MEASUREMENTS OF MINOR CONSTITUENTS IN THE STRATOSPHERE

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INTRODUCTION

The capability of spacetlab to carry payloads of weight and size an order of magnitude larger than was possible with other vehicles will give a new dimension to investigations of the earth homosphere from space. The use of more sophisticated instruments will be possible as well as their association allowing comparison between various types of measurements that will lead to a better accuracy of the data gathered on a global basis.

Particularly in the stratosphere, the geographic and vertical distribution of minor constituents is a key factor of the understanding of the chemical and dynamical processes taking place in that atmospheric region where the ozone abundance is of crucial importance for life on earth and is at the center of all physical and chemical stratospheric processes as discussed by other speakers at this symposium.

The analysis of the experimental work already performed in this field with presently available vehicles and methods is usefull as a guidance for the definition of spacetlab borne payload parts dedicated to this type of observations. Such an analysis will be summarized here. Our present knowledge of the minor stratospheric constituents originates from the alternative interactions between model calculations and observations. These have been obtained from various platforms: satellites, rockets, balloons, aircrafts and the earth surface. The methods can be
put in two different categories: those based on in situ measurements on one hand and those based on remote sensing on the other hand. The latter ones only can be applied from spacetab while the other will possibly contribute indirectly in a broad framework by providing verifications of remote measurements gathered from space.

THE IN-SITU MEASUREMENT METHODS

These relate to local sampling or action on stratospheric air followed by immediate or delayed application of analytical techniques. In such cases the use of an adequate vehicle implies balloon, aircraft and rocket flights. Samplings from balloon have already been conducted at the end of the nineteenth century (Pfotzer, 1972).

Meteorological balloons are now routinely carrying chemical ozone sondes pumping the ambient air for immediate electrochemical analysis (Brewer and Milford, 1960). Chemiluminescent reactions of ozone with Rhodamine B, and ethylene have also been applied to ozone measurements. Ridley et al. (1974) and Lowenstein et al. (1975) have determined the abundance of stratospheric nitric oxide through its luminescent reaction with ozone respectively observed in sampling experiments on balloon gondolas and aircrafts. Even more complex chemical procedures have been applied to the in situ detection of carbon monoxide from aircraft (Seiler and Junge, 1969) by observing optically mercury atoms release by reduction of mercury oxide.

Physical processes have been applied in situ to the determination of various minor constituents. To study the conditions of contrail formation behind high flying aircrafts, Dobson et al. (1945) have obtained the first evidence for the stratospheric dryness. Methane (Bainbridge and Heidt, 1966), freons and nitrous oxide (Schmeltekopt et al., 1975) have been determined by means of laboratory gas chromatography in air samples collected by balloons in pre-evacuated containers. Cryopumping on board of balloon and rocket payloads followed by laboratory analysis of in situ trapped samples has been applied to the determination of several trace species. The only information on the abundance of stratospheric H$_2$ is due to this method (Ehhalt et al., 1975). Collection of trace elements on paper filters has yielded data on nitric acid and on halogens (Lazrus et al., 1975). Air samples have been analysed inside an absorption cell on board of a balloon gondola by means of a spin flip Raman laser source to detect nitric oxide.
and water vapor (Patel et al., 1974). The most recently developed method is based on atomic resonance fluorescence in conjunction with a parachute borne flowthrough module (Anderson, 1975). Results have been so obtained on O and OH. The in situ measurement methods are summarized in Table I.

**THE REMOTE SENSING METHODS**

These are up to now essentially based on the observation of luminous phenomena in the wavelength range from the ultraviolet to the far infrared. The observation of stratospheric phenomena related to traces species is historically very old since the presence of volcanic dust and of nacreous clouds is known since a long time. Ground based observations of optically active substances formed in the stratosphere and absent from the troposphere is possible at wavelengths where the lowest atmospheric layers do not interfere. The best example appears to be ozone currently monitored by application of its ultraviolet absorption from 290 to 340 nm (Götz et al. 1934). It is however more generally suitable to observe the stratosphere from high altitude by means of instruments carried by balloons rockets or satellites. Since the molecular properties lead to a characteristic spectrum of narrow lines for each species, the use of high resolution spectroscopic instruments ensures the specificity and the sensitivity of the method. The tangential observation of the atmosphere ensures long pathes and vertical resolution and can be made in absorption or in emission. In the first case, an extra-atmospheric light source must be used such as the sun or stars. The light intensity, I, received at the observation point equals

\[ I = I_0 e^{-\tau} \]

where \( I_0 \) is the light intensity in absence of absorption and \( \tau \) is the optical thickness, the product of the absorption cross section by the number of molecules on the path. In the second case the discrete emission of the atmospheric gas is observed which is related to the amount of absorber in a similar but more complex fashion. The measured intensity

\[ I_E = I_0(T) (1 - e^{-\tau}) \]

is related to the black body function \( I_0(T) \) which depends on the temperature of the medium. The stratospheric emission peaks at about 10 \( \mu m \).
<table>
<thead>
<tr>
<th>CONSTITUENTS</th>
<th>METHODS OF MEASUREMENT</th>
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<tr>
<td><em>CO₂</em></td>
<td>UV: ground based satellite</td>
</tr>
<tr>
<td><em>H₂O</em></td>
<td>IR: from aircraft, balloon or rocket</td>
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<tr>
<td><em>O₃</em></td>
<td>Em: from satellite</td>
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<tr>
<td><em>CH₄</em></td>
<td>IR: from aircraft, balloon or rocket</td>
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<tr>
<td><em>N₂O</em></td>
<td>Absorption</td>
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<td><em>CO</em></td>
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<td>(NO)</td>
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<td>(NO₂)</td>
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<tr>
<td>HNO₃</td>
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<td>CₓHₓ</td>
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<tr>
<td>X</td>
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<td>(HHalogen)</td>
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**Range of number densities [log n(cm⁻³)]**

- 13-16: CO₂
- 11-14: H₂O
- 10-13: O₃
- 9-13: CH₄
- 8-12: N₂O
- 9-12: CO
- 8-12: H₂
- 9-13: (O)
- 8-12: (NO)
- 7-10: (NO₂)
- 7-9: HNO₃
- 6-9: CₓHₓ
- 6-8: X

**METHODS OF MEASUREMENT**

- **REMOTE SENSING**
  - UV: ground based satellite
  - IR: from aircraft, balloon or rocket
  - Em: from satellite
  - Absorption

- **IN SITU**
  - Frost point hygrometer
  - Chemiluminescence
  - IR LASER on sample in situ
  - Resonant scattering
  - General analytical methods applied in the lab, on in situ trapped samples

1 Based on actually published performance.
2 Constituents in parenthesis present in sunlit stratosphere only.
3 X stands for halogen.
Both emission and absorption methods require the knowledge of molecular parameters such as energy levels, line intensities, line widths to perform the inversion of integrated optical depths in order to determine vertical distributions of constituents. While the absorption method is almost independent of the temperature, the availability of the external light source limits its use in time. On the other hand the emission method can operate at any time but relies on the absolute determination of intensity which depends on temperature. In addition, when the atmospheric total density becomes too low, at high altitude \( I_0(T) \) does not follow the Boltzman formula and the source function must be determined by absorption measurements for instance.

The possibility of detecting minor stratospheric constituents by limb observations (Ackerman, 1963) began only recently with the availability of sophisticated high altitude balloon borne equipment dedicated to stratospheric observations. The first measurements were on nitric acid (Murcray et al., 1968), methane and nitrogen dioxide (Ackerman and Frimout, 1969) and water vapor (Murcray et al., 1969). All of these were in absorption using the sun as a source as well as the more recent on nitric oxide (Ackerman et al., 1975), chlorofluorocarbons (Williams et al., 1975) and hydrochloric acid (Farmer et al., 1976 and Ackerman et al., 1976).

The first stratospheric limb observations in emission have yielded information in the submillimeter-wave range (Harries, 1973) and in the middle infrared range (Murcray et al., 1973 and Chaloner et al., 1975) mainly on the odd nitrogen species \( \text{NO}, \text{NO}_2 \) and \( \text{HNO}_3 \) and on \( \text{H}_2\text{O} \). Satellite observation of the \( \text{H}_2\text{O} \) limb emission is now underway for the low stratosphere from Nimbus 6 and Nimbus G will perform measurements of the emission of several minor species by means of several instruments.

The instruments used are of two types: the spectrometers-interferometers and the correlation radiometers. All have to be of large sensitivity and of high resolution in order to achieve measurements of low concentrations as shown in figure 1, as well as to separate the spectral features due to various gases. Figure 2 shows as an example HCl absorption lines in the 3 \( \mu \text{m} \) methane band. In order to perform occultation absorption measurements from an orbiting vehicle the spectral scanning time must be short which excludes the use of large path difference interferometers. It should eventually be mentioned that ozone is now routinely measured from the observation of ultraviolet backscattered solar radiation.
Fig. 1. - General view of the abundance of minor constituents in the stratosphere, mesosphere and low thermosphere.
Fig. 2.- Stratospheric spectra (upper part) taken at various zenith angles in degree by means of a grille spectrometer and showing HCl absorption lines (2944.92, 2942.74 cm\(^{-1}\)) in the CH\(_4\) 3\(\mu\)m band and laboratory spectra of CH\(_4\) (R. Toth, private communication) showing the need of high resolution.
The results obtained up to now (table I), by all means are still preliminary, many discrepancies exist between the results obtained by various methods and very few information exist on geographic, seasonal and long term trends in the concentrations of minor species. Of the great wealth of the electromagnetic spectrum from the ultraviolet to submillimeter waves very little has been inspected. The difficulties of the actual experiments limit their number as well as their geographic and time distribution. Such limitations will be overcome by the use of jointly instrumented payloads on orbit allowing inter comparisons of observations performed at any location and at any time.


LOWENSTEIN, M. and H. SAVAGE (1975), Latitudinal measurements of NO and O₂ in the lower stratosphere from 5.5° to 82° North, *G.R.L.*, 2, 448.


WILLIAMS, W.J., J.J. KOSTERS, A. GOLDMAN and D.G. MURCRAY (1975), Simultaneous stratospheric measurements of fluoro-carbons and odd nitrogen compounds, private communication to be published.