

ATMOSPHERIC ABSORPTION MEASUREMENT BY FOURIER TRANSFORM DOAS

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Summary

Two instruments - a Fourier transform spectrometer (FTS) AND a grating spectrometer using a diode array detector or a CCD detector - described earlier, have been improved. The grating spectrometer has been tested and compared to the FTS. Both have participated in an instrument intercomparison campaign held in September in 1992 in Brussels. Since then modifications have been made to the FTS which lead to better signal to noise ratio and a shorter measuring time.

Aims of the Research

- To develop new instrumentation procedures to improve the DOAS technique
- To compare the capabilities of different instruments in the frame of an intercomparison campaign

Activities during the year

During 1992 tests of the grating spectrometer (with a photodiode array or a CCD detector) have been carried out. Improvements of the experimental conditions concerning the FTS and the grating spectrometer have been made. Different software algorithms have been tested and improved. Two instruments have participated in the intercomparison campaign organized in the frame of TOPAS.

Principal experimental results

1) Development and tests of the grating spectrometer

The grating spectrometer is a 1/8 m Czerny-Turner from ORIEL. Two detectors have been used : a 1024 pixels photodiode array and a 512*512 pixels CCD. Several entrance slits have been tested in combination with several gratings. For a combination of a 100 µm entrance slit with a 600 gr/mm grating, the FWHM is about 1.2 nm for both detectors.

The hardware and software have been modified in order to be adapted to the optical system used by the FTS of the Laboratoire de Chimie Physique Moléculaire of the Université Libre de Bruxelles (ULB). Preliminary tests have been carried out at the ULB. More tests will be carried out systematically next year.

2) Systematic pollution monitoring with the FTS

Systematic measurements of the atmospheric pollution at the Campus of the ULB have been carried out during the past year. Nearly each month concentrations of SO₂, NO₂ and O₃ have been monitored during 24 hours periods.

3) Instrument Intercomparison Campaign September 1992

An intercomparison campaign was held in Brussels at the Laboratoire de Chimie Physique Moléculaire during the period 7-19 September 1992. 8 groups participated in this campaign, representing 5 nations (France, Germany, Sweden and United Kingdom, Belgium). Three commercial companies selling or developing DOAS instruments were represented. Five optical path lengths - of 232, 464, 474, 774 and 1007 m - were available. In several instances the light from the 774 m path length was distributed simultaneously to several spectrometers. Moreover an open 15 m White absorption cell and spectrograph was installed on the roof of the main building. It was decided that NO₂, SO₂ and O₃ would be the priority species to be monitored. Additional molecules such as H₂CO, HNO₂ or hydrocarbons were measured by some groups. In addition, calibration measurements of standard lamp source and of gas cells (SO₂, NO₂, O₃ and H₂CO) were performed by all the instruments. O₃ concentration values measured by chemiluminescence and meteorological data were provided continuously during the campaign. Coordinated observation periods of 12 (night or day) and 24 consecutive hours were devoted to simultaneous measurements of the imposed species.

The two previously described instruments were operated in the following conditions :

grating spectrometer + photodiode array :

600 gr/mm	
100 µm entrance slit	=> FWHM = 1.2 nm
integration time = 2.5 - 5 s	
number of scans = 100 - 250	=> experience time = 10 min
wavelength interval	285 - 610 nm
wavelength dispersion/pixel	0.3 nm
molecules detected (detection limit)	
SO ₂	299.5 - 302.5 nm (5.0 ppb)
NO ₂	425.0 - 433.5 nm (5.0 ppb)

Fourier transform spectrometer :

resolution	16 cm ⁻¹
number of scans	1600
experience time	50 min
wavenumber interval	25000 - 40000 cm ⁻¹
detector	solar blind UV Vacuum diode
molecules detected (detection limit)	
SO ₂	33400 cm ⁻¹ (0.1 ppb)
NO ₂	28700 cm ⁻¹ (5.8 ppb)
O ₃	35300 cm ⁻¹ (1.6 ppb)

Preliminary results are shown in figures 1.a, 1.b and 1.c, where concentrations of respectively SO₂, NO₂ and O₃ are represented for the 24 hours period 14-15 September 1992. Error bars have not been represented in order not to confuse the graphs.

Some remarks can be drawn from these plots :

a. concerning SO₂ measured with the grating spectrometer :

Concentration values seem to be constantly below the average value. This can be explained by the etaloning effect which greatly affects this spectral region.

b. concerning O₃ measured with the FTS :

Problems have been encountered with the elimination of interfering absorption structures of O₂. As no absorption cross sections of O₂ in this region are available from laboratory experiments, those cross sections have to be defined from an atmospheric spectrum from which absorption structures of other constituents are removed. Such a cross section depends greatly on the experimental conditions. It seems that for example the aging of the lamp has an important influence. More accurate absorption cross sections of O₂ should be determined.

4) Improvement of the signal to noise ratio of the FTS

In order to improve the signal to noise ratio of the spectra taken with the FTS, a pre-disperser prism has been used. This prism has been placed in the path of light entering the FTS just before the entrance aperture. There it acts like a filter, defining the band pass of the entire system. This enables the use of a Si diode detector which has a far better signal to noise ratio than the original solar blind UV diode. Moreover, since the Si diode detector has a faster response, the moving mirror can be operated at greater speed leading to the diminution of the experiment time. New values of the detection limits attainable with this new set up are compared in Table 1 to those obtained before. From this table it can be seen that values of the detection limits have been greatly improved, particularly in the case of NO₂. This is due to the fact that without the prism, the band pass of the

system is such that around 28700 cm^{-1} , the signal is very low. By using the prism the band pass can be adjusted so that the signal in this region is greatly increased. With such detection limits the measurement of other molecules present in lower concentration in the atmosphere should be possible.

	ν (cm^{-1})	detection limit*	
		before (Res: 16 cm^{-1} ; 1000 scans; exp time : 45 min)	with the prism (Res: 16 cm^{-1} ; 1000 scans; exp time : 15 min)
SO ₂	33340	0.1	0.05
NO ₂	28710	5.8	0.4
O ₃	35305	1.6	0.6

* for an optical path of 778 m

Table 1 : Detection limits

5) Laboratory measurements

Absolute absorption cross sections of CS₂ have been measured with the experimental set up described in Carleer et al.(1993). The $29500\text{-}34500\text{ cm}^{-1}$ (290-340 nm) spectral range was investigated at a resolution of 16 cm^{-1} (about 0.1 nm).

Main conclusions

The two instruments have been successfully improved during 1992. The software and the experimental set up have been modified in such a way that detection limits have been increased. Comparisons between a grating spectrometer and the FTS have been carried out. The participation in the intercomparison campaign have shown some limitations of the two systems (experiment time and need of better absorption cross sections for O₂ for the FTS, etaloning interference with the SO₂ absorption for the grating system, ...). Some of them have already been solved.

Aims of the coming year

The main objectives of the coming year are to refine the software analysis by improving the algorithms and the reference cross sections (i.e. for O₂) and to increase the number of detected molecules (H₂CO, HNO₂, toluene, benzene,...) especially for the FTS for which signal to noise ratios have been greatly improved. Both instruments should be totally automated. This has partially been done for the grating spectrometer.

The measuring capabilities will be increased by the purchase of a portable Fourier transform spectrometer, which will be entirely dedicated to atmospheric related measurements. The periods of measurement should be increased by the permanent installation of the grating spectrometer and the

use of the portable FTS. To perform this, the optical set up will be slightly modified : the intermediate mirror will be replaced by the lamp source, thus reducing the optical path length to 390 m but allowing easier automation procedures.

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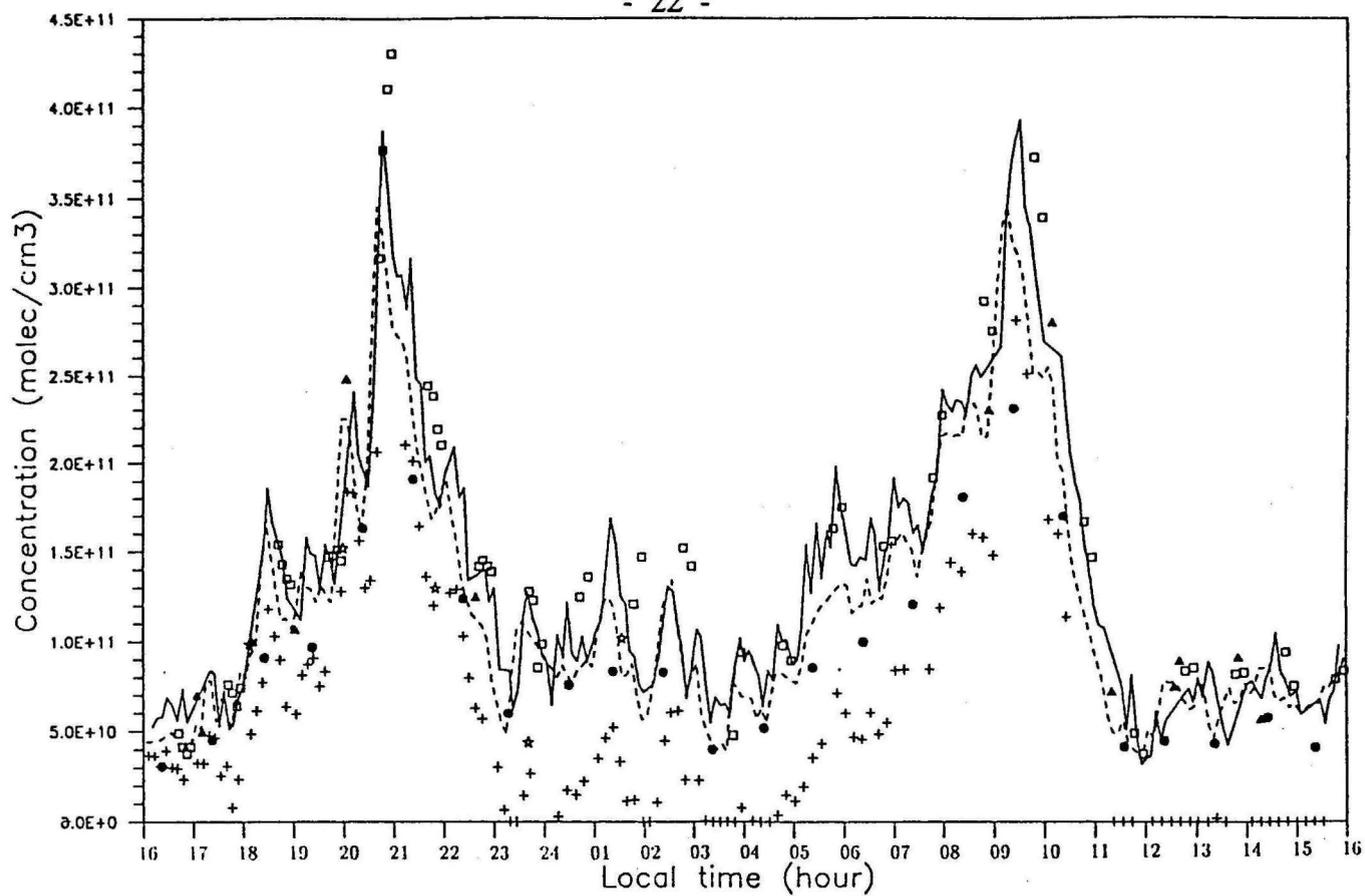
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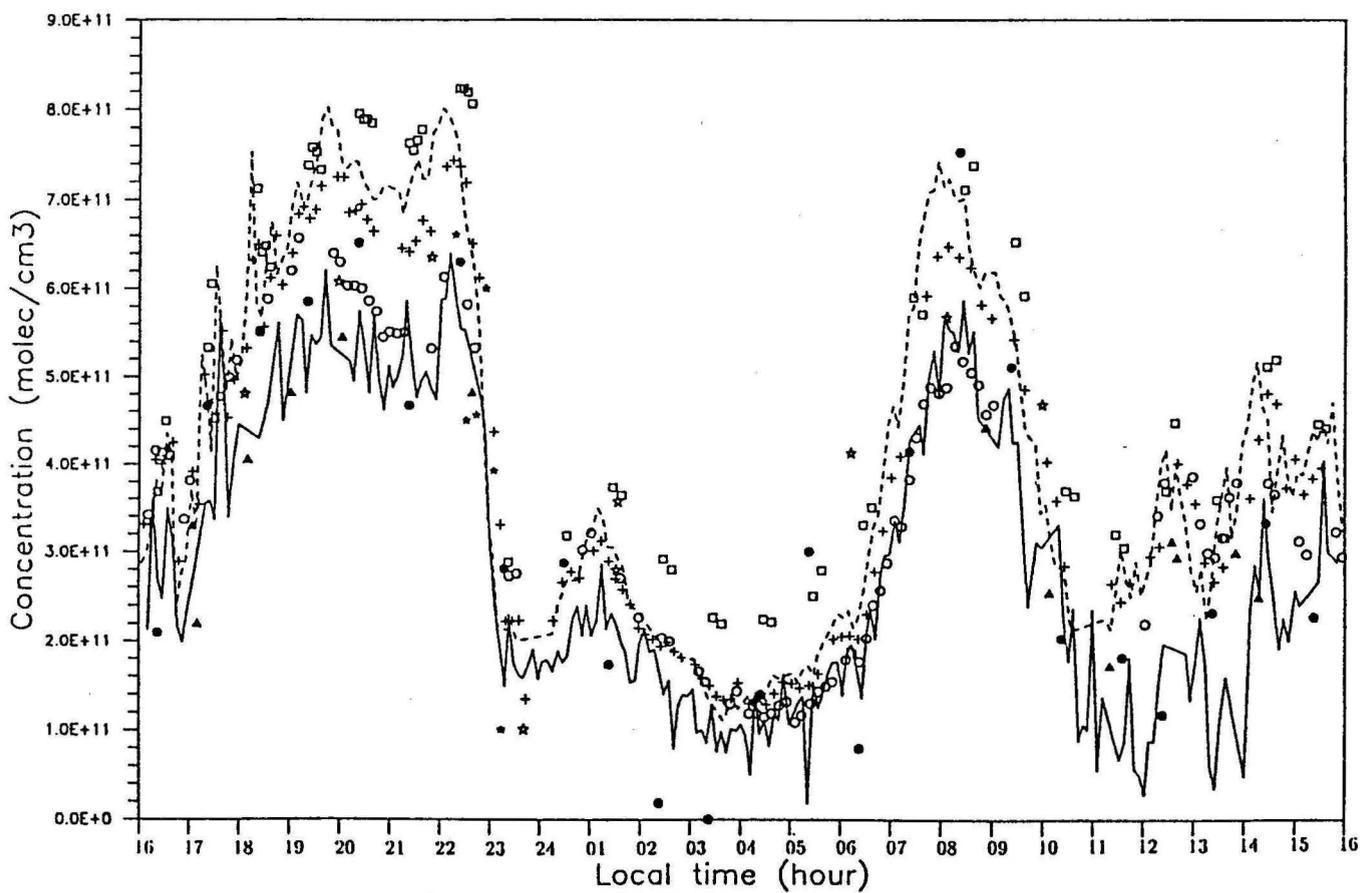
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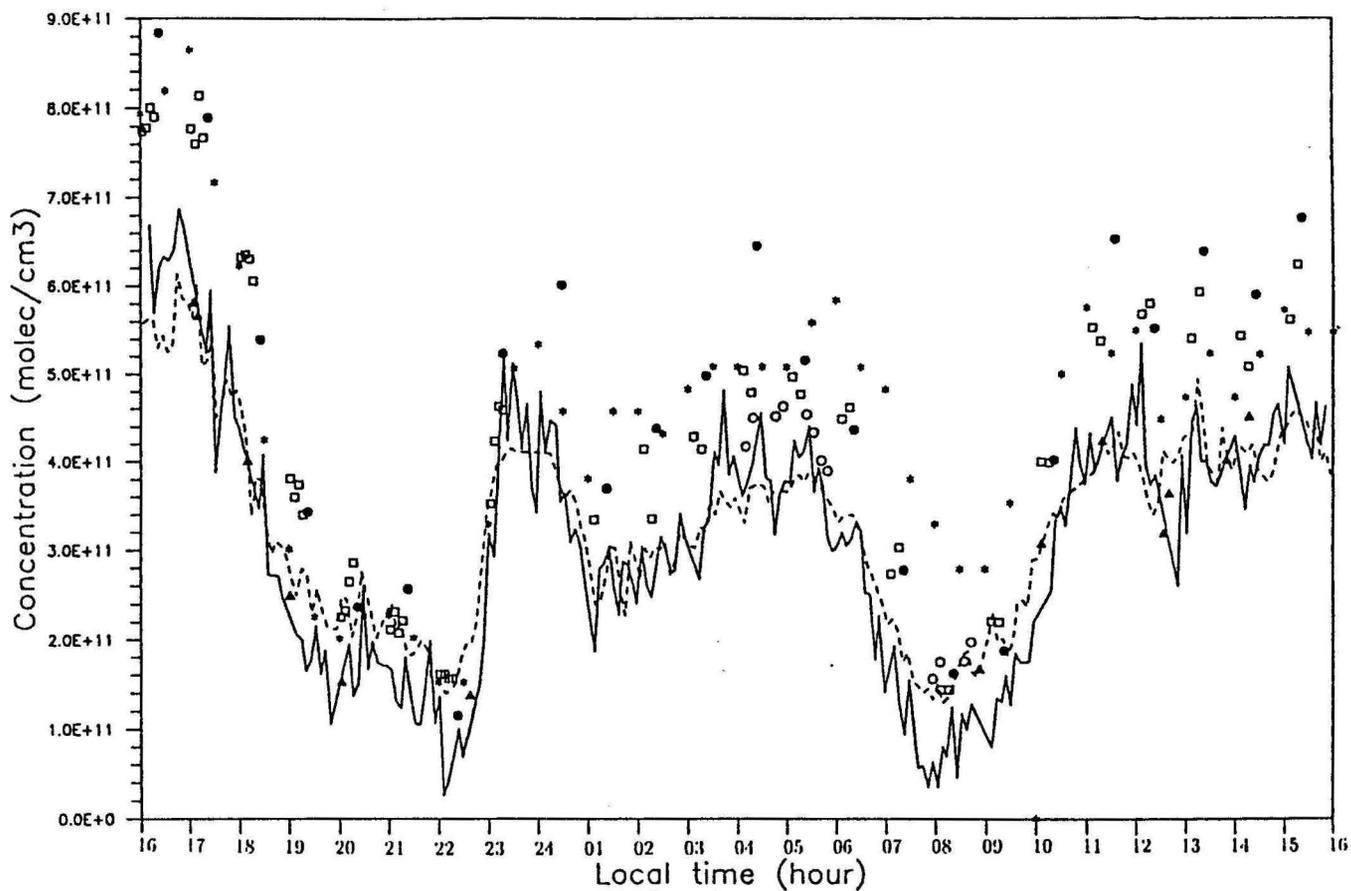
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A



B



C

Figure 1 : Concentration profiles of a. SO₂, b. NO₂ and c. O₃ for the 24 hours period 14-15 September 1992.

- : CNRS, France, 293 m absorption path;
- ▲ : CNRS, France, 788 m absorption path;
- : SERI, Sweden, 220 m and 1.7 km absorption paths;
- : SERI, Sweden, 788 m absorption path;
- : ULB, Belgium, 788 m absorption path;
- + : IASB, Belgium, 788 m absorption path;
- : UEA, United Kingdom, 788 m absorption path;
- ☆ : UH, Germany, 1.7 km absorption path;
- ★ : UH, Germany, open white cell