been observed to be desorbed from Mount St. Helens ash on heating (8). The sulfur carried in the aerosol as sulfate [the range is 0.5 to 1.5 ppb (by volume) when converted from parts per billion (by mass) as reported in (7)] is comparable with the sulfur carried in the plume gases as COS and CS_2 .

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order of 5 ppb for CO, 0.85 ppm for CO₂, and 0.004 ppm for CH₄. The precision of the method is indicated by the standard deviations of six replicate analyses of a sample: 0 percent for CO ($\hat{x} = 170$ ppb); 0.4 percent for CH₄ ($\hat{x} = 1.53$ ppm); and 0.08 percent for CO₂ ($\hat{x} = 340$ ppm). A 2-ml aliquot is needed for each analysis 2-ml aliguot is needed for each analysis. A 2-mi anduot is needed for each analysis.
 Calibration is accomplished by the use of a large cylinder of a gas mixture (in N₂) purchased from and certified by Scott. The assigned concentrations in this cylinder are 0.98 ppm for CO₂.
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- 9. for universal time.
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Stratospheric Nitrogen Dioxide in the Vicinity of Soufriere, St. Vincent

Abstract. In April 1979, measurements of nitrogen dioxide in the upper atmosphere were made near Soufriere Volcano by twilight optical-absorption techniques. The derived value of 5×10^{15} molecules per square centimeter column implies an enhancement of 25 percent over earlier abundances measured in the same latitudinal regions. This enhancement may represent the normal stratospheric variability of nitrogen dioxide in the equatorial region but in any case may be considered an upper limit to the volcano's effect on the total nitrogen dioxide abundance.

On 15 April 1979, a series of flights of a NASA P-3 aircraft, coordinated with the SAGE (Stratospheric Aerosol and Gas Experiment) satellite, was scheduled in the vicinity of Barbados (13.03°N, 59.48°W) in order to investigate the possible stratospheric effect of the 13 to 14 April series of volcanic eruptions of Soufriere. The first flight was on 17 April; the major eruption of the volcano took place while the aircraft was airborne and headed toward St. Vincent. The flight plan consisted of a series of circles taken around the volcano, outside the region of the plume.

During the next 2 days, additional flights were made in an attempt to deduce the drift pattern and altitudinal extent of the volcanic aerosols in the atmosphere at and above the level of the aircraft. Unfortunately, it was quite

cloudy during this whole period. As the NO₂ measurements obtained from the visible spectrophotometer required clear skies or at least uniform cloud coverage, subsequent NO₂ measurements were made on the ground in Barbados just before each aircraft flight on 18 and 19 April. The aerosol results from the lidar (light detection and ranging) measurements and the in situ quartz crystal microbalance cascade impactor are reported in (1) and (2).

The absorption features of the NO_2 molecule cover a large region of the visible spectrum. The most intense absorption bands are in the region from 4250 to 4550 Å and are easily accessible by means of modern spectrophotometric systems. Noxon et al. (3) made a detailed study of the observed twilight absorption by NO_2 . They obtained a series of curves relating the relative absorption (between the maximum absorption near 4395 Å to the minimum absorption near 4420 Å) to the solar zenith angle for different model NO₂ height distributions at a fixed total abundance of 1.1×10^{16} molecules per square centimeter column. We scaled the data obtained in our program to the height profile curves taken from Noxon et al. (3), as corrected by Noxon (4), to deduce the NO_2 abundance.

To obtain the amount of absorption at each solar zenith angle, we used essentially the technique of Noxon *et al.* (3)and an instrument with 3-Å resolution. The zenith scattered light versus wavelength for the sun at a zenith angle of less than 75°, where there is little NO_2 absorption (less than 0.5 percent) because of the small optical depth, was divided point by point into data obtained at higher solar zenith angles. A smooth line drawn through the resultant curve determines the percent absorption of each of the three absorption maxima of NO₂ in this wavelength region.

The flight data for 5 April near 37°N, for 12 to 14 April south of the equator, and for 17 April near the volcano, as well as the 18 and 19 April ground-based observations in Barbados, show a considerable degree of scatter with respect to any NO₂ height profile. Figure 1 presents the data obtained for the 17, 18, and 19 April evening twilights. The percent absorption scale was varied to make these data points fall within the group of altitude curves given by Noxon et al. (3). We then used the relative scale factor together with the total abundance of 1.1×10^{16} molecules per square centimeter column, used to produce Noxon's curves, to deduce the abundance that would produce the observed data points. Although it is difficult to select a specific representative altitude curve for these data points, the curve should be the same for the three data sets obtained here, because we do not expect much of a latitudinal variation in the height distribution for this time of the year (5). The percent absorption obtained in the three latitudinal regions translates into various total amounts of NO₂ at each latitude. We plotted these values as large black dots on the graph of latitudinal variation in NO₂ observed by Noxon (5) [corrected by Noxon (4)] (Fig. 2). We have also included in Fig. 2 similar NO₂ data obtained on another SAGE-coordinated series of flights at high latitudes in July 1979.

Our data for 5 April and for 12 to 14 April are higher than Noxon's by about a factor of 1.4. This difference could be due to a change in the NO₂ abundance from 1977 to 1979 or to some systematic difference in measurement or analysis technique. However, because all our data in April 1979 were scaled the same way, we would expect this same factor to exist for the data taken on 17, 18, and 19 April at the latitude of the volcano. This would infer a value of 4×10^{15} molecules per square centimeter column compared with the actual measured value of 5×10^{15} molecules per square centimeter column. Thus, our data indicate an enhancement of about 25 percent over that expected from Noxon's data.

To presume that the apparent enhancement is due to the volcanic activity is highly speculative, and we cannot be



Fig. 1. Calculated (3) relative absorption between 4395 and 4420 Å versus solar zenith angle for various height distributions and a total NO₂ abundance of 1.1×10^{16} molecules per square centimeter column. Dots are average observed values on 17, 18, and 19 April 1979; the lengths of the vertical lines represent the variation in absorption between the three absorption features. The ratio of the calculated to the observed absorption yields an abundance of 5×10^{15} molecules per square centimeter column.



Fig. 2. Latitudinal variation of NO_2 abundance from Noxon (5) as corrected by Noxon (4). Flight values from this study are indicated by large dots.

more definitive without a systematic set of observations made in the immediate vicinity of the volcano both before and after the eruptions. The apparent enhancement can only be used as an upper limit to the effects the volcano could have on the total NO₂ abundance. Factors that would influence this value, such as circulation changes and stratospheric temperature effects, have not been considered and may well be the main cause of this enhancement. Tropospheric enhancements are also possible. Enhancements in tropospheric or lower stratospheric NO₂ abundances due to volcanic activity might be expected. Halogen species ejected into this region by the volcano could influence the NO₂ abundance through reactions with chlorine of the form

$$ClO + NO \rightarrow Cl + NO_2$$

Additional effects could also be caused by bromine and fluorine compounds (6). Injection of NO₂ directly into the stratosphere from explosive eruptions such as that of Soufriere may also be important, but little is known about the amounts of nitrogen species in volcanic gases. We do know that increased amounts of SO₂ were injected into the atmosphere during this series of eruptions (7). Our general lack of knowledge of volcanic gases and the possibility of a 25 percent enhancement in NO₂ associated with such an event emphasize the importance of various satellite programs designed to monitor the global distribution of minor constituents. Only in this way will we be able to determine accurately the relative effect of natural and anthropogenic sources on the atmosphere.

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