

Urban pollution monitoring by DOAS Fourier Transform Spectroscopy

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In the framework of the TOPAS (Tropospheric Optical Absorption Spectroscopy) EUROTRAC subproject supported by the Belgian State Science Policy Office - Prime Minister's Service, and the "Fonds National de la Recherche Scientifique", a long path (788m) absorption system has been constructed on the urban site of the campus of the Université Libre de Bruxelles. A schematic of this set up is presented in Fig.1. A light source S (either a high pressure 800W Xe-lamp for the UV region, or a 250W Tungsten filament lamp for the visible part of the spectrum) is placed at the focal point of a first Cassegrain-type telescope (ET) some 30cm in diameter. A long focal length mirror (M) placed at a distance of 394m reflects the light into a second similar telescope (RT). The light collected by this second telescope is focused on the entrance aperture of a BRUKER IFS120HR high resolution Fourier Transform Spectrometer.

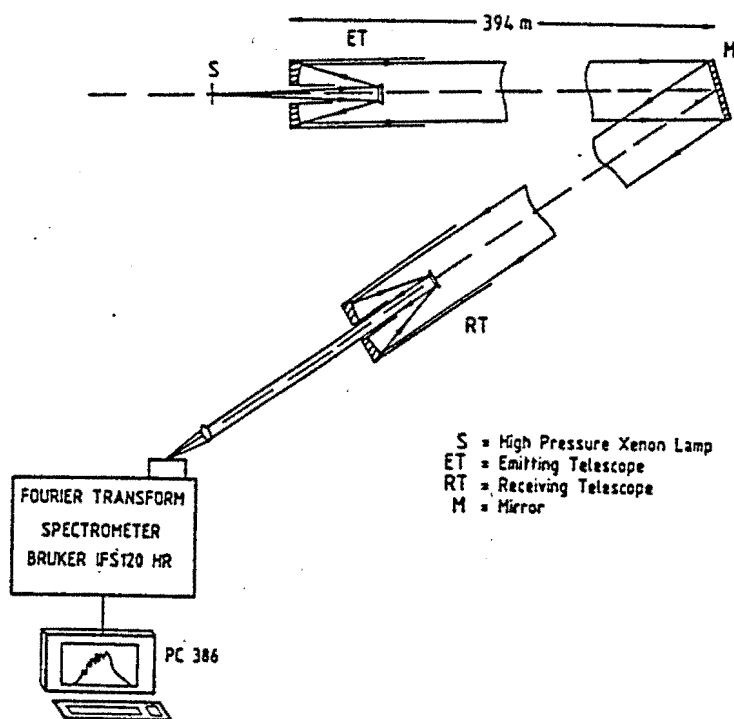


Figure 1. Experimental set up : S = High Pressure Xenon Lamp or Tungsten filament, ET = Emitting Telescope (30 cm \varnothing), RT = Receiving Telescope (30 cm \varnothing), M = Long Focal Retroreflector Mirror.

Absorption spectra are recorded in the visible region ($30000\text{-}14000\text{cm}^{-1}$, $330\text{-}700\text{nm}$) using a Silicon photodiode detector and a blue-green filter to cut off most of the infrared radiation. In the UV region ($38000\text{-}26000\text{cm}^{-1}$, $260\text{-}380\text{nm}$), the detector is either a solar-blind vacuum UV diode, or a newer setup consisting of a UV-enhanced Si photodiode placed behind a quartz prism based predispersor to eliminate the unwanted visible and IR radiation. The spectra are recorded at an unapodized resolution of 16cm^{-1} (roughly $0\text{-}15\text{nm}$ in the UV, 0.25nm in the visible). Fig.2 shows a typical spectrum recorded with the UV vacuum diode. The most visible absorption structures seen in this figure are due to the SO_2 molecule and the bell shaped appearance of the spectrum is mainly due to the frequency response of the detector.

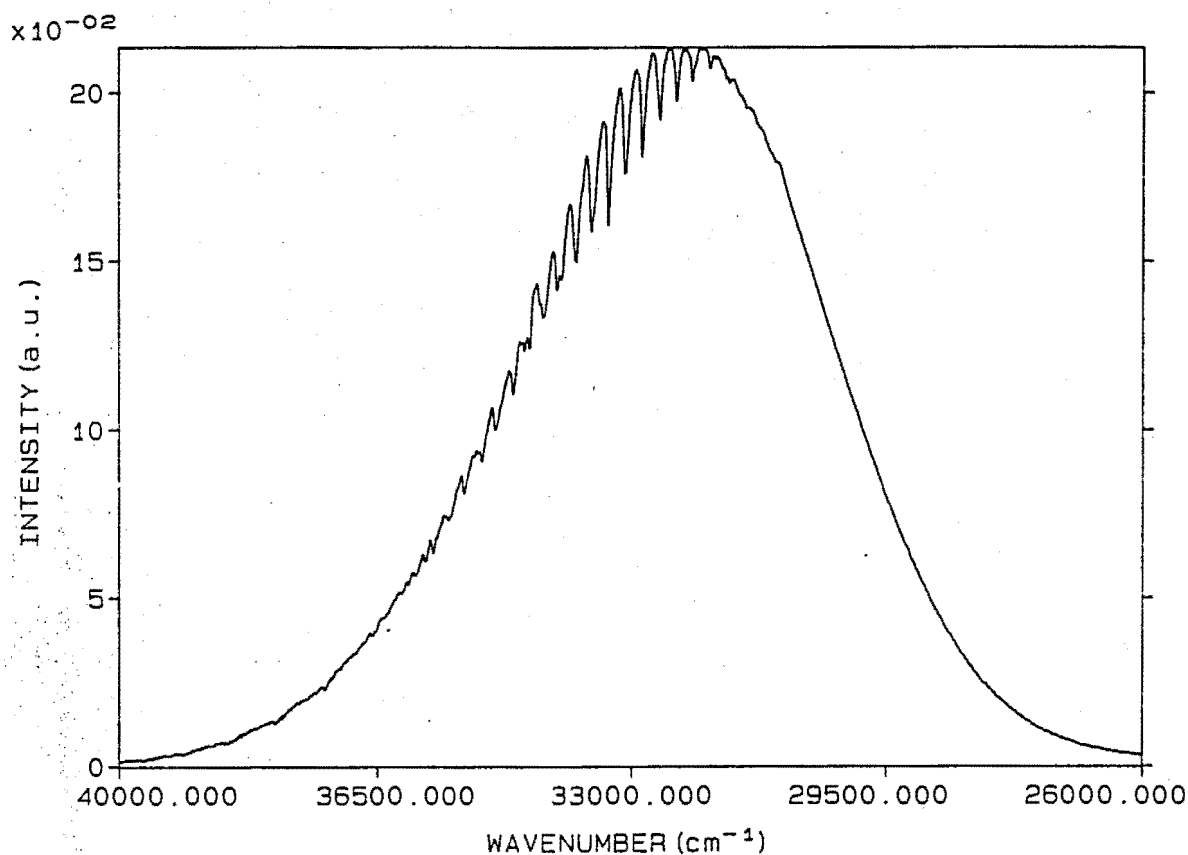


Figure 2. UV vacuum diode recorded absorption spectrum with a long path distance of 788m.

The concentration of each of the absorbing species is measured using the Beer-Lambert law :

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

where I is the measured intensity, I_0 the measured intensity from which all absorption structures have been removed using low pass Fourier filtering, n is the concentration, d the absorption path length and $\Delta\sigma$ is the so-called differential cross-section of the molecule.

Using this experimental set up and a specially developed iterative least squares PC program to treat the data, we are routinely measuring by Differential Optical Absorption Spectroscopy (DOAS) the concentrations of 3 minor constituents of the troposphere : SO_2 , NO_2 and O_3 . The differential cross-sections of SO_2 and NO_2 used have been measured in the laboratory on the same spectrometer [1]. Cross-sections of O_3 have been taken from the literature [2]. An estimation of the detection limits for the three molecules is given in Table 1 in which the second column gives the spectral regions where the concentrations are measured for each molecule. The better sensitivity for NO_2 in the visible region comes from the more intense absorbance structures of this molecule in this region. As can be seen from this table, the use in the UV of the newly developed Si photodiode based setup instead of the original solar blind diode greatly improves the detection limit for NO_2 , and also shortens the recording time by a factor of 5, from 50 down to 10 minutes per spectrum.

TABLE 1 : S/N ratios and detection limits for SO_2 , NO_2 and O_3 .

Molecule	ν (cm ⁻¹)	UV (vacuum diode) ¹		UV (Si diode) ²		Visible (Si diode) ²	
		S/N	ppb	S/N	ppb	S/N	ppb
SO_2	33340	3200	0.1	6500	0.05		
NO_2	28710 22300	500	5.8	7250	0.4	4000	0.3
O_3	35310	1700	1.6	4550	0.6		

1. 50 minutes recording time

2. 10 minutes recording time

Daily variations of the concentrations of SO_2 , NO_2 and O_3 for three different dates in 1991 are presented in Fig.3, representing different pollution levels on the urban site of the Université Libre de Bruxelles. One can see on the three different graphs the awaited anti-correlation for the NO_2 and O_3 concentrations.

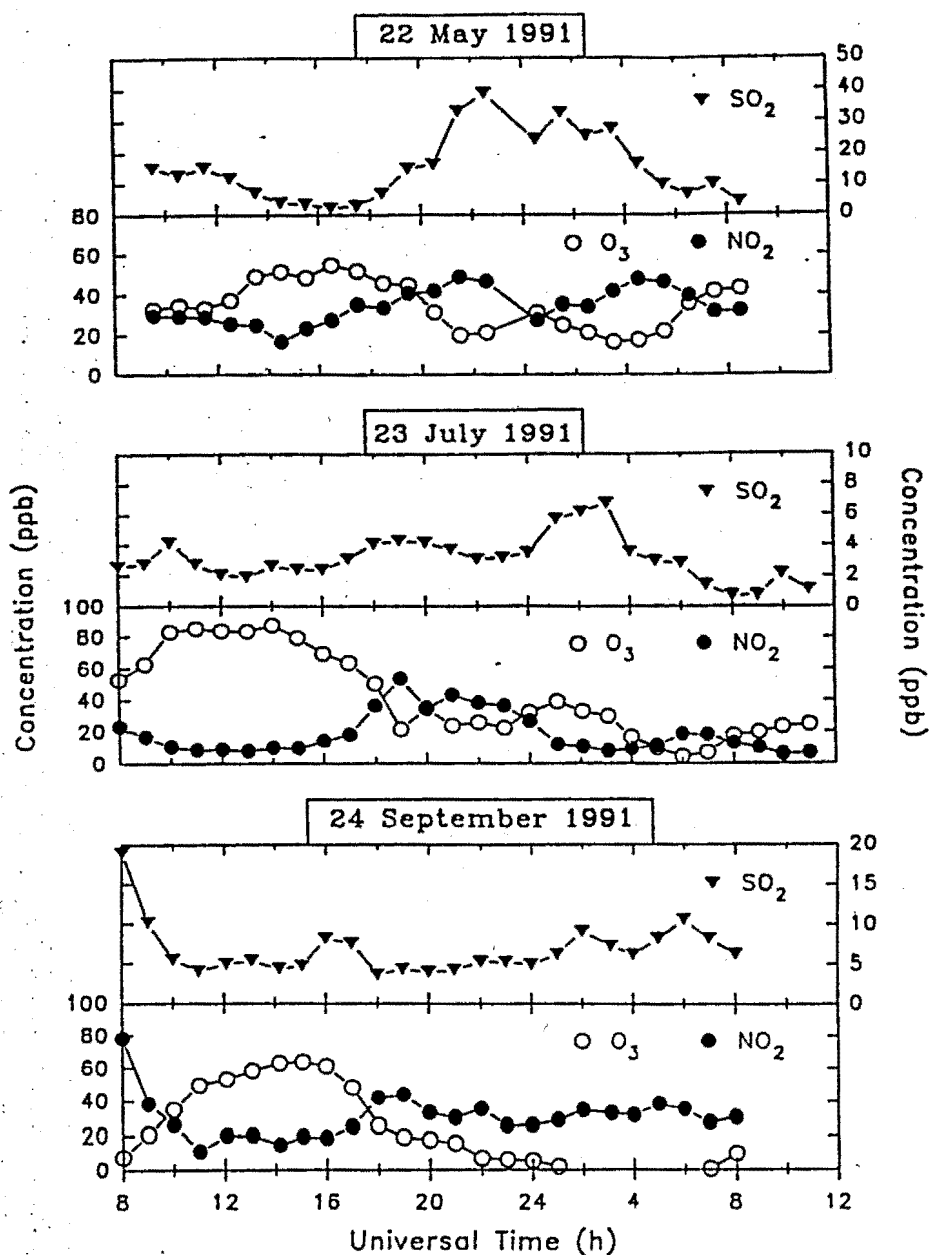


Figure 3. Concentration profiles for SO_2 , NO_2 and O_3 on 22 May 1991, 23 July 1991 and 24 September 1991.

One important characteristic of these measurements is the use of a Fourier Transform Spectrometer. This instrument shows two main advantages over more traditional grating spectrographs :

- a higher sensitivity due in part to the bigger surface of a circular entrance aperture than for a conventional slit, and also because at all times roughly half the incoming light reaches the detector, allowing the recording of spectra