

Intercomparison of Instruments for Tropospheric Measurements using Differential Optical Absorption Spectroscopy

A contribution to subproject TOPAS

C. Camy-Peyret¹, M. Carleer², C. Clerbaux², R. Colin², A.C. Vandaele³, C. Hermans³, P.C. Simon³, B. Bergquist⁴, B. Galle⁴, C. Fayt⁵, F. Goutail⁶, M. Nunes-Pinharanda⁶, J.P. Pommereau⁶, M. Hausmann⁷, F. Heintz⁷, U. Platt⁷, I. Pundt⁷, T. Rudolph⁷, J. Plane⁸ and N. Smith⁸

¹*Université Pierre et Marie Curie, Paris, France*

²*Université Libre de Bruxelles, Brussels, Belgium*

³*Institut d'Aéronomie Spatiale de Belgique, Brussels, Belgium*

⁴*Swedish Environmental Research Institute, Göteborg, Sweden*

⁵*Université de Mons-Hainaut, Mons, Belgium*

⁶*Service d'Aéronomie CNRS, Verrieres-le-Buisson, France*

⁷*Universität für Umweltphysik, Heidelberg, Germany*

⁸*University of East Anglia, Norwich, England*

In order to assess the accuracy and the advantages of instruments using the Differential Optical Absorption Spectroscopy technique, it was decided to organize an international intercomparison campaign of instruments. This campaign took place in an urban site in Brussels in September 1992. Eight different instruments were present and measured simultaneously several atmospheric constituents, in the same portion of the troposphere. All measurements were made in the UV and visible region and were based on the DOAS technique. This technique is based on the recognition of the spectroscopic signatures of the absorbants and the fact that no reference spectrum, without any absorption features, is obtainable. Critical parameters in this method are the absorption cross sections of the molecules to be detected. It was decided that each group should use the same references [1–3].

A brief description of all participating instruments can be found in Table 1, where the type of instrument and detector, the absorption path denomination, the measured molecules and the recording time are indicated. All the instruments were installed in the same laboratory at an altitude of about 20 m from ground level and pointing in the NW direction towards a set of sources and retroreflectors placed at various distances. It was decided to limit the intercomparison to the species NO₂, O₃ and SO₂, however most of the instruments present could detect more constituents. It can be seen from Table 1 that the instruments can be classified in three groups, depending on their recording time. It was decided to compare the instruments on three different time scales: 5, 20 and 45 minutes.

Fig. 1 shows the evolution of the concentrations of NO₂, O₃ and SO₂ for the 24 hour period starting at 4.00 pm on the 14th of September, as measured by all the instruments. The measurements integrated over a period of 45 min are presented in

Table 1. Description of the participating instruments

Institution	Instrument & Detector	Optical path	Measured Molecules	Recording Time
Swedish Environmental Research Institute	grating spectrom. PMT + slotted disc grating spectrom. CCD (1024)	A, D	NO ₂ , O ₃ , SO ₃ , H ₂ CO	20 min/molec
		C	NO ₂ , O ₃ , SO ₂	20 min
Universite Libre de Bruxelles	Fourier Transform Spectrom. Solar blind UV Photodiode	C	NO ₂ , O ₃ , SO ₂	45 min
Service d'Aeronomic CNRS	grating spectrom. PDA (512)	B, C	NO ₂ , O ₃ , SO ₂ , H ₂ CO, HNO ₂ , hydrocarbons	5 min
Universität Heidelberg	grating spectrometer PMT + slotted disc grating spectrom. PDA (1024)	A, D	NO ₂ , SO ₂	20 min/molec
		White cell	NO ₂ , NO ₃	10 min
University of East Anglia	grating spectrom. PDA (1024)	C	NO ₂ , O ₃	15 min
Institut d'Aeronomic Spatial de Belgique	grating spectrom. PDA (1024)	C	NO ₂ , SO ₂	6 min

A: Retroreflector at 230 m; B: Source at 230 m; C: Mirror at 390 m; D: Retroreflector at 1010 m.

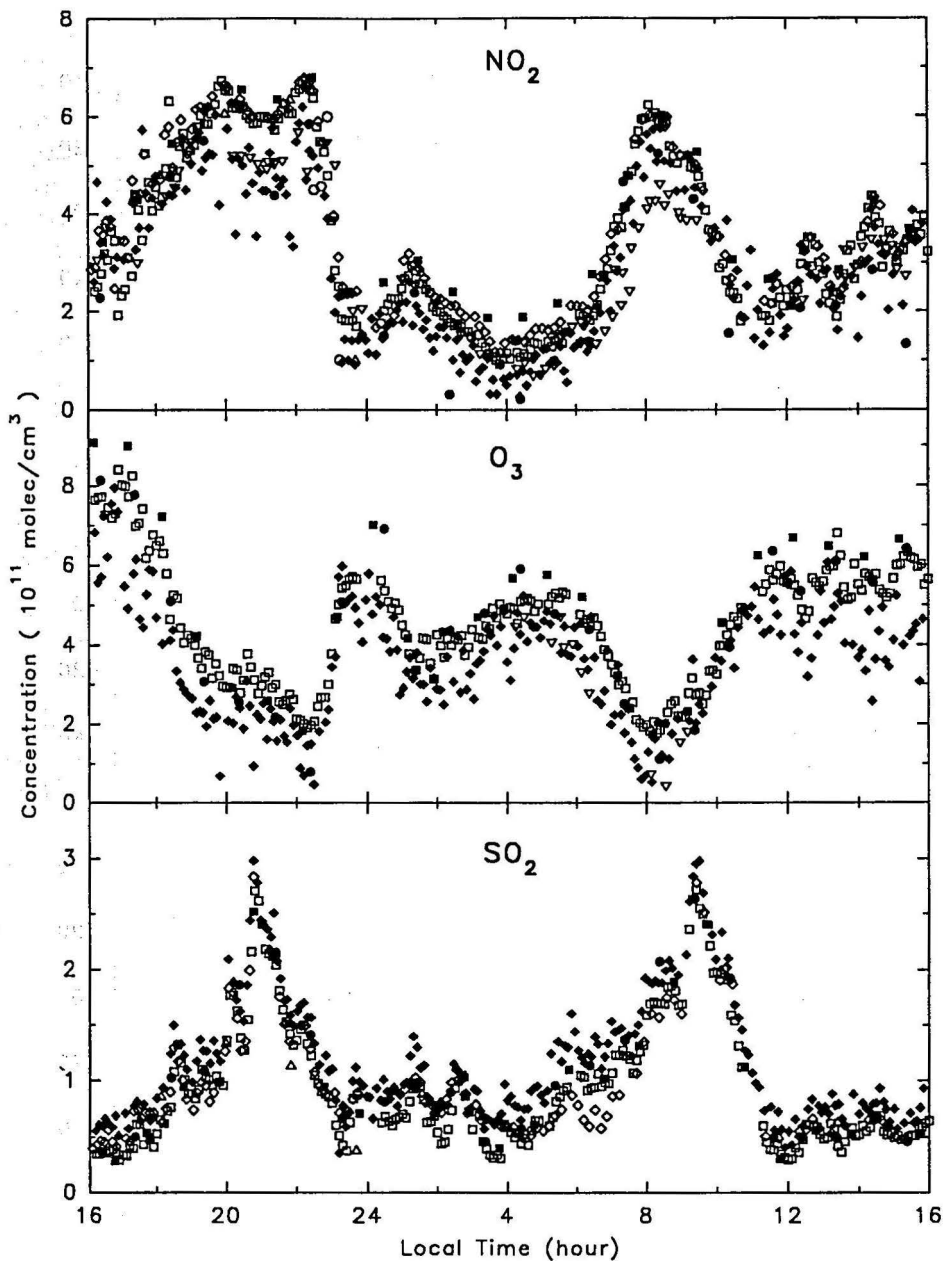


Figure 1. Concentration evolution of NO_2 , O_3 , and SO_2 during the 24 hour period starting at 4.00 pm on the 14th of September (\bullet ULB, \diamond IAS, \square and \blacksquare SERI, \blacklozenge CNRS, Δ and \circ UH, ∇ UEA)

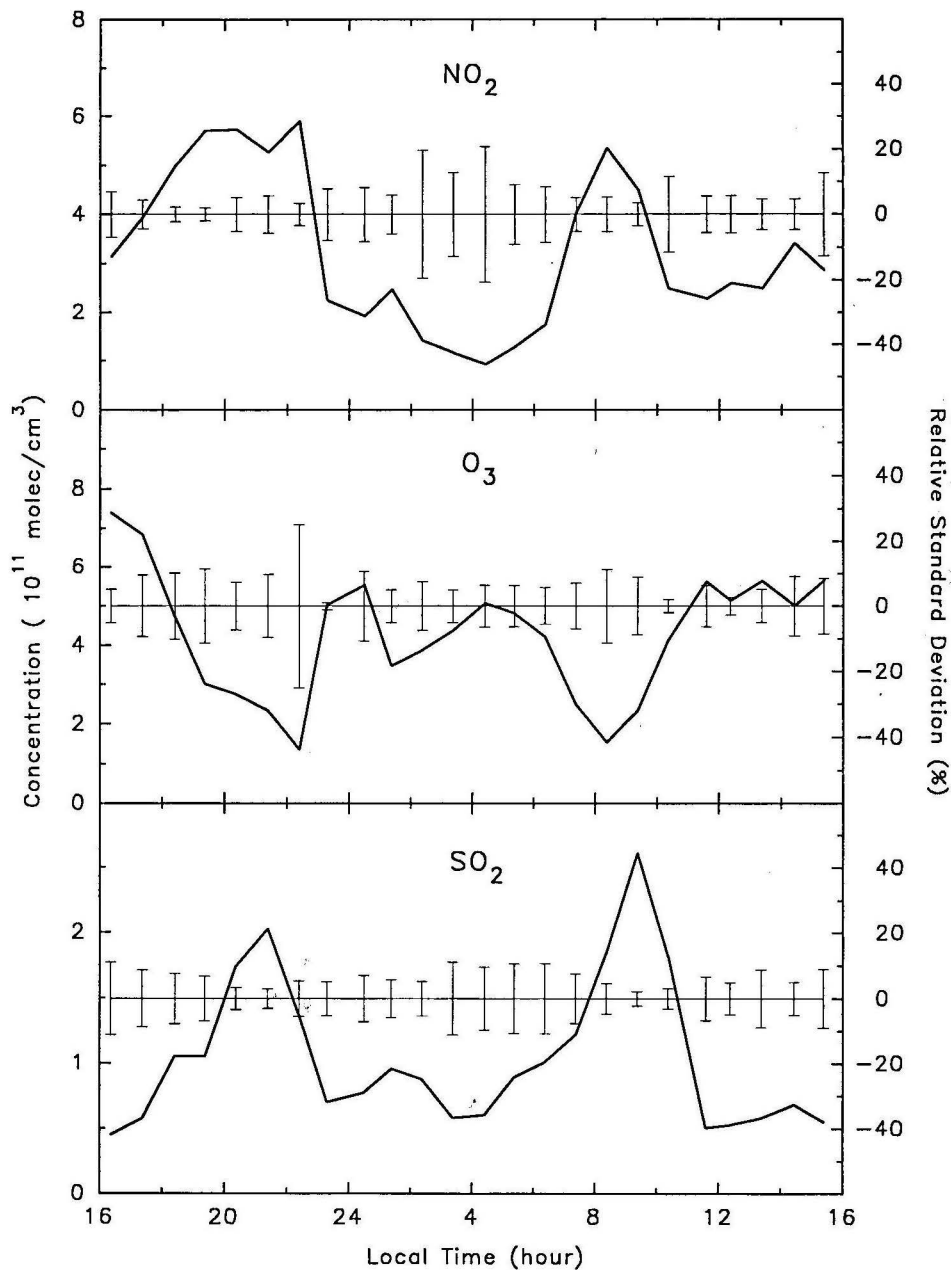


Figure 2. Mean concentration and dispersion of NO₂, O₃, and SO₂ during the 24 hour period integrated over 45 min

Fig. 2, where their mean value and their standard deviation are plotted against time. Only those instruments using the short paths A, B and C and which performed at least one measurement every 60 min throughout most of the 24 hour period have been retained. The dispersions of all these instruments on the three molecules are respectively 5×10^{10} , 7×10^{10} and 2×10^{10} molec/cm³.

The comparison presented in Fig. 2 shows that rapid fluctuations in concentrations are not responsible for the discrepancies between the instruments. It may therefore be stated that the dispersion of the results are entirely due to the instruments themselves. They are due to the different algorithmic treatments used by each group in the DOAS technique: the technique used to adapt the resolution of the cross sections to the resolution of the instrument, the fact that several molecules are measured simultaneously or not, the filtering procedure used to eliminate the broad band component of the recorded spectrum are but a few examples. A further effort should be made to compare in more detail the various retrieval methods used. This point, as well as the study of the detection limits of the instruments, will be addressed in a forthcoming campaign scheduled to take place in September 1994 in East Anglia (U.K.).

References

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