N in July is indicated by the large dot; it appears to be consistent with the overall latitudinal trend inferred by Murcray *et al.* (1975).

## 6 Summary and Conclusions

The distribution of the volume mixing ratio of nitric acid as function of altitude was measured at 58.7°N on 22 July 1974. Although no significant diurnal variation was expected, it should be noted that the measurement was made in

the late afternoon between 2317 and 0130 GMT. The nitric acid layer was peaked at 24 km with a maximum mixing ratio of 5.5 ppbv. The total amount above the tropopause was 0.32 matmcm. The measured distribution is consistent with other available measurements of nitric acid. A factor of two discrepancy between the thermal-emission technique and the *in situ* filter technique has been noted. A detailed comparison of the observed nitric acid distribution with theory is carried out by Evans *et al.* (1976).

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