

GROUND-BASED MEASUREMENTS OF STRATOSPHERIC OCIO, NO₂ AND O₃ AT HARESTUA, NORWAY (60°N, 10°E) DURING SESAME

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ABSTRACT

Within the scope of the Second European Stratospheric Arctic and Mid-latitude Experiment (SESAME), stratospheric OCIO, NO₂ and O₃ were measured by ground-based UV-visible spectroscopy in Harestua, Norway (60°N, 10°E). The measurements were carried out from the middle of January until the end of March 1994 (SESAME phase I) and from the beginning of November 1994 until the end of March 1995 (SESAME phase III). During January-February 1995, the NO₂ and O₃ measurements were complemented by direct Sun observations of the same constituents using a Fourier transform UV-visible spectrometer. During both winter periods, significant OCIO signatures were observed in January and March. As expected, the abundance of OCIO is correlated to the potential vorticity at 475 K, the largest OCIO columns being seen inside the polar vortex. There is a general anti-correlation between OCIO and NO₂, large OCIO contents appearing to be mainly driven by the stratospheric temperature.

1. INTRODUCTION

Ground-based remote sensing measurements of stratospheric species have been extensively used to increase the scientific understanding of stratospheric processes at high and mid-latitudes. Several campaigns have been performed during winter and spring period, in both hemispheres. The European Arctic Stratospheric Experiment (EASOE) co-ordinated by the European Commission (EC) during the winter 1991/1992 has demonstrated the need for such a complementary approach between high quality ground-based observations, aircraft and balloon measurements, combined with satellite data and model calculations.

Despite the international effort and the important results obtained during the Arctic and Antarctic campaigns, several scientific issues mainly related to ozone depletion outside the polar regions remain controversial due to the

complex coupling between chemistry and dynamics, specifically in the northern hemisphere.

For the Second European Stratospheric Arctic and Mid-Latitude Experiment (SESAME), it was decided to expand the ground-based instruments for stratospheric monitoring around 60° N to fill in the geographical gap between the observing sites situated beyond the Arctic circle and the mid-latitude Alpine stations situated around 45° N and contributing to the Network for the Detection of Stratospheric Changes (NDSC), in order to study the connection between these latitudinal ranges. The selected observing sites could be at or near the edge of the polar vortex during winter in order to determine the extent of chemically-induced loss of stratospheric ozone and to investigate transport from high latitude, mainly during late winter-early spring. The observations are based on two main techniques, the Fourier transform spectroscopy in the infrared (FTIR) and the UV-visible differential absorption spectroscopy (UV-Vis). These measurements include total amounts of several reservoir species (FTIR) with ozone, nitrogen dioxide and OCIO (UV-Vis).

In total, ground-based instruments were operated at about 35 sites, mainly in Europe. The purpose of this work is to describe the UV-visible instruments deployed by the Belgian Institute for Space Aeronomy (BISA) and the "Université Libre de Bruxelles" (ULB) during SESAME at Harestua (60° N, 10° E, Norway) and to show some preliminary results. The final results obtained during the winters 1993/94 and 1994/95 need to be further analysed and will be published elsewhere.

2. INSTRUMENT AND DATA ANALYSIS

Most of the measurements presented in this paper were carried out using two grating spectrographs looking at the zenith-scattered sunlight. In addition, some direct Sun measurements were performed between January and March 1995 using a Fourier transform spectrometer operated in the UV-visible range.

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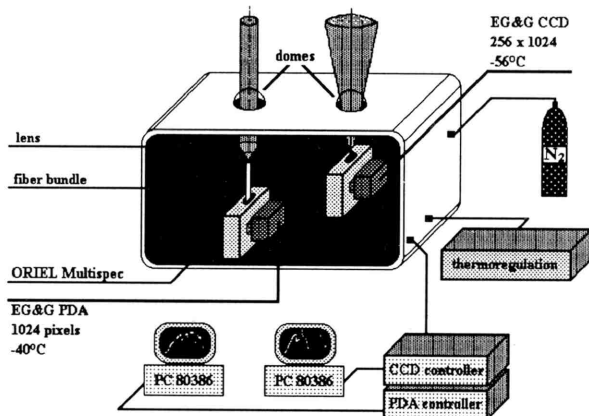


Fig. 1 Schematic description of the BISA ground-based UV-visible instruments.

2.1 Grating spectrometers

The grating instrument is an improved version of the one described in *Van Roozendaal et al. (1994)*. It is based on two spectrometers recording UV and visible spectra of the zenith scattered sunlight, and mounted together in a waterproof protection case (Fig. 1). The UV spectrometer looks directly at the zenith through a hemispherical quartz dome. For the visible spectrometer, a quartz-fibre bundle is used. Its circular cross section is changed to rectangular (2.5 mm times 100 μm) and serves as the entrance slit. The protection case is thermally regulated at 33°C to avoid any deformation of the optics (mirrors, gratings) which would be induced by thermal stress variations. Each spectrometer consists of a grating spectrograph (Oriel MultiSpec) coupled to a cooled detector. The Oriel MultiSpec is a crossed Czerny-Turner system of 12 cm focal length. In order to improve the straylight rejection, special ribs are cast in position to baffle unwanted light paths. This spectrograph offers minimal optical aberrations and an extended flat field allowing the use of large photodiode arrays. The first spectrometer was designed for OCIO and BrO detection. It is equipped with an EG&G CCD detector (256x1024 pixels) cooled at -56°C and covers the UV spectral range from 340 to 395 nm with a resolution of 0.6 nm (FWHM) and a sampling ratio of 10 pixels/FWHM. The second spectrometer, devoted to NO₂ and O₃ measurements, uses an EG&G Reticon photodiode array (1024 pixels) cooled to -40°C. The spectral range extends from 400 to 560 nm (resolution of 0.7 nm and sampling ratio of 6 pixels/FWHM). The whole case is flushed with dry nitrogen in order to avoid condensation of ambient water vapour on the refrigerated parts of the system. Coolers consist of Peltier elements, connected to a primary circuit of methanol cooled down to -20°C. In order to optimise the performances of the system, the spectrometers and

detectors were carefully characterised in the laboratory before being operated in the field, with the aim to identify and quantify possible sources of instrumental artefacts. In particular the following aspects were studied in detail:

- stray-light level in the spectrometer
 - polarisation response of the gratings
 - thermal and mechanical stability
 - inter-pixel variability of the array detectors
 - etaloning effect
 - linearity of the detectors
 - dark current level
 - influence of the sampling ratio on the interpolation noise (*Roscoe et al., 1994*)
 - optimal choice of spectral range and resolution
- A paper on this characterisation work is in preparation.

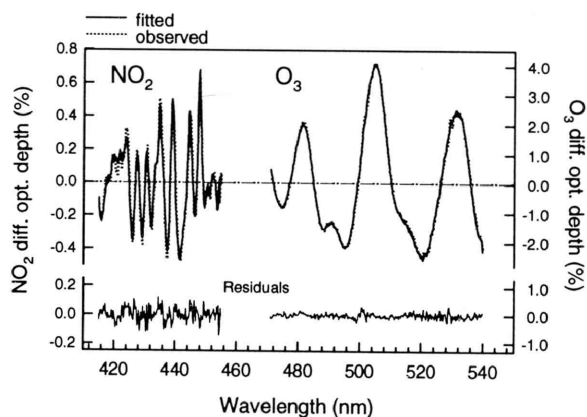


Fig. 2 Typical example of fitted and observed optical depths for NO₂ and O₃ shown together with residuals, as measured with the BISA instrument (91° SZA).

The retrieval of NO₂, O₃ and OCIO column amounts is based on the well known method of differential absorption spectroscopy (see e.g. *Noxon, 1979*). A twilight spectrum, a control spectrum, absorption cross sections of NO₂, O₃, O₄, H₂O and OCIO as well as a pseudo cross section for the Ring effect are fitted together using a coupled linear/non-linear least-squares algorithm written at BISA. Ozone, O₄ and OCIO cross sections are taken from the literature (*Johnston, unpublished results, Greenblatt et al., 1990, Wahner et al., 1987*). NO₂ cross sections are obtained from cell measurements scaled on the recent data of *Merienne et al. (1995)*. For H₂O, a line-by-line calculation of the high resolution absorption spectrum is performed using the HITRAN data base (*Rothman et al., 1992*) assuming realistic H₂O and temperature vertical profiles. The result is subsequently convolved to the actual instrumental resolution. Ring cross sections are obtained empirically from high-pass filtering of the control spectrum. The conversion from slant to vertical columns is accomplished using air-mass factors (AMFs) calculated according to *Solomon et al. (1987)*.

For NO_2 and O_3 retrievals, a single reference spectrum is used. On the contrary, OCIO data are analysed by reference to a control spectrum taken at 82° SZA each twilight. This procedure minimises the instrumental noise that might be introduced by slight mechanical or thermal instabilities. Fig. 2 and Fig. 3 present typical NO_2 , O_3 and OCIO fits. The figures show the fitted and observed differential optical depth of each constituent, after removal of all other absorption signatures. Residual levels displayed on the bottom illustrate the quality of the measurements.

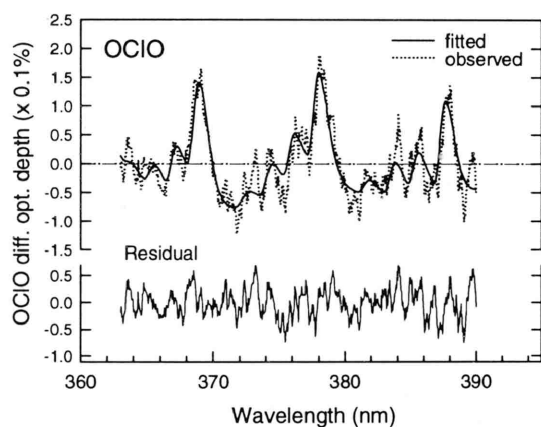


Fig. 3 Same as Fig. 2, but for OCIO

The BISA instrument has been qualified for the NDSC (NO_2 measurements) after participation to the Intercomparison of UV-visible spectrometers for measurements of stratospheric NO_2 for the Network for the Detection of Stratospheric Change held in Lauder during the period May 12-23, 1992 (Hofmann *et al.*, 1995). In addition, it took part to the UV-visible instrument intercomparison organised by the Aberystwyth University at Camborne (Wales) during September 1995 as part of SESAME activities.

2.2 Fourier transform spectrometer

The mobile Fourier Transform Spectrometer (FTS) *BRUKER IFS120M* was operated at the Harestua observatory from 20 January to 3 March 1995. The optical design of the instrument is given in Fig. 4. A Fourier transform spectrometer combines the advantages of a large spectral interval investigated in one scan and a built-in wavenumber calibration. This last advantage is achieved by the presence of a He-Ne laser, which allows the interferogram to be digitised at equal and well-known intervals of retardation. The detector used was a GaP diode, which allowed to record the 20000 to 30000 cm^{-1} spectral region suitable to measure O_3 and NO_2 column amounts. Although interferograms were recorded at various resolutions during the campaign, the results shown here were

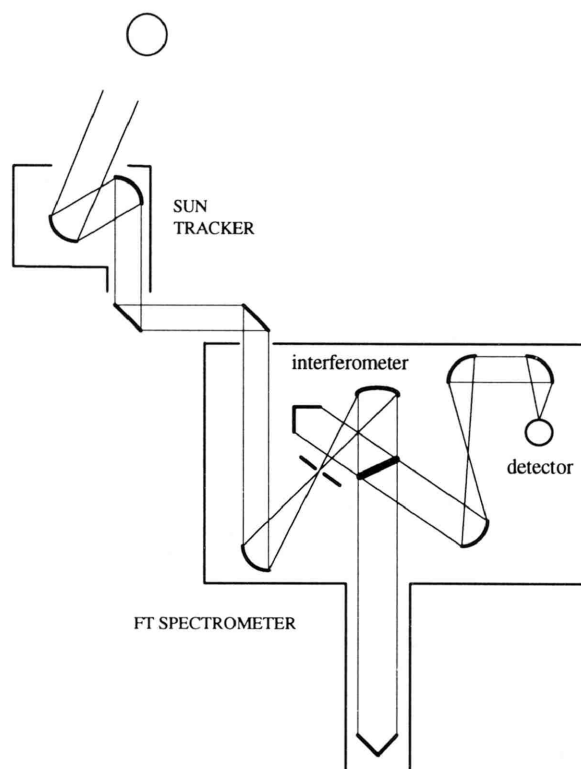


Fig. 4 Schematic description of the Fourier transform spectrometer *BRUKER IFS120M*.

obtained from spectra calculated for a resolution of 64 cm^{-1} (0.6 nm at 300 nm). Two spectral regions were used to derive the O_3 and NO_2 total columns (18400 - 21500 cm^{-1} and 22200 - 23800 cm^{-1}). In each of these regions, O_3 , NO_2 , O_4 and H_2O total amounts were determined. In order to eliminate most of the Fraunhofer structures, the observed spectrum was first divided by a reference spectrum recorded at low solar zenith angle and chosen for minimal absorption by NO_2 and O_3 . However residuals of some strong Fraunhofer lines were found in these ratios whose origin is still unexplained. Empirically, they were fitted using a calculated pressure broadened profile obtained from the line positions, well referenced in the literature. NO_2 absorption cross sections were measured by Carleer *et al.* (1994). The other cross sections as well as the least-squares procedure applied to derive the total columns from the spectra are similar to the one used by the grating instrument. Fig. 5 shows an example of fitted and observed differential optical depths together with residuals for NO_2 and O_3 , as obtained with the analysis programme. Although residuals are still larger than with the grating spectrometers, these first reported FTS measurements of stratospheric species in the UV-visible range are in good agreement with co-located instrument results.

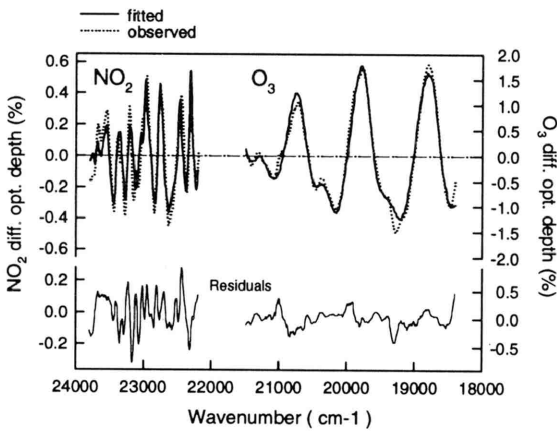


Fig. 5 Example of NO₂ and O₃ fits obtained with the FTS BRUKER IFS120M in direct-sun geometry.

3. RESULTS AND DISCUSSION

Fig. 6 and Fig. 7 show a summary of the observations achieved during SESAME phase I and phase III. Time series of NO₂, OCIO and O₃ column amounts are presented together with 50 hPa temperatures and

potential vorticities (PV) produced by the European Centre for Medium-term Weather Forecast (ECMWF) at the 475 and 550 K isentropic levels. The limits of the vortex at both isentropic levels are indicated by horizontal lines (PV contours at 36 and 102x10⁻⁶ K m²/kg s).

3.1 Stratospheric meteorology

Low stratospheric temperatures were experienced during SESAME phase III as compared to phase I, especially from mid-December until the end of January when the northern hemisphere minimum temperature (NH min) remained close to or below the limit of PSC type II (ICE) formation. Temperature and PV at 475 K and 550 K are anti-correlated, episodes of low temperature at Harestua corresponding to excursions of the polar vortex above the site. Two significant inside-vortex episodes were monitored during phase I and phase III, both years at the end of January and mid-March. PVs at 475 K and 550 K show similar evolution indicating no large vertical distortion of the polar vortex when above or close to Harestua.

3.2 NO₂ and OCIO column amounts

Morning and evening NO₂ amounts are averages of

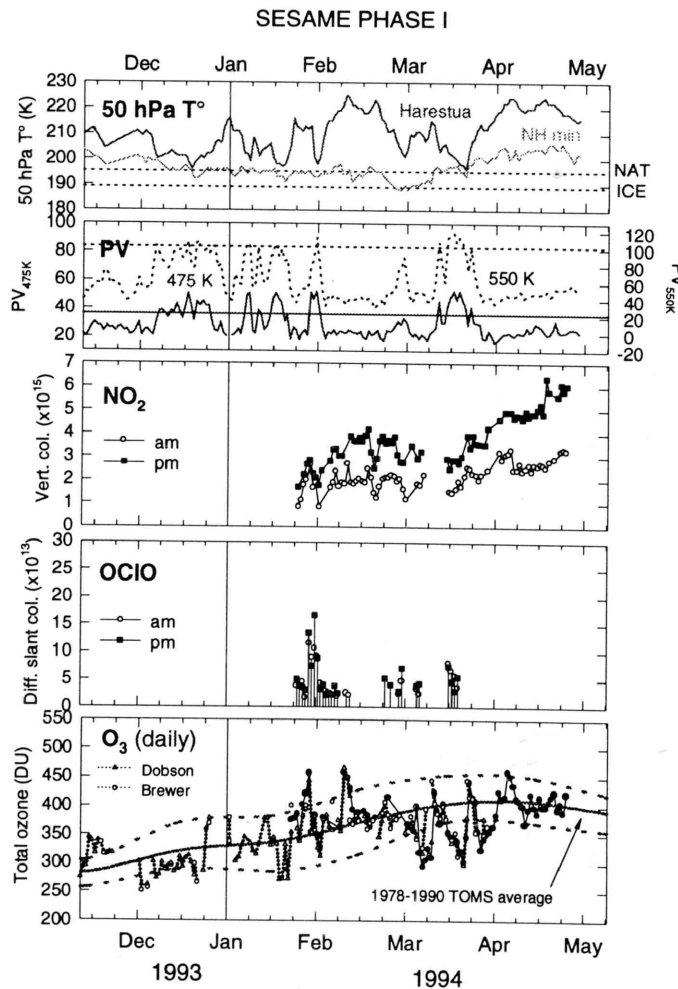


Fig. 6 Time series of NO₂, OCIO and O₃ observations performed at the Harestua station during SESAME phase I, together with stratospheric temperatures and potential vorticities.

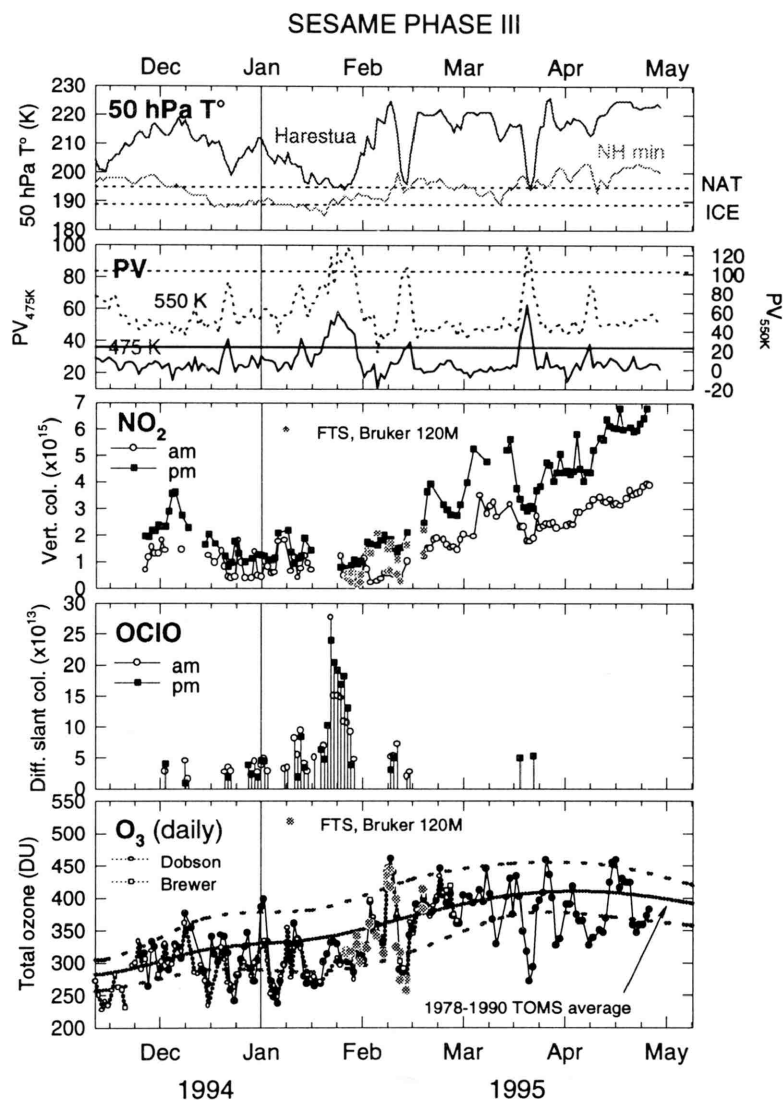


Fig. 7 Same as Fig. 6, but for SESAME phase III.

measurements between 87° and 91° SZA (weighted by the inverse of the error on the individual measurements). In the case of the direct Sun data obtained from January to March 1995 with the FTS instrument (Fig. 7) the average is usually made between 83° and 88° SZA. Despite this zenith-angle difference, the agreement between the direct Sun and zenith-sky results is quite satisfactory. OCIO data are differences in slant column amount between 91° and 82° SZA.

The NO_2 time series shows the well-known seasonal variation primarily due to the change in illumination. In addition, NO_2 column amounts are much lower in January-February 1995 than during the same period in 1994. This is to be related to the occurrence of very cold stratospheric temperatures during this period which are believed to favour NO_x conversion to their reservoirs as well as possible denitrification of the polar stratosphere by condensation of nitric acid on polar stratospheric clouds (PSCs). Corollary, the OCIO contents inside the polar vortex during January 1995 are quite large as compared to January 1994 indicating larger chlorine activation in January 1995. Most OCIO observations are obtained inside or at the edge of the polar vortex which indicates that the

activation is essentially limited to the vortex region. However significant OCIO amounts were detected outside the vortex as well, for example at the beginning of January 1995.

3.3 Ozone column amounts

The ozone column amounts determined from zenith-sky and direct Sun observations (daily averages) are obtained from measurements made between 80° and 85° SZA. In the case of the zenith-sky data, it was decided to restrict the SZA interval at rather small values in order to minimise the uncertainty on the zenith-sky AMF for O_3 which can be rather large at high latitude due to the important variability of the O_3 vertical distribution (Sarkissian *et al.*, 1995). This choice was also justified as giving the best agreement (less than 5 % difference in average) with the Dobson and Brewer O_3 data from Oslo. Fig. 6 and Fig. 7 (bottom) show a comparison of the O_3 time series with the long term (1978-1990) TOMS climatology above Oslo (average of monthly means in solid line, minimum and maximum values in dotted lines). It is interesting to point out that O_3 values were rather low

in March 1994 and 1995 when the polar vortex was moving above Harestua (as compared to the 12-year TOMS climatology). These measurements are consistent with episodes of O₃ chemical destruction inside the polar vortex in March 1994 and 1995, reported from other SESAME observing sites.

4. CONCLUSION

UV-visible measurements of OCIO, NO₂ and O₃ column amount were performed at Harestua, 60° N during SESAME phases I and III. A careful laboratory characterisation as well as the development of a new analysis software made significant improvements of the instrumentation. Its sensitivity for the detection of poorly abundant constituents like OCIO and NO₂ in high latitude winter conditions was increased as compared to the first measurements made during the EASOE campaign. The quality of the spectral data should enable the measurement of BrO whose analysis is presently in progress.

The good agreement of the FTS measurements with the other instrument results demonstrates the feasibility of the stratospheric UV-visible measurements as a new application of the Fourier Transform Spectroscopy. Higher resolution spectra (8 and 0.5 cm⁻¹) were recorded and are still to be investigated. From these spectra, more accurate results for NO₂ and O₃ are expected as well as measurements of additional molecules (possibly OCIO and BrO).

A first comparison of the results obtained during the two SESAME winter periods shows large differences in the NO₂ and OCIO column amounts reflecting large differences in the stratospheric meteorology. Low O₃ column amounts (as compared to the long term climatology derived from TOMS data) are measured in March both during SESAME phase I and phase III.

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