Detection of Minor Tropospheric Constituents using Fourier Transform Spectroscopy

M. Carleer, R. Colin (Université Libre de Bruxelles, Laboratoire de Chimie Physique Moléculaire, CP 160, 50 av. F.D. Roosevelt, 1050 Brussels, Belgium, Tel.: +32-2-6502415, Fax : +32-2-6504232),

A.C. Vandaele, P.C. Simon (Institut d'Aéronomie Spatiale de Belgique, 3 av. Circulaire, 1180 Bruxelles, Belgium, Tel.: +32-2-3751579, Fax: +32-2-3748423)

In the frame of TOPAS (Tropospheric OPtical Absorption Spectroscopy), an EUROTRAC subproject supported by the Belgian State - Prime Minister's Service - Science Policy Office and the "Fond National de la Recherche Scientique", a long path (788 m) absorption system has been constructed on the urban site of the campus of the Université Libre de Bruxelles. It consists of a Xenon high pressure emission source connected to a 30 cm Cassegrain type telescope. A parabolic mirror placed at a distance of 394 m reflects the light back into a similar telescope connected to a high resolution Fourier Transform spectrometer BRUKER IFS120HR. The two telescopes are mounted on alignment devices and the external mirror is equipped with a driving system operated from the laboratory. This system has been in operation since October 1990. Absorption structures of O_2, O_3, NO_2 and SO_2 have been observed in the UV region (25000-45000 cm^{-1}). The spectra are recorded at a dispersion of 8 cm^{-1}.

A PC program has been developed for the analysis of the data. It consists in filtering the spectra by a Fourier transform technique, so that high frequency components of the signal are eliminated. The spectrum obtained in such a manner represents the source emission spectrum without any absorption from atmospheric molecules. The concentrations of the measured constituents are then derived using the Beer-Lambert law :

$$I(\lambda) = I_0(\lambda)e^{-n\Delta\sigma(\lambda)d}$$

where $I(\lambda)$ is the measured intensity,
$I_0(\lambda)$ the intensity without atmospheric structures,obtained by Fourier filtering of I
n the concentration,
d the optical path (788m) and
$\Delta\sigma(\lambda)$ the differential absorption cross section of the molecule.

The differential cross sections of SO_2 and NO_2 have been measured in the laboratory with the same instrument and at the same resolution. For O_3, cross sections measured by Daumont et al. [1] were used.

The detection limits of the different constituents are listed in Table 1. It should be noted that the use of a Fourier Transform spectrometer lowers the minimum detectable limit compared to conventional grating spectrometers, since the signal to noise ratio is better[2].

Table 1

	Differential Absorption Cross Section (cm^2 $molec^{-1}$)	at $\overline{\nu}$ (cm^{-1})	Detection Limit[a] (ppb)
SO_2	$5.0\,10^{-19}$	33050	0.2
NO_2	$4.0\,10^{-19}$	28700	1.3
O_3	$1.1\,10^{-19}$	35280	1.4

[a]calculated for an absorption path of 788m

Daily average concentrations of SO_2, NO_2 and O_3 at the Université Libre de Bruxelles campus site have been found to be respectively 15 ppb, 50 ppb and 20 ppb. Correlation studies have shown that NO_2 and O_3 are strongly chemically associated. SO_2 is highly dependant on dynamical transport, particularly on wind direction. A typical daily survey of the three constituents is given in Fig. 1.

References

[1] Daumont D., Barbe A., Brion J., Malicet J., New absolute absorption cross section of O_3 in the 195-350 nm region, personnal communication

[2] Finlayson-Pitts B.J., Pitts J.N., Atmospheric Chemistry : fundamentals and experimental techniques, J. Wiley & Sons, New York, 1986, pp. 337-346

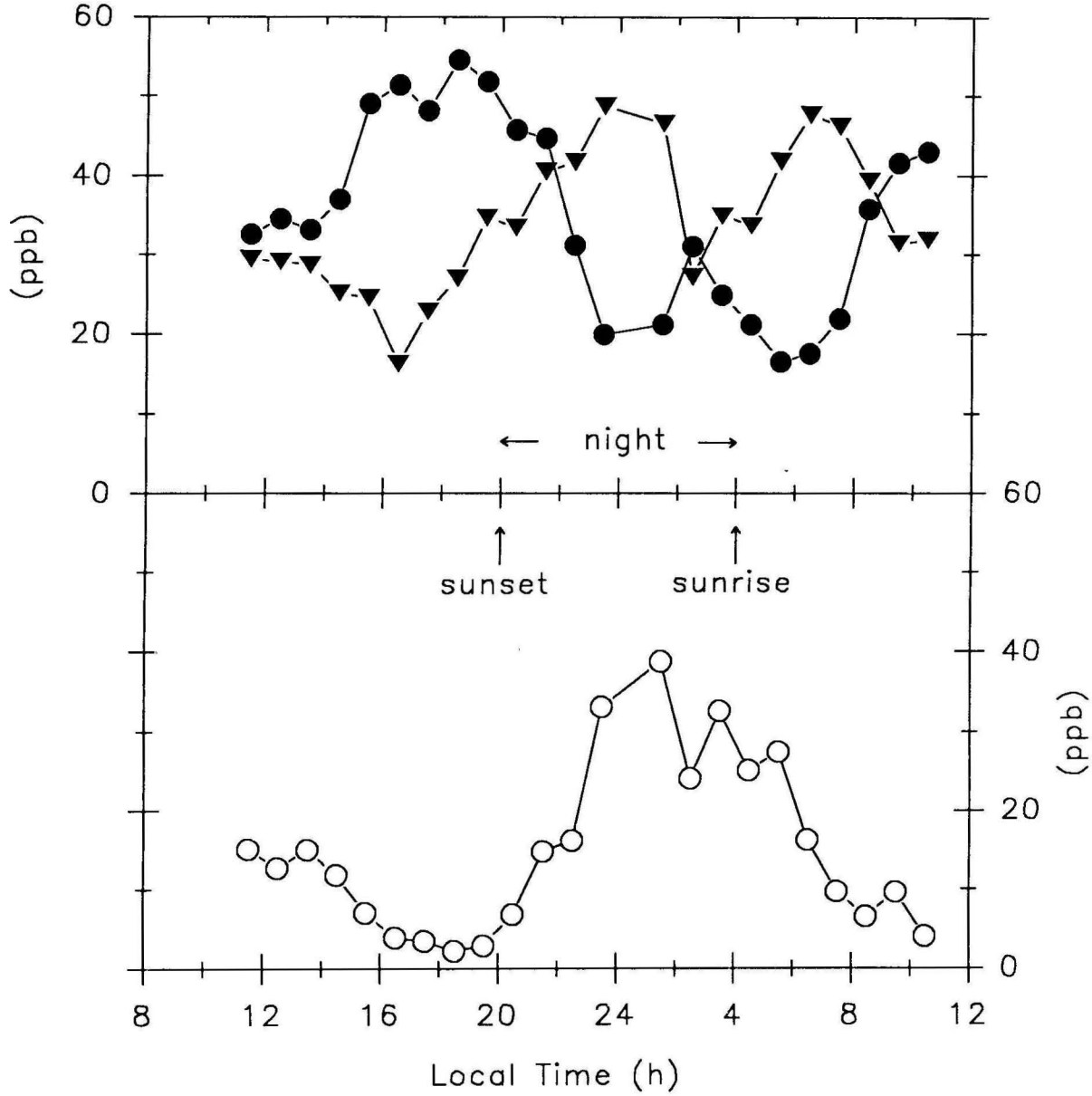

Fig. 1 : Diurnal variation of the concentrations of NO_2 (▼), O_3 (●) and SO_2 (O) during May 22–23, 1991 at Brussels (Lat : 50°48'N, Long : 4°21'E)