

Detection of tropospheric pollutants in a urban site

A contribution to the EUROTRAC subproject TOPAS

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Summary

Data obtained during the Instrument Intercomparison Campaign, which took place at Brussels in September 1992, were analysed. Different intercomparisons were carried out between the various groups depending on the time scales used by their instruments. Moreover data from the CNRS group were used to compare different algorithms.

A new instrument setup based on a grating spectrometer and a CCD detector, has been developed. A Fourier Transform Spectrometer BRUKER 120M has been acquired and preliminary tests have been performed on a wide variety of detectors and filters.

Measurements of absorption cross sections were carried out with the new Fourier Transform Spectrometer. SO₂, CS₂ and NO₂ absorption cross sections were obtained at high resolution.

Aims of the research

- to finalise the intercomparisons of the data obtained during the 1992 TOPAS Campaign
- to compare different DOAS algorithms
- to develop a new measurement setup based on the Fourier transform spectrometer BRUKER 120M
- to develop a new measurement setup based on a CCD detector
- to measure the absorption cross sections of some atmospheric gases (SO₂, CS₂ and NO₂) in various conditions of resolution and temperature

Activities during the year

1. Intercomparison Campaign in September 1992

a. Analysis of the results

An intercomparison campaign of instruments based on the Differential Optical Absorption Spectroscopy technique has been held in September 1992 at Brussels. Two instruments were present : the BRUKER IFS120HR Fourier Spectrometer of the Laboratoire de Chimie Physique Moléculaire of the ULB and a grating spectrograph associated to a PDA type detector.

The analysis of the data acquired during the campaign has been carried out during 1993. Several improvements of the analysis procedure have been introduced.

Moreover the intercomparison of the results of all the participants has been assigned to the Institut d'Aéronomie Spatiale. The intercomparison only concerned NO₂, O₃ and SO₂. This comparison was complicated by the fact that each instrument measured the atmospheric constitution on a different time basis. It was then decided to compare the results on three different time scales (5, 20 and 45 min). The results of this intercomparison show the considerable importance of the absorption cross sections and of the analysis algorithms (see common report for more information).

b. Comparison of algorithms

In order to compare the behaviour of the different analysis algorithms, it was decided to exchange raw spectra recorded during the campaign between the different groups. The IASB analysed three spectra recorded by the instrument of the CNRS (France). One of these spectra is a cell measurement, containing only SO₂ at high concentration. The two other spectra are atmospheric spectra recorded when the concentration of SO₂ was low (~ 1 ppb) and high (~ 10 ppb). Moreover concentrations of NO₂ for the two atmospheric spectra have been determined. Table 1 shows the results. The concentrations are in molec/cm³, and the figures between brackets are the estimated errors on the concentrations.

From Table 1, it can be seen that the values agree fairly well in the case of the cell measurement, if we consider the initial value given by the CNRS group (2%). There is roughly 25% difference when considering the new value from CNRS.

Concerning the concentrations of SO₂ and NO₂ in the atmospheric spectra, the comparison is far less good. CNRS values are systematically greater for SO₂ and lower for NO₂, with approximately a factor 2 in each case.

As the spectra are the same, the discrepancies can only come from the analysis procedures, particularly from the calculation of the differential cross sections and the fitting procedure.

| | SO ₂ | | NO ₂ | |
|-------------------|----------------------------|----------------|-----------------|---------------|
| | CNRS | IASB | CNRS | IASB |
| Cell Measurement | 3.78e17 (i) 4.96e17 (n) | 3.70e17 (4e15) | - | - |
| Atmos. Spectrum 1 | 6.7e10 (6e9) | 3e10 (1e10) | 4.3e11 (2e10) | 6.9e11 (9e10) |
| Atmos. Spectrum 2 | 2.51e11 (7e9) | 1.7e11 (1e10) | 5.8e11 (2e10) | 8.4e11 (7e10) |

(i) initial value

(n) new value

Table 1 : Algorithm Comparison

2. Instrumental developments

In the course of the year, a Fourier Transform Spectrometer BRUKER 120M has been acquired. This spectrometer, which works in the UV-Visible region as well as in the IR, has been conceived to be moveable. It has two detector compartments allowing simultaneous measurements in two different spectral regions. Its maximum attainable resolving power is 10^6 . Preliminary tests have been carried out on a wide range of detectors and filters in order to determine its optimum characteristics.

3. Measurements of absorption cross sections of atmospheric species

Accurate absorption cross sections are needed to deduce the concentrations of atmospheric constituents when using the absorption spectroscopy technique. Absorption cross sections of SO_2 , NO_2 and CS_2 have been measured at different resolutions. Spectra have been recorded using a Fourier Transform Spectrometer BRUKER IFS120HR at room temperature. Moreover spectra of NO_2 absorption at 250K and 273K have also been obtained. Two resolutions have been used, namely 2 and 16 cm^{-1} , corresponding approximately to the resolutions of 0.02 and 0.1 nm at 300 nm. These resolutions were chosen to provide spectra which could be directly used in atmospheric experiments, as the resolution most commonly used for these applications range from 0.3 nm to 1.5 nm. Future satellite observations like the Global Ozone Monitoring Experiment (GOME) requires even higher resolution (0.02 nm).

The gas (SO_2 , UCAR, stated purity of 99.98%; NO_2 , UCAR, stated purity 99%, CS_2 , courtesy of the Chemistry Laboratory of the ULB) is introduced in a 21.1 cm cell located in the sample compartment of the Fourier Transform Spectrometer; oxygen is added to obtain a total pressure of 1 atm. The cell (Hurtmans et al., 1993) is made of anodised aluminium and has quartz windows. The partial pressure of the analysed gas is measured with a 100 Torr full scale Baratron gauge and the temperature of the gas is monitored inside the cell with a temperature transducer. The latter is characterised by an accuracy of 0.2K in the temperature range used in the present work. The cooling and the stability ($\pm 1\text{K}$) of the temperature inside the cell is achieved via a commercial thermostat/cryostat.

Spectra have been recorded in single sided mode, during the forward movement of the mobile mirror only and a boxcar apodization function has been used. Each spectrum is the average of a number of scans depending in the spectral region being investigated. Blank spectra, i.e. with 1 atm pure oxygen, have been recorded before and after each measurement. A high pressure Xenon source, a Tungsten filament and a quartz Suprasil beamsplitter combined with a Si diode, a UV diode or a GaAsp diode have been used in order to cover the entire spectral region from 10000 to 40000 cm^{-1} . The various combinations are summarised in Table 2, which also reports the experimental conditions.

Absorption cross sections are derived from the experimental data using Beer-Lambert law. The concentration of the gas is obtained from its partial pressure inside the cell. In the case of NO_2 , it is necessary to take into account the presence of its dimer N_2O_4 . Partial pressures of NO_2 and N_2O_4 are calculated using the value of the equilibrium constant K_p taken from Hurtmans et al.(1993). Hurtmans et al. reviewed the values of the equilibrium constant found in the literature and determined an empirical relation for the temperature dependence of the constant. The dependence was expressed by the following fourth degree polynomial expansion

$$\log(K_p) = -22.482 + 0.10469 T - 4.9033 \cdot 10^{-5} T^2 - 3.2255 \cdot 10^{-7} T^3 + 4.2181 \cdot 10^{-10} T^4$$

| Molecule | Resolution cm ⁻¹ | Temperature K | Pressure hPa | Detector | Spectral region cm ⁻¹ |
|-------------------|--------------------------------|------------------|------------------------------|-----------------|-------------------------------------|
| CS ₂ | 16 | 293 | 0.08, 2.08, 14.90 | Si-diode | 25000-35000 |
| SO ₂ | 16 | 296 | 1.96 | GaAsp- diode | 25000-35000 |
| | 16 | 296 | 1.65 | UV- diode | 30000-40000 |
| | 2 | 296 | 1.02 | UV- diode | 30000-40000 |
| NO ₂ * | 16 | 294 | 10.04 | Si-diode | 8000-17000 |
| | 16 | 294 | 5.28 | Si-diode | 13000-22000 |
| | 16 | 294 | 5.12, 10.18, 30.50, 50.50 | Si-diode | 15000-30000 |
| | 16 | 294 | | GaAsp- diode | 25000-35000 |
| | 16 | 294 | 2.0, 5.28, 9.95 | UV- diode | 30000-40000 |
| | 16 | 253 | 10.35, 32.05 | Si-diode | 15000-30000 |
| | 16 | 272 | 30.60 | Si-diode | 10000-25000 |

*The indicated pressure corresponds to the pressure of the mixture NO₂/N₂O₄

Table 2 : Experimental conditions

At 294K, the value of the constant K_p is 104.056 hPa. From spectra taken under different pressure conditions, N₂O₄ absorption cross section has been deduced and then removed from the absorption spectra of NO₂. Contrarily to the measurements of Schneider et al.(1987), which showed that the absorption due to N₂O₄ became negligible below 43000 cm⁻¹, N₂O₄ has been seen to show strong absorption in the entire 20000-45000 cm⁻¹ spectral region. N₂O₄ absorption cross sections at 294K are represented in Figure 1. The NO₂ absorption cross sections, corrected for the presence of its dimer, is plotted in Figure 2 for the entire spectral region. Figure 3 shows the absorption cross sections of SO₂ at 296K and cross sections of CS₂ are represented in Figure 4.

Error on the absorption cross sections have been determined to be of the order of 2% for CS₂, SO₂, and NO₂, and up to 20% for N₂O₄. Comparison with data from the literature shows good agreement (better than 5 %).

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