A Concurrent Multi-axis Differential Optical Absorption Spectroscopy System for the Measurement of Nitrogen Dioxide and other Trace Species.

Thesis submitted for the degree of
Doctor of Philosophy
at the University of Leicester

by

Roland Leigh
Department of Physics and Astronomy
University of Leicester

September 2005
Abstract

This thesis describes the development of a novel instrument configured for the measurement of nitrogen dioxide and other trace species in an urban environment. Despite improvements in efficiency in many combustion processes including vehicular engines, the level of nitrogen dioxide in the typical urban environment continues to impact on human health and requires regular monitoring.

The concurrent multi-axis differential optical absorption spectroscopy (CMAX-DOAS) system developed in this work has a temporal resolution of a minute or less, and has the capability to spatially resolve different air masses as they travel over the instrument. Such sampling capabilities are unique to a ground-based scattered-light DOAS system and are very-well suited to analysis of rapidly moving and distinct plumes in an urban environment.

The CMAX-DOAS instrument was built in 2002, and tested and validated during an intercomparison campaign in Norway in 2003. During 2004 concurrent measurements from multiple viewing geometries were made in Leicester (52.6 N, 1.12 W). Measured slant columns of nitrogen dioxide from the CMAX-DOAS instrument have errors calculated at less than 2% for a single axis, and 4 to 6% for analysis using a reference spectrum from another axis. These measurements identified significant boundary layer concentrations (up to 80 µg m⁻³) of nitrogen dioxide which clearly correlate with anthropogenic activity over diurnal, weekly and annual timescales.

Through concurrent measurement of different air masses, considerable information on individual plumes has been obtained, including estimates of source location, plume size and concentration. Such measurements are unique in terms of the information they can provide on nitrogen dioxide emissions on an urban scale and are necessary to determine the link between urban activity, nitrogen dioxide emissions, air quality and ultimately human health.
Journal Publications resulting from this work.


Acknowledgements

This thesis represents many years of effort to produce something tangibly worthwhile in my lifetime and I have many friends family and colleagues to thank for their considerable support in getting me to this point.

Firstly must come Gary Corlett, my indefatigable post-doc who has spent many long days, weeks and months on campaign with me during this PhD, as well as attempting tirelessly to educate me in correct instrumental technique and the (purely theoretical) virtues of a tidy lab. Secondly my supervisor, Paul Monks, who gave me time and space to work independently while providing tremendous support and “encouragement” when I needed it. John Remedios and Udo Frieß also deserve particular mention for their considerable assistance during this project, along with the other members of EOS who have helped to preserve my sanity over the last 4 years.

During this PhD many colleagues in the DOAS community in Europe have provided significant assistance, and particular mention should go to Michel van Roozendael and Caroline Fayt for the considerable time they willingly gave to instruct me in the ways of WinDOAS.

A broad acknowledgement must go out to the University Badminton club, and Carisbrooke Tennis Club for giving me healthy and wholesome distractions from work when needed. Thanks also to Dave (Amos), Helen, Hilke, Dave (Moore), Lisa, Grant, Zoe, Nigel, Louisa and Pete for providing fine drinking partners to keep me sane, both in terms of beer in the evenings, and tea in the day.

Above all thanks must go out to my mother and father, for all their support over the last 30 years, and to whom I dedicate this thesis.
## Contents

1  The Scientific Context ............................................................................................................ 1
   1.1 General Introduction to the atmosphere ................................................................. 2
   1.2 General Atmospheric Composition and Chemistry .................................................. 4
   1.3 Tropospheric ozone and NOx Chemistry ................................................................... 6
       The Leighton relationship or the “photostationary state” ..................................... 12
   1.4 Tropospheric NO2 concentrations and trends .......................................................... 13
   1.5 Stratospheric ozone and NOx chemistry ................................................................. 16
   1.6 Summary ...................................................................................................................... 24

2  The Theory of Concurrent Multi-Axis DOAS .............................................................. 25
   2.1 Introduction .................................................................................................................. 25
       2.1.1 The Beer-Lambert Law ..................................................................................... 26
       2.1.2 Scattering ............................................................................................................ 28
           2.1.2.1 Rayleigh Scattering ....................................................................................... 28
           2.1.2.2 Mie Scattering ................................................................................................ 29
       2.1.3 Fitting Parameters ............................................................................................. 30
           2.1.3.1 Polynomial fitting to eliminate scattering effects ..................................... 30
           2.1.3.2 The instrument line shape (ILS) .................................................................. 30
           2.1.3.3 The Ring effect .............................................................................................. 31
       2.1.4 The Solar I0 effect ............................................................................................... 32
           2.1.4.1 The Trace Species Absorption Cross Sections ......................................... 33
               2.1.4.1.1 Ozone ....................................................................................................... 34
               2.1.4.1.2 NO2 ........................................................................................................... 36
               2.1.4.1.3 O4 ............................................................................................................. 38
               2.1.4.1.4 H2O .......................................................................................................... 39
       2.1.5 The DOAS Fit ....................................................................................................... 40
   2.2 Radiative transfer and the interpretation of Slant Column measurements .......... 44
       2.2.1 The SCIATRAN Radiative Transfer Model ................................................... 45
       2.2.2 Tropospheric and Stratospheric Air Mass Factors .......................................... 46
   2.3 Conclusions .................................................................................................................. 49
3 The CMAX-DOAS Instrument ..................................................................................... 50
3.1 Overview of the Total System ................................................................................ 51
3.2 The Head Unit .......................................................................................................... 51
3.3 The Spectrometer System ........................................................................................ 56
  3.3.1 The F-number matcher ....................................................................................... 56
  3.3.2 The Imaging Spectrometer .................................................................................. 59
  3.3.3 The Spectrometer Gratings ................................................................................ 60
  3.3.4 The Entrance Slit ............................................................................................... 61
  3.3.5 The CCD Detector .............................................................................................. 61
      3.3.5.1 Frame transfer capabilities ........................................................................ 64
      3.3.5.2 Dark Current .............................................................................................. 65
  3.3.6 Instrument Performance and Stability .............................................................. 66
      3.3.6.1 Performance with and without entrance slit ............................................. 67
            3.3.6.1.1 Sensitivity to temperature changes ............................................. 69
  3.4 The PC-based Analysis Environment ...................................................................... 70
  3.4.1 Overall description ............................................................................................ 70
  3.4.2 The Visual Basic™ programming environment .............................................. 70
  3.4.3 The CCD to PC connection .............................................................................. 70
  3.4.4 Extracting spectra from the CCD image ......................................................... 71
      3.4.4.1 Averaging over multiple images .............................................................. 72
      3.4.4.2 Averaging over multiple rows ................................................................... 72
      3.4.4.3 Correcting for Pixel-to-pixel variability ............................................... 73
      3.4.4.4 Removing Dark Current .......................................................................... 75
  3.4.5 The DOAS fit ..................................................................................................... 75
      3.4.5.1 The wavelength Calibration Routine ..................................................... 77
  3.5 Summary .................................................................................................................. 77
4 The NDSC intercomparison campaign in Andøya, Norway (69.3°N, 1.16°E) 80

4.1 Introduction to the campaign .................................................................................... 80
4.2 The format of the intercomparison exercise ........................................................... 81
4.3 Meteorological Conditions during the campaign ................................................... 82
4.4 The participating institutes and instruments ........................................................... 83
4.5 Instrumental setup for the Leicester CMAX-DOAS. .............................................. 85
  4.5.1 Stray light tests ................................................................................................... 86
  4.5.2 Instrument Line Shape ...................................................................................... 87
  4.5.3 CCD performance .............................................................................................. 90
    4.5.3.1 Full-well capacity ........................................................................................ 90
    4.5.3.2 Sensitivity to the Ultra-violet ........................................................................ 90
  4.5.4 Modifications during the campaign ................................................................ 91
4.6 Fitting Parameters used during the campaign ......................................................... 93
4.7 Results .......................................................................................................................... 95
  4.7.1 Concentrations of target species measured during the campaign ............... 95
  4.7.2 Comparison of slant columns from each instrument ..................................... 96
4.8 Conclusions ................................................................................................................ 102

5 Measurements in Leicester During 2004 ................................................................. 104

5.1 Introduction ................................................................................................................ 104
5.2 Instrumental Location .............................................................................................. 104
5.3 Instrumental Alterations from the Andøya Campaign ........................................... 106
5.4 Pre calibration and stabilization .............................................................................. 107
5.5 Error analysis with the Leicester Installation ....................................................... 107
  5.5.1 Instrument Line Shape Errors ......................................................................... 110
5.6 Recording period ....................................................................................................... 114
5.7 Other calibration and measurement stations ....................................................... 114
5.8 Meteorological measurements .............................................................................. 114
5.9 Results .......................................................................................................................... 115
  5.9.1 A Self-Consistency test using two zenith telescopes .................................. 115
  5.9.2 Summary of instrumental error analysis ...................................................... 119
5.10 Example measurements from “Normal” Operation ................................. 120
5.10.1 Measurements of stratospheric ozone .............................................. 123
5.10.2 Tropospheric NO\textsubscript{2} ................................................................. 128
5.10.3 Analysis of 17\textsuperscript{th} January 2004 .......................................... 131
5.11 Conclusions ......................................................................................... 138

6 Analysis of NO\textsubscript{2} events in Leicester .......................................... 140
6.1 Introduction ......................................................................................... 140
6.2 Spatial analysis using 4 Northerly-pointing off-axis views .................... 140
6.2.1 Viewing Geometry Assumptions ....................................................... 143
6.2.2 Plume reconstruction ....................................................................... 145
6.2.3 Source Location and strength estimation ......................................... 150
6.3 Additional Azimuthal Geometries ........................................................ 153
6.4 Conclusions ......................................................................................... 161

7 Conclusions .......................................................................................... 162
7.1 Summary of development and key results .......................................... 162
7.2 Conclusions on instrumental capabilities and limitations ..................... 164
7.3 Future work, and development possibilities ......................................... 166
7.4 Final Conclusions ................................................................................ 171
List of Figures

Figure 1-1 The atmospheric temperature profile defining the boundaries between layer classifications.......................................................... 2
Figure 1-2 General atmospheric circulation driven by convection and Coriolis forces .... 4
Figure 1-3 A selection of trace species demonstrating the relationship between chemical lifetime and spatial scale.......................................................... 5
Figure 1-4 Measurements of NO₂, NO and oxidant including ozone from 25th July 1973 in Pasadena.......................................................... 13
Figure 1-5 Tropospheric NO₂ from the SCIAMACHY instrument on the satellite ENVISAT. .......................................................... 14
Figure 1-6 Estimated UK emissions of NOx .......................................................... 15
Figure 1-7 Zonally averaged rate of ozone formation (molecules cm⁻³ s⁻¹) from the photolysis of O₂ .......................................................... 17
Figure 1-8 The spatial variability of total column (stratosphere plus troposphere) ozone on 1st October 2003 .......................................................... 18
Figure 1-9 Retrieved ozone concentrations from the SCIAMACHY instrument on board ENVISAT. .......................................................... 18
Figure 1-10 Total Column ozone values over Birmingham, UK (52.48N, 1.53W) as measured by the TOMS instrument .......................................................... 19
Figure 1-11 Mixing ratio profiles for principal NOy species determined by balloon-borne FTIR spectroscopy (35 N, sunrise, September) .......................................................... 22
Figure 1-12 Primary NOx reactions in the stratosphere and troposphere .......................................................... 23
Figure 2-1 Illustration of the parameters in the Beer-Lambert Law .......................................................... 26
Figure 2-2 Rayleigh scattering phase function for unpolarised light .......................................................... 29
Figure 2-3 An example of the literature absorption cross section for NO₂ .......................................................... 31
Figure 2-4 Ring spectrum calculated by WinDOAS using the wavelength-dependent instrument line shape measured on 17th January 2004 .......................................................... 32
Figure 2-5 Absorption Cross Section of Ozone from 250 to 800 nm .......................................................... 34
Figure 2-6 Temperature dependence of the ozone cross section in the visible region .......................................................... 35
Figure 2-7 The Influence of the $I_0$ correction on the Ozone cross section in the fitting window from 430 to 510 nm ........................................................................................................... 35
Figure 2-8 The NO$_2$ absorption cross section in the UV/Visible region from 250 to 800 nm. ........................................................................................................................................... 36
Figure 2-9 The temperature dependence of the UV/Visible NO$_2$ absorption cross section ........................................................................................................................................... 37
Figure 2-10 The influence of $I_0$ Correction on the NO$_2$ absorption cross section in the 430 to 510 nm fitting window .................................................................................................................. 37
Figure 2-11 O$_4$ Absorption cross section used in this work .......................................................................................................................... 38
Figure 2-12 Water Vapour Cross section used in this work ............................................................................................................................. 39
Figure 2-13 An Example DOAS Fit from the zenith view on 17th January 2004.......... 42
Figure 2-14 Geometry for single scattering situations with multi-axis DOAS .......... 46
Figure 2-15 NO$_2$ profile used in Air Mass Factor calculations where a 5 ppbv tropospheric concentration was required ........................................................................................................... 47
Figure 2-16 Air Mass Factors for all viewing angles using the profile shown in Figure 2-15......................................................................................................................................................... 48

Figure 3-1 Overview Schematic of the CMAX-DOAS system ...................................................................................................................................................... 51
Figure 3-2 Graphical representation of the head unit including photographs from the instrument's installation in Leicester ........................................................................................................... 52
Figure 3-3 Front View of design of head unit, with attachment for Andøya campaign... 53
Figure 3-4 Side View of the head unit, with additional desiccant holder and space for sheathed fibre-optic cables .......................................................................................................................... 54
Figure 3-5 Alignment of fibre-optic outputs at the end of the multi-track fibre ......... 56
Figure 3-6 F-number matcher used to minimize stray light within the spectrometer, and ensure optimal focus on the CCD chip. .................................................................................................................. 58
Figure 3-7 The MS257 Spectrometer system used in this work ......................... 59
Figure 3-8 Physical configuration of traditional CCD designs (left) and the back-illuminated CCD design (right) .................................................................................................................. 63
Figure 3-9 Quantum Efficiency of typical 48-20 CCD's.. ........................................... 64
Figure 3-10 The relationship between chip temperature and dark current for the 48-20 CCD chip ................................................................. 66
Figure 3-11 Instrument line shape in two-dimensional imaging plane with the slit at 150 μm ................................................................. 68
Figure 3-12 The instrument line shape as measured by the WinDOAS software after the removal of the entrance slit ................................................................. 68
Figure 3-13 Typical image from the CCD showing the five spectra from the different viewing geometries ......................................................... 71
Figure 3-14 Spectra recorded of the Quartz-tungsten radiometric calibration lamp from each fibre plotted with lamp absolute output ........................................ 74
Figure 3-15 Correction factors for 21st November 2003 for all fibres ........................................ 74
Figure 3-16 Slant column densities retrieved from 2 independent sets of zenith sky spectra by the established WinDOAS software, and the Visual Basic™ software. 76
Figure 3-17 Correlation plot of the slant columns retrieved by WinDOAS and the Visual Basic™ software on 9th November 2004 ................................................................. 76
Figure 3-18 Data processing steps for the CMAX-DOAS analysis ........................................ 79

Figure 4-1 Location of the NDSC campaign: Andøya Rocket Range facility at Andenes, Norway .................................................................................. 82
Figure 4-2 Atmospheric Conditions during the Andøya campaign ....................................... 83
Figure 4-3 Location of the Leicester CMAX-DOAS instrument, and its installation configuration on the roof of the building ........................................ 85
Figure 4-4 Instrument line shapes for the instruments participating in the intercomparison plotted with the derived ILS as calculated by the WinDOAS software ....................................................................... 88
Figure 4-5 Resolution of each instrument on the campaign .................................................. 89
Figure 4-6 A comparison of clear-sky zenith spectra taken with the 47-20 CCD and the UV-coated 48-20 Chip .............................................................................. 91
Figure 4-7 Evolution of the concentration of target species during the campaign, plus at the bottom, charts of potential vorticity and temperature ....................................................................... 96
Figure 4-8 Measured Slant columns of NO₂ from each group for 25th Feb (Julian day 55) to 27th Feb (Julian day 57). ........................................................................................................... 97
Figure 5-16 Air Mass Factors for all viewing angles using the profile shown in Figure 2-15, with a tropospheric concentration of 10 ppbv and 5 ppbv.

Figure 5-17 Residual Air Mass Factors for tropospheric columns of 10 ppbv and 5 ppbv when a noon reference spectrum from the zenith view is used.

Figure 5-18 Residual Air Mass Factors for all viewing angles, with the air mass factor for the noon view from each viewing angle subtracted.

Figure 5-19 Residual Air Mass Factors from all angles when a reference spectrum from the zenith view at a given time is used.

Figure 5-20 4 Volume mixing ratios calculated from residual tropospheric slant columns from the 15°, 10° and 5° viewing geometries.

Figure 5-21 Schematic of the assumptions made in tropospheric calculations.

Figure 5-22 Derived boundary layer volume mixing ratios from the CMAX-DOAS measurements, and measured concentrations of NO₂ from the city centre.

Figure 5-23 Derived NO₂ volume mixing ratios from the CMAX-DOAS instrument and a chemiluminescence detector in the city centre for 1st to 22nd August 2004.

Figure 5-24 Derived NO₂ volume mixing ratios from the CMAX-DOAS instrument and a chemiluminescence detector in the city centre for 6th to 12th May 2004.

Figure 5-25 Average concentrations of NO₂ for each day of the week as derived from measurements by the CMAX-DOAS instrument in Leicester during 2004.

Figure 6-1 Measured slant columns for 17th January 2004 for NO₂ and O₄.

Figure 6-2 Expansion of the main two pollution peaks on 17th January 2004.

Figure 6-3 Simplified plume geometry for plume analysis.

Figure 6-4 Scaled schematic of the evolution of the plume which passed over the CMAX-DOAS instrument at 9.37am.

Figure 6-5 Scaled schematic of the evolution of the plume which passed over the CMAX-DOAS instrument at 9.46am.

Figure 6-6 Illustration of the relationship between the eccentricity of an elliptical plume and the path length through that plume.

Figure 6-7 Calculation of positions and concentrations for plume 1 using a Y/X ratio of 0.4 and 0.2.
Figure 6-8 Calculation of positions and concentrations for plume 2 using a Y/X ratio of 0.4 and 0.2

Figure 6-9 Ozone concentration in ppbv as measured by the automated monitoring station operated by Leicester City Council

Figure 6-10 Map of Leicester city centre, showing the location of the CMAX-DOAS instrument and the main train station

Figure 6-11 CCD image when 7 fibres are concurrently imaged with only 50-rows between the centre of each imaged spectrum

Figure 6-12 Wind speed and direction on the 14th November 2004 during the 7-Axis configuration

Figure 6-13 Slant columns of NO\textsubscript{2} from the five northerly-pointing telescopes on 14th November 2004

Figure 6-14 O\textsubscript{4} Slant Columns measured by the zenith and northerly-pointing telescopes on 14th November 2004

Figure 6-15 Slant columns of NO\textsubscript{2} from the three telescopes at 15° elevation, showing the progression of three individual plumes as they are blown from West to East

Figure 6-16 Slant columns of O\textsubscript{4} for the morning of 11th November 2004, showing predominantly clear sky conditions

Figure 6-17 Details of the three plumes of NO\textsubscript{2} shown in Figure 6-15, showing measurements from the 4 available elevation angles

Figure 6-18 O\textsubscript{4} slant columns for the 5 elevation views on 11th November 2004 showing predominantly clear sky conditions

Figure 7-1 Design for individual, adjustable telescope units

Figure 7-2 Possible viewing geometries for monitoring plume progression

Figure 7-3 Possible plume geometries suitable for monitoring broad areas, or tracking plumes as they are blown across the view of the instrument

Figure 7-4 Possible viewing geometry, best suited to tracking plumes being blown over the instrument, or for producing profiles of NO\textsubscript{2}

Figure 7-5 Possible configuration of 2 CMAX-DOAS instruments designed to measure NO\textsubscript{2} over Leicester City Centre
List of Tables

Table 1-1 Typical tropospheric concentrations of major trace species........................................ 7
Table 2-1 Summary of the cross sections used in the DOAS fits in this work......................... 39
Table 3-1 Milestones in the development of the CMAX DOAS instrument.......................... 50
Table 3-2 The technical specifications of the gratings used in this work.............................. 60
Table 3-3 Summary technical specifications of the CMAX-DOAS instrument................... 78
Table 4-1 Summary specifications of the instruments participating in the intercomparison campaign................................................................................................................ 84
Table 4-2 Spectrometer settings during the measurement phase of the campaign............. 92
Table 4-3 Specifications of the fitting parameters for TC1 and TC2................................. 93
Table 4-4 TC0 parameters for each group.............................................................................. 94
Table 4-5 Results of the regression analysis performed on the TC0 data...................... 101
Table 5-1 Summary of calculated error contributions from various aspects of the CMAX-DOAS procedure............................................................................................................. 113
Table 5-2 Summary of the calculated errors on CMAX-DOAS measurements derived from four independent techniques................................................................. 119
Table 5-3 Residual Tropospheric Air Mass Factors calculated for 3 periods on 17th Jan 2004................................................................. 132
Table 6-1 Details of the two pollution peaks shown in Figure 6-2................................. 142
1 The Scientific Context

Introduction

The relatively thin layer of gas known as the atmosphere which surrounds the earth is critical to the survival of virtually all life as the majority of terrestrial life uses the oxygen and carbon dioxide in air for some form of respiration. The atmosphere also plays a critical role in the interaction with potentially harmful solar radiation, modulating surface conditions including temperature in the process. The ability of the atmosphere to fulfil these vital functions varies with the abundance of constituents of relatively low concentration known as “trace” species.

The concentration of trace species varies naturally with solar cycles, and significant natural events such as volcanic eruptions and biomass burning. Anthropogenic (human-induced) influences have been shown to have a significant impact on global trace gas concentrations particularly since the industrial revolution. Some atmospheric trace species which can be in relatively high concentrations in urban environments are directly harmful to human health when inhaled. Accurate measurement and prediction of atmospheric composition is therefore a critical component in the effort to optimise human health and life expectancy.

The Concurrent Multi-Axis Differential Optical Absorption Spectroscopy (CMAX-DOAS) system described in this work provides a new and original technique for the measurement of trace species in the urban and rural environment. This thesis documents the scientific context for such measurements, the theory of the technique used, the technical specifications and innovations of the instrument and the key results obtained.
1.1 General Introduction to the atmosphere

An atmosphere can be defined as: "The gas bound gravitationally to a planet". For the purposes of nomenclature the atmosphere is commonly classified into distinct layers defined at their boundaries by atmospheric temperature inversions.

![Figure 1-1 The atmospheric temperature profile defining the boundaries between layer classifications source: [Wayne, 2000]](image)

Approximately 99% of the Earth’s atmospheric mass lies below the stratopause and approximately 50% is below 5 km. As atmospheric density above the stratosphere is so low, the vast majority of chemistry takes place in the lower two layers. Tropospheric air surrounds much of life on earth and is used by the majority of it for respiration. Understanding of the composition of the troposphere and the mechanisms which may alter the concentrations of constituents is therefore vital to the health of many species.
The temperature inversion between the stratosphere and the troposphere marks the boundary for dynamic vertical mixing. The stratosphere is dominated by circulation at constant altitude, with only occasional vertical mixing. The troposphere however is characterised by strong circulatory patterns both vertically and horizontally, forming the familiar weather systems. The lowermost section of the troposphere is affected by surface features and emissions, and is termed the boundary layer. The boundary layer is therefore characterised by turbulent mixing and distinct air masses influenced by topographic features and emissions from natural and anthropogenic (human-induced) sources.

The large scale motion of the atmosphere is driven predominantly by heating due to solar radiation and the effect of Coriolis forces. Incoming solar radiation causes differential heating of the surface and atmosphere, driving large circulatory patterns. The most influential effect is the heating of the atmosphere above the equator, resulting in warm air rising from the troposphere to the stratosphere. The air then moves away from the equator, cooling as it does, and then sinks back down to the surface nearer the poles. Many other smaller surface features also induce smaller-scale effects. The Coriolis force results from the motion of the atmosphere over a rotating sphere and the requirement for the conservation of angular momentum. For example, a packet of air travelling north from the equator will reduce its distance from the earth’s axis of rotation as it travels away from the equator, and therefore its angular velocity will increase as angular momentum is conserved. This results in the air packet moving east (the direction of rotation) relative to the surface of the earth.

Radiative forcing and the Coriolis effect result in the major circulatory patterns as shown in Figure 1-2.
1.2 General Atmospheric Composition and Chemistry

For a dry atmosphere, 99.965% of atmospheric volume is composed of molecular nitrogen $\text{N}_2$ (78.084%), molecular oxygen $\text{O}_2$ (20.947%), and Argon Ar (0.934%). Although the concentrations of these species do vary very slightly, for most purposes their concentrations may be considered to be constant. Discussions of atmospheric composition from this point onwards will therefore focus on the “trace” species which constitute the remaining 0.035% of the atmosphere.

The relative abundance of trace species in the atmosphere is a complex balance between sources, sinks, dynamical transport and reservoir species. Sources of a specific species may include natural and anthropogenic emissions, and chemical transformations including those initiated by photolysis and lightning. Typical sinks include chemical transformations, wet and dry deposition to the surface. Reservoir species are relatively stable compounds which are formed through reactions involving more reactive, shorter-
lived species. The reservoir species can then be transported long distances before being destroyed, reforming the more reactive species once again. Such reservoir species play a vital role in the transport of reactive compounds in the atmosphere. The spatial distribution of trace species in the atmosphere is a function of their source location, the dynamical motion of the atmosphere, and the chemical lifetime of the species including the effect of reservoir species. A selection of major atmospheric trace species and their spatial distributions is shown in Figure 1-3.

![Figure 1-3 A selection of trace species demonstrating the relationship between chemical lifetime and spatial scale. Source: The academic sciences entering the twenty-first century, National Academic Press, Washington DC, 1998](image)

For the purposes of this work, the majority of the complexities of atmospheric chemistry will be put aside, and focus will be given to the primary processes affecting the species measurable in this study by the CMAX-DOAS technique, namely nitrogen dioxide (NO₂) and ozone (O₃).
Ozone is an allotrope of oxygen, containing 3 bound atoms. It was first discovered in 1840 by Christian Friedrich Schönbein, and was found to be a valuable absorber of UV radiation in the atmosphere by Cornu in 1879 and Hartley in 1881 [Cornu, 1879; Hartley, 1881]. The absorption by ozone of UV radiation below 330 nm is the cause of the warming of the stratosphere and therefore the temperature inversions at the tropopause and stratopause.

Nitrogen dioxide is a reddish-brown gas which has one atom of nitrogen bound to two atoms of oxygen in each molecule. It was discovered in the 1770’s by Joseph Priestly shortly after his discovery of Oxygen in 1770, and NO in 1772. Owing to the rapid and numerous conversion paths between NO and NO$_2$ in the atmosphere the combination of both products, NO$_x$, is often used (NO$_x$ = NO + NO$_2$).

### 1.3 Tropospheric ozone and NO$_x$ Chemistry

Given the sensitivity to highly variable emission and meteorological factors, it is necessary to classify tropospheric air into “clean” tropospheric air in which short-term anthropogenic emissions are not a factor, and polluted “urban” air.

A comprehensive list of trace gases and their typical abundances can be found in [Graedel et al., 1986]. The more concise list in Table 1-1 details the species of particular interest to this study, and their typical concentrations in both clean tropospheric air and highly polluted urban air, as detailed by Seinfeld in 1986.

Concentrations of these trace species vary considerably both temporally and spatially, and are influenced by a huge variety of natural and anthropogenic factors including meteorology, incident solar radiation, surface albedo and vegetation.
Species | Typical Concentration in clean tropospheric air /ppbv | Typical concentration in highly polluted urban air /ppbv
--- | --- | ---
SO₂ | 1-10 | 20-200
CO | 120 | 1,000-10,000
NO | 0.01-0.05 | 50-750
NO₂ | 0.1-0.5 | 50-250
O₃ | 20-80 | 100-500
HNO₃ | 0.02-0.3 | 3-50<sup>a,b</sup>
NH₃ | 1 | 10-25<sup>b</sup>

Table 1-1 Typical tropospheric concentrations of major trace species. Source: [Seinfeld, 1986] except<sup>a</sup> [Hanst et al., 1982]<sup>b</sup> [Tuazon et al., 1981]

Unlike stratospheric ozone, which protects life on earth from potentially harmful radiation, tropospheric ozone has been shown to cause respiratory health problems particularly in asthma sufferers, and is a major constituent of photochemical smog. [Schwartz, 1994; Dokic and Howarth, 1998]. Therefore, tropospheric ozone production and destruction cycles are of particular interest, although for markedly different reasons to stratospheric ozone.

Tropospheric nitrogen dioxide has also been shown to correlate with reported cases of asthma and acute chest illnesses in a considerable volume of medical research literature [Hoek and Brunekreef, 1994; Anderson et al., 1995; Pilotto et al., 1997]. These correlations are often described as weak, with the UK Medical Research Council Institute of Environmental Health [Humfrey et al., 1996] summarising the associations as follows:

- Nitrogen dioxide concentrations are linked with acute chest illness through consistent evidence of association, with uncertainty about the causality.
- Nitrogen dioxide concentrations are also linked with cases of asthma through inconsistent evidence with occasional reports, anecdotes or case studies.
The complexity of the chemical pathways and inter-dependencies between different species in the troposphere is immense. This section covers the fundamental processes governing the concentration of target species, NO₂, ozone and water vapour.

In remote regions, where there are no direct sources of nonmethane hydrocarbons and other anthropogenic emissions, NOx and ozone chemistry is driven by methane, carbon monoxide and the hydroxyl radical.

\[
\begin{align*}
\text{OH} + \text{CO} & \rightarrow \text{CO}_2 + \text{H} \\
\text{H} + \text{O}_2 + \text{M} & \rightarrow \text{HO}_2 + \text{M} \\
\text{HO}_2 + \text{NO} & \rightarrow \text{NO}_2 + \text{OH} \\
\text{NO}_2 + \text{hv} & \rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} & \rightarrow \text{O}_3 + \text{M}
\end{align*}
\]

Net: \[\text{CO} + 2\text{O}_2 + \text{hv} \rightarrow \text{CO}_2 + \text{O}_3\] (1.6)

Where M is a background molecule termed a “reaction chaperone”, necessary to balance the energy states in the reaction.

\[
\begin{align*}
\text{OH} + \text{CH}_4 & \rightarrow \text{CH}_3 + \text{H}_2\text{O} \\
\text{CH}_3 + \text{O}_2 + \text{M} & \rightarrow \text{CH}_2\text{O}_2 + \text{M} \\
\text{CH}_2\text{O}_2 + \text{NO} & \rightarrow \text{CH}_3\text{O} + \text{NO}_2 \\
\text{CH}_2\text{O} + \text{O}_2 & \rightarrow \text{HO}_2 + \text{CH}_2\text{O} \\
\text{HO}_2 + \text{NO} & \rightarrow \text{HO} + \text{NO}_2 \\
2(\text{NO}_2 + \text{hv}) & \rightarrow \text{NO} + \text{O} \\
2(\text{O}_2 + \text{O} + \text{M}) & \rightarrow \text{O}_3 + \text{M}
\end{align*}
\]

Net: \[\text{CH}_4 + 4\text{O}_2 + 2\text{hv} \rightarrow \text{CH}_2\text{O} + \text{H}_2\text{O} + 2\text{O}_3\] (1.14)
Ozone and NO\textsubscript{x} are both lost from the remote troposphere by wet and dry deposition. NO\textsubscript{x} is readily converted into HNO\textsubscript{3}, its primary tropospheric reservoir before (predominantly dry) deposition.

\[ \text{NO}_2 + \text{OH} + \text{M} \rightarrow \text{HNO}_3 + \text{M} \]  

\textit{(1.15)}

In the absence of NO\textsubscript{x}, the CO cycle above can turn into an ozone destruction cycle:

\[ \text{OH} + \text{CO} \rightarrow \text{CO}_2 + \text{H} \]  

\textit{(1.16)}

\[ \text{H} + \text{O}_2 + \text{M} \rightarrow \text{HO}_2 + \text{M} \]  

\textit{(1.17)}

\[ \text{HO}_2 + \text{O}_3 \rightarrow \text{OH} + 2\text{O}_2 \]  

\textit{(1.18)}

\begin{align*}
\text{Net:} & \quad \text{CO} + \text{O}_3 \rightarrow \text{CO}_2 + \text{O}_2 \\
\textit{(1.19)}
\end{align*}

Furthermore, in relatively high H\textsubscript{2}O concentrations, ozone destruction, and the formation of OH occur in the following cycle:

\[ \text{O}_3 + \text{hv} \rightarrow (^{1}\text{D}) + \text{O}_2 \text{ <340nm} \]  

\textit{(1.20)}

\[ \text{O}(^{1}\text{D}) + \text{M} \rightarrow \text{O} + \text{M} \]  

\textit{(1.21)}

\[ \text{O}(^{1}\text{D}) + \text{H}_2\text{O} \rightarrow 2\text{OH} \]  

\textit{(1.22)}

The presence of the sufficient concentrations of water vapour prevents all O(\textit{1D}) atoms being quenched back to the ground state and being recombined into ozone. The most significant source of water vapour in the atmosphere is evaporation and its concentration is therefore a function of temperature, pressure, and hydrology.

Urban NO\textsubscript{x} and ozone chemistry is complicated by the additional influence of Peroxy radicals (RO\textsubscript{2}), nonmethane hydrocarbons (RH) and carbonyl products (R'CHO). With these constituents in much higher concentrations than remote areas, reactions 1.23 to 1.28 become an important ozone production mechanism.
\[
\begin{align*}
OH + RH & \rightarrow R + H_2O \\
R + O_2 + M & \rightarrow RO_2 + M \\
RO_2 + NO & \rightarrow RO + NO_2 \\
RO + O_2 & \rightarrow HO_2 + R'CHO \\
HO_2 + NO & \rightarrow OH + NO_2 \\
2(NO_2 + h\nu & \rightarrow NO + O)
\end{align*}
\]

Where R is any organic molecule.

\[
\text{Net: } 2(O + O_2 + M \rightarrow O_3 + M)
\]

\[\text{Net: } 2(O + O_2 + M \rightarrow O_3 + M)\]

NO\textsubscript{X} in urban environments has very significant surface sources as it is both a primary and secondary product of combustion processes [Miller and Bowman, 1989]. NO is produced in combustion processes from the combination of oxygen atoms with molecular nitrogen in the Zel'dovich mechanism [Zel'dovich, 1946].

\[
\begin{align*}
O + N_2 & \leftrightarrow N + NO \\
N + O_2 & \leftrightarrow O + NO \\
N + OH & \leftrightarrow H + NO
\end{align*}
\]

This mechanism is very highly temperature dependent owing to the high activation energy of the O+N\textsubscript{2} reaction, with a 10,000-fold increase in the rate of reaction as the temperature increases from 1,200 °C to 2,000 °C. [Baulch et al., 1994]

A second process known as the prompt-NO mechanism is also a significant source of NO in fuel-rich combustion sources. [Hayhurst and Vince, 1980; Miller and Bowman, 1989];

\[
\text{CH} + N_2 \rightarrow HCN + N
\]

Both HCN and N then react rapidly with oxidant to form NO.
Enhanced NO concentrations have two significant effects on ozone concentrations. Firstly, the availability of peroxy radicals is reduced through the following reaction:

$$RO_2 + NO \rightarrow RO + NO_2$$  \hspace{1cm} (1.34)

The limited availability of RO\textsubscript{2} places a limit on the production of ozone via reaction 1.34. Ozone concentrations are further reduced through the oxidation of NO by reaction with ozone.

$$NO + O_3 \rightarrow NO_2 + O_2$$  \hspace{1cm} (1.35)

NO\textsubscript{2} can be further oxidized by ozone to produce the nitrate radical, NO\textsubscript{3}. During the day, NO\textsubscript{3} is very rapidly photolysed effectively rendering this a null cycle. During the night the NO\textsubscript{3} can be much longer lived, and serves as a direct sink of NO\textsubscript{2}, as well as activating the N\textsubscript{2}O\textsubscript{5} reservoir through the following reaction.

$$NO_2 + NO_3 + M \rightarrow N_2O_5 + M$$  \hspace{1cm} (1.36)

At night, NO\textsubscript{2}, NO\textsubscript{3} and N\textsubscript{2}O\textsubscript{5} are in dynamic equilibrium in the troposphere. As this work is based on measurements with sunlight, and is therefore presently limited to daytime measurements, no further explanation of NO\textsubscript{3} or nighttime NO\textsubscript{x} chemistry will be given.
The Leighton relationship or the "photostationary state"

In an atmosphere poor in organics the relationship between NO$_2$, NO and ozone is dominated by the following three reactions:

\[ \text{NO}_2 + h\nu(\lambda \leq 420 \text{ nm}) \rightarrow \text{NO} + O(3P) \]  
(1.37)

\[ \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \]  
(1.35)

\[ O(3P) + \text{O}_2 \rightarrow ^m O_3 \]  
(1.38)

The relative concentrations in steady state conditions in which other reactions are neglected can therefore be stated as:

\[ \frac{[\text{O}_3][\text{NO}]}{[\text{NO}_2]} = \frac{k_{1.37}}{k_{1.35}} \]  
(1.39)

or

\[ \frac{[\text{NO}_2]}{[\text{NO}]} = [\text{O}_3] \frac{k_{1.35}}{k_{1.37}} \]  
(1.40)

In other words, the relative concentrations of NO$_2$ and NO are modulated by the concentration of ozone. For this reason, the oxidation of NO to NO$_2$ depletes the supply of tropospheric ozone. When this supply is exhausted, no more NO$_2$ is created through reaction 1.35. While sufficient ozone is available, NO is quickly oxidized, and NO$_2$ is the primary NO$_x$ species.

The relationship between NO$_2$, NO and ozone is nicely demonstrated in a study by Finlayson-Pitts and Pitts in 1977 in Pasadena, California. In this study the concentrations of NO$_2$, NO and ozone were monitored during over a particularly polluted summer day. The results can be seen in Figure 1-4.
Figure 1-4 measurements of NO₂, NO and oxidant including ozone from 25th July 1973 in Pasadena, California showing the rapid conversion of NO to NO₂ in the presence of high oxidant levels (source: [Finlayson-Pitts and Pitts, 1977])

As can be seen in Figure 1-4 the presence of oxidants including ozone after 7am leads to the rapid oxidation of emitted NO to produce NO₂ during this severe episode of photochemical air pollution.

1.4 Tropospheric NO₂ concentrations and trends.

Recent developments in satellite technology and techniques have permitted high resolution retrievals of tropospheric NO₂ from space-borne platforms [Martin et al., 2002; Richter and Burrows, 2002; Beirle et al., 2004]. Figure 1-5 shows tropospheric NO₂ over Europe as measured by the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY). The industrial sources of NO₂ are clearly evident, as is the limited lifetime of the NO₂ in the troposphere as it is destroyed before travelling too far from the source.
Measurements of NO\textsubscript{2} in urban environments in this thesis are all performed in the United Kingdom. In 2000 in the United Kingdom, 49% of total emissions of NO\textsubscript{x} were produced by vehicular transport, with this percentage rising to 68% in urban areas such as London [DEFRA, 2003]. The link between ambient NO\textsubscript{x} concentrations in urban environments and source strengths and locations is therefore of significant importance as public health concerns need to be balanced with the need for combustion processes within major conurbations. Sources of NO\textsubscript{x} in the United Kingdom from 1980 and projected until 2010 are shown in Figure 1-6.
Figure 1-6 Estimated UK emissions of NOx [IPCC, 2001]

The UK National Atmospheric Emissions Inventory (NAEI) of NOx is compiled each year by estimating emission strengths from different sources such as stationary combustion sources and road transport onto a 1 km by 1 km grid. Currently, road transport is the largest source of NOx emitted within the UK [DEFRA, 2003] with most of the NOx emitted as NO but, particularly for large diesel vehicles, more and more NOx is emitted as primary NO2. Estimates of NOx levels across the UK are provided by utilising the emissions inventories within simple empirical dispersion models. In the UK, annual mean concentrations of NOx above the EU requirement level of 40 μg m$^{-3}$ (21 ppbv) were measured at most roadside and kerbside sites in London and at over half the background sites in the year 2000 with similar results observed at roadside and kerbside measurement sites in cities outside London. Outside of cities, dispersion models used to extend the analysis from the sparse measurements to the entire UK show that the limit of 40 μg m$^{-3}$ is still exceeded over 34 - 68 % of the total area [DEFRA, 2003].
Across the UK, and indeed across most of Europe emissions of NO\textsubscript{x} have been declining since 1996, a trend that is predicted to continue towards 2010 and beyond as shown in Figure 1-6 owing to continued improvements in combustion technology. Even though NO\textsubscript{x} emissions are declining, the levels forecast for 2010 show that most cities within the UK will still exceed the EU concentration limit of 40 µg m\textsuperscript{-3} at the time it is enforced [DEFRA, 2003]. In addition, extremely poor air quality days with hourly episodes higher than 200 µg m\textsuperscript{-3} are noted to be increasing [DEFRA, 2003]; such days are classified into two types a) winter episodes caused by poor dispersion of primary NO\textsubscript{x} and secondary NO\textsubscript{2} produced from the unusual reaction of NO with oxygen (O\textsubscript{2}) and b) summer episodes caused by elevated secondary NO\textsubscript{2} concentrations attributed in part to an increase in baseline ozone increasing the oxidising capacity of rural air entering urban areas.

1.5 Stratospheric ozone and NO\textsubscript{x} chemistry.

Ozone's main stratospheric production and destruction cycles were first hypothesised by Sir Sydney Chapman in the 1930's [Chapman, 1930], and are now known as the Chapman cycle:

\[
\begin{align*}
\text{O}_2 + hv &\rightarrow 2\text{O} & (1.41) \\
\text{O} + \text{O}_2 &\xrightarrow{M} \text{O}_3 & (1.36) \\
\text{O} + \text{O}_3 &\rightarrow 2\text{O}_2 & (1.42) \\
\text{O}_3 + hv &\rightarrow \text{O} + \text{O}_2 & (1.43)
\end{align*}
\]

Under steady state conditions the Chapman cycle keeps a constant profile concentration of ozone in the Stratosphere. The Photolytically-driven reaction 1.36 is the primary production mechanism, resulting in a correlation between solar flux and ozone production. Ozone production is highest at the solar equator in the upper stratosphere as shown in Figure 1-7.
Global ozone concentrations show considerably more structure than apparent in Figure 1-7 as the ozone is transported by dynamic motions and destroyed by catalytic cycles. A typical spatial distribution of stratospheric ozone during the annual ozone hole event is shown in Figure 1-8, showing significant large and small-scale features. Two-dimensional atmospheric concentration cross sections of ozone are provided by several satellite platforms including the Scanning Imaging Absorption Spectrometer for Atmospheric Chartography (SCIAMACHY) instrument on board ENVISAT, and a typical example is shown in Figure 1-9. The predominantly stratospheric nature of ozone concentrations is clearly visible, combined with the changing height of the tropopause, which is higher at the equator owing to the convective uplifting described earlier.

Figure 1-7 Zonally averaged rate of ozone formation (molecules cm$^{-3}$ s$^{-1}$) from the photolysis of O$_2$ [Johnston, 1975]}
Total ozone (DU) / Ozone total (UD), 2003/10/04

Figure 1-8 The spatial variability of total column (stratosphere plus troposphere) ozone on 1st October 2003. Source: http://woudc.ec.gc.ca/e/ozone/Curr_map.htm

Figure 1-9 Retrieved ozone concentrations from the SCIAMACHY instrument on board ENVISAT. Data from 13th February 2004, Orbit 10226. Image courtesy of Christian von Savigny, University of Bremen.
The annual solar cycle modulates stratospheric ozone concentration, with a pronounced cycle peaking with maximum solar flux. This is illustrated by ozone measurements from the Total Ozone Mapping Spectrometer (TOMS) over Birmingham from 1996 to 2004 shown in Figure 1-10.

\[ X + O_3 \rightarrow XO + O_2 \]  
\[ XO + O \rightarrow X + O_2 \]  
Net: \[ O + O_3 \rightarrow O_2 + O_2 \]

Where X can be H, OH, NO, Cl or Br.
Catalytic destruction cycles involving Chlorine and Bromine compounds are responsible for the most marked ozone destruction in the Antarctic spring where heterogeneous chemistry on the surface of particles in polar stratospheric clouds cause the "ozone hole" first reported by Farman in 1985 [Farman et al., 1985]. This work will concentrate however on Northern mid-latitude ozone chemistry, where there are no polar stratospheric clouds and catalytic cycles involving NOx and HOx are of greater influence.

The hydroxyl radical, OH, is produced in the stratosphere by the oxidation of H2O, CH4 and H2:

\[
\begin{align*}
H_2O + O(¹D) &\rightarrow 2OH \\
CH_4 + O(¹D) &\rightarrow CH_3 + OH \\
H_2 + O(¹D) &\rightarrow H + OH
\end{align*}
\]

(1.47) (1.48) (1.49)

The primary HOx cycles involved in the destruction of ozone are:

\[
\begin{align*}
OH + O_3 &\rightarrow HO_2 + O_2 \\
HO_2 + O &\rightarrow OH + O_2
\end{align*}
\]

(1.50) (1.51)

\[
\text{Net: } O + O_3 \rightarrow 2O_2
\]

(1.52)

and (predominantly below 30km)

\[
\begin{align*}
OH + O_3 &\rightarrow HO_2 + O_2 \\
HO_2 + O_3 &\rightarrow OH + 2O_2
\end{align*}
\]

(1.53) (1.18)

\[
\text{Net: } 2O_3 \rightarrow 3O_2
\]

(1.54)
The largest source of NOx in the stratosphere is from the oxidation of naturally produced
nitrous oxide, N\textsubscript{2}O. N\textsubscript{2}O is emitted by biological processes in soils, and has a sufficiently
long chemical lifetime to be transported into the stratosphere where it is oxidized to form
NO.

\[
N\textsubscript{2}O + O(\text{I} D) \rightarrow 2NO
\]  

NO then reacts with ozone in the following catalytic cycles to destroy ozone

\[
NO + O_{3} \rightarrow NO_{2} + O_{2} \\
NO_{2} + O \rightarrow NO + O_{2}
\]

\[
\text{Net: } O + O_{3} \rightarrow 2O_{2}
\]

\[
NO + O_{3} \rightarrow NO_{2} + O_{2} \quad (1.35)
\]

\[
NO_{2} + O_{3} \rightarrow NO + 2O_{2} \quad (1.58)
\]

\[
\text{Net: } 2O_{3} \rightarrow 3O_{2} \quad (1.59)
\]

The amount of NOx available in the stratosphere for the destruction of ozone is
moderated not only by the production and destruction cycles already mentioned, but also
by certain reservoir species, such as HNO\textsubscript{3}, ClONO\textsubscript{2}, BrONO\textsubscript{2} and N\textsubscript{2}O\textsubscript{5} which can be
formed through the following reactions:

\[
NO_{2} + OH + M \rightarrow HNO_{3} + M \quad (1.60)
\]

\[
ClO + NO_{2} + M \rightarrow ClONO_{2} + M \quad (1.61)
\]

\[
BrO + NO_{2} + M \rightarrow BrONO_{2} + M \quad (1.62)
\]

\[
NO_{2} + NO_{3} + M \rightarrow N_{2}O_{5} + M \quad (1.63)
\]

HNO\textsubscript{3} is transported from the lower stratosphere to the troposphere, where it is removed
through wet deposition. ClONO\textsubscript{2} and BrONO\textsubscript{2} are both very significant NO\textsubscript{2} reservoirs as

21
far as ozone destruction is concerned, as Br\textsubscript{2}O, ClO and NO\textsubscript{2} are all catalysts in ozone destruction cycles, and therefore the destruction of ClONO\textsubscript{2} or BrONO\textsubscript{2} releases two catalytic molecules rather than just one.

The conversion of NO\textsubscript{2} and NO\textsubscript{3} into N\textsubscript{2}O\textsubscript{5} results in the diurnal cycle of stratospheric NO\textsubscript{2}. The nitrate radical, NO\textsubscript{3} is produced by the oxidation of NO\textsubscript{2}, and is very rapidly photolysed, resulting in very low concentrations during the day. However, at night, sufficient NO\textsubscript{3} is present for a significant reservoir of N\textsubscript{2}O\textsubscript{5} to accumulate. This reservoir is slowly photolysed the following day, back into NO\textsubscript{2}, which increases during the day, and NO\textsubscript{3}, which is rapidly destroyed.

Typical stratospheric concentrations of these NO\textsubscript{y} species are shown in Figure 1-11.

![Figure 1-11 Mixing ratio profiles for principal NO\textsubscript{y} species determined by balloon-borne FTIR spectroscopy (35 N, sunrise, September). Source: [Sen et al., 1998]](image-url)
Measurements of stratospheric composition are not the key focus of this work. However, the CMAX-DOAS system does provide certain information on NO\textsubscript{2} and ozone in the stratosphere which is discussed further in Chapter 5.

A summary of NO\textsubscript{x} Chemistry is shown in Figure 1-12 including its interaction with ozone. Figure 1-12 encapsulates the key chemical pathways discussed in this chapter relating to NO\textsubscript{2}.

![Primary NO\textsubscript{x} reactions in the stratosphere and troposphere.](image-url)

Figure 1-12 Primary NO\textsubscript{x} reactions in the stratosphere and troposphere.
1.6 Summary

Of the multitude of trace species which comprise 0.035% of atmospheric volume, this study will concentrate on NO$_2$ and ozone. Both these species are present in significant quantities in both the stratosphere and troposphere and are produced by both natural and anthropogenic sources. Stratospheric ozone has a very important role in the absorption of radiation below 330 nm. Stratospheric NO$_2$ is involved in significant ozone destruction cycles and reservoir species. Both tropospheric ozone and NO$_2$ have been shown to have harmful effects on human health in significant quantities. Knowledge of the current concentrations of these species, and their medium and long-term trends is crucial to establish implications on human health of changing UV radiation exposure and variable air quality in urban environments.

Modeling NO$_2$ and ozone concentrations in the urban environment is extremely difficult owing to the complexity of the dynamics involved and the strong dependence on source strength and locations. This complexity increases the importance and reliance on measurement, particularly within urban environments. Although significant advances are being made in spatially resolving emission estimates, and in developing more analytical models several key questions remain unanswered owing to limited measurements on the spatial extent of pollutant concentrations.

The concurrent multi-axis differential optical absorption spectroscopy (CMAX-DOAS) instrument developed in this work provides a technique capable of measuring NO$_2$ in the urban environment with sufficient spatial and temporal resolution to link these emissions to specific urban areas, processes and timescales. Results from this study therefore have the potential to develop knowledge of the links between urban emission sources and ambient air quality, and thus assist in future urban emission planning.
2 The Theory of Concurrent Multi-Axis Differential Optical Absorption Spectroscopy

2.1 Introduction

This chapter explains the technique used to measure the concentration of trace species in this work from the principles of molecular absorption, through compensation for instrumental effects, to the calculation of atmospheric concentrations through modelling of radiative transfer through the atmosphere. The absorption principles behind this technique have been known since the 18th century, the adjustments required for differential optical absorption spectroscopy have been refined over the last few decades and continue to be refined with the radiative transfer calculations each year.

The technique of Differential Optical Absorption Spectroscopy [Platt, 1994] uses the unique pattern of absorption of solar radiation by different molecules to measure the amount of each target species. The Beer-Lambert law provides the basis for the technique which is then enhanced by the inclusion of procedures which compensate for atmospheric processes such as Mie and Rayleigh scattering to produce trace gas measurements which include information on spatial variability.
2.1.1 The Beer-Lambert Law

The Beer-Lambert law states that the absorption of radiation by a gas is given by the following relationship (see Figure 2-1):

$$\frac{I_{(\lambda)}}{I_{0(\lambda)}} = e^{-\sigma(\lambda)N\ell}$$

(2.1)

where:

- $I_{0(\lambda)}$ is the incident intensity at a given wavelength, $\lambda$.
- $I_{(\lambda)}$ is the transmitted intensity at a given wavelength, $\lambda$.
- $\sigma(\lambda)$ is the absorption cross section of the given gas at a given wavelength.
- $N$ is the concentration of the gas
- $\ell$ is the path length through the given gas

the exponent $\sigma N \ell$ is equivalent to $\ln \left( \frac{I_{0(\lambda)}}{I_{(\lambda)}} \right)$ and both are referred to as the optical depth, denoted by the symbol $\tau$.

Figure 2-1 Illustration of the parameters in the Beer-Lambert Law, with incoming radiation $I_0$ passing through a concentration of gas $N$, with a cross section $\sigma$ and a path length $\ell$

The Beer-Lambert Law as illustrated in Figure 2-1 is the simplest case scenario using a homogeneous concentration and a single absorber. However, atmospheric DOAS requires the simultaneous retrieval of several trace species concentrations using a variable source
of incoming radiation (the sun) and a system for compensating for various atmospheric extinction processes.

For a cell containing more than one gas, a more complete expression of the Beer-Lambert Law is as follows:

\[
\frac{I(\lambda)}{I_0(\lambda)} = \exp\left(-\sum_i \sigma_i(\lambda) \cdot N_i \cdot l\right) \tag{2.2}
\]

The absorption cross sections (\(\sigma_i\)) are dependent upon wavelength (\(\lambda\)), temperature (\(T\)) and pressure (\(p\)). For clarity the subscripts for pressure and temperature have not been included in the equations. Taking the natural logarithm of both sides gives:

\[
\ln\left(\frac{I(\lambda)}{I_0(\lambda)}\right) = -\sum_i \sigma_i(\lambda) \cdot N_i \cdot l \tag{2.3}
\]

or

\[
\ln\left(\frac{I_0(\lambda)}{I(\lambda)}\right) = \sum_i \sigma_i(\lambda) \cdot N_i \cdot l \tag{2.4}
\]

In atmospheric DOAS, the term \(I_0\) is the intensity of the reference spectrum which takes the shortest path through the atmosphere (often taken at solar noon). The term \(I\) is the intensity of a spectrum taken at any other time, which takes a longer path through the atmosphere, and is therefore subject to increased absorption throughout the extra path length. However, absorption by trace species is not the only influence on solar intensity in the atmosphere. Scattering, absorption and emission processes from air molecules, cloud droplets and aerosols also attenuate incoming radiation. These processes and their effects are covered in detail in this chapter.
2.1.2 Scattering

When a photon interacts with matter, two outcomes are possible. Firstly, the energy of the photon and the matter is unaffected. This is known as an elastic scattering process. The second scenario is the conversion of energy during the interaction, resulting in complete absorption of the photon, or a photon of different energy level being emitted after the collision. This is known as inelastic scattering.

Both elastic and inelastic scattering occur in the atmosphere between photons, air molecules and particles. These scattering processes are known as Rayleigh scattering, Mie scattering, and rotational raman scattering.

2.1.2.1 Rayleigh Scattering

Elastic scattering of photons by air molecules and particles which are small compared with the wavelength of the incident light is known as Rayleigh scattering. The Rayleigh scattering cross section was first given by Lord Rayleigh in 1899 [Rayleigh, 1899]

\[ I = I_0 \frac{8\pi^4 \alpha^2 N}{\lambda^4 R^2} (1 + \cos^2 \theta) \]  \hspace{1cm} (2.5)

where:

- \( R \) is the distance from the scatterer.
- \( N \) is the number of scattering molecules.
- \( \alpha \) is a measurement of the polarisability of air molecules.
- \( \lambda \) is the wavelength of the incident radiation.
- \( \theta \) is the phase angle of scattered radiation.

The most important aspect of the Rayleigh scattering equation is the \( 1/\lambda^4 \) coefficient, which not only is the primary cause for blue sky but more importantly to this work, results in only broad scattering features. Applying the Rayleigh scattering formula in the atmosphere relies on the assumption that \( \text{O}_2 \) and \( \text{N}_2 \) act as ideal dipoles. Advancements on the basic Rayleigh equation for use in atmospheric theory have been published [Penndorf, 1957] and find the \( 1/\lambda^4 \) coefficient to be roughly correct in atmospheric
conditions. The Rayleigh scattering phase function, which describes the probability of an incident photon being scattered in a given direction, is shown in Figure 2-2.

![Figure 2-2 Rayleigh scattering phase function for unpolarised light. The dotted line shows the contribution of light polarised parallel to the scattering plane, while the dot-dashed line shows the contribution from light polarised perpendicular to the scattering plane. Taken from [Hönninger, 2002]](image)

2.1.2.2 Mie Scattering

Elastic and inelastic scattering of photons by particles with diameters larger than about one tenth of the wavelength of the incident light is known as Mie scattering [Mie, 1908]. Like Rayleigh scattering, Mie scattering results in broadband structures. However, the resultant radiation from the scattering event is less strongly dependent on the wavelength of the incident radiation than Rayleigh scattering. The predominance of Mie scattering from larger particles in clouds and haze is the reason these phenomena appear white to the human eye. The phase function for Mie scattering varies with particle size but is always asymmetric with the significant majority of resultant radiation emitted in the direction of the incident radiation. Such phase functions are critical in the radiative transfer calculations used to interpret slant column measurements from DOAS instruments. Equation 2.4 can now be expanded to isolate absorption from trace species of interest, and extinction due to Rayleigh and Mie scattering.

\[
\ln \left( \frac{I_{0}(\lambda)}{I(\lambda)} \right) = \sum_{i} \sigma_{i}(\lambda) \cdot N_{i} \cdot I + \left( \sigma_{\text{Ray}}(\lambda) \cdot N_{\text{air}} \right) + \left( \sigma_{\text{Mie}}(\lambda) \cdot N_{\text{particles}} \right) \cdot I \tag{2.6}
\]
2.1.3 Fitting Parameters

Mie and Rayleigh scattering both result in broadband structure in the measured spectra i.e., there are no extinction effects with structure narrower than 20 nm. This therefore provides the opportunity to distinguish analytically between absorption by trace species with strongly structured absorptions, and spectral features caused by scattering processes. Once narrowband features have been isolated, the DOAS method involves the assignment of each feature to a known atmospheric process, including absorption by target species.

2.1.3.1 Polynomial fitting to eliminate scattering effects

By fitting an appropriate polynomial, the slowly varying broadband structures caused by scattering can be removed. The order of the polynomial depending upon the width of the fitting window, and the width of the widest trace gas absorption feature to be fitted. For example, in a fitting window from 429 nm to 509 nm, the broadest absorption feature is the O₄ peak at 477 nm, which is approximately 20 nm wide. Therefore for an 80 nm window, to isolate structure finer than 20 nm, a third-order polynomial is appropriate.

2.1.3.2 The instrument line shape (ILS)

Narrowband features are influenced by the instrument line shape (ILS) of the spectrometer and detector configuration used in the DOAS hardware. The ILS is defined as the response of the instrument to a monochromatic signal of a given intensity at a given wavelength. The instrument response is spatially dispersed on the detector as a result of the width of the spectrometer entrance slit, and the properties of the diffraction grating, thus registering on several channels (pixels) of the detector. The ILS, which would ideally have a narrow Gaussian distribution, varies over the focal plane of the instrument, and is very sensitive to changes in the alignment of the optical components. Therefore the instrument line shape is measured, as detailed in Chapter 3, and all known atmospheric absorption features are convolved with this measured instrument line shape, so that they accurately represent the signal which this specific instrument will produce. The examples shown in this chapter use the instrument line shape measured on 17th January 2004. An example is shown in Figure 2-3.
Figure 2-3 An example of the literature absorption cross section for NO$_2$ [Vandaele et al., 1998], measured on an instrument with a high spectral resolution, and the spectrum after convolution with the CMAX-DOAS instrument line shape, showing how the NO$_2$ spectrum would look if measured by this instrument

2.1.3.3 The Ring effect

Narrowband structure is introduced into the absorption spectra through in-filling of Fraunhofer structure which is widely accepted to occur because of inelastic rotational raman scattering [Fish and Jones, 1995], otherwise known as the Ring effect [Grainger and Ring, 1962]. The increased rotational raman scattering occurring at high solar zenith angles results in a broadening of Fraunhofer features compared with a spectrum at low solar zenith angles. Therefore any comparison of two spectra recorded at different solar zenith angles will include features caused by this effect.

The most popular method for compensating for the ring effect was proposed by Solomon et al. in 1987 [Solomon et al., 1987]. This technique involves the calculation of a “Ring spectrum”, which contains the narrowband structure introduced by infilling, and fitting
this spectrum with the main DOAS fitting procedure. For analysis of CMAX DOAS spectra a ring spectrum was calculated by the WinDOAS software using the measured instrument line shape. An example ring spectrum used in January 2004 is shown in Figure 2-4.

![Ring Spectrum calculated by WinDOAS using a measured ILS from 17th Jan 2004.](image)

Figure 2-4 Ring spectrum calculated by WinDOAS using the wavelength-dependent instrument line shape measured on 17th January 2004 across a fitting window of 430 nm to 520 nm.

### 2.1.4 The Solar I₀ effect

A correction is required to the fitted cross sections as a result of the use of the highly structured Fraunhofer spectrum as the initial light source, whereas fitted cross sections are measured in the laboratory with light sources with very broad structure. As both spectra involved in the DOAS fit are filtered by the ILS of the instrument prior to the commencement of the DOAS procedure, the complete removal of highly structured Fraunhofer structures is not possible.
If as a simplest case scenario we take the reference spectrum to have no atmospheric absorption, the resulting spectrum can be defined as:

\[ I_r(\lambda) = \int I_o(\lambda) W(\lambda' - \lambda) d\lambda' \]  

Where \( I_r(\lambda) \) is the reference spectrum measured by the DOAS instrument, \( I_o(\lambda') \) is the solar Fraunhofer spectrum and \( W(\lambda' - \lambda) \) is the normalised instrument line shape. The target spectrum with atmospheric absorption features is given as:

\[ I(\lambda) = \int I_o(\lambda') e^{-r(\lambda)} W(\lambda' - \lambda) d\lambda' \]  

Where \( r(\lambda) \) is the optical depth of the atmosphere. The DOAS procedure which aims to remove original Fraunhofer structure, leaving just atmospheric influences, relies on taking the negative log ratio of the target spectrum to the reference spectrum. However, this does not result in the removal of all structure unless either the initial light source \( I_o(\lambda) \) or the absorption features \( r(\lambda) \) are constant. Therefore, the fitted cross sections with fine structure need to be corrected for use with sky-viewing instrument. This is most important in this instance for NO\(_2\), and to a lesser extent, ozone. As the I\(_o\) features are dependent upon the depth of the absorption features from each absorber, an initial estimate of the slant column value is used in the I\(_o\) correction procedure. This initial slant column estimate was set as 5x10\(^{16}\) mol/cm\(^2\) for NO\(_2\) and 1x10\(^{20}\) mol/cm\(^2\) for Ozone.

2.1.4.1 The Trace Species Absorption Cross Sections

The absorption cross section \( \sigma \) seen in Equation 2.1 is the measure of absorption of incident photons at different wavelengths by a particular gaseous species. In the visible region of the spectrum from around 400 nm to 600 nm, the primary absorbers are NO\(_2\), ozone, water vapour, and the oxygen dimer, O\(_4\). The choice of fitting window is dictated by the strength of the absorption features of the target species which should be maximised, and the possibility of interference with other species, which should be
minimised. Where possible, the fitting window should also avoid strong Fraunhofer structures which will lead to strong ring effects in the resulting differential spectrum.

2.1.4.1.1 Ozone

Figure 2-5 Absorption Cross Section of Ozone from 250 to 800 nm.

The ozone absorption structure in the UV/Visible region is split into 4 major bands, as indicated in Figure 2-5. The narrow-band structures of the rising edge of the Chappuis band are used in this thesis. These structures arise from quantum mechanical interferences between two interacting excited electronic states [Orphal, 2003]. Although the temperature dependence of the features is not as strong in the Chappuis band as in the Huggins band there are still significant variations. The temperature-dependent intensity and wavelength shift in the O₃ absorption cross sections in the 400-500nm region is shown in Figure 2-6 [Burrows et al., 1999]. As the primary ozone absorption takes place in the stratosphere, a cross section measured at 223 K was used [Bogumil et al., 2003]
The WinDOAS software [Fayt and Van Roozendael, 2001] was used to calculate the corrected $I_0$ cross section for ozone. The influence of the $I_0$ effect on ozone in the visible region is minimal, as shown in Figure 2-7.

Figure 2-7 The Influence of the $I_0$ correction on the Ozone cross section in the fitting window from 430 to 510 nm. Values plotted are the $I_0$ corrected cross section minus the same uncorrected $O_3$ cross section. The cross section used in this Figure was from [Bogumil et al., 2003] with a concentration of $1 \times 10^{-20}$ mol/cm$^2$. 

Figure 2-6 Temperature dependence of the ozone cross section in the visible region. [Burrows et al., 1999]
2.1.4.1.2 NO$_2$

The absorption cross section of NO$_2$ in the UV/Visible region has both broadband and fine structure, as shown in Figure 2-8. Structures in the visible region above 400 nm are due to B-X and A-X bands, as well as a contribution from the forbidden C-X transition. The highly structured nature of the NO$_2$ absorption cross section from 400 to 500 nm is owing to the density of the energy levels and the strong coupling between the ground and first excited electronic states [Orphal, 2003]. It is this highly structured nature of the cross section that renders NO$_2$ such a strong candidate for DOAS retrievals in the UV and visible regions.

![The NO$_2$ absorption cross section in the UV/Visible region from 250 to 800 nm. [Vandaele et al., 1998]](image)

The temperature dependence of NO$_2$ in the UV/Visible region is significant [Vandaele et al., 1998] with a considerable change in the depth of fine absorption features. The use of the correct temperature cross section is therefore crucial to obtaining accurate slant column densities. As the target of this analysis was urban plumes, a cross section measured at 293 K was used.
The $I_0$ effect is more pronounced in the NO$_2$ cross section than in ozone, with features particularly evident in the 430 to 450 nm region as shown in Figure 2-10.

Figure 2-10 The influence of $I_0$ Correction on the NO$_2$ absorption cross section in the 430 to 510 nm fitting window. Values plotted are the $I_0$ corrected cross section minus the same uncorrected NO$_2$ cross section. The cross section used in this Figure was from [Vandaele et al., 1998] with a concentration of $5 \times 10^{16}$ mol/cm$^2$. 
2.1.4.1.3 $O_4$

$O_4$ is the dimer of $O_2$, and has absorption features in the UV/visible region. $O_4$ is the collisional complex of molecular oxygen, rather than the bound dimer or a van der Waals complex. The concentration of $O_4$ is therefore proportional to the square of the concentration of molecular oxygen, with a resultant dependence on atmospheric pressure [Greenblatt et al., 1990; Van Roozendael et al., 1994]

With a well-defined profile which varies only slowly with changing atmospheric pressure, the $O_4$ absorption measured by DOAS gives information on the photon path length through the atmosphere [Wagner et al., 2004]. Through radiative transfer modelling, the photon path length derived from $O_4$ measurements can provide information on the scattering properties of the atmosphere and thus on aerosols. This concept is explored in more detail later in this chapter. The $O_4$ cross section used in this work [Greenblatt et al., 1990] is shown in Figure 2-11, with significant peaks at 447 and 477 nm.

![Figure 2-11 O₄ Absorption cross section used in this work (Greenblatt et al., 1990).](image)

38
2.1.4.1.4 $\text{H}_2\text{O}$

The final significant absorber in the visible region covered by this instrument is water vapour ($\text{H}_2\text{O}$). The water vapour cross section was taken from the HITRAN database [Rothman et al., 2003] and is shown in Figure 2-12.

![Water Vapour Cross Section](image)

**Figure 2-12 Water Vapour Cross section used in this work. [Rothman et al., 2003]**

A summary of all cross sections used in this work is shown in Table 2-1.

<table>
<thead>
<tr>
<th>Species</th>
<th>Reference</th>
<th>T/K</th>
<th>Convolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ozone</td>
<td>[Bogumil et al., 2003]</td>
<td>223</td>
<td>Wavelength dependent Gaussian with $I_0$ correction ($1 \times 10^{20}$ mol/cm$^2$)</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>[Vandaele et al., 1998]</td>
<td>293</td>
<td>Wavelength dependent Gaussian with $I_0$ correction ($5 \times 10^{16}$ mol/cm$^2$)</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>Hitran Database[Rothman-et al., 2003]</td>
<td></td>
<td>Wavelength dependent Gaussian</td>
</tr>
<tr>
<td>O$_4$</td>
<td>[Greenblatt et al., 1990] (with Burkholder - 0.2nm shift)</td>
<td></td>
<td>Wavelength dependent Gaussian</td>
</tr>
<tr>
<td>Ring</td>
<td>WinDOAS (calculated)</td>
<td></td>
<td>Wavelength dependent Gaussian</td>
</tr>
</tbody>
</table>

Table 2-1 Summary of the cross sections used in the DOAS fits in this work, including temperature dependence, $I_0$ correction and convolution properties where appropriate.
2.1.5 The DOAS Fit

The cross sections for all known absorbers, the polynomial, stray-light correction and ring spectrum are fitted concurrently to the differential spectrum. With zero uncertainty in the wavelength calibration of the cross sections and the differential spectrum, this fitting procedure can be performed rapidly using matrix algorithms. The solution to a linear fit can be calculated directly as follows [Albritton et al., 1976]:

\[ \beta = (X^T X)^{-1} X^T J \]  

(2.9)

where \( J \) is the spectrum to be analysed, comprising of \( n \) pixels, and \( X \) is a matrix of coefficients to be fitted, comprising of \( r+1 \) polynomial arguments and \( m \) reference spectra including cross sections, the ring spectrum and stray light corrections. The covariance matrix is calculated as:

\[ \Sigma = \sigma^2 (X^T X)^{-1} \]  

(2.10)

Where

\[ \sigma^2 = [n-(m+r)]^{-1} [J-X\beta]^T [J-X\beta] \]  

(2.11)

The error on an element of the results matrix, \( \beta \) is given by:

\[ \Delta \beta_j = [\Theta_{jj}]^{1/2} \]  

(2.12)

The WinDOAS software and the Visual Basic™ CMAX-DOAS software use equation 2.12 to calculate error bars on parameters determined with a linear fit.

In many cases it is necessary to incorporate in the DOAS routine a Non-linear least squared (NLLS) fitting technique such as Levenberg-Marquardt [Levenberg, 1944; Marquardt, 1963]. A NLLS fitting routine is an iterative process, in which additional parameters to those being linearly fitted to the differential cross section are adjusted
between each fitting attempt until an optimum solution is found. These additional parameters are necessary in the DOAS procedure to adjust to slight wavelength changes in the recorded spectra and small uncertainties in the wavelength calibrations in the cross sections used. Stutz and Platt calculate that a shift equivalent to $1/20^{th}$ of the width of absorption bands can produce a result that differs by 70% from the true value [Stutz and Platt, 1996]. Therefore, additional steps are required to ensure optimal wavelength calibration for the linear fit. The additional parameters employed in the NLLS routine are termed “shift” and “squeeze”. The shift parameter allows a uniform shift of $x$ pixels across the entire fitting window, while the squeeze procedure allows for slight adjustments of the resolution of the spectrum. Each iteration involves a linear fit and the calculation of a chi-square value as a measure of a success of the fit. The non-linear parameters of shift and squeeze are then adjusted within defined parameters and the next iteration performed. Once the iterative process has settled at an optimum solution, the shift and squeeze parameters are expanded to ensure that the minimum found is not just a local minimum within the solution space, but the global minimum sought. If no better minimum is found within the defined limits, the iterative process is complete, and the results are returned.

This NLLS fit procedure is used within the WinDOAS software, and was incorporated into the Visual Basic code written specifically for the CMAX-DAOS instrument. An example fit from the Visual Basic™ CMAX-DOAS code is shown in Figure 2-13.
Figure 2-13 An Example DOAS Fit from the zenith view on 17th January 2004. The blue line is the measured spectrum, the red line the fitted spectrum. The panels show (in order of decreasing differential optical depth) (a) - O₃, (b) - O₃', (c) - NO₂, (d) - H₂O, (e) – Residual spectrum.
The overall quality of the DOAS retrieval can be estimated from the magnitude of the unassigned signal remaining after the NLLS fitting process (Figure 2-13, panel E). This residual contains random noise, and systematic features resulting from errors in the contributory elements of the DOAS fitting procedure. The relative contributions from each source are investigated in chapter 3. The root mean square (RMS) residual is a calculated from the residual spectrum as follows:

\[
\text{RMS} = \sqrt{\frac{\sum_{i=0}^{n} x_i^2}{n}}
\]  

(2.13)

Where \( n \) is the number of pixels in the spectrum and \( x_i \) is the value of the residual spectrum at a given pixel. The shape of the residual structure contains important information on the source of the unassigned signal which the RMS calculation removes. However, the calculation of a single RMS figure to represent the magnitude of the residual gives a straightforward method for quantifying the quality of the DOAS fit and is used throughout the DOAS community.

The Detection limits of a given DOAS system with a known noise level \( \sigma \), using a fitting window of \( n \) pixels can be approximated as follows [Stutz and Platt, 1996]

\[
\overline{D_{\text{limn}}} \approx \sigma \cdot \frac{6}{\sqrt{n-1}}
\]

(2.14)

This detection limit is defined as the point at which \( \Delta \beta/\beta_j = 0.5 \). This simple approximation for the detection limit was tested by Stutz and Platt using Monte Carlo modelling, and was found to produce results within 10-20% of the modelled answer.
2.2 Radiative transfer and the interpretation of Slant Column measurements.

The retrieved values from the non-linear least-squares DOAS fit give a measure of the increased absorption from a given absorber as the solar zenith and azimuthal angles change and the average photon path length increases. The degree of absorption by a given molecule is dependent upon its integrated concentration along the effective light path through the atmosphere of photons received at the instrument. This light path is in reality an infinite number of different light paths taken by each individual photon. The measure of the trace gas concentration along this effective light path is termed the slant column density, and is defined as:

$$SCD = \int_{0}^{L} N(s) ds$$  \hspace{1cm} (2.15)

where $L$ is the effective photon path length and $s$ is a unit of length along the effective photon path.

The increased absorption measured by the DOAS method is the due to the additional photon path length at any time of day other than solar noon. This measurement is termed the differential slant column density (DSCD) and can be expressed as:

$$DSCD = SCD - SCD_{ref}$$  \hspace{1cm} (2.16)

where:

$SCD$ is the slant column density for the spectrum being analysed.

$SCD_{ref}$ is the path length of the average photon for the reference spectrum

Due to the dependence of the SCD on solar zenith angle, azimuthal angle, wavelength and atmospheric conditions, it is desirable to convert this SCD into a vertical column density (VCD) defined as:

$$VCD = \int_{0}^{\infty} N(z)dz$$  \hspace{1cm} (2.17)
This VCD is therefore a measure of the integrated amount of a given molecule in a vertical direction above the measurement site. In order to derive a VCD from the calculated DSCD, it is necessary to calculate the average path of received photons as they pass through the atmosphere to the instrument. Radiative transfer models such as TRACY [von Friedeburg, 2003] or SCIATRAN [Rozanov et al., 2001] are used for such calculations. Multiple scattering calculations within these models are based on a considerable number of input parameters including viewing geometry, solar zenith angle, azimuthal angle, cloud conditions, surface albedo, trace gas profiles and aerosol concentrations and properties.

The radiative transfer model produces an air mass factor (AMF) as a measure of photon path length for a set of input parameters. The air mass factor is defined as:

\[ AMF(\lambda, \vartheta, \varphi, \phi) = \frac{SCD(\lambda, \vartheta, \varphi, \phi)}{VCD} \]  

(2.18)

2.2.1 The SCIATRAN Radiative Transfer Model

The radiative transfer model SCIATRAN was developed at the Institute of Environmental Physics at the University of Bremen. Version 2.1 of the model was used for the CMAX-DOAS calculations. In this version a full spherical geometry is used with initial estimates for diffuse radiation calculated from a pseudo-spherical approach. This permits accurate radiative transfer calculations for the required viewing geometries, while minimising computational time. Details of this model can be found in Rozanov et al., 2000, 2001 [Rozanov et al., 2000; Rozanov et al., 2001] with validation of the output for use in multi-axis systems available in Wittrock et al., 2000 [Wittrock et al., 2000].
2.2.2 Tropospheric and Stratospheric Air Mass Factors

The concept of Multi-Axis DOAS relies on AMF differences between photons collected by different viewing geometries. The dependence of the AMF on stratospheric and tropospheric concentrations can be approximated by using a single scattering approximation as shown in Figure 2-14 [Honninger et al., 2004].

Figure 2-14 Geometry for single scattering situations with multi-axis DOAS [Honninger et al., 2004]. Panel A represents the situation of a significant stratospheric absorber and panel B the equivalent for a tropospheric concentration of the target gas.

The approximation that the photon is only scattered once through its path through the atmosphere results in a relatively simple air mass factor calculation. The SCD for an absorber with a fraction $a$ of its total vertical column below the scattering altitude is given by the following equation [Honninger et al., 2004]:

$$\text{SCD} = a \cdot \frac{1}{\sin \alpha} + (1 - a) \cdot \frac{1}{\cos \delta} \cdot VCD \ (a \leq 1)$$ (2.19)
Although radiative transfer models negate the need for any computation to be performed using such a simplified AMF calculation, equation 2.19 does highlight the \( \frac{1}{\sin \alpha} \) dependence upon viewing geometry for tropospheric concentrations, and \( \frac{1}{\cos \theta} \) dependence for stratospheric concentrations. The significant differences in sensitivity to tropospheric concentrations from different viewing geometries is the fundamental concept behind multi-axis DOAS. Using the radiative transfer model, SCIATRAN, AMFs for a typical NO\(_2\) profile can be calculated using multiple scattering calculations, and appropriate parameters for surface albedo and aerosols. For example, the NO\(_2\) profile shown in Figure 2-15, with both tropospheric and stratospheric components produces Air Mass Factors shown in Figure 2-16.

![Figure 2-15 NO\(_2\) profile used in Air Mass Factor calculations where a 5 ppbv tropospheric concentration was required.](image)

AMFs for all elevation angles were calculated from 44 to 95° SZA with tropospheric concentrations below 5 km of 5 and 10 ppbv. The resulting AMFs are shown in Figure 2-16. The increasing separation between the elevation angles can be seen as the tropospheric concentration is increased from 5 to 10 ppb.
When spectra from off-axis views are analysed using a reference spectrum from the zenith view at noon, the Air Mass Factors for the resulting differential slant column concentrations are as shown in Figure 2-16.

![Figure 2-16 Air Mass Factors for all viewing angles using the profile shown in Figure 2-15, with a tropospheric concentration of 10 ppbv (solid lines) and 5 ppbv (dashed lines).](image)

The increased separation of the AMFs for different viewing geometries, as the tropospheric concentration is increased from 5 to 10 ppbv, demonstrates the sensitivity of off-axis measurements to tropospheric concentrations. The influence of the stratospheric component of the profile is evident in the increase in AMF from 80 to 95° SZA. The increase in total vertical column amount when the tropospheric concentration is increased to 10 ppbv reduces the influence of the constant stratospheric component, resulting in lower AMF values at high SZAs despite the increased concentrations. Further AMF scenarios and calculations are shown in Chapter 5 as multi-axis measurements are analysed and tropospheric and stratospheric components distinguished.
2.3 Conclusions

The technique of differential optical absorption spectroscopy permits the measurement of trace species through their absorption of incoming solar radiation. Such measurements rely on accurate radiative transfer models to calculate the correct air mass factor for each measurement. Stratospheric and tropospheric concentrations of trace species can be differentiated through the dependence of the absorption on viewing angle and SZA. Stratospheric absorption increases with increasing SZA, while absorption from tropospheric species increases with decreasing view geometry elevation angle.

The dependence of the tropospheric AMF on viewing geometry permits multi-axis DOAS to glean profile information from measurements from different viewing geometries. In an unchanging and horizontally homogeneous atmosphere, the sequential sampling through these viewing geometries would provide sufficient information for profile retrieval. However, in an environment characterised by changing and inhomogeneous concentrations and distinct unmixed air parcels a sequential technique is insufficient. A concurrent system is required to capture maximum possible information on the spatial distribution of trace gases at a given time. The distinct air masses sampled by each viewing geometry in given atmospheric conditions can then be simulated in a radiative transfer model to calculate the variability of trace gas concentrations in the spatial and temporal domains.
3 The CMAX-DOAS instrument

Introduction.

The CMAX-DOAS instrument used in this work is an entirely new instrument built during 2001 and 2002. As with any research project to develop instrumentation, the configuration of the hardware and software went through many alterations over the project timeline. The instrumental configuration described in this chapter is correct for Autumn 2004 and encapsulates the optimum operating mode that the instrument achieved. The instrument was operated in alternative configurations during several field campaigns and details of these early stages will be explored in other chapters and improvements made will be identified. The overall development timetable for the instrument is shown in Table 3-1.

<table>
<thead>
<tr>
<th>Date</th>
<th>Stage of Hardware Development</th>
<th>Stage of Software Development</th>
</tr>
</thead>
<tbody>
<tr>
<td>Feb 2002</td>
<td>Components assembled for first time</td>
<td>None</td>
</tr>
<tr>
<td>July 2002</td>
<td>System first basically operational with open head system and little automation.</td>
<td>Relied on third-party software to operate CCD and perform zenith DOAS fit.</td>
</tr>
<tr>
<td>February 2003</td>
<td>System operational in automated mode. Closed head system used for Andøya campaign.</td>
<td>Leicester software written to operate system and perform DOAS.</td>
</tr>
<tr>
<td>December 2003</td>
<td>System fully automated. All 5 axes working.</td>
<td>Fully automated software saving images, extracting spectra, performing multi-axis DOAS fits and updating to web.</td>
</tr>
</tbody>
</table>

Table 3-1 Milestones in the development of the CMAX DOAS instrument.
3.1 Overview of The Total System

The CMAX-DOAS system comprises of three primary components, namely the head unit, the spectrometer system, and a PC-based analysis environment, as shown schematically in Figure 3-1.

![Figure 3-1 Overview Schematic of the CMAX-DOAS system](image)

3.2 The Head Unit.

The head unit is the photon collection portion of the instrumentation and consists of five telescopes connected to the spectrometer by five fibre-optic cables. Pictures of the actual head unit and a representation of the concept can be seen in Figure 3-2, detailed schematics can be seen in Figures 3-3 and 3-4.
The telescopes comprise of aluminium alloy tubes of 5 cm in diameter with an f/2 plano-convex lens fixed at one end and an SMA type fibre-optic bushel at the focal point of the lens at the other end. These telescopes are securely mounted onto an aluminium frame encased within a weather-proof box. The entrance windows of this box are made from anti-reflection coated glass (Edmund Optics BK7) and are placed 7.5 cm from the plano-convex lenses of the telescopes. The windows are slanted to be parallel to the telescopes, and a black-anodized aluminium alloy tube between the window and the telescope ensures that only light coming through a particular window will arrive at a given telescope. Every piece of aluminium alloy in the head assembly is black anodized to minimize stray light.

Figure 3-2 Graphical representation of the head unit including photographs from the instrument's installation in Leicester.
Figure 3-3 Front View of design of head unit, with attachment for Andoya campaign (Chapter 4)  
(Image courtesy of Barry Towell, University of Leicester)
The nature of the plano-convex lens assembly combined with the anti-reflective entrance windows produces a very constrained viewing geometry. This is desirable to maximize the differentiation between the air-masses sampled by the photons collected in each telescope.
For operation in cold conditions heating pads were installed in the head assembly. These consisted of 6 strips of resistive material which were wrapped around the mounting frame and connected via 10 m cables to a separate 12 V power supply. This avoided problems with ice or snow accumulation on the entrance windows and optics. To avoid condensation on the telescope windows and lenses a container of desiccant was incorporated into the design. This container could be accessed without opening the main headpiece and contained enough silica gel for many weeks of normal operation. This modification reduced the likelihood of liquid water absorption lines appearing in the spectra.

During the NDSC campaign in Andøya the head unit was mounted directly on to a wooden barrier (see Figure 3-3 and section 4.1 for details). In Leicester, the headpiece was mounted on a four-metre extendable pole which was securely fastened at the base. This pole, with an incorporated winch permitted the head piece to be lowered for inspection and maintenance, and then raised again to its full 4m height to ensure unobstructed viewing geometries on all axes.

The final component of the light collection system assembly is the connection to the spectrometer, which comprises of five 200 µm-diameter quartz fibre-optic cables. At one end these are connected to the SMA connectors on the telescopes placing the fibre-optic opening at the focal point of the plano-convex lens. The other ends of the fibres are connected to a commercial 9-way multi-track fused silica fibre optic [Oriel, 2001] which aligns the outputs of all fibres into a vertical array as shown in Figure 3-5.
3.3 The Spectrometer system

The Spectrometer subsystem consists of three primary components. The spectrometer housing including the mirrors remained fixed for the duration of this work. The spectrometer gratings and F/# matcher were both adjusted to optimise spectrometer performance.

3.3.1 The F-number matcher.

In any optical system, the focal properties of the different components need to be matched in order to minimise signal loss and stray light problems. In this system the initial constraining factor on the focal properties was the limited options for fibre optic numerical apertures.
The numerical aperture (NA) of a fibre-optic is defined by Snell’s Law as:

\[
NA = n_0 \cdot \sin a_0 = \sqrt{n_1^2 - n_2^2}
\]  

(3.1)

Where
\[n_0 = \text{refractive index of the surrounding medium}\]
\[n_1 = \text{refractive index of the fibre core}\]
\[n_2 = \text{refractive index of the fibre cladding}\]
\[a_0 = \text{critical angle to the optical axis}\]

The fused silica fibre-optics used in this experiment have a numerical aperture of 0.22. The 5 cm diameter telescope lenses with a 10 cm focal length were designed to completely utilise the 24.8° acceptance cone angle of the fibres.

The F-number (F/#) of an optical component is defined as:

\[
F/\# = \frac{1}{2 \cdot NA}
\]  

(3.2)

The F/# of the fibres was therefore 2.27. However, the MS257 spectrometer system used in this experiment has an f-number of 3.9. In order to maintain sufficient vertical separation in the imaging spectrometer and to get the best results from the entire system these F/#’s need to be converged. This was achieved by the use of an F/# matcher which consists of two mirrors which change the focal length of the fibre exit cone and refocus the cone onto the entrance slit of the spectrometer. This is shown in Figure 3-6.
Figure 3-6 F-number matcher used to minimize stray light within the spectrometer, and ensure optimal focus on the CCD chip [Oriel, 2001].
3.3.2 The imaging spectrometer

The commercial imaging spectrograph used in this work (Oriel MS257i, [Oriel, 2001]) is a Czerny-Turner design with corrected toroidal optics for multi-track spectroscopy. This system provides the wavelength dispersion in the x-axis while maintaining the necessary separation of input signals in the y-axis. The corrected toroidal optics reduce astigmatism in the vertical plane of the resulting image increasing comparability of resulting signals from different locations on the focal plane. The overall layout of the MS257 spectrometer is shown in Figure 3-7. The axial port was used in all experiments to minimize the number of components in the optical path.

Figure 3-7 The MS257 Spectrometer system used in this work [Oriel, 2001]
The spectrometer and F/# matcher produced a combined magnification of the end of the multi-track fibre optic of 3. This resulted in the separation of 400 μm at the end of the fibre-optic translating to a separation of approximately 1.2 mm on the detector.

### 3.3.3 The Spectrometer Gratings.

The MS257 is fitted with an automatic grating turret which holds three separate gratings and allows them to be inter-changed via commands from a PC. The gratings fitted in the Leicester instrument are detailed in Table 3-2. These gratings were chosen to provide sufficient intensity in the UV/Visible range, with bandpass and resolution properties suitable for the retrieval of spectral features of approximately 1 nm FWHM over a window approximately 80 nm wide. Due to the configuration of the detector within the spectrometer, only half of the full bandpass was sampled. Therefore, to achieve a sampled spectrum over 80 nm for analysis of NO$_2$ in the visible, the use of grating 2 (with 600 lines / mm) was necessary, resulting in a resolution of approximately 0.08 nm / pixel.

<table>
<thead>
<tr>
<th>Line Density (l/mm)</th>
<th>Blaze Wavelength (nm)</th>
<th>Type</th>
<th>Peak Efficiency (%)</th>
<th>Reciprocal Dispersion (nm/mm)*</th>
<th>Multichannel Array Bandpass (nm)**</th>
<th>Resultant resolution per pixel of the detector (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>500</td>
<td>Ruled</td>
<td>80</td>
<td>12.8</td>
<td>325</td>
<td>0.16</td>
</tr>
<tr>
<td>600</td>
<td>400</td>
<td>Ruled</td>
<td>85</td>
<td>6.5</td>
<td>165</td>
<td>0.08</td>
</tr>
<tr>
<td>1200</td>
<td>350</td>
<td>Ruled</td>
<td>80</td>
<td>3.2</td>
<td>81</td>
<td>0.04</td>
</tr>
</tbody>
</table>

**Table 3-2 The technical specifications of the gratings used in this work**

- * At Blaze wavelength
- ** Across a 1 inch array, with grating centered at blaze wavelength
3.3.4 The Entrance Slit.

The MS257 spectrometer system is equipped with an adjustable electronic entrance slit. This provides the potential to dynamically adjust the instrument line shape and diffraction characteristics. The slit also gave the potential to reduce the light intensity entering the system, providing a simple means of reducing over-exposure. During early campaigns the slit was used extensively, however before installation at the University of Leicester the slit was opened to its widest setting and left there, effectively removing it from the optical system. This resulted in the multi-track fibre acting as an effective spectrometer entrance slit with a width of 200 μm. With the electronic entrance slit in place the alignment of the fibre-optics with the entrance slit was exceptionally sensitive to even slight movements of the instrument. As this alignment between the F/# matcher and the slit changed, so did the influence of each side of the slit on the instrument line shape at the imaging plane. This sensitivity would result in every small vibration causing considerable changes in instrument response which would not only vary over time, but would also vary between fibres, as the vertical alignment of the multi-track outputs could not be relied upon to be perfectly aligned with the vertical slit to within accuracies of a micron or two. Variability in line shape between fibres is of considerable importance as spectra from each fibre are compared with spectra from the zenith fibre. This results in measurement errors if significant differences exist between instrument line shapes from the different axes as discussed later in this work.

3.3.5 The CCD Detector

The detector used in this system is a Marconi 48-20 back-illuminated, frame-transfer, UV-coated Charge Coupled Device (CCD). This CCD chip has 1033 rows and 1072 columns of pixels each of which is 13 μm wide by 13 μm high giving a total imaging area of approximately 13.4 mm x 13.9 mm.
The basic principle of a CCD is the measurement of charge produced following the absorption of a photon, the excitation of an electron into the conduction band, and the creation of an electron-hole pair. The traditional CCD design is shown in the left panel of Figure 3-8. The incident radiation travels through the polysilicon gates and the silicon dioxide insulators and triggers electron-hole pairs in the very top layer of the Silicon substrate. These electron-hole pairs are then registered by the polysilicon gate. At the end of the designated integration time, the charge registered by each gate (pixel) is read out to a PC or similar device (see Janesick 2001 for full details of this read-out procedure).

One important constraint of the traditional CCD design is the absorbance of wavelengths below 400 nm by the polysilicon gate structures. This results in very poor sensitivity to these wavelengths in traditional designs. This problem can be resolved by the use of a back-illuminated CCD design as illustrated in the right panel of Figure 3-8. In this design the silicon substrate is thinned to approximately 12 μm. The thinning enables the gate to register electron-hole pairs initiated by photons which strike the silicon substrate from the back. This avoids problems with absorption by the gates and, coupled with an anti-reflection coating, significantly increases UV sensitivity.
Traditional CCD Design | Back-illuminated CCD’s

Silicon Dioxide | Polysilicon Gate

Silicon Substrate | Thinned Silicon Substrate

Incoming light | Incoming light

Figure 3-8 Physical configuration of traditional CCD designs (left) and the back-illuminated CCD design (right)

The efficiency of the CCD in producing cascades of electrons for each photon incident on the surface is known as the Quantum Efficiency (or QE). The QE is dependent on wavelength and is different for each detector. The standard QE curve for a 48-20 chip is shown in Figure 3-9. As can be seen from Figure 3-9 the typical response from a back-illuminated CCD drops dramatically below 350 nm without the anti-reflection coating. The effect of this coating can be seen in measurements from the CMAX-DOAS instrument from the Andoya campaign detailed in section 4.5.3.2.
Figure 3-9 Quantum Efficiency of typical 48-20 CCD's. The one used in this experiment was the "Enhanced UV Coated" version which has significant sensitivity below 360 nm (Marconi, 48-20 technical notes).

3.3.5.1 Frame transfer capabilities.

In many spectrometer systems using a CCD as a detector, a shutter is used at the entrance to the spectrometer. This shutter limits the integration time of the CCD, and produces dark conditions while the shutter is closed during which the CCD can be read out. In order to eliminate any moving parts from this design the need for an entrance shutter was removed through the use of the frame transfer capabilities of the CCD.
A frame transfer CCD is capable of rapidly transferring the charge from the imaging pixels to a secondary array, which can then be read out while the next image is forming on the imaging pixels. Such a system removes the need for a mechanical shutter, and increases the number of images which can be taken over a given period, thus improving signal to noise. However, some smearing of the image does occur during transfer, contributing to the asymmetry of the instrument line shape. Errors caused by such smearing are included in the analysis of instrument line shape asymmetry in Chapter 5 which concludes that total line shape asymmetry causes less than 0.5% errors. Therefore the advantages of using a frame transfer device considerably outweigh the errors introduced in the system.

3.3.5.2 Dark Current

Within the CCD structure radiation is emitted due to the thermal energy of the materials involved. Such radiation is inevitable from any substance with a temperature above absolute zero and this causes problems with every CCD as this triggers electron cascades in the silicon substrate and charge build-up in the pixels even when the CCD is in total darkness. For this reason, this charge is termed the “dark current” and varies strongly with the temperature of the CCD chip itself. The CCD is therefore cooled to as low a temperature as practically possible. The CCD was held inside a cryostat which was pumped to pressures of approximately $5 \times 10^{-4}$ mbar. This permitted the CCD to be cooled without ice formation on the chip which damages the chip and causes significant spectral features.

The CCD was attached to a two-stage Peltier cooler which in turn was cooled by an external refrigeration unit which constantly pumped water of approximately 10 °C around the system. The Peltier cooler was powered by a regulated supply which monitored the temperature of the CCD through a platinum resistance thermometer (PRT). In this way the CCD temperature was kept at a constant temperature of -35 °C, being the coldest achievable temperature before ice formation occurred on the surface of the CCD. The relationship between CCD temperature and dark current is shown in Figure 3-10.
3.3.6 Instrument Performance and stability

The established method of sequential multi-axis DOAS [Honninger et al., 2004; Wittrock et al., 2004] benefits from the utilisation of a single optical system for the measurement of all spectra. This results in the effects of instrumental artifacts such as instrument line shape variability and spatial variations in detector sensitivity being obviated by the mechanics of the DOAS technique [Platt, 1994]. The challenge of concurrent MAX-DOAS is to minimise or compensate for such effects as spectra from different optical systems are used in the same analysis. Although the spectrometer and CCD are single units, it is a different part of each mirror, a different part of the grating and different pixels on the CCD which are used for each viewing angle, and therefore they must be considered as different optical systems.
Stray light and dark current corrections are applicable to sequential MAX-DOAS as they have potential temporal variability. The primary additional variables necessary to include in concurrent MAX-DOAS are the variability of sensitivity of the optical systems to each specific wavelength for each fibre input and the variability of the instrumental response across the focal plane. The variability of the instrument sensitivity is a function of grating efficiency, mirror efficiency, obstructions (dirt, dust etc) in the optical path, and above all, sensitivity of individual CCD pixels. The summation of all these effects is termed the specific instrument sensitivity as it is manifested in the response of a given pixel measuring a given wavelength to a specific intensity of input. The specific instrument sensitivity changes the shape of the measured spectrum, which has considerable consequences for a DOAS fit. It is necessary to be able to know to a appropriate level of accuracy, what any given spectrum would have looked like had it been measured using the same optical system as the zenith spectrum. The level of accuracy required is dependent upon the optical depth of the differential structure of the absorber being retrieved. In the case of NO$_2$ in the visible in an urban environment this optical depth is relatively high at approximately 0.02 at 439 nm for a slant column of $1 \times 10^{17}$ mol cm$^{-2}$.

The influence of instrumental artefacts on retrievals using such optical depths is explored in the rest of this chapter and continued in Chapter 5 during the instrumental installation in Leicester.

### 3.3.6.1 Performance with and without entrance slit.

With the entrance slit in place, the instrument alignment was adjusted until the instrument line shape was made as uniform as possible across the focal plane of the CCD detector. Atmospheric spectra were taken through each viewing geometry and the instrument line shape was analysed from these spectra using the WinDOAS software [Fayt and Van Roozendael, 2001]. By restricting the fitting window to a fairly narrow band (435 to 475 nm) the range of full-width half-maximum (FWHM) measured instrument line shape values across all fibres, as approximated by a Gaussian, was measured as 0.78 +/- 0.06 nm. The FWHM along each fibre is plotted in Figure 3-11. This gives a measure of the performance of the imaging spectrometer in the two-dimensional imaging plane.
With the entrance slit removed the instrument line shape was fixed at a fairly broad 1.1 to 1.8 nm as shown in Figure 3-12 and the overall intensity of the signal could not be attenuated by use of the slit. However the advantages gained were the relative insensitivity of the instrument to small changes in alignment and the uniform Gaussian instrument line shape achieved from all axes in the focal plane.

Figure 3-11 Instrument line shape in two-dimensional imaging plane with the slit at 150 μm.

Figure 3-12 The instrument line shape as measured by the WinDOAS software after the removal of the entrance slit.
3.3.6.1.1 Sensitivity to temperature changes.

The system was found to be sensitive to moderate temperature changes (+/- 1 °C) in laboratory conditions, inducing a wavelength shift and minor fluctuations in instrument line shape. In order to reduce these effects the instrument was boxed within a large metal flight case filled with foam. This reduced air circulation around the system. In order to minimize temperature gradients within the box all power to the spectrometer was turned off for normal operation. This removed the heat source of the spectrometer electronics. The remaining source of temperature variability inside the flight container was the CCD housing which was constantly well below lab temperature (5 °C approximately) due to the water cooling of the Peltier coolers. This constant source was deemed unavoidable with the current system and remained in place throughout the instrument developmental lifecycle. It was not considered to be a significant source of temperature gradient once the instrument had temperature stabilized and the heat source of the spectrometer electronics had been removed.

With the spectrometer encased within the insulated flight container, and the CCD operating under normal conditions, the temperature of the spectrometer was monitored over a 3 day period within the normal operating conditions in the air-conditioned optics lab at the University of Leicester. The temperature of the spectrometer was found to be stable at 19 °C +/- 0.2 °C which minimized variability in optical properties of the spectrometer and other optical components. The wavelength calibration over this time was found to be stable to within 1 pixel, or 0.08 nm.

The errors caused by the operating conditions and the limits of the optical properties of the spectrometer and detector system were calculated and detailed in chapter 5 for operation at the University of Leicester.
3.4 The PC-based analysis Environment.

3.4.1 Overall description

The spectrometer, temperature probes and the electronics for the 48-20 CCD chip were controlled by a window-based Personal computer (PC). The PC was used to monitor lab conditions, change spectrometer settings, acquire data from the CCD and store and analyse this data. The programming language used was Microsoft Visual Basic™ (version 6.0) with several separate dynamic link libraries (DLL's) included in the code where third-party software was incorporated.

3.4.2 The Visual Basic™ programming environment.

Visual Basic™ was chosen as the programming language for this project as it enabled very rapid application development with a flexible yet powerful interface capability with attached hardware. The processing speed was not as fast and certain mathematical procedures required more lines of code and more time than other packages available (eg. Fortran, IDL). However, Visual Basic™ was selected as offering the most complete solution.

3.4.3 The CCD to PC connection.

The CCD electronics were developed at the University of Leicester and incorporated into this project. The camera head which housed the CCD and associated vital components was connected to a control box by a high-speed data link. This control box was in turn connected to the PC via a USB cable and a high-speed data cable.

The USB cable was used to send commands to the CCD control box, which in turn retrieved data from the CCD and fed the data back to the PC via the high-speed data cable. This control box gave the flexibility to alter integration times, and readout patterns (number of rows, columns etc) from within the VB programming environment.
3.4.4 Extracting spectra from the CCD image.

An Example CCD image returned from the control box is shown in Figure 3-13. The spectra are dispersed over the horizontal direction with the fibres separated vertically, with the zenith fibre at the top, followed by the 15, 10, 5, and 0 degree elevation angles. The whole image is 550 rows high by 1052 pixels wide. The CCD electronics permitted a zone of the CCD to be specified and read without reading out the whole chip. As such read-outs were achieved more quickly by specifying the 550 rows required of the 1033 total available. Read-out times were reduced by almost half through this technique. The same option was available to reduce the number of columns read, however it was decided to keep as much spectral information as possible. Therefore 20 columns were discarded from the left edge of the CCD which were dominated by random noise, but the other 1052 columns of the total 1072 were retained and saved by the PC.

Figure 3-13 Typical image from the CCD showing the five spectra from the different viewing geometries.
3.4.4.1 Averaging over multiple images
In order to reduce the noise on each spectrum it was necessary to average over multiple images. This required the determination of a certain period of time, the saving of all CCD data over that period, and the averaging of values from all saved images to produce a final less noisy product which represented the average spectral value over that period. The choice of period determined the temporal resolution of the instrument and therefore it was desirable to have as short a period as possible. However, with a root-n reduction in noise available, it was valuable to average as many images averaged over a period as possible. A further consideration was the rate at which concentrations were likely to change, and therefore the temporal resolution required to capture detailed atmospheric conditions. For example, with the instrument installed at the University of Leicester to measure NO$_2$ there was potential to cope with fairly noisy spectra due to the strength of the absorber in question, while at the same time the NO$_2$ concentrations were likely to be subject to rapid changes with highly variable local sources from traffic levels and industry. Therefore the temporal resolution was set at 1 minute, which at midday with the shortest integration times resulted in about 20 images being included in each averaged dataset, with an improvement in signal to noise of approximately 4.5.

3.4.4.2 Averaging over multiple rows.
Further signal to noise improvements were achieved through the averaging of several rows of the CCD to create each spectrum. The resolution of the imaging spectrometer in terms of the vertical dispersion of inputs and the overall magnification of the system determine over how many rows each fibre is imaged. In this system the spectral images covered approximately 30 rows. Therefore all 30 rows were averaged to produce the spectrum for that fibre. Although the best signal to noise is achieved at the centre row of this 30-row segment, the first and last rows still contribute significant although much smaller amounts to the signal strength, while the noise remains randomly distributed, resulting in an improved total signal to noise of the averaged figure.
3.4.4.3 Correcting for Pixel-to-pixel variability.

Specific instrument sensitivities are measured using a stabilised Quartz-Tungsten-Halogen lamp which is applied to each input fibre in turn. Spectra are recorded on each fibre using exactly the same retrieval mechanism applied during normal measurement operation. A correction factor (R) is then calculated for each pixel as follows:

\[ R_{(\alpha,\eta)} = \frac{I_{(\text{zen},\eta)}^c}{I_{(\alpha,\eta)}^c} \]  \hspace{1cm} (3.3)

where, \( I_{(\text{zen},\eta)}^c \) is the intensity of the zenith spectrum at that pixel and \( I_{(\alpha,\eta)}^c \) is the intensity of the off-axis spectrum at that pixel.

An example set of spectra and resultant correction factors are shown in Figures 3.13 and 3.14. In this case small features are clear in fibres 1 and 3 around pixel 840, and a strong broad feature is evident in the fibre 3 reading around pixel 500. These features are almost certainly due to artifacts on the surface of the CCD.

These correction factors are applied to their relevant pixels in each set of off-axis spectra to produce spectra which are more directly comparable to those recorded by the zenith optical system. These correction factors are measured regularly and are stable under normal static operation but highly variable if the system alignment is altered.
Figure 3-14 Spectra recorded of the Quartz-tungsten radiometric calibration lamp from each fibre plotted with lamp absolute output as provided by the manufacturer (Ocean Optics).

Figure 3-15 Correction factors for 21st November 2003 for all fibres.
3.4.4.4 Removing Dark Current.

The dark current, as explained in section 3.3.5.2, introduces additional noise to the CCD image. The Dark Current noise is generally a broad-band feature which reflects the temperature of different sections of the CCD chip. As such, the dark current needed to be measured frequently to guard against changes in CCD temperature, and as close to the fibre images as possible to capture the spatial dark current characteristics. To this end, spectra were taken from the 50th row either side of the central spectral peak. These spectra were sufficiently far from the central peak to contain negligible spectral information from the fibres, and yet the average of the two dark current spectra either side of a fibre image gave a good approximation of the background dark current level for that section of the chip. The relative intensities of the spectra and the areas between the imaged spectra can be seen in Figure 5-2, demonstrating the very low intensities between spectra. These averaged dark current spectra were then subtracted from the retrieved spectrum for each fibre to achieve a final set of spectra which were saved to disk.

3.4.5 The DOAS fit

The mechanics of the DOAS fitting routine have already been discussed in chapter 2. A new DOAS fitting routine was written in Visual Basic™ for this project. This was necessary to allow total flexibility for the corrections described above, and to permit multi-axis analysis to be performed in all the configurations required. In the early stages of development this project relied heavily upon the WinDOAS software [Fayt and Van Roozendael, 2001] written and supplied by IASB in Brussels. As the project progressed many of these functions were incorporated into the Visual Basic™ code. A comparison of the Visual Basic™ retrieval function, and WinDOAS was performed on 9th November 2004 using 2 concurrent sets of zenith data (further details of these data can be found in section 5.9.1). Both sets of zenith spectra were analysed using the WinDOAS software, and the Visual Basic™ code with results shown in Figures 3-16 and 3-17. Although some differences do exist between the retrieved slant column densities, these are acceptable within the error bars of DOAS retrievals and the Visual Basic™ code was used for the majority of the DOAS retrievals in this work.
Figure 3-16 Slant column densities retrieved from 2 independent sets of zenith sky spectra by the established WinDOAS software, and the Visual Basic™ software written for this project.

\[ y = 1.0056x + 0.0428 \]

\[ R^2 = 0.9993 \]

\[ y = 0.9956x + 0.065! \]

\[ R^2 = 0.9991 \]

Figure 3-17 Correlation plot of the slant columns retrieved by WinDOAS and the Visual Basic™ software on 9th November 2004.
3.4.5.1 The wavelength Calibration Routine.

The overall detailed wavelength calibration was performed by the WinDOAS software which performs a shift and squeeze calibration using multiple sub-windows [Fayt and Van Roozendael, 2001].

The stability of the wavelength calibration was found to be accurate to within 0.08 nm over the period of a week. Off-axis spectra were often shifted but never significantly stretched or otherwise distorted from the calibration of the zenith spectrum. Therefore off-axis shift calculations were performed by the retrieval software to maximize comparability of spectra from all axes.

3.5 Summary

The CMAX-DOAS instrument used in this work was built specifically for this project during 2001 and 2002 with ongoing enhancements and alterations being undertaken into 2004. The fundamental technical specifications are detailed in Table 3-3. The ability to concurrently record spectra from multiple axes necessitated a custom-built head unit, a carefully-aligned imaging spectrometer and well-characterised two-dimensional detector with enhanced sensitivity below 450 nm. The spectrometer and detector were aligned and stabilized, and subsequently sealed to minimize thermal variability. The potential sources of error from the optical properties of each component of the system are calculated in chapter 5 during operation in Leicester.

Data processing steps were performed by bespoke Visual Basic™ code, and the WinDOAS software. The data processing steps and the software used in each stage are shown in Figure 3-18.
<table>
<thead>
<tr>
<th>Component</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Telescope Diameter</td>
<td>5 cm</td>
</tr>
<tr>
<td>Telescope Focal length</td>
<td>10 cm</td>
</tr>
<tr>
<td>Fibre-optic length</td>
<td>10 m</td>
</tr>
<tr>
<td>Fibre-optic f-number</td>
<td>2</td>
</tr>
<tr>
<td>Fibre-optic diameter</td>
<td>200 μm</td>
</tr>
<tr>
<td>Spectrometer</td>
<td>Oriel MS257</td>
</tr>
<tr>
<td>Spectrometer Focal length</td>
<td>25 cm</td>
</tr>
<tr>
<td>Spectrometer Mirrors</td>
<td>2 x Toroidal</td>
</tr>
<tr>
<td>Spectrometer f-number</td>
<td>3.9</td>
</tr>
<tr>
<td>Spectrometer Entrance Slit</td>
<td>150 μm – or removed completely.</td>
</tr>
<tr>
<td>CCD Description</td>
<td>Marconi 48-20, Back-illuminated, Frame Transfer, UV-Coated</td>
</tr>
<tr>
<td>CCD dimensions</td>
<td>1072 Columns x 1033 Rows</td>
</tr>
<tr>
<td>CCD imaging area used</td>
<td>1052 Columns x 550 Rows</td>
</tr>
<tr>
<td>CCD integration time</td>
<td>Variable, 0.1 seconds to 60 seconds</td>
</tr>
<tr>
<td>Grating line density</td>
<td>600 lines/mm</td>
</tr>
<tr>
<td>Grating Blaze Wavelength</td>
<td>400 nm</td>
</tr>
<tr>
<td>Wavelength range recorded</td>
<td>428 nm to 510 nm</td>
</tr>
<tr>
<td>Fitting Window Used</td>
<td>431 nm to 508 nm</td>
</tr>
<tr>
<td>Spectral Sampling</td>
<td>0.078 nm per pixel</td>
</tr>
<tr>
<td>Instrument line shape</td>
<td>Gaussian, variable from 1.05 nm to 1.2 nm.</td>
</tr>
<tr>
<td>Wavelength calibration</td>
<td>Kurucz Solar Spectrum</td>
</tr>
<tr>
<td>Wavelength accuracy</td>
<td>&lt;0.04 nm</td>
</tr>
<tr>
<td>Temperature Stability</td>
<td>19 °C +/- 0.2 °C</td>
</tr>
</tbody>
</table>

Table 3-3 Summary technical specifications of the CMAX-DOAS instrument.
Figure 3-18 Data processing steps for the CMAX-DOAS analysis.
4 The NDSC intercomparison campaign in Andøya, Norway (69.3 °N, 1.16 °E)

An intercomparison campaign of ground-based zenith-sky viewing UV-visible spectrometers was held at the Andøya Rocket Range (69.3 °N, 1.16 °E) at Andenes, Norway from 12th February to 8th March 2003. This campaign was within the framework of the Network for the Detection of Stratospheric Change (NDSC) and was the primary test ground for the CMAX-DOAS instrument. Eight groups from institutes in England, Germany, Norway, New Zealand, France and Spain participated in the campaign which aimed to assess the capabilities of zenith-sky viewing DOAS spectrometers and quantify the quality and the consistency of data distributed through the NDSC.

4.1 Introduction to the campaign

The Network for the Detection of Stratospheric Change (NDSC) was formed in 1986 and formally started in 1991. The network provides a global ground-based network making uniformly accurate measurements of stratospheric composition and structure for the earliest detection of stratospheric change, as well as providing a long term reference data set for sometimes relatively short-term satellite data sets. Central to maintaining measurements of the highest uniformity and quality throughout the NDSC is the use of instrument and analysis intercomparisons. The first UV-Visible spectrometer intercomparison, for the measurements of stratospheric NO$_2$, was held in May 1992 at the NDSC southern hemisphere mid-latitude primary site at Lauder (45 °S, 170 °E) in New Zealand \cite{Hofmann et al., 1995}. The second NDSC UV-Visible spectrometer intercomparison, for the measurement of stratospheric NO$_2$ and O$_3$ was held in June 1996 at the Observatoire Haute Provence (44 °N, 6 °E) in France \cite{Aliwell et al., 2002; Roscoe et al., 1990}.
The Leicester CMAX-DOAS instrument participated in the third NDSC intercomparison campaign of ground-based UV-visible instruments which was held at high latitude, at the Andøya Rocket Range facility at Andenes, Norway (69 °N, 16 °E) in the winter from 12th February to 8th March 2003 when polar vortex conditions are likely above this location [Vandaele et al., 2005].

4.2 The format of the intercomparison exercise

The intercomparison exercise is termed “blind” and coordinated by a campaign referee, A.C. Vandaele, from the Université Libre de Bruxelles. During the campaign daily slant column data were submitted by each group the following morning at 10 am. These data were reviewed at 5 pm the same day, using graphics which illustrated the general agreement of all data sets, without giving precise data values or the institutes of origin for each dataset. This format permitted a degree of blindness and independence to the datasets from each institute, while also making it possible to identify major problems with specific datasets at an early point in the campaign, so that improvements could be implemented, and procedures and data quality improved. Final consolidated datasets were also submitted by each institute within 2 months of the end of the campaign. These datasets were indicative of final data products which each institute would release after a full period for analysis and correction.

The campaign location is shown in Figure 4-1. Andøya is a small island off the northwest coast of Norway which provides a convenient location for the study of the stratospheric arctic vortex underlain by relatively clean tropospheric marine air. Measurements of meteorological data, such as temperature, pressure, wind speed and direction as well as the relative humidity are performed routinely in Andøya. The facility also encompasses another measurement station, ALOMAR, the Artic Lidar Observatory for Middle Atmosphere Research, located at the top of the 379 m high Ramman Mountain. The ALOMAR observatory is equipped with a Water Vapour Radio spectrometer, several irradiance sensors, a Brewer spectrophotometer and three Lidars (RMN, ozone and Na-Lidar). These provide information on the polar stratospheric clouds, temperature, winds, OH and O₃ vertical profiles.
Two UV-vis zenith sky viewing instruments, the SYMOC 1 and 2, are also permanently stationed in Andøya. Both participated in the intercomparison campaign and are termed NILU_1 and NILU_2. Furthermore, two ozone sondes were launched on the 17th and 26th of February and vertical profiles of temperature and ozone were obtained with the O₃-Lidar during the 20th, 21st, 26th of February and 2nd of March.

The first week of the campaign was devoted to the installation and testing of the various instruments. The intercomparison exercise began on 21st of February, when all instruments were sufficiently stabilized, and lasted until the 6th of March. Owing to a delay in shipping, the Leicester instrument did not arrive in Andøya until 19th February, allowing only 48 hours for installation, calibration and stabilisation before the start of the intercomparison exercise. This resulted in difficulties for the Leicester instrument in the first few days of the campaign.

4.3 Meteorological Conditions during the campaign

Figure 4-2 illustrates the evolution of the meteorological parameters during the NDSC campaign. The conditions were rather exceptional for the location and time of year. This was the warmest February-March period for the previous 44 years. Temperatures were rarely below zero, with a considerable amount of rain during the campaign. The first part of the period, until day 58 (27th Feb) was very warm (6 °C) for the season and
particularly wet with significant wind (13-18 m/s) blowing from the W-SW. It was followed by four relatively cooler (0 to 2 °C) and dryer days in lighter and variable winds swinging from NW to SW, and terminated by warmer weather ahead from a low pressure system.

![Figure 4-2 Atmospheric Conditions during the Andoya campaign (Vandaele et al. 2004).](image)

**4.4 The participating institutes and instruments**

Four of the eight institutes operated two instruments, and each instrument on the campaign had slightly differing technical specifications. A summary of the different instruments is given in Table 4-1.
<table>
<thead>
<tr>
<th>Group</th>
<th>Type</th>
<th>Grating (g/mm)</th>
<th>Slit width (µm)</th>
<th>Field of view (°)</th>
<th>Light input system</th>
<th>Pol.</th>
<th>Detector</th>
<th>Spec Range (nm)</th>
<th>No of Pixels</th>
<th>Res (FWHM, nm)</th>
<th>Samp Ratio</th>
<th>MAX-DOAS</th>
<th>NO₂</th>
<th>BrO</th>
<th>OCIO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Service d'Aéronomie du CNES</td>
<td>John/Voy CP200</td>
<td>360</td>
<td>50</td>
<td>10</td>
<td>Quartz window</td>
<td>no</td>
<td>Hamamatsu PDA Ambient</td>
<td>300-620</td>
<td>1024</td>
<td>0.8-1.5</td>
<td>2.5-5</td>
<td>x</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>INASB_1</td>
<td>Spectra PRO-350 Action Res</td>
<td>1200</td>
<td>200</td>
<td>0.15* x 2'</td>
<td>Loss</td>
<td>no</td>
<td>Perkin Elmer NTE CCD 1340 400B-40°C</td>
<td>335-450</td>
<td>1340</td>
<td>0.75</td>
<td>9</td>
<td>x</td>
<td>-</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>INASB_2</td>
<td>TRIAX 180</td>
<td>1800</td>
<td>300</td>
<td>0.15* x 2'</td>
<td>Loss P</td>
<td>P</td>
<td>Hamamatsu</td>
<td>334-395</td>
<td>1024</td>
<td>0.7</td>
<td>11</td>
<td>x</td>
<td>-</td>
<td>x</td>
<td>-</td>
</tr>
<tr>
<td>Instituto Nacional de Técnica Aeroespacial</td>
<td>John/Voy TRIAE 180</td>
<td>900</td>
<td>100</td>
<td>25</td>
<td>Fiber bundle</td>
<td>no</td>
<td>Perkin Elmer NTE PDA</td>
<td>325-460</td>
<td>1024</td>
<td>0.55-0.7</td>
<td>4-5</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>-</td>
</tr>
<tr>
<td>Inst. of Environmental Physics, Brommen</td>
<td>IUPB_1 ARC 500 Action Res</td>
<td>600</td>
<td>150</td>
<td>1</td>
<td>Fiber bundle</td>
<td>no</td>
<td>Perkin Elmer NTE CCD 1340 400B-40°C</td>
<td>324-408</td>
<td>1340</td>
<td>0.4</td>
<td>6</td>
<td>x</td>
<td>-</td>
<td>x</td>
<td>-</td>
</tr>
<tr>
<td>Inst. of Environmental Physics, Heidelberg</td>
<td>IUPH ARC 500 Action Res</td>
<td>600</td>
<td>120</td>
<td>1</td>
<td>Fiber, lens</td>
<td>no</td>
<td>Hamamatsu PDA ST3904-10ºC</td>
<td>340-420</td>
<td>1024</td>
<td>0.55</td>
<td>7</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Norwegian Institute for Air Research</td>
<td>NILU_1 SpectraPro 275 (Action Res)</td>
<td>1200</td>
<td>200</td>
<td>18</td>
<td>Fiber bundle</td>
<td>no</td>
<td>Spec 10: 100B CCD (Laser)</td>
<td>339-410</td>
<td>1034</td>
<td>0.45</td>
<td>9</td>
<td>-</td>
<td>x</td>
<td>x</td>
<td>-</td>
</tr>
<tr>
<td>National Institute of Water and Atmosphere</td>
<td>NILU_2 SpectraPro 275 (Action Res)</td>
<td>600</td>
<td>150</td>
<td>18</td>
<td>Fiber bundle</td>
<td>no</td>
<td>Perkin Elmer PDA Array-10ºC</td>
<td>400-550</td>
<td>1024</td>
<td>1.2-1.4</td>
<td>8-9</td>
<td>x</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>National Institute of Water and Atmosphere</td>
<td>NTWA_1 ISA HR330</td>
<td>1200</td>
<td>200</td>
<td>14</td>
<td>Fiber</td>
<td>no</td>
<td>Hamamatsu CCD-30ºC</td>
<td>330-390</td>
<td>1024</td>
<td>0.55</td>
<td>11</td>
<td>-</td>
<td>x</td>
<td>x</td>
<td>-</td>
</tr>
<tr>
<td>National Institute of Water and Atmosphere</td>
<td>NTWA_2 SPEX 270M</td>
<td>964</td>
<td>250</td>
<td>5</td>
<td>Mirror</td>
<td>no</td>
<td>Hamamatsu CCD-20ºC</td>
<td>400-490</td>
<td>1024</td>
<td>0.66</td>
<td>8</td>
<td>x</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Space Research Centre, Brussels</td>
<td>ULEB Oriel MS2570</td>
<td>564</td>
<td>250</td>
<td>5</td>
<td>Fiber, lens</td>
<td>no</td>
<td>Monsel 49-20 CCD</td>
<td>395-480</td>
<td>1072</td>
<td>0.8-1.0</td>
<td>9</td>
<td>x</td>
<td>x</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>
4.5 Instrumental setup for the Leicester CMAX-DOAS.

The instrument was located on the roof of an old lidar building approximately 50 metres from the main site of the Andøya Rocket Range. The site and the positioning of the head unit can be seen in Figure 4-3.

Figure 4-3 Location of the Leicester CMAX-DOAS instrument, and its installation configuration on the roof of the building, showing the northerly view over the ocean.

The instrumental setup used in Andøya was similar to that described in Chapter 3. The primary modifications were to allow for the extreme weather conditions during Spring in the North-West of Norway. Temperatures varied from -1 °C to +8 °C with winds reaching 18 m/s. In addition the marine air provided a highly corrosive environment for the instrumentation. Heating pads were installed in the head unit to maintain a temperature above freezing, and minimise moisture build-up within the telescope assembly.
At this early stage in the design project, the entrance slit supplied with the MS257 Spectrometer was still in place. This led to a narrower instrument line shape, and a greater resolution, but introduced errors owing to the problematic alignment of the entrance optics with the slit, and the subsequent asymmetry of the instrument line shape. This is discussed in more detail in Section 4.5.2.

As can be seen in Figure 4-3 the head unit was securely strapped to the roof of the permanent building which housed the spectrometer, PC and other equipment. The fibre optic cables were enclosed within reinforced corrugated plastic tubing and passed through a conduit to the lab below. The off-axis viewing geometries were pointed in a northerly direction; however the off-axis analysis was insufficiently advanced at this stage to retrieve any viable data. Inside the building the spectrometer and PC were configured as detailed in chapter 3. The CCD camera vacuum seal had a small leak, and therefore was continuously pumped during the campaign to improve the cooling potential of the CCD system.

4.5.1 Stray light tests

The NDSC protocol requires measurements of stray light for each participating instrument. A set of Schott filters were used to determine the stray light level. This was obtained by taking the ratio of a zenith-sky spectrum to a spectrum close in time and filtered in the 350-370 nm region. Those instruments, for which this ratio was found to be smaller than 0.005 at 360 nm were considered as having a good or very good stray light rejection capability. The Leicester CMAX-DOAS instrument achieved this threshold of 0.005 [Vandaele et al., 2005]. The constrained entrance optics, and the enclosure of the spectrometer inside a light-tight box ensure the minimisation of stray light issues for a single fibre. When multiple fibres are used stray light from other fibres becomes a factor, however this was not the case in Andøya. Other instruments, such as IASB_1, INTA, NILU_1, and NILU_2 exhibited stray-light levels greater than 0.005 (typically a factor of 10 higher), and could therefore be expected to show larger sensitivity to stray-light in their analysis.
4.5.2 Instrument Line Shape

As requested by the NDSC protocol, instrumental functions were measured on site using a Mercury line lamp. Accurate knowledge of the instrumental spectral response function is essential for the convolution of the high-resolution laboratory cross sections of the measured species. It must be noted that some of the retrieval codes can also estimate this function and, more interestingly, its evolution with wavelength from the zenith sky spectra themselves. In order to evaluate the reliability of such a software facility, the measured slit functions were compared with functions deduced using the WINDOAS program, developed at Belgian Institute for Space Aeronomy (IASB/BIRA)[Fyt and Van Roozendael, 2001]. Results of the slit function comparison are plotted in Figure 4-4. For most of the instruments, the best agreement was found using a Gaussian type instrumental function. The IASB_1, NIWA_1, and NIWA_2 slit functions were however best reproduced using an error function.
Figure 4-4 Instrument line shapes for the instruments participating in the intercomparison (dots), plotted with the derived ILS as calculated by the WinDOAS software. From [Vandaele et al., 2005]
The instrument line shape for the Leicester CMAX-DOAS exhibited a degree of asymmetry owing to the influence of the imperfect alignment of the multi-track fibre optic and the spectrometer entrance slit.

The resolution of each instrument can be calculated from the instrument line shape, and is plotted in Figure 4-5 with the wavelength regions for each analysis window indicated (see section 4.6 for details of these analysis windows). The grating position for the Leicester CMAX-DOAS instrument was chosen to produce the optimal resolution across the primary fitting windows used in this campaign. These fitting windows are termed TC1 and TC2 and are detailed in section 4.6.

Figure 4-5 Resolution of each instrument on the campaign (● CNRS, ■ IASB_1, ○ IASB_2, ▲ INTA, ▽ IUPB_1, ▼IUPB_2, ♦ IUPH, # NILU_1, ○ NILU_2, × NIWA_1, □ NIWA_2, ∆ ULEI). Taken from [Vandaele et al., 2005] Marked at the top of the Figure are the fitting windows used during the campaign which are detailed in section 4.6.
4.5.3 CCD performance

During the campaign, performance characteristics of the Marconi 47-20 chip were investigated in order to establish their influence on retrievals.

4.5.3.1 Full-well capacity.

Each CCD pixel has a maximum number of counts which can be registered on a single read. This maximum value is known as the “full well capacity”, and for the 47-20 chip was measured at 4,400 counts. Charge bleeding between CCD pixels was found to occur as usage neared full-well capacity which resulted in a changing instrument line shape, depending on CCD usage for a given CCD image. The higher the CCD usage, the wider the instrument line shape, as charge from the centre of the peak leaked into the weaker spectral features. Such changes in instrument line shape lead to significant errors in DOAS analysis.

CCD usage was regulated by software which altered integration times according to the level of incoming solar radiation. This software was altered from a target of 90-95% CCD full-well usage, to a level of 55-70%. Below 70% full-well usage, charge bleeding was found to be negligible, thus providing a more consistent instrument line shape.

4.5.3.2 Sensitivity to the Ultra-violet.

The 47-20 chip used during the campaign was not equipped with an UV coating which limited the sensitivity of the pixels at wavelengths below 360 nm. An alternative chip was not available during the campaign. However, after the campaign, the effect of this reduced sensitivity to the UV was explored by taking comparable atmospheric spectra with the 48-20 UV enhanced chip detailed in Chapter 3, and the 47-20 chip used in Andøya. These two spectra were taken within an hour of each other, in clear sky conditions and are shown in Figure 4-6.
As can be seen in Figure 4-6 the structures below 370 nm are reduced using the non-UV enhanced 48-20 chip. The reduced amplitude of these structures considerably decreases the sensitivity of retrievals in fitting windows below 370 nm.

### 4.5.4 Modifications during the campaign

The grating position was altered on several occasions during the campaign to test the suitability and sensitivity of differing fitting windows and resolutions and to test the optimal position of the fitting window in the total recorded spectrum. The gratings and wavelengths measured are shown in Table 4-2. As can be seen, the focus of attention switched from the UV early in the campaign, to the visible, and then back to the UV.

The low sensitivity to the UV, coupled with the asymmetry of the instrument line shape and the charge bleeding on the CCD led to large errors in retrievals for BrO and OCIO. The fitting windows below 380 nm and the fine structure of the cross sections involved made these retrievals particularly susceptible to such instrumental effects. Although considerable efforts were made to correct for such effects during the campaign, it was
decided on 25th Feb (Julian day 56) to move the grating to the visible and concentrate on the NO$_2$ fitting window until a reliable retrieval had been achieved. On 5th Feb the grating was moved back to the UV to have a last attempt at BrO and OCIO, however no reliable retrieval was possible.

The grating position for the NO$_2$ visible window was chosen to provide the greatest resolution and most symmetrical ILS as possible in the fitting window from 425-450 nm, which were the recommended settings for the campaign.

<table>
<thead>
<tr>
<th>Date</th>
<th>Wavelength setting (centre)</th>
<th>Wavelength Min (nm)</th>
<th>Wavelength Max (nm)</th>
<th>Grating (lines/mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>22/02/2003</td>
<td>369.5</td>
<td>341</td>
<td>383</td>
<td>1200</td>
</tr>
<tr>
<td>23/02/2003</td>
<td>372</td>
<td>343.5</td>
<td>385.5</td>
<td>1200</td>
</tr>
<tr>
<td>24/02/2003</td>
<td>397</td>
<td>342</td>
<td>428</td>
<td>600</td>
</tr>
<tr>
<td>25/02/2003</td>
<td>452.5</td>
<td>400</td>
<td>484</td>
<td>600</td>
</tr>
<tr>
<td>26/02/2003</td>
<td>452.5</td>
<td>400</td>
<td>484</td>
<td>600</td>
</tr>
<tr>
<td>27/02/2003</td>
<td>452.5</td>
<td>400</td>
<td>484</td>
<td>600</td>
</tr>
<tr>
<td>28/02/2003</td>
<td>452.5</td>
<td>400</td>
<td>484</td>
<td>600</td>
</tr>
<tr>
<td>01/03/2003</td>
<td>447.5</td>
<td>394</td>
<td>479</td>
<td>600</td>
</tr>
<tr>
<td>02/03/2003</td>
<td>447.5</td>
<td>394</td>
<td>479</td>
<td>600</td>
</tr>
<tr>
<td>03/03/2003</td>
<td>447.5</td>
<td>394</td>
<td>479</td>
<td>600</td>
</tr>
<tr>
<td>04/03/2003</td>
<td>447.5</td>
<td>394</td>
<td>479</td>
<td>600</td>
</tr>
<tr>
<td>05/03/2003</td>
<td>372</td>
<td>343.5</td>
<td>385.5</td>
<td>1200</td>
</tr>
<tr>
<td>06/03/2003</td>
<td>372</td>
<td>343.5</td>
<td>385.5</td>
<td>1200</td>
</tr>
</tbody>
</table>

Table 4-2 Spectrometer settings during the measurement phase of the campaign
4.6 Fitting Parameters used during the campaign

Following a consultation process between the campaign referee and participants at the very start of the campaign, sets of fixed retrieval parameters were established. For each target species, an optimal target window was established that all groups would use for retrieval. Fitting parameters within this window were also fixed, such as cross sections used, offset correction applied, and the degree of the polynomial used in the DOAS fit. This unilateral primary fitting configuration was known as TC1 (Test Case 1). In addition to this TC1 setting, each group submitted retrievals using parameters which they considered to be optimal for their own given instrument, this retrieval was known as TC0. In some cases the accuracy of alternative windows were also examined, with these configurations being termed TC2, TC3 and so on. Given the early stage of development of the Leicester CMAX-DOAS instrument, the campaign settings of TC1 were also used for the TC0 analysis of data from this instrument.

Details of each configuration for NO\textsubscript{2} are given in Table 4-3 and Table 4-4. In these tables, cross sections are referred to by shortcut initials as follows; B: [Burrows et al., 1998]; Bd: Bogumil deconvoluted [Bogumil et al., 2003]; BR: [Coeur et al., 2002]; Gr: [Greenblatt et al., 1990] corrected for shift and stretch; H: [Hermans et al., 2002]; Ha:[Harder et al., 1997]; Har : [Harder and Brault, 1997]; Hi: Hitran 2000 [Rothman et al., 2003]; K:[Kromminga et al., 2003]; V:[Vandaele et al., 1998]; Vrz: Ring calculated with WINDOAS [Fayt and Van Roozendael, 2001]. Numbers after these acronyms represent the temperatures at which the cross sections were obtained and the numbers in brackets signify the I\textsubscript{0} correction factors used.

<table>
<thead>
<tr>
<th>Test case</th>
<th>Wavelength Interval (nm)</th>
<th>Abs. Cross Sections</th>
</tr>
</thead>
<tbody>
<tr>
<td>TC1</td>
<td>425-450</td>
<td>O\textsubscript{3} (Bd 223K). NO\textsubscript{2} (V 220K). O\textsubscript{4} (Gr). H\textsubscript{2}O (Hi)</td>
</tr>
<tr>
<td>TC2</td>
<td>400-418</td>
<td>NO\textsubscript{2} (V 220K). OC\textsubscript{1}O (K 213K)</td>
</tr>
</tbody>
</table>

Table 4-3 Specifications of the fitting parameters for TC1 and TC2. Taken from [Vandaele et al., 2005]
<table>
<thead>
<tr>
<th>CNRS</th>
<th>JASB</th>
<th>INTA</th>
</tr>
</thead>
<tbody>
<tr>
<td>O&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Bd 223</td>
<td>O&lt;sub&gt;i&lt;/sub&gt;</td>
</tr>
<tr>
<td>NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>V 220 (1x10&lt;sup&gt;10&lt;/sup&gt;)</td>
<td>NO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>O&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Gr mod</td>
<td>O&lt;sub&gt;i&lt;/sub&gt;</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Hi</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td>Ring From Ref spectrum</td>
<td>Offset</td>
<td>Offset</td>
</tr>
<tr>
<td>Offset -</td>
<td>Poly 4</td>
<td>Offset</td>
</tr>
<tr>
<td>Poly -</td>
<td>Poly 4</td>
<td>Poly 3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>IUPB</th>
<th>IUPH</th>
<th>NIWI</th>
</tr>
</thead>
<tbody>
<tr>
<td>O&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Bd 223</td>
<td>O&lt;sub&gt;i&lt;/sub&gt;</td>
</tr>
<tr>
<td>NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>V 220 (1x10&lt;sup&gt;10&lt;/sup&gt;)</td>
<td>NO&lt;sub&gt;2&lt;/sub&gt;</td>
</tr>
<tr>
<td>O&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Gr</td>
<td>O&lt;sub&gt;i&lt;/sub&gt;</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>BR</td>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
</tr>
<tr>
<td>Ring Bremen</td>
<td>Offset cst</td>
<td>Ring Vrz</td>
</tr>
<tr>
<td>Offset cst</td>
<td>Poly 2</td>
<td>Offset cst</td>
</tr>
<tr>
<td>Poly 2</td>
<td>Poly 2</td>
<td>Poly 3</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>NIWA</th>
<th>ULEI</th>
</tr>
</thead>
<tbody>
<tr>
<td>O&lt;sub&gt;i&lt;/sub&gt;</td>
<td>Bd 223 (1x10&lt;sup&gt;5&lt;/sup&gt;)</td>
</tr>
<tr>
<td>NO&lt;sub&gt;2&lt;/sub&gt;</td>
<td>V 220 (1x10&lt;sup&gt;10&lt;/sup&gt;)</td>
</tr>
<tr>
<td>O&lt;sub&gt;i&lt;/sub&gt;</td>
<td>H</td>
</tr>
<tr>
<td>H&lt;sub&gt;2&lt;/sub&gt;O</td>
<td>Hu</td>
</tr>
<tr>
<td>Ring Vrz + slope</td>
<td>Offset</td>
</tr>
<tr>
<td>Offset cst</td>
<td>Poly 2.3</td>
</tr>
<tr>
<td>Poly 2.3</td>
<td>Poly 2.3</td>
</tr>
</tbody>
</table>

Table 4-4 TC0 parameters for each group. These parameters were chosen by each group as the preferred settings for their particular instrument. Taken from [Vandaele et al., 2005]
4.7 Results.

4.7.1 Concentrations of target species measured during the campaign

Slant column measurements of BrO, OCIO, and NO$_2$ were submitted by campaign participants from the 23$^{\text{rd}}$ Feb (Julian day 54) to 6$^{\text{th}}$ March (Julian day 65). The progression in the column density of these species can be seen in Figure 4-7. The DSCD values plotted in Figure 4-7 use the slant column value at 90 degrees solar zenith angle, with a reference spectrum taken at 80 degrees solar zenith angle. Potential vorticity (PV) and temperature at 50 hPa are also plotted to provide information on stratospheric conditions.

The arrival of the polar vortex above Andøya can be seen on the afternoon of 25$^{\text{th}}$ Feb (Julian day 56) with a significant increase in PV, and decrease in stratospheric temperature. The associated chemical changes are also evident with activation of the Br and Cl reservoirs, and subsequent increases in BrO and OCIO concentrations accompanied by a reduction in stratospheric NO$_2$ levels characteristic of polar vortex denoxification.

The magnitude of the BrO slant column at 90$^{\circ}$ sza in the vortex is similar to that reported in polar regions during previous winters [Tornkvist et al., 2002]. In contrast, the 6-7 x10$^{13}$ OCIO mol/cm$^2$ are 3-4 times lower than the 2.5x10$^{14}$ molec/cm$^2$ reported by the same authors at Ny-Ålesund during chlorine activation episodes. The vortex was only partially activated in February 2003.
Figure 4-7 Evolution of the concentration of target species during the campaign, plus at the bottom, charts of potential vorticity and temperature.

4.7.2 Comparison of slant columns from each instrument
The slant columns densities measured during the campaign by each group are shown in Figure 4-8.
Figure 4-8 Measured Slant columns of NO\textsubscript{2} from each group for 25th Feb (Julian day 55) to 27th Feb (Julian day 57). Note the arrival of the polar vortex during the 26th, resulting in a reversed diurnal variation.

The generally good agreement between most datasets for NO\textsubscript{2} can be seen in the above figure. Data from the Leicester instrument is marked with Δ’s. Although the individual datasets are rarely distinguishable in Figure 4-8, the Leicester data can be clearly seen diverging from the consensus measurement in the evening of the 25\textsuperscript{th} Feb. This was only the second day on which the Leicester instrument submitted data, and the charge bleeding issue detailed in section 4.5.3.1 was not resolved until later in the campaign. This may have been the cause of this particular divergence.
The primary obstacle in calculating the accuracy of each instruments’ measurements is the absence of independent NO$_2$ measurements by another technique to which those of the UV-visible spectrometers could be compared. The choice of the campaign referee was to use a method suggested by Roscoe et al. [1999] for defining a reference based on objective criteria. The method is based on the analysis of the linear regression between different data sets of different groups. It allows a quantitative analysis of how well instruments’ measurements agree.

For example, Figure 4-9 and Figure 4-10 show the regression analysis of all groups’ data against data from the second instrument from NIWA. Such analysis repeated for each group permits the identification of a core subset of instruments whose measurements are in generally good agreement. An average of measurements from this core subset can then be considered as the reference dataset against which the accuracy of all measurements can be judged. The reference groups chosen for NO$_2$ were NIWA, INTA and IASB, and each dataset was analysed against an average of measurements from these three instruments.
Figure 4-9 Regression analysis, showing the agreement of all groups' data with data from the second instrument from NIWA.
Regression analysis of each dataset provides figures for the slope and intercept of the best-fit line through the data, as well a residual figure indicating the spread of the data. These three figures are used as a quantitative measure of the ability of each group to measure the "correct" differential slant column densities of NO₂. Furthermore, this analysis can be performed on the sunrise (SR) or sunset (SS) datasets from each day, or a combination of the two. The results from this analysis are shown in Table 4-5.
Table 4-5 Results of the regression analysis performed on the TCO data. Average values of the daily regression parameters, intercept (I), slope (S) and rms residual (R), with their standard deviations are given for each instrument and considering only sunrise data (SR), sunset data (SS), and all data combined (SR+SS).

<table>
<thead>
<tr>
<th></th>
<th>I (x10^{13} molec/cm^2)</th>
<th>S (x10^{13} molec/cm^2)</th>
<th>R (x10^{13} molec/cm^2)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Mean Std. Dev.</td>
<td>Mean Std. Dev.</td>
<td>Mean Std. Dev.</td>
</tr>
<tr>
<td>CNRS</td>
<td>SR 0.1 28.3</td>
<td>1.013 0.043</td>
<td>6.6 1.8</td>
</tr>
<tr>
<td></td>
<td>SS 2.3 18.1</td>
<td>1.008 0.031</td>
<td>8.9 3.6</td>
</tr>
<tr>
<td></td>
<td>SR+SS 1.1 23.3</td>
<td>1.010 0.038</td>
<td>7.7 3.0</td>
</tr>
<tr>
<td>IASB</td>
<td>SR -0.1 8.7</td>
<td>0.992 0.024</td>
<td>3.1 1.4</td>
</tr>
<tr>
<td></td>
<td>SS -4.2 8.7</td>
<td>0.989 0.007</td>
<td>4.4 2.8</td>
</tr>
<tr>
<td></td>
<td>SR+SS -1.8 8.7</td>
<td>0.990 0.017</td>
<td>3.8 2.3</td>
</tr>
<tr>
<td>INTA</td>
<td>SR 1.8 6.4</td>
<td>0.997 0.026</td>
<td>3.4 1.5</td>
</tr>
<tr>
<td></td>
<td>SS 0.1 11.5</td>
<td>0.993 0.060</td>
<td>3.2 1.1</td>
</tr>
<tr>
<td></td>
<td>SR+SS 1.1 9.0</td>
<td>0.994 0.020</td>
<td>3.3 1.3</td>
</tr>
<tr>
<td>IUPB</td>
<td>SR 3.1 11.6</td>
<td>1.022 0.032</td>
<td>8.7 4.1</td>
</tr>
<tr>
<td></td>
<td>SS 1.2 8.4</td>
<td>1.045 0.009</td>
<td>10.7 3.4</td>
</tr>
<tr>
<td></td>
<td>SR+SS 2.4 10.0</td>
<td>1.036 0.024</td>
<td>9.7 3.8</td>
</tr>
<tr>
<td>IUPH</td>
<td>SR -1.0 13.5</td>
<td>1.032 0.035</td>
<td>4.5 1.1</td>
</tr>
<tr>
<td></td>
<td>SS -6.4 18.5</td>
<td>1.014 0.025</td>
<td>4.8 1.2</td>
</tr>
<tr>
<td></td>
<td>SR+SS -3.7 15.8</td>
<td>1.019 0.034</td>
<td>4.6 1.1</td>
</tr>
<tr>
<td>NILU</td>
<td>SR 3.1 18.9</td>
<td>1.039 0.041</td>
<td>7.9 4.3</td>
</tr>
<tr>
<td></td>
<td>SS 1.8 14.5</td>
<td>1.062 0.028</td>
<td>9.6 4.6</td>
</tr>
<tr>
<td></td>
<td>SR+SS 2.5 16.5</td>
<td>1.053 0.035</td>
<td>8.8 4.4</td>
</tr>
<tr>
<td>NIWA</td>
<td>SR -2.1 5.5</td>
<td>1.003 0.013</td>
<td>3.2 1.3</td>
</tr>
<tr>
<td></td>
<td>SS 0.1 6.9</td>
<td>1.008 0.007</td>
<td>3.5 1.5</td>
</tr>
<tr>
<td></td>
<td>SR+SS -1.1 6.3</td>
<td>1.006 0.012</td>
<td>3.4 1.4</td>
</tr>
<tr>
<td>ULEI</td>
<td>SR -3.6 16.2</td>
<td>0.903 0.055</td>
<td>10.6 4.9</td>
</tr>
<tr>
<td></td>
<td>SS 14.6 55.0</td>
<td>1.056 0.083</td>
<td>13.4 5.6</td>
</tr>
<tr>
<td></td>
<td>SR+SS 5.6 39.0</td>
<td>1.027 0.118</td>
<td>12.0 5.3</td>
</tr>
</tbody>
</table>

Analysis of the residuals from this regression analysis gives an indication of the accuracy of each instrument. Figure 4-11 shows histogram analysis of these residuals, with a best fit curve applied to provide a mean difference and standard deviation for each set of measurements from the reference set.
Figure 4-11 Histograms of the DSCD differences for each instrument in case of TC1. The abscissa are the absolute differences observed between one instrument and the reference, and the y-axis represents the number of occurrences of one specific difference value. The red Gaussian fit represents a normal curve having the same mean and standard deviation as the data.

The University of Leicester instrument through this analysis has a best fit curve with a mean difference of $3 \times 10^{14}$ mol/cm$^2$, and a standard deviation of $8.5 \times 10^{14}$ mol/cm$^2$.

4.8 Conclusions

Despite its very early stage of development, the CMAX-DOAS instrument successfully participated in the intercomparison campaign. The lack of sensitivity to wavelengths below 360 nm, coupled with the inherent loss of light through small fibres led to very poor performance in the retrieval of BrO and OCIO.
The retrieval of NO$_2$ in the visible window from 425 to 450 nm provided the Leicester instrument with a quantitative measure of its accuracy, with measurements having a mean difference from the campaign standard of $3 \times 10^{14}$ mol/cm$^2$, with a standard deviation of $8.5 \times 10^{14}$ mol/cm$^2$.

The error margins for the Leicester instrument are relatively high compared with the established NSDC instruments which are designed for the sensing of relatively low levels of NO$_2$ in remote locations. However, when compared with typical slant columns in a moderately polluted urban environment ranging from $1 \times 10^{16}$ to $5 \times 10^{17}$ mol/cm$^2$, these error margins are acceptable, given the advantages offered to temporal resolution and spatial sampling of the concurrent multi-axis design.

It should also be noted that improvements in instrument design, such as the removal of the spectrometer entrance slit, will have considerably improved error margins in subsequent measurements.
5 Measurements in Leicester During 2004

5.1 Introduction

The CMAX-DOAS instrument was installed on the roof of the Space Research Centre at the University of Leicester (52.62 °N, 1.12 °W) at the end of 2003. The location of the instrument in relation to the city-centre environment and the presence of several in situ chemiluminescence monitors provided an invaluable opportunity to investigate the urban boundary layer with the CMAX-DOAS instrument. As described in Chapter 1, urban NO\textsubscript{2} concentrations are the subject of several EU directives, and a concern for human health. The concurrent sampling through multiple viewing geometries possible with the CMAX-DOAS instrument provides a unique tool for sampling distinct air masses above an urban city centre.

5.2 Instrumental Location

The instrument was installed on a 4 m pole, on the roof of the Space Research Centre at the University of Leicester. A clear view to the North was available, unobstructed by tall buildings and trees. The location of the installation with respect to the town centre and main traffic routes is shown in Figure 5-1. Figure 5-1 shows modeled mean annual NO\textsubscript{2} concentrations in the Leicester Area, and the location of 8 automated monitoring stations, operated by Leicester City Council. The northerly-pointing off-axis views sampled air masses over the main urban city centre in Leicester. The heterogeneity of the air-masses sampled by the different viewing directions limited the profiling capabilities of the CMAX-DOAS instrument using existing techniques. However, the concurrent nature of the multi-axis measurements did permit innovative simultaneous analysis of different air-masses.
Mean Annual Concentrations for 2001 Interpolated From Modelled Points. Monitoring Station Locations Shown

Legend

Mean Annual NO2 Conc 2001

- 26.61 - 29.47
- 29.48 - 32.05
- 32.06 - 34.53
- 34.54 - 36.82
- 36.83 - 39.11
- 39.12 - 42.17
- 42.18 - 51.05

Points for the interpolation produced by Leicester City Council using the dispersion model ADMS-Urban 1.6 developed by Cambridge Environmental Research Consultants. It shows predicted annual mean concentrations of nitrogen dioxide in micrograms per cubic metre for 2001. This plot is only applicable to the areas shown within the Leicester City Council boundary.

Figure 5-1 Modelled NO2 concentrations in the Leicester Area, produced by the ADMS model, using assimilated data from the automated monitoring stations marked on the map. The location of the CMAX-DOAS instrument is also shown.
5.3 Instrumental Alterations from the Andøya Campaign.

The instrument was modified in several ways before installation in Leicester.

1. The entrance slit on the spectrometer was removed completely from the optical system. This resulted in a much broader instrument line shape (ILS), but removed much of the variability across the focal plane. It also reduced the dependence of the ILS on the alignment of the F/# matcher with the spectrometer, significantly enhancing the stability of the system.

2. The 47-20 CCD chip used during the Andøya campaign was replaced with a Marconi 48-20 UV enhanced chip. This was a result of problems owing to the lack of UV sensitivity in Andøya and damage sustained during the return transit of the chip to Leicester. The 48-20 had certain disadvantages over the 47-20, including a smaller full-well capacity of only 4400 counts. The 48-20 chip also had no dump gate, which handles accumulating charge during the read-out phase, causing the build-up of charge at the top of the chip.

3. In order to achieve the most consistent long-term dataset possible, the vacuum pumping system was removed from the CCD camera head. This resulted in a lower vacuum in the CCD chamber, and therefore a higher operating temperature. The advantages were the avoidance of any vibration caused by the connection of the pump to the CCD housing, and the resulting stability of entire optical system. The noise levels in the laboratory were also significantly reduced to a level suitable for long-term operation.

4. Metal-sheathed fibre-optic cables were installed on all viewing geometries. This permitted full 5-axis viewing which had not been possible in Andøya.
5.4 Pre calibration and stabilization

In Leicester, the Spectrometer, F-number matcher and CCD camera assembly were sealed inside a foam-padded container. This provided a degree of temperature stability for the whole optical system. The laboratory was air-conditioned to maintain a constant operating temperature. The resultant temperature inside the box, monitored over several days, was 19 °C +/- 0.2 °C. This degree of temperature stability minimized expansion and contraction of the optical elements over the day, and therefore added to the consistency of the ILS.

5.5 Error analysis with the Leicester Installation.

One primary advantage of the installation at the University of Leicester, was the opportunity to undertake a complete analysis of the performance of the instrument, and the potential sources of errors. Errors in a DOAS fit arise from two primary components, namely instrument noise and systematic errors. The instrument noise results from two principal sources, photo electron noise from the detector, and electronic noise from the various components between the CCD pixel and the PC [Stutz, 1991]. The systematic error results from inaccuracies in the many components used in the DOAS analysis, including the cross sections, the Ring effect, the instrument line shape and the wavelength calibration.

The photo electron noise is caused by the statistical distribution of the number of detected photo electrons in the CCD device. This is proportional to the square root of the number of observed photo electrons. As the integration time of the CMAX-DOAS system was automatically monitored to maximise the CCD usage, the number of observed photo electrons was maximised for each reading and remained reasonably constant throughout a measurement period.

The detector noise is caused by characteristics of the electronic components used to collect the signal from the CCD pixel. Such detector noise is proportional to the number of CCD images used for each spectrum.
Systematic errors are obviously eliminated where possible, however, instrumental constraints still produce certain inaccuracies. Each potential source of systematic error was independently investigated to establish the likely contribution to the total fitting error.

Stray light between fibres is a potential source of systematic error. This could occur in the spectrometer optical system if the imaging qualities of the spectrometer were insufficiently precise or light from sources other than the fibres entered the system. The degree of stray light signal between fibres was investigated by monitoring signal strength between the imaged fibres. Any variability over the day in the signal strength between the fibres would indicate that the signal contained either stray light not entering the system via the fibre-optic system, or photons scattered from one of the fibres. The signal strength on 9th November 2004 at points on each fibre, and points between all fibres is shown in Figure 5-2.

![Figure 5-2 Signal strength measured on each viewing geometry over a normal day, with the six dark current measurements all plotted in black but barely distinguishable from each other as they exhibit so little structure above the background signal.](image)

Figure 5-2 Signal strength measured on each viewing geometry over a normal day, with the six dark current measurements all plotted in black but barely distinguishable from each other as they exhibit so little structure above the background signal.
In Figure 5-2 the data from the clear morning and evening demonstrate the relative intensities of the different viewing geometries in non-cloudy conditions. The arrival of cloud at 7am coincides with the initiation of the automatic integration-time software, which keeps the maximum value on the CCD to between 50 and 70% of full-well usage. The number of images averaged for each reading varies depending upon the integration time used, with 1 reading per measurement during low-light conditions in the morning, to a maximum of 20 images per measurement during brighter intervals. The signal strength between fibres are all plotted in Figure 5-2 although they lie so closely together that their individual signals are indistinguishable. These low measurements indicate negligible stray light signal, with negligible errors caused by either stray light entering the system, or through signals being diffracted by the spectrometer optics, and superimposed on another signal. The negligible signal monitored above the zenith fibre also confirms the lack of influence of the charge build-up between frames.

The variability of the stray light signal between the fibres, gives a measure of electronic noise. The RMS from the mean daily value is 2.5 counts. Using the approximation of an average signal strength on the fibres of 1500 counts, this produces an uncertainty of approximately 0.2%. The signal strength on the 2 degree view is significantly lower, with an average signal between 90 deg SZA at dawn, and 90 deg SZA at dusk of only 46 counts above the measured dark current. This leads to errors from electronic noise of approximately 5.3 % on this fibre in these atmospheric conditions. It should be noted that cloud structures very strongly influence the relative intensities of each viewing geometry, and these errors are therefore subject to significant daily variability. The low intensity on the 2 degree view on this day could be considered as a worse case scenario.
5.5.1 Instrument Line Shape Errors

Systematic errors are also introduced through assumptions made in the convolution of cross sections and other fitted parameters with a given instrument line shape. The first of these assumptions, is that the instrument line shape is Gaussian. With the spectrometer entrance slit removed, this assumption is reasonably accurate. However, certain asymmetries still exist. The instrument line shape was measured with a mercury line lamp and a Gaussian was fitted to this measured instrument line shape to estimate the errors introduced through the use of a Gaussian line shape to convolve cross sections. The results of this fitting process are shown in Figure 5-3. The errors caused by this asymmetry are calculated as 0.5%. As the spectrometer entrance slit had been removed, variability in the instrument line shape across the CCD focal plane was reduced, although some uncertainty remained as to the errors introduced by the variability of this asymmetry across the CCD chip.

![Figure 5-3](image-url)  
*Figure 5-3 The measured instrument line shape plotted with a fitted Gaussian curve, demonstrating the slight asymmetry of the line shape.*
The dependence of the instrument line shape on the horizontal and vertical position in the focal plane was investigated with recorded atmospheric spectra using the WinDOAS software. As part of a rigorous wavelength calibration procedure including shift and squeeze procedures the WinDOAS software fits standard instrument line shape parameters (e.g., full-width half-maximum (FWHM)) to sub-windows of recorded spectra. This procedure permits accurate wavelength calibration, and investigation of the variability of the line shape both within an individual spectrum, and between spectra imaged in different areas of the focal plane. Figure 5-4 shows the measured instrument line shape from all five viewing geometries introduced in Chapter 3.

![Figure 5-4](image-url)

Figure 5-4 The instrument line shape calculated by the WinDOAS software from spectra measured on each section of the CCD. Values plotted are the FWHM of fitted Gaussian curves along the spectrum.

The errors owing to the variability of this instrument line shape are introduced when spectra from one fibre are used as reference spectra for another fibre. The errors introduced in such a procedure vary according to the FWHM of the two spectra at a given...
wavelength. A calculation of these errors can be achieved by calculating the error from two normalised Gaussian curves of the appropriate FWHM's. From the data in Figure 5-4, errors varied across the fitting window and between fibres, and with a maximum around 470 nm with values of approximately 3.5% for analysis of 15-degree spectra with a zenith reference.

The wavelength calibration of the spectra was performed by the WinDOAS software, and this calibration was used to shift reference spectra where necessary to be on the same grid as the off-axis spectra. Wavelength calibrations were taken to be accurate to within half a pixel, or 0.04nm. Possible errors introduced through inaccurate wavelength calibration were calculated to be 0.8 % through analysis of shifted Guassian curves with a FWHM of 1.4 nm. A summary of contributory errors in the DOAS fit can be found in table 3.

The total estimated fitting error of 1.5% for individual fibre measurements applies for analysis of spectra from a single viewing geometry. Errors introduced by the variability of the instrument line shape affect analysis of off-axis spectra with a zenith reference only, and increase the theoretical error to approximately 5%.

Additional errors on slant column measurements will be introduced by errors in measured cross sections. Subsequent calculations of absolute concentrations and profile shapes will be subject to errors in calculations of photon paths through the atmosphere. Statements of errors for DOAS analysis are problematic, due to the variability of the influence of a given variability in signal with the strength of the differential absorption features between the reference spectrum, and the spectrum under analysis. For spectra with very weak differential structure, even the slightest instrumental inaccuracy can introduce very significant errors, which are difficult to quantify in a theoretical calculation.
<table>
<thead>
<tr>
<th>Source</th>
<th>Error Estimate</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wavelength Calibration</td>
<td>0.8%</td>
</tr>
<tr>
<td>Electronic Noise</td>
<td>0.2%</td>
</tr>
<tr>
<td>Stray Light</td>
<td>Neg.</td>
</tr>
<tr>
<td>Asymmetry of Instrument Line Shape</td>
<td>0.5%</td>
</tr>
<tr>
<td>Total single fibre fitting error</td>
<td>1.5%</td>
</tr>
<tr>
<td>Variability of instrument line shape</td>
<td>3.5% (total 5%)</td>
</tr>
<tr>
<td>Additional error due to low signal on 2 deg view</td>
<td>5.3% (total 10.3%)</td>
</tr>
</tbody>
</table>

Table 5-1 Summary of calculated error contributions from various aspects of the CMAX-DOAS procedure

The calculated error margins on the 2 degree elevation are considerably higher owing to the very low intensity of the image and is an inherent disadvantage of this instrumental system. The integration time of the CCD is determined by the brightest viewing geometry, which changes with cloud conditions and solar zenith angle. The telescope pointing at 2 degrees elevation consistently receives the lowest scattered flux, and therefore the signal has a larger relative contribution from CCD dark current and electronic noise. For this reason data from the 2 degree elevation view is only used with a 2 degree reference spectrum.

An additional method for quantifying errors in the CMAX-DOAS measurements was developed using 2 concurrent zenith views. Results from this technique are detailed in section 5.9.1.
5.6 Recording period

The instrument was operating in Leicester whenever possible during 2004. Gaps in the data appear due to instrumentation changes, and software alterations. Gaps were also caused by technical difficulties with the interface between the CCD electronics, and the PC controlling the system. This interface was rendered more stable over the year with various software patches.

5.7 Other calibration and measurement stations

As seen in Figure 5-1, other NO\textsubscript{2} monitoring activities take place within the Leicester city area. Leicester City Council operates 8 automated NO\textsubscript{2} monitoring stations using chemiluminescence detectors to obtain in-situ measurements at key locations in the local area. These measurements are key parameters used to constrain the ADMS model which produced Figure 5-1 and is used by Leicester City Council to produce annual average NO\textsubscript{2} concentration statistics.[LCC, 2000]

5.8 Meteorological measurements

Data from two meteorological stations are used in this work. Leicester City council operates a permanent recording station located to the East of the University which provides wind speed and direction data at hourly intervals.

An Oregon Scientific WMR968 meteorological station was installed at the Space Research Centre on 5\textsuperscript{th} Feb 2004. This station recorded humidity, temperature, wind speed, wind direction, and rainfall. This station was linked to the same PC as the CMAX-DOAS system, and recorded data every 2 minutes.
5.9 Results

Results from measurements in Leicester fall into 3 broad categories.

- Stratospheric ozone measurements were undertaken with each operation, and a long-term record was constructed that are compared with satellite measurements.

- NO$_2$ measurements were performed with the zenith and off-axis telescopes during normal operation giving information on stratospheric and tropospheric NO$_2$.

- Several alternative configurations and viewing geometries were tested to examine the capabilities of the instrument.

The first results presented are from an alternative configuration which provides an additional technique to assess the errors in measurements from the CMAX-DOAS instrument. A verification of the retrieval through comparison of derived total column ozone concentrations with satellite measurements is then presented. This is an established technique and is not the primary goal of this instrument. The majority of the results presented relate to the retrieval of tropospheric NO$_2$ concentrations through the use of the off-axis viewing geometries.

5.9.1 A Self-Consistency test using two zenith telescopes.

In order to establish the true capabilities of the instrument, a self-consistency test was performed with two independent zenith telescopes. The lowest elevation angle telescope was replaced with a temporary telescope pointing to the zenith. This additional telescope was mounted outside the main head unit and had the same dimensions as the original telescopes and was fitted with an 8 cm cylindrical baffle to avoid direct sunlight entering the telescope.
Spectra from both telescopes were imaged 300 rows apart on the CCD to simulate an average image separation and variability of instrument function. The spectra were extracted from the CCD and analyzed using the method and parameters used in normal operation (see Chapter 3). The correlation between measurements from both telescopes was tested to establish the ability of the CMAX-DOAS instrument to produce consistent concurrent slant column results from two independent inputs. In addition to comparing slant columns from the two telescopes, the influences of using a reference spectrum from another area of the CCD was investigated through analysis of both sets of spectra with exchanged reference spectra. These reference spectra were shifted to the correct wavelength grid, but no other corrections were applied. Four sets of data were therefore generated all measuring the same air mass at the same time. These datasets are termed as follows:

- Prim/Prim, for the original (primary) zenith view using its own reference.
- Sec/Sec, for the secondary zenith view, using its own reference.
- Prim/Sec, for the primary zenith spectra, using a reference spectrum from the secondary zenith view.
- Sec/Prim, for the Secondary zenith spectra, using a reference spectrum from the primary zenith view.

The results are shown in Figure 5-5 and Figure 5-6.
Figure 5-5: Slant columns of NO₂ measured using the four different methods of analysis; Prim/Prim, Sec/Sec, Prim/Dec and Sec/Prim (see text for details).

Figure 5-6: A correlation plot of the four datasets in Figure 5-5, using Prim/Prim on the x-axis. Also included are linear best-fit lines for each dataset, with equations showing intercept, gradient and R² values.
The generally good agreement between the sets of measurements can be seen as almost indistinguishable lines in Figure 5-5. The slant column values in the range from $1 \times 10^{16}$ to $2.5 \times 10^{17}$ mol/cm$^2$ are typical in Leicester. At such levels, the errors in individual measurements are a low proportion of the total signal. The extent of the differences between measured slant columns can be seen in the correlation plot in Figure 5-6. The comparability of the two datasets can be initially seen in the best fit line between Prim/Prim and Sec/Sec, with an offset of $4 \times 10^{14}$ mol/cm$^2$, and an $R^2$ value of 0.9979. The gradient of this line is significantly below 1, at 0.9764, with measurements from the new zenith measuring on average 2.4% lower than the original zenith. These marginally lower measurements may have been the result of the limit of the viewing accuracy of the telescopes, resulting in a slightly different viewing geometry. The correlation between Prim/Prim and Prim/Sec is the initial test of the errors introduced through the use of an alternative reference spectrum from another section of the CCD. The agreement within less than 0.5%, with an offset of $7 \times 10^{14}$ mol/cm$^2$ and an $R^2$ value of 0.9999 indicate that the difference in instrument function between these two fibres has introduced only very minimal errors to the DOAS system.

The technique of calculating the error in a DOAS fit directly from the covariance matrix in the fitting process was covered in Section 2.1.5. This technique, was also used to assess the errors on each of the four datasets taken on 9th November 2004. The calculated errors for each measurement were converted to a percentage of the derived slant column value and are shown in Figure 5-7. It is worth noting that there is a very strong anti-correlation between the percentage error and the slant column amount. Therefore it is difficult to accurately express the error bars given by this technique. Values at the minor peak at 1 pm, and the major peak at 3 pm are used as an indication of error ranges under favourable conditions.
Figure 5-7 Errors on retrieved slant column amounts shown in Figure 5-5 as calculated by the Stutz and Platt method and expressed as a percentage of slant column value. The Y-axis is limited to 20% as very high percentage values are calculated when slant column measurements become negligible.

5.9.2 Summary of instrumental error analysis

The four techniques for assessing the quality of the data produced by the CMAX-DOAS instrument are summarised in Table 5-2.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Single-Axis error (%)</th>
<th>Error using a ref. spectrum from other axis(%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Theoretical calculations in Chapter 5</td>
<td>1.5</td>
<td>3.4</td>
</tr>
<tr>
<td>Andøya error calculations, assuming 2 standard deviations and a slant column of 5 x 10^{16} mol cm^{-1}.</td>
<td>1.7</td>
<td>N.A.</td>
</tr>
<tr>
<td>Dual Axis Calculations</td>
<td>&lt;1% (with a 2.4% bias)</td>
<td>&lt;1% (plus bias depending on dataset)</td>
</tr>
<tr>
<td>Stutz and Platt error bars – based on slant column values of (a) 5 x 10^{16} and (b) 2.5 x 10^{17} molcm^{-1}</td>
<td>(a) 2.0%</td>
<td>(a) 5.8%</td>
</tr>
<tr>
<td></td>
<td>(b) 1.0%</td>
<td>(b) 1.8%</td>
</tr>
</tbody>
</table>

Table 5-2 Summary of the calculated errors on CMAX-DOAS measurements derived from four independent techniques.
5.10 Example measurements from “Normal” Operation.

The primary configuration of operation during 2004 was automated measurements every 2 minutes, using the zenith, 15, 10, 5 and 2 degree views. Due to instrument line shape differences already discussed, the 2 degree view was not included in analyses where a zenith reference spectrum was used. A day of data from summer 2004 can be seen in Figure 5-8. These data demonstrate the ability of the CMAX-DOAS system to concurrently measure NO₂, O₃, O₄ and H₂O. In this analysis, the reference spectrum from the zenith view was used as reference for the off-axis views, providing maximum spatial information.

![Figure 5-8](image)

*Figure 5-8 Slant columns for all retrieved absorbers from Thursday 20th May 2004 for all axes. Panels are as follows: (a) NO₂, (b) O₃, (c) O₄, (d) H₂O*

The stratospheric dominance of the ozone signal can be seen in the lack of dependence of measurement on viewing geometry, with a slant column purely dependent upon solar zenith angle. The NO₂ and O₄ slant columns demonstrate both tropospheric and stratospheric signals while the H₂O signal as expected is dominated by tropospheric signal. The constant and known profile of O₄ permits information to be gleaned on the...
abundance of cloud or haze on a given day [Wagner et al., 2004]. Clouds and haze influence photon path lengths by altering atmospheric scattering properties. While thick clouds can increase path lengths through increased scattering between and within clouds, thin cloud or haze will reduce path lengths in off-axis measurements, as scattering of photons is more likely to occur near the CMAX-DOAS instrument. Therefore, on this day, the O$_4$ slant columns indicate light non-uniform cloud as shown by the non-smooth curves, and the proximity of measurements from different axes when compared with Figure 5-9. More cloud and haze effects are evident in the morning than the evening where dusk measurements almost resemble clear-sky conditions.

The NO$_2$ slant column contains information on stratospheric NO$_2$, contained in the solar zenith angle dependence of measurements at dawn and dusk, particularly in the zenith measurement which is least influenced by tropospheric concentrations. The diurnal increase in stratospheric NO$_2$ can be seen in the increased SZA dependence in the dusk measurements over dawn. In addition, tropospheric concentrations are clearly evident in the separation of the off-axis signals, and short temporal features. The most significant features which do not coincide with cloud events are at about 12 noon and 6.30pm. Path length changes indicated in O$_4$ measurements will also influence NO$_2$ measurements. For example, cloudy features appearing in the O$_4$ columns at 10am and 3pm also appear as enhancements in the NO$_2$ slant columns.

Two further example days of measurements are shown in Figure 5-9 and Figure 5-10. Figure 5-9 shows data from Friday 7$^{th}$ May 2004 and demonstrates the strength of the NO$_2$ signal during the weekday morning rush-hour during constant cloud conditions. Figure 5-10 strongly contrasts Figure 5-9, showing data from Sunday 9$^{th}$ May, where the morning rush-hour is clearly absent (note also the different y-scales on the NO$_2$ panes in these figures).

Slant column data were produced for every day on which measurements were taken. Long-term analysis was therefore possible to establish weekly, seasonal and annual trends.
Figure 5-9 Slant columns for all retrieved absorbers from Friday 7th May 2004 for all axes. Panels are as follows: (a) NO$_2$, (b) O$_3$, (c) O$_4$, (d) H$_2$O

Figure 5-10 Slant columns for all retrieved absorbers from Sunday 9th May 2004 for all axes. Panels are as follows: (a) NO$_2$, (b) O$_3$, (c) O$_4$, (d) H$_2$O
5.10.1 Measurements of stratospheric ozone.

With purely stratospheric absorbers, the atmospheric concentration can be derived relatively simply from a Langley Plot. The Langley plot involves the fitting of a linear best-fit line to a scatter plot of ozone slant column concentration against AMF. For a uniform and constant stratospheric concentration, the relationship between slant column concentration and AMF should be linear. The gradient of the best fit line gives the stratospheric concentration as it is an indication of the additional ozone measured for each additional unit of AMF. The AMF’s used in the calculations of ozone vertical column densities were calculated at 432 nm using SCIATRAN. The solar zenith angle of each measurement was used to calculate an appropriate AMF for Ozone at 432 nm. The Visual Basic™ CMAX-DOAS program produced a Langley plot for each day’s ozone columns automatically, and one example product from 2\textsuperscript{nd} July 2004 is shown in Figure 5-11.

![Figure 5-11 Example Langley plot for 2nd July 2004. Gaps in the data are due to system resets caused by the interface between the PC I/O card and the hard drive. The derived ozone vertical column concentration for this day was 319 Dobson units from the morning data, and 327 Dobson units from the evening data.](image)
The accuracy of these derived concentrations can be verified against total ozone column concentrations measured by current satellites and ground stations. Figure 5-11 shows a composite map derived from data from the World Ozone and Ultraviolet Radiation data centre (WOUDC) (http://www.msc-smc.ec.gc.ca/wouldc).

Total ozone (DU) / Ozone total (UD), 2004/07/02

Figure 5-12 Map of Total Ozone for 2nd July 2004, courtesy of the Meteorological Service of Canada (http://exp-studies.tor.ec.gc.ca/e/ozone/Curr_allmap_g.htm) Marked in red are the azimuthal angles sampled as the solar zenith angle progressed between 86 and 90 degrees in the morning (East) and evening (West).

The azimuthal range covered by the measurements from 86 to 90 ° SZA during this measurement on 2nd July 2004 was 59 to 65 ° in the morning, and 299 to 305 ° in the evening. These azimuthal ranges are shaded red in Figure 5-12 and provide information on the section of the stratosphere which is sampled by measurements at any particular time. On 2nd July the ozone distribution over the European region was reasonably uniform, and therefore the CMAX-DOAS instrument was able to produce a Langley plot with reliable fit lines, producing a measurement of ozone of approximately 325 Dobson Units.
However, the stratospheric ozone concentration is not always uniform across the viewing geometry of the instrument, as demonstrated on 24th May 2004. On this day, data from the WOUDC shows clear structures to the East and West of the UK, which will influence measurements. These structures result in a Langley plot with significant spread, and derived ozone values in the morning which are significantly lower than the evening measurement. Ozone values from the WOUDC are shown in Figure 5-13 with the shaded red areas showing the azimuthal sampling on this day, which were from 87° to 93° in the morning and 267° to 273° in the evening.

Figure 5-13 Map of Total Ozone for 24th March 2004, courtesy of the Meteorological Service of Canada (http://exp-studies.tor.ec.gc.ca/e/ozone/Curr_allmap_g.html) Marked in red are the azimuthal angles sampled as the solar zenith angle progressed between 86 and 90 degrees in the morning (East) and evening (west).
Figure 5-14 Example Langley plot for 24th March 2004. The increased spread in this plot is an indication of the spatial variability of stratospheric ozone concentrations.

In mid-latitudes the turbulent mixing and production mechanisms discussed in Chapter 1 result in stratospheric ozone concentrations with a variable spatial dependence.

Figure 5-15 shows total column ozone measurements from the TOMS satellite for the sites shown in Figure 5-13. Plotted with these TOMS values is the derived total column ozone measured by the CMAX-DOAS instrument in Leicester. The CMAX-DOAS instrument correctly measures the significant features of the ozone variability between 3th April 2004 and 28th April 2004 and values lie within the expected range given the spatial variability of the stratospheric ozone field.

Measurements of stratospheric ozone are neither a primary objective of this work nor a strength of the CMAX-DOAS system when compared with traditional dedicated ozone measurement devices. However, the generally good agreement between the CMAX Measurements, and measurement from the TOMS instrument provide a degree of cross-calibration as the ozone retrieval is fundamentally linked to the retrieved quantities of the other trace species through the mechanics of the DOAS technique. The extent to which
information can be derived on the spatial variability of ozone concentrations would be a useful subject for future work. Using a broader range of SZA and azimuthal angles could obtain significant information on stratospheric ozone variability as photons pass through different sections of the stratosphere. However the focus of this work remains the use of multiple axes to derive detailed information on tropospheric NO\textsubscript{2} concentrations.

Figure 5-15 Total Column Ozone measurements over selected sites from the TOMS satellite instrument and the Leicester CMAX-DOAS instrument. The considerable variability in the measured total column values demonstrates the degree of spatial inhomogeneity in stratospheric ozone concentrations.
5.10.2  Tropospheric NO₂

Where a zenith reference is used with off-axis measurements, the tropospheric component of the signal can be distinguished using a relatively simple technique which is facilitated by the concurrent nature of the measurements. As the stratospheric absorption is identical for all axes, the entire stratospheric signal can be removed by subtraction of the zenith slant column measurement from the off-axis slant column amounts. This process also removes a portion of the tropospheric signal leaving a slant column amount given by the function:

\[
SC_{R trop}^{O A} = N_{Trop} \cdot (AMF_{Trop}^{O A} - AMF_{Trop}^{Zen})
\]

(5.2)

Where:

\(N_{Trop}\) is the tropospheric concentration

\(AMF_{Trop}^{O A}\) is the tropospheric component of the Air Mass Factor in the off-axis direction

\(AMF_{Trop}^{Zen}\) is the tropospheric component of the Air Mass Factor in the zenith direction.

This enhanced tropospheric signal is now distinct from the stratospheric signal and also independent of the amount in the reference spectrum. Using the radiative transfer model SCIATRAN [Rozanov et al., 2001], \(AMF_{Trop}^{O A}\) and \(AMF_{Trop}^{Zen}\) can be calculated for a given NO₂ profile shape as discussed in Section 2.2.2. The NO₂ profile shown in Figure 2-15 was used for AMF calculations in this chapter to demonstrate the derived values of \((AMF_{Trop}^{O A} - AMF_{Trop}^{Zen})\) given alternative analysis configurations.

When spectra from off-axis views are analysed using a reference spectrum from the zenith view at noon, the Air Mass Factors for the resulting differential slant column concentrations are as shown in Figure 2-16 (a repeat of Figure 2-16).
Figure 5-16 Air Mass Factors for all viewing angles using the profile shown in Figure 2-15, with a tropospheric concentration of 10 ppbv (solid lines) and 5 ppbv (dashed lines).

Figure 5-17 Residual Air Mass Factors for tropospheric columns of 10 ppbv (solid lines) and 5 ppbv (dashed lines) when a noon reference spectrum from the zenith view is used.
When spectra from each off-axis view are analysed using a reference spectrum from that same off-axis view, the resulting Air Mass Factors are shown in Figure 5-18.

![Graph showing Air Mass Factors for various viewing angles and concentrations.]

**Figure 5-18 Residual Air Mass Factors for all viewing angles, with the air mass factor for the noon view from each viewing angle subtracted. Solid lines are AMFs using a tropospheric concentration of 10 ppbv, dashed lines use a tropospheric concentration of 5 ppbv.**

For analysis in which the slant column value for the zenith view at a given time is subtracted from the off-axis slant column value as that time, the resulting Air Mass Factors are shown in Figure 5-19. These air mass factors are relevant for tropospheric analysis as the influence of the stratospheric concentration has been removed.
Figure 5-19 Residual Air Mass Factors from all angles, using 10 ppb and 5 ppb tropospheric columns, when a reference spectrum from the zenith view at a given time is used.

Figure 5-19 shows the fundamental concept behind the CMAX-DOAS instrument as sensitivity of off-axis measurements to tropospheric concentrations increases as the elevation angle is decreased. The removal of the stratospheric signal through subtraction of the zenith view results in clearly separated AMF curves, with a relatively small solar zenith angle dependence. Therefore analysis using this technique produces a quantified measurement of tropospheric NO₂.

5.10.3 Analysis of 17\textsuperscript{th} January 2004

As a primary dataset for tropospheric analysis, data from the 17\textsuperscript{th} January was analysed, using a zenith reference spectrum at noon for the DOAS fit on all axes. The zenith slant columns at a given time were subtracted from the off-axis slant columns, to leave tropospheric residual slant columns, with air mass factors comparable to those shown in Figure 5-19. These air mass factors vary with aerosol concentrations, as tropospheric path lengths for photons detected in the off-axis views reduce dramatically in the presence of aerosols. Air mass factors for three scenarios were calculated, and applied to data from three time-periods on 17\textsuperscript{th} Jan 2004. The calculated tropospheric Air Mass Factors are shown in Table 5-3.
<table>
<thead>
<tr>
<th>Time Period</th>
<th>15° Viewing angle AMF</th>
<th>10° Viewing angle AMF</th>
<th>5° Viewing angle AMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;10</td>
<td>2.5</td>
<td>3.5</td>
<td>4.7</td>
</tr>
<tr>
<td>10-12.30</td>
<td>2.5</td>
<td>3.2</td>
<td>3.8</td>
</tr>
<tr>
<td>&gt;12.30</td>
<td>2.5</td>
<td>2.9</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Table 5-3 Residual Tropospheric Air Mass Factors calculated for 3 periods on 17th Jan 2004.

The residual slant columns for 17th Jan were divided by the air Mass Factors to give comparable tropospheric column values for each axis. Tropospheric column values from each axis were then divided by 30,000 cm, to give a volume mixing ratio given the assumption that the total tropospheric NO₂ column was uniformly distributed in the lower 300 m of the troposphere. An assumption of a box profile is invariably incorrect in the urban environment with distinct and un-mixed air masses, however it is a necessary first step towards a more complete analysis. The resulting volume mixing ratios are shown in Figure 5-20.

Figure 5-20 4 Volume mixing ratios calculated from residual tropospheric slant columns from the 15°, 10° and 5° viewing geometries. Three sets of air mass factors were used to analyse the full day of data, and volume mixing ratios were calculated using the assumption of a uniform 300 m NO₂ profile.
The accuracy of the aerosol calculations and the profile shape assumptions can be validated by analysing the agreement between the three off-axis measurements over the clear morning period. Furthermore, the derived concentration can be compared with the in situ chemiluminesence detector located in Leicester city centre. The absolute volume mixing ratio derived from the CMAX-DOAS instrument is dependent upon the depth of the tropospheric column assumed, and cannot therefore be reliably included in a validation. However, the diurnal variation in the measurements does agree well with the city centre monitor, and the measurements from all three axes agree well, given the three sets of air-mass factors used over the entire day’s measurements. These two factors provide significant evidence of reliable tropospheric concentration measurements from this instrument, although the absolute volume mixing ratio is not well constrained with these calculations. Data from 17th January are further analysed in Chapter 6.

Consistent and comparable measurements were started by the CMAX-DOAS instrument from the middle of March 2004. These measurements were taken whenever technically possible to gather information on diurnal, weekly and seasonal cycles of NO₂ in the urban environment. In order to build up a long time series of tropospheric NO₂ concentrations, a simple algorithm was developed. This algorithm relies on the following assumptions:

1. The absorption by NO₂ outside of the polluted boundary layer is the same from both the zenith and off-axis viewing geometries.
2. Clouds when present are a uniform layer above the polluted boundary layer PBL, and scattering causing increased absorption is identical in both the zenith and off-axis views.
3. The 5° viewing angle samples a 4km path of the polluted boundary layer, which is not sampled by the zenith view.
4. The concentration of NO₂ in the urban boundary layer is taken as the average concentration along this 4 km additional off-axis path photon path length.

The four assumptions made are summarised in Figure 5-21.
Relatively low NO₂ concentrations
Similar NO₂ absorption on all axes above PBL

Polluted Boundary Layer

4+ x km

x km

Figure 5-21 Schematic of the assumptions made in tropospheric calculations. Absorption on all axes is assumed to be similar above the PBL, while within the PBL the off-axis view has a 4km path length through the PBL.

From these assumptions, the following algorithm can be derived for the average concentration of the polluted boundary layer along the line of sight of the instrument in \( \mu g \, m^{-3} \):

\[
Conc_{PBL} = \frac{S_{R10}^{OA}}{4 \times 10^5 \, cm \times 1.29 \times 10^{10} \, mol \, m^{-3} \, \mu g^{-1} \, cm^{-3}} \]

(5.2)

Where
4\( \times \)10^5 is the number of cm of additional path length
1.29\( \times \)10^{10} mol m^{-3} \( \mu g^{-1} \) cm^{-3} is the conversion factor from mol cm^{-3} to \( \mu g \) m^{-3} for NO₂.

Using this rough algorithm, all data from 2004 was analysed, and is plotted with data from the chemiluminescence detector in the city centre in Figure 5-22. The Y-axis on the right for the CMAX-DOAS measurements is a factor of two larger than the in situ scale, to facilitate comparison of features.
Figure 5-22 Derived boundary layer volume mixing ratios from the CMAX-DOAS measurements, and measured concentrations of NO₂ from a chemiluminescence detector in the city centre.

In this long-term series, the spread of data available during 2004 is shown. The annual cycle caused by the increased destruction of NO₂ through photolysis (equation 1.36) during the summer is evident. Increased levels of NO₂ during winter may also be due to increased use of private cars and heating fuel, which are furthermore dispersed more slowly in winter due to the reduction in convection-induced dynamic motion of air-masses.

Details from a period in May, and August can be seen in Figure 5-23 and Figure 5-24.
Figure 5-23 Derived NO$_2$ volume mixing ratios from the CMAX-DOAS instrument (red) and a chemiluminescence detector in the city centre (blue) for 1$^{st}$ to 22$^{nd}$ August 2004.

Figure 5-23 demonstrates the level of agreement between the CMAX-DOAS measurements and the measurements from the chemiluminesce detector over a period of a few weeks. The weekly cycle is clearly evident, with low measurements from both instruments on the three Sundays during this period. Given the difference in spatial sampling of the two measurements, the degree of agreement is significant. The absolute concentrations measured by the CMAX-DOAS instrument are directly dependent upon the path-length assumption included in algorithm. However, the trends are not dependent upon any assumptions made, and are directly derived from the mechanics of the DOAS fit. The reproduction of the weekly trend, and the identification of short-term features is therefore a significant piece of evidence that the CMAX-DOAS instrument is able to reliably measure the NO$_2$ concentration in the polluted urban boundary layer, directly measuring the times and relative intensities of emission events. Figure 5-24 shows another period during May 2004 in which individual peaks can be identified in both sets of measurements. From Friday 7$^{th}$ May to Tuesday 11$^{th}$ May, morning and evening rush hours can be seen on week days, with lower concentrations and different diurnal patterns evident during Saturday and Sunday.
Figure 5-24 Derived NO$_2$ volume mixing ratios from the CMAX-DOAS instrument (red) and a chemiluminescence detector in the city centre (blue) for 6th to 12th May 2004.

From all the data collected with the CMAX-DOAS instrument, it is possible to derive average concentrations for a given time on a given day of the week. Figure 5-25 shows 30-minute binned average concentrations from all available CMAX-DOAS data in 2004. The increase in NO$_2$ during week days after 7am is clear as cars and public transport start the morning rush hour. A further increase after 5pm is also evident on weekdays at the end of the working day. Concentrations on Saturdays are a significant proportion of the weekday levels, demonstrating the level of shopping, work and leisure activity in a typical British city on a Saturday. Sunday levels are significantly lower.
5.11 Conclusions

With the instrument installed at the University of Leicester, a complete characterisation was possible. The accuracy of the slant column measurements from the CMAX-DOAS instrument was assessed using 4 independent measures of instrument errors. Error margins estimated using these techniques all provide errors bars less than 2% for a single viewing geometry and 4-6% in analysis using a reference spectrum from a second viewing geometry. Such error margins are well within acceptable ranges for the study of the polluted urban boundary layer.

The instrument was operated on all available occasions during 2004, and slant column data calculated. Using traditional Langley plots, stratospheric ozone concentrations could be derived. Total column ozone measurements from the CMAX-DOAS instrument agree with measurements from the TOMS satellite, within the constraints imposed by the spatial sampling of the instrument, and the spatial variability of stratospheric Ozone. Such measurements provide a degree of validation of the operation of the CMAX-DOAS
instrument, however the viewing geometries are not ideally suited to such stratospheric measurements in the mid-latitudes.

The strengths of the CMAX-DOAS instrument lie in the ability to concurrently measure slant columns within a rapidly-changing urban environment. In such an environment, the ability to take a reference spectrum with the zenith view at the same time as a measurement over the city centre with an off-axis view, gives an instant measurement of the NO$_2$ in the air-mass above the city. This measurement was calculated using slant columns from the zenith and 5° elevation angles, where the noon reference from the zenith view had been used as a reference spectrum. Using a set of stated assumptions, the influence of the stratospheric NO$_2$ concentration, and the tropospheric NO$_2$ concentration above the polluted boundary layer can be negated through the subtraction of slant column amounts measured by the zenith view. The remaining slant column concentrations measured by the elevation angle provide a measure of the concentration of NO$_2$ above the city centre.

Derived PBL concentrations were compared with data supplied by an in situ chemiluminescence detector in the city centre. The annual cycle of NO$_2$ was clearly evident, as was the ability of the CMAX-DOAS measurements to identify emission features detected by the in situ monitor. Monthly, weekly and diurnal patterns are shown in the CMAX-DOAS data as industrial and vehicular activity in the city centre varies. The absolute concentrations of NO$_2$ in the PBL are dependent upon an assumption of a 4 km path length through the PBL from the off-axis view. This path length is reasonable given the dimension of Leicester’s city centre, and provide reasonable results, with concentrations approximately half of those measured in situ.

Given the ability to measure individual emission characteristics using 2 concurrent axes, the use of all 5 viewing geometries in theory opens up the possibility of validating tropospheric measurements, and gathering further spatial information on NO$_2$ concentrations at a given instant. The possibilities of spatial distribution measurements are explored further in Chapter 6.
6 Analysis of NO$_2$ events in Leicester

6.1 Introduction

The temporal resolution of the CMAX-DOAS instrument provides a unique opportunity to analyse relatively rapid changes in NO$_2$ concentrations in the air-masses sampled by each viewing geometry. The design with 4 northerly-pointing off-axis views permits sequential sampling of the same air mass in Northerly and Southerly winds, as the plume is blown through each viewing angle in turn. Data from the 17$^{th}$ January 2004 will be used to demonstrate this principle. The addition of supplementary azimuthal telescopes permits sequential sampling of Easterly and Westerly moving air masses. Data from 14$^{th}$ November 2004 will be used to further demonstrate the potential of this observation geometry.

6.2 Spatial analysis using 4 Northerly-pointing off-axis views

As an example of the spatial analysis possible using high time resolved CMAX-DOAS data, measurements from the morning of 17$^{th}$ January 2004 will be analysed. A subset of the data used in Chapter 5 is presented in Figure 6-1, demonstrating the variability of the NO$_2$ signal while O$_4$ curves remain smooth indicative of clear-sky conditions.

![Figure 6-1 Measured slant columns for 17th January 2004 for NO$_2$ (left) and O$_4$ (right).](image)
Further analysis of this clear-sky morning period demonstrates the potential of the CMAX-DOAS instrument to gain information about the dynamical progression of individual air masses. For this analysis the DOAS retrieval was adapted, with the noon reference spectrum from each individual axis being used as the reference for the spectra from that axis, instead of using the zenith reference for all analysis. This loses certain information on the vertical profile of the gases, but also removes any influence of the changing instrument line shape over the surface of the CCD. Therefore residuals on all axes were reduced for the 1-minute analysis to between 1.3% for the zenith view and 0.61% for the 15 degree elevation. This analysis technique also permitted the use of a 2 degree viewing angle which was unreliable in the initial analysis owing to its low intensity and excessive differences in instrument line shape compared to the zenith view.

Figure 6-2 shows the morning period between 9.20 and 9.50am with an expanded time axis. This highlights the distinct peaks sampled by the instrument, confirming the presence of discrete plumes of NO\textsubscript{2} in the viewing direction of the instrument. The clear temporal shifts between peaks as they are measured by each axis allows the dynamical progression of the air mass to be quantified.

![Figure 6-2 Expansion of the main two pollution peaks on 17th January 2004.](image-url)
The analysis of the finer structure of these peaks provides information on the transport of these two plumes, their spatial extent, and their concentration of NO$_2$. The wind speed on the 17th Jan 2004 was approximately 1.6 ms$^{-1}$ coming from a northerly direction. As the instrument is placed to the south of the city centre, this would result in plumes from the city centre being transported slowly through each viewing direction of the CMAX-DOAS instrument. The progression through the viewing geometries can be clearly seen. Owing to the nature of the recording cycle in the CCD to PC interface, a measurement is missed every 6 to 10 minutes. In this time period, measurements are missing at 9:22, 9:29, 9:33 and 9:42. The missing measurements at 9:29 and 9:42 are particularly unfortunate in this particular case as they coincide with the two peaks, and cautious interpolations of the peak shapes around these missing points need to be made.

Information on these plumes can be gained from the amplitude of these peaks, their width, and the temporal shift between each viewing direction. These values can be found in Table 6-1.

<table>
<thead>
<tr>
<th></th>
<th>Peak 1 (overhead at 9:37am)</th>
<th>Peak 2 (overhead at 9:46am)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amplitude (mol/cm$^2$x10$^{16}$)</td>
<td>Width (minutes)</td>
</tr>
<tr>
<td>2 Degree</td>
<td>2.2</td>
<td>6.5</td>
</tr>
<tr>
<td>5 Degree</td>
<td>6.5</td>
<td>9.5</td>
</tr>
<tr>
<td>10 Degree</td>
<td>7</td>
<td>8.5</td>
</tr>
<tr>
<td>15 Degree</td>
<td>5.5</td>
<td>9</td>
</tr>
<tr>
<td>Zenith</td>
<td>1</td>
<td>4</td>
</tr>
</tbody>
</table>

Table 6-1 Details of the two pollution peaks shown in Figure 6-2.
6.2.1 Viewing Geometry Assumptions

A relatively straightforward geometric analysis can be performed given four assumptions. The first assumption is that the wind speed is constant over the spatial and temporal domain. The wind speed is taken from the Leicester City Council meteorological station, which measures wind speed hourly. The 9 am reading was 1.8 ms\(^{-1}\), the 10 am reading was 1.4 ms\(^{-1}\). Therefore the assumed wind speed for the period around 9.30 am is 1.6 ms\(^{-1}\).

The second assumption which is necessary is a vertical uplift of the plume. In the absence of information required for quantitative calculation of the plume rise rate using the Briggs equations [Briggs, 1975] such as emission speeds and temperatures, a rough estimation of 25 cm per second, or 10 degrees in a 1.6 m/s wind was used. The third assumption is that the plume is spherical in such a slow wind. Such a simplistic assumption will introduce errors, however future instrumental developments involving additional viewing geometries will allow the plume shape to be more accurately assessed. For this first demonstration the mathematical simplicity gained by such simple assumptions is paramount in the absence of significant additional plume shape information.

The final assumption required is that the plume is travelling directly towards the instrument and the centre of the plume is sampled by the off-axis and zenith geometries. Given the instrument position to the south of the city centre, and a measured Northerly wind, this assumption is justified within the parameters of this initial analysis. Leicester city centre is situated in a slight valley, and is approximately 50m below the level of the instrument based to the south of the city. This height difference would result in a degree of additional dynamical movement of the plume prior to the first sampling by the 2 degree view resulting in potential inaccuracies in the derived plume source location. However, such influences were not considered in this analysis as the height difference does vary over the potential emission source, and is relatively small.
These assumptions establish a relatively simple triangular geometry of the plume through the viewing angles of the CMAX-DOAS instrument, as illustrated in Figure 6-3.

Figure 6-3 Simplified plume geometry for plume analysis

From this geometry several properties of the plume can be estimated. Firstly the diameter of the plume when it is measured by a given viewing direction can be estimated from the time taken for it to be blown through that viewing direction at a given wind speed. This can be expressed as:

\[ D(\theta) = U \cdot \left( T_f(\theta) - T_s(\theta) \right) \]  

(6.1)

where \( U = \sqrt{W^2 + R^2} \)  

(6.2)

- \( D(\theta) \) = plume diameter when passing through a given viewing angle.
- \( U \) = plume speed along its line of transport
- \( T_s(\theta) \) = start time of plume measurement from a given viewing angle
- \( T_f(\theta) \) = finish time of plume measurement from a given viewing angle
- \( W \) = Wind speed as measured by in-situ monitors
- \( R \) = estimated plume rise rate.
The distance traveled between detection by subsequent viewing geometries can also be estimated through calculation of the distances CD, DE, EF, and FG.

For example

\[ FE = (T_p(\theta_3) - T_p(\theta_2)) \times U \]  

(6.3)

where:

FE is the distance between points F and E in Figure 6-3.

\[ T_p(\theta_3) \]  

is the time of peak plume intensity from viewing angle 3.

Once the distance FE has been calculated, the triangle AFE can be solved, calculating distances to the plume centres when the peak concentrations are being measured.

\[ AF = \frac{\sin(5^\circ) \times FE}{\sin(155^\circ)} \]  

(6.4)

6.2.2 Plume reconstruction

Using the elevation angles of each viewing geometry and the calculated distance of the plume from the instrument, the horizontal (\(H^F\)) and vertical (\(V^F\)) displacement of the centre of the plume can be calculated at the time \(T_p(\theta_3)\).

\[ V^F = \sin(15^\circ) \times AF \]  

(6.5)

\[ H^F = \cos(15^\circ) \times AF \]  

(6.6)

The maximum absorption of the plume can be measured from the amplitude of the plume peak above the background NO\textsubscript{2} concentration. Given the assumption of spherical plumes and the assumption used in Chapter 5 that most photons are scattered behind the
plume, the absorption path length through the plumes is given by the measured diameter $D(\theta)$. The average concentration in mol cm$^{-3}$ within the plume can be calculated from:

$$N_a = \frac{A_\theta}{D(\theta)}$$

(6.7)

where $A_\theta$ is the amplitude of the peak as measured by the view geometry with elevation angle $\theta$ (mol cm$^{-2}$).

The results of these calculations therefore provide estimations of the size of the plume, its position, and its concentration. This analysis was performed on the two plumes identified in Figure 6-2, and results plotted to scale in Figure 6-4 and Figure 6-5.

Figure 6-4 Scaled schematic of the evolution of the plume which passed over the CMAX-DOAS instrument at 9.37am. Figures shown are the average plume concentration, the time (T) since the plume was first detected, and the diameter.

Figure 6-5 Scaled schematic of the evolution of the plume which passed over the CMAX-DOAS instrument at 9.46am. Figures shown are the average plume concentration, the time (T) since the plume was first detected, and the diameter.
Plotted in Figures 6-4 and 6-5 are the calculated positions and sizes of the plumes as they pass through each viewing geometry. Even with the assumption of spherical plumes, a first approximation of plume concentrations can be derived. However, the weakness of the assumption is evident as the plume concentration is calculated to decrease significantly as the plume is measured by the zenith view. This is chemically inconsistent with existing knowledge of urban NO$_2$ chemistry, and a much more likely scenario is a shallower, flatter plume which for a given concentration would cause a smaller amount of absorption in the vertical plane than the horizontal. The possibility that the zenith view is only measuring the edge of the plume must also be considered. The assumption that at each stage we are measuring the centre of the plume is a considerable one, especially as the calculated distance between the 15° measurement and the zenith measurement is 600 to 800 m. It is very likely that to some degree the zenith measurements for both plumes are lower due to the plume being blown through the off-axis viewing geometries and then to the side of the instrument rather than directly overhead. Without the use of additional azimuthal geometries it is difficult to quantify the extent of this effect. The use of additional azimuthal viewing geometries is discussed later in this Chapter, and in Chapter 7. The remainder of this analysis will be done under the assumption that the middle of the plume is measured on each occasion in order to develop a technique which could be used in a situation where sufficient azimuthal views were available.

Adjusting the assumption of spherical plumes to allow for a more elliptical geometry permits a more realistic modeling of likely plume dimensions. Using an assumed eccentricity, the path length through a plume with an elliptical cross section can determined and used in concentration calculations, as illustrated in Figure 6-6.
The eccentricity of the ellipse is defined as:

$$
\varepsilon = \sqrt{1 - \left(\frac{Y}{X}\right)^2}
$$

(6.8)

With wind fields of 1.6 m/s$^{-1}$ horizontally, and 0.25 m/s$^{-1}$ vertically, an Y/X value of 0.2 was used as an initial estimation of plume shape. An intermediate step using Y/X of 0.4 was also calculated to provide a measure of the sensitivity of calculated concentrations to this Y/X factor. Results from these calculations are shown in Figure 6-7 and Figure 6-8.
Figure 6-7 Calculation of positions and concentrations for plume 1 using a Y/X ratio of 0.4 (top) and 0.2 (bottom).

Figure 6-8 Calculation of positions and concentrations for plume 2 using a Y/X ratio of 0.4 (top) and 0.2 (bottom).
6.2.3 Source Location and strength estimation

As discussed in Chapter 1, the primary source of NO\textsubscript{2} in the urban atmosphere is the emission of NO from combustion sources, and the subsequent conversion of this NO to NO\textsubscript{2} through reaction with ozone.

\[ NO + O_3 \rightarrow NO_2 + O_2 \]  

The concentration of ozone as measured by an in-situ monitor operated by Leicester City Council is shown in Figure 6-9. The reduction in ozone concentrations during the morning rush hour is clearly evident as NO from vehicular traffic is oxidized to form the significant NO\textsubscript{2} concentrations measured and discussed in Chapter 5. The in situ ozone monitor is situated near to busy roads at ground level, and therefore available ozone will be used sooner here than at other sites in the city. The night-time peak of 25 ppb of ozone is an indication of the oxidizing capacity of the Leicester Urban atmosphere, and therefore plumes of 25ppb of NO\textsubscript{2} are a reasonable possibility given a sufficiently large and distinct source of NO.

Figure 6-9 Ozone concentration in ppbv as measured by the automated monitoring station operated by Leicester City Council.
The total mass of NO₂ in the plumes can be roughly estimated through calculation of the volume of the elliptical plumes. If the assumption is made that the concentration is constant throughout the plume, and that the elliptical plume has the same dimensions in the vertical and East-West dimension, then the total mass of NO₂ within the plume can be calculated for any of the ellipses drawn in Figure 6-7 and Figure 6-8.

For example, for plume 1 measured by the 15° elevation angle, using an assumed Y/X factor of 0.2, the measured diameter is 877 m, and the concentration is 26 ppb. Therefore the total mass of NO₂ in that plume, given the above assumptions is calculated as follows:

\[
\text{Total Volume} = \frac{4}{3} \pi \times (877 \times 0.5) \times (877 \times 0.4 \times 0.5) \times (877 \times 0.4 \times 0.5) = 1.46 \times 10^7 \text{ m}^3
\]

1 ppb = 1.913 μg m⁻³

26 ppb = 49.738 μg m⁻³ = 4.974 x 10⁻⁸ kg m⁻³.

Therefore the total mass of NO₂ in the plume = 4.974 x 10⁻⁸ x 1.46 x 10⁷ = 0.73 kg.

This is a significant mass of NO₂, which would require a repeated and distinct emission source. The estimated source position can be calculated by extrapolating back from the measured plume positions from the different axes and calculating the distance AB in Figure 6-3. For both plumes the source location is calculated to be between 1.2 and 1.4 km to the north of the CMAX-DOAS instrument.
Figure 6-10 Map of Leicester city centre, showing the location of the CMAX-DOAS instrument, and a prime candidate for emission of plumes between 1.2 and 1.4 km to the north, the main train station. (map courtesy of Ordinance Survey).

As shown in Figure 6-10, the main train station in Leicester is located approximately 1.3 km to the north of the site of the CMAX-DOAS instrument. The acceleration of diesel trains out of the station is therefore a significant possible source of such plumes.

Emissions from diesel trains are poorly quantified at present [Hickman, 1999; Goodwin and Coleman, 2002; DEFRA, 2003], although an initial estimate of the volume of NO produced by an accelerating diesel engine can be gained from a study of German Diesel trains by Jørgensen and Sorenson [Jørgensen and Sorenson, 1997].

In this study, an Intercity passenger train was monitored for energy consumption over an 81.8 km route on two separate occasions. On the first occasion the train did not make any
stops, and used a total of 6.545 x 106 KJ, or 1818 kWh of energy. On the second trip, 3 stops were made and a total of 9.385 x 106 KJ or 2609 kWh was used. The three stops used an average of 264 kWh of energy per stop to accelerate the train back to full speed. The average emissions of NOx for a diesel train are 6 – 16 g kWh⁻¹, although the variation in this emission range when the locomotive is accelerating is poorly defined. Using a value of 10 g kWh⁻¹, a total emission of NOx for a train to accelerate from rest to full speed can be calculated as 2.64 kg. Although there are many assumptions made in this simple calculation, it does conclude that diesel trains are a credible source for distinct regular plumes of between 0.5 and 1 kg of NO₂ in Leicester City Centre, given sufficient ozone concentrations to act as an oxidizing agent.

### 6.3 Additional Azimuthal Geometries

On 11th November 2004, two additional viewing geometries were temporarily added to the CMAX DOAS instrument. These geometries were at 15° elevation angle, with one telescope pointing at 20° and the other at 340° ± 2° azimuthal angles (i.e. One telescope 20° east of the permanent view geometries, and one 20° west). These additional viewing geometries permitted the tracking of individual plumes as they were blown by an easterly or westerly wind through the different viewing geometries. The use of 7 concurrent fibres necessitated the concentration of the images on the CCD chip. Normal operation with 5 fibres used alternate inputs into the 9-way multi-track fibre giving a spacing between images of approximately 100 rows, and negligible stray-light concerns. The spacing between the imaged spectra was halved for this experiment, to 50 rows in order to accommodate the additional fibres, and a resultant image is shown in Figure 6-11.
This configuration therefore not only tests the utility of the additional viewing geometries, but also the capability of the existing CCD and spectrometer system to accommodate additional viewing geometries.

The wind conditions, as measured by the WMS 987 weather station on top of the Space Research Centre at the University of Leicester, are shown in Figure 6-12. Clear sky conditions were available during the morning period around 8am, when the wind direction was approximately 210° with an average wind speed of 1.5 m/s. Therefore plumes detected around this time would be traveling from the South West to the North East at approximately 1.5 m/s.
Figure 6-12 Wind speed and direction on the 14th November 2004 during the 7-Axis configuration.

Slant columns of NO$_2$ from the available elevation angles are shown in Figure 6-13. Reference spectra from each viewing angle were used, rather than using a single zenith reference spectrum. The influence of a South West wind can be seen from the fact that structures in the off-axis measurements are not repeated in the zenith view. Plumes detected over the city centre by the 2, 5, 10 and 15 views are not blown over the CMAX-DOAS instrument, and are therefore not measured by the zenith view. The cloud conditions for this day can be derived from the O$_4$ slant columns shown in Figure 6-14.

The day was mostly clear of significant cloud, resulting in fairly smooth, clearly separated slant column measurements of O$_4$ from each elevation angle. The two periods of cloud during the day demonstrate the influence of scattering by clouds in multi-axis measurements. The zenith view, which has the shortest average photon path normally experiences increased absorption as multiple scattering within the cloud causes an increase in path length and retrieved slant column concentrations. The off-axis views measure smaller slant column concentrations under these cloud conditions.

Scattering
within the clouds effectively blocks photons scattered from long distances away with long tropospheric path lengths, and instead photons scattered within the cloud are the dominant source for off-axis measurements. These photons scattered within the clouds have a shorter total tropospheric path length than those measured by the same viewing geometry in clear sky conditions that are scattered some distance away. This change in average photon path results in the observed reduction in retrieved slant column density of O₃ under cloudy conditions.

Figure 6-13 Slant columns of NO₂ from the five northerly-pointing telescopes on 14th November 2004. Slant columns from each telescope were calculated using the noon reference spectrum from that same telescope.
Figure 6-14 O$_4$ Slant Columns measured by the zenith and northerly-pointing telescopes on 14th November 2004. Distinctive cloud features can be seen around midday.

The pollution peak between 8 and 9 am on the morning of the 14$^{th}$ November is used to demonstrate the capabilities of the additional azimuthal geometries. Retrieved slant columns from the three different azimuthal viewing geometries for a selected morning period are shown in Figure 6-15. Three plumes in Figure 6-15 can be seen to progress through the Westerly view, the northerly-viewing geometries, and finally the most Easterly telescope. O$_4$ slant columns for the same period are shown in Figure 6-16, demonstrating that although there is some structure, suggesting a little cloud cover on this particular morning, there are not the three significant structures shown in the NO$_2$ data. These two figures demonstrate the ability of the CMAX-DOAS to track individual plumes of NO$_2$ as they are blown across the instrument viewing geometries.

The permanent viewing geometries were also operating concurrently, and therefore provide information on the spatial extent and transport of the plumes in the north-south direction. Data from the zenith, 15°, 10° and 5° views are shown in Figure 6-17, the 2° view contained significant additional structure from the city centre, and is therefore
shown dashed to clarify the plume structure. The O₄ columns from the elevation views demonstrate the clear sky conditions, including the reliable retrieval from the 2° viewing geometry.

Figure 6-15 Slant columns of NO₂ from the three telescopes at 15° elevation, showing the progression of three individual plumes as they are blown from West to East.

Figure 6-16 Slant columns of O₄ for the morning of 11th November 2004, showing predominantly clear sky conditions.
Figure 6-17 Details of the three plumes of NO₂ shown in Figure 6-15, showing measurements from the 4 available elevation angles.

Figure 6-18 O₃ slant columns for the 5 elevation views on 11th November 2004 showing predominantly clear sky conditions.
The irregular shapes of these three plumes render the analysis rather more complex than in section 6.2.2. Initial information is available from the plume amplitudes, which are approximately $2 \times 10^{16}$ mol cm$^{-2}$, therefore these plumes are less concentrated than plume 1 in Figure 6-2 from 17th January 2004. With a wind speed of 1.5 m s$^{-1}$ at 210° the components of the wind speed in the South-North, and West-East directions are 1.3 and 0.75 m s$^{-1}$ respectively. Transit times of 4-6 minutes through the viewing geometries give an initial estimation of diameter of 720 m. Gaps of approximately 1 minute between peak detection in the azimuthal directions for all 3 peaks gives an estimated distance from the instrument of approximately $(60 \times 0.75)/\tan 20 = 125$ m.

Although spatial information is still sparse, the following observations can be made from the available 7 viewing geometries.

- With all three plumes, the lowest viewing geometry at 5° elevation angle is the first to see the plume, therefore a local source should be suspected, especially with a southerly wind.

- The three plumes are of similar dimensions, concentrations, and are spaced 12 minutes apart.

- The fact that the 15° elevation westerly view and the 5° northerly views see the plume at approximately the same time for each plume, suggests an irregular plume shape.

- Sequential viewing of plumes through increasing elevation angles in a southerly wind suggests a rapid rate of plume transport upwards after emission.
6.4 Conclusions

Sensitivity tests shown in Chapter 6 have demonstrated the reliability of fine structure visible in slant columns measured in urban environments with the CMAX-DOAS instrument. By analysing this fine structure, individual plumes of NO₂ can be identified as they are blown through the instrument viewing geometries. The concurrent nature of the measurements from the CMAX-DOAS instrument enables limited spatial information to be derived from peaks which are visible in multiple axes.

In favourable wind conditions, in which the original source of the plume is directly downwind of the instrument, a simplified geometry can be used to reconstruct plume dimensions, concentrations and source location. This simplified geometry makes numerous assumptions owing to the very limited spatial information available. However, despite the significant assumption uncertainties, derived plume dimensions and concentrations are within expected parameters and a credible source location was identified.

The existing CCD and spectrometer system is capable of accommodating additional viewing geometries, with minimal stray light problems caused by a 50-row separation between imaged spectra. Additional azimuthal telescopes can be used to track the spatial extent and transit of plumes in all wind conditions. With only 2 additional azimuthal telescopes, the amount of spatial information is very limited. However the irregular plume shapes expected, and suggested by initial investigations demonstrate the utility of each additional view.
7 Conclusions

7.1 Summary of development and key results.

The primary science driver for this work was the requirement for improved nitrogen dioxide monitoring in the urban environment. Elevated concentrations of nitrogen dioxide in the urban environment have been linked to respiratory health problems, and are the subject of several EU directives. The spatial sampling capabilities of in situ chemiluminescence monitors are limited, requiring significant numbers of instruments and considerable modelling interpolations to produce data over urban spatial scales. The development of a scattered-light spectroscopic system for determining the concentration of distinct air-masses in the urban environment would contribute considerably to air quality monitoring capabilities.

The primary instrumental focus was the development of a scattered-light DOAS system capable of simultaneous imaging of multiple viewing directions. The instrumental challenges included the design and construction of suitable entrance optics, the alignment of optical components to produce distinct and comparable spectra, and the reading out of such signals rapidly from a CCD detector. In addition to such hardware challenges, software was required to operate such a system, including assessment of instrument line shapes, wavelength calibrations, and autonomous analysis of sets of spectra using a variety of reference spectra. For analysis of weekly, monthly and seasonal trends, the instrument was required to operate in all weather conditions, and as autonomously as possible. From the DOAS analysis, and the slant columns retrieved from concurrent measurements, new techniques were required to gather information from these unique datasets.

Through a series of testing stages and measurement campaigns, the instrumental and software capabilities were incrementally improved. The ability to produce accurate slant columns from a single axis was first confirmed in early 2003 during the Andoya
campaign. The development of capabilities to concurrent multi-axis measurements occurred during the latter part of 2003, and reliable data were taken with the new instrument in 2004. An automated software environment was developed to analyse data from all axes simultaneously, with the appropriate reference spectrum for a given situation.

Reliable slant columns were retrieved using spectra from an off-axis view with a reference spectrum from the zenith view, despite the fact that these spectra were recorded through different optical systems. Through hardware alterations and very careful spectrometer alignment, instrument line shape differences were minimised and stray light issues negated. Detector characterisation permitted a significant reduction in spectral features introduced through detector sensitivity. With the use of such techniques, the errors on DOAS retrievals in the urban environment from a single axis were measured at less than 2%. Errors when using a reference spectrum from a different axis were calculated at between 4 and 6%. Four different techniques for analysing errors were used to derive these figures.

The unique measurements taken with this instrument permit simultaneous knowledge of slant columns of NO$_2$ and other trace species in multiple directions. The time resolution of this instrument is theoretically less than 10 seconds, although for this work, measurements were averaged into bins of 2 minutes to reduce noise. Measurements from the urban environment demonstrate strong signals of NO$_2$ with a clear correlation to anthropogenic activity. The concentration of tropospheric NO$_2$ was estimated through the use of several basic assumptions resulting from the location of the instrument in the Leicester City area.

Concentrations of NO$_2$ in the boundary layer derived from measurements from the CMAX-DOAS instrument were within the expected range, and agree well with in situ measurements from chemiluminescence detectors. This is the first time that diurnal, weekly and seasonal trends have measured using an scattered-light DOAS system in an urban environment.
The high-resolution and concurrent nature of the measurements permit spatial information to be gathered on individual plumes in the urban environment. With the correct meteorological conditions and viewing geometries, the development of a plume can be monitored. Not only is an estimation of plume concentration and size possible, but with a few basic assumptions, a reasonable estimate of the origin of the plume can be obtained. These are the first measurements of individual plume concentrations, origins and dimensions using an open-path DOAS system in an urban environment. A significant source of distinct plumes in the Leicester city area was found to be the main train station, with an estimated mass of NO$_2$ in plumes reaching 0.75 kg.

### 7.2 Conclusions on instrumental capabilities and limitations.

The design of this instrument imposed several restrictions on the sensitivity of measurements. The use of fibre optic cables with a diameter of only 50 µm limited the amount of light entering the optical system, and thus the number of photons detected. For measurements of a strong absorber in the visible region of the spectrum, this limitation in light entering the system was not a constraint. However, measurements of weaker absorbers, requiring faster integration times and more averaging, or measurements in a weaker part of the solar spectrum such as the UV, may be constrained by the amount of light transmitted by such fibres.

The use of a single detector to measure the signal from all axes places a limitation on the integration time used for the CCD detector. The integration time must be set to avoid saturation of the brightest viewing geometry. The weakest signal therefore cannot be enhanced through an increase in the integration time used on the CCD, resulting in poor signal to noise characteristics from certain geometries under certain solar zenith and azimuthal angles. Figure 3-12 demonstrates this effect with the weak signal on the 2° view geometry. An increase in the number of elevation or azimuthal viewing geometries will exacerbate this problem as the variability in the irradiance in each telescope will increase. As with fibre-size, this limitation was not found to be too much of a constraint.
for such a strong absorber as NO₂ for viewing angles above 3°, but problems may arise in retrievals with more stringent signal to noise requirements.

The changes in instrument line shape across the detector were calculated in this work to produce errors of 4 to 6%. These errors are for a relatively high concentration of a strong absorber (NO₂), in the strong part of the solar spectrum from 400 to 500 nm. Furthermore, for measurements from elevation angles below 3° where signal to noise ratios were low, the NO₂ retrieval became unreliable when a zenith reference spectrum was used. Although this instrument could obtain significant and groundbreaking measurements despite these additional uncertainties, the removal of such influences would open up new possibilities of enhanced sensitivity. The ability for each viewing geometry to obtain its own zenith noon reference spectrum would significantly enhance the potential of a CMAX-DOAS instrument. Possible instrumental adaptations to address this issue are explored later in this chapter.

Despite the inherent instrumental limitations of the current design, a significant amount of information is available in the recorded slant columns of O₄, Ozone and NO₂. In an environment with high concentrations of NO₂, measurements of an accuracy of a few percent are easily achievable, and such measurements have considerable value to the monitoring of urban air quality. Through the use of a zenith reference spectrum from the same time as an off-axis spectrum, an instant measurement of NO₂ in the PBL was produced using a slight variation to the standard software. Real time measurements are available using such a system, with time resolution of less than a minute, and a delay of approximately 5 seconds for analysis. Such measurements of the air quality above a city centre would not only provide a source for public information, but would also provide valuable data to the modeling community, to constrain models of urban chemistry which are currently limited by the use of a network of in situ monitors which are only able to provide point measurements at ground level.

The use of 5 and 7 viewing axes to monitor the progression of a single plume demonstrates the potential of concurrent multi-axis DOAS to examine individual distinct
pollution events and trace the evolution of plumes following emission. Individual pollution sources could be targeted with such a device, with viewing geometries adapted to the source location and meteorological conditions, to maximise the information gained on that specific source and the NO\textsubscript{2} emitted.

The future potential of the technique is explored further through the proposal of alternative instrument designs, which remove some of the constraints already mentioned in this chapter, and maximise the positive aspects of current CMAX-DOAS capabilities.

### 7.3 Future work, and development possibilites.

In order to retrieve weaker absorbers or cope with the low signals demonstrated by the 2 degree viewing geometry in this work, a technique for removing instrument line shape differences is essential.

The most straightforward solution is to incorporate stepper motors into the telescope mounts which would permit each telescope to be rotated to a zenith view at solar noon. This would require the manufacture of a new head unit, which permits unobstructed zenith views and freedom of movement for all telescopes. Each telescope would also require a baffle to avoid direct sunlight entering the during the zenith exposure. This baffle would require a non-UV absorbing window over the end to avoid the baffle filling with water when it rains. A simple design for such adjustable telescope units is shown in Figure 7-1. Such units could be placed in a row on a railing for example, to provide the necessary viewing geometries.

The significant draw-back of such a system, is the incorporation of moving parts to the instrument design. With the current CMAX-DOAS system, there are no moving parts, significantly increasing instrumental stability. The effectiveness of a system using stepper motors would depend upon the reliability and reproducibility of the motors, including operation during rain, hot summer, and cool winter conditions.
The 7-axis experiment detailed in section 6.3 demonstrated the potential for imaging individual fibres only 50 rows apart on the CCD. This can be considered as a minimum separation while still ensuring negligible stray light problems between the fibres. Through the use of the full CCD imaging area, a total of 21 individual fibres could be simultaneously imaging using the current spectrometer and CCD configuration. The dump gate charge build up seen in Figure 3-12 does not occur when a full CCD image is captured and so would not be an issue. The manufacture of a multi-axis fibre similar to be used in this experiment with 21 fibres instead of 9 would be complex but feasible and not prohibitively expensive. (Ocean Optics – personal communication). With 21 telescopes, much more spatial distribution information could be retrieved, and using adjustable mounts with stepper motors would provide the flexibility to alter the configuration depending upon the target plume. For example, individual units based on the design shown in Figure 7-1 could be mounted on a single rail which ran from east to west. The stepper motors could be easily controlled via a PC to configure any desired viewing geometries, including taking a zenith measurement at solar noon.

Desirable Viewing geometries could include any of the patterns shown in Figures 7-2 to 7-4. With 21 telescopes, there is considerable flexibility in the areas of the sky monitored.
Broad areas of the horizon could be monitored with the configuration shown in Figure 7-3. Significant information on the vertical distribution of NO2 could be gathered using a configuration shown in Figure 7-4, or plumes could be tracked as they progressed over the instrument. Obviously such configurations of 7x3 telescopes could be altered to 4 x 5 with one zenith view, as illustrated in Figure 7-2, or indeed 10 x 2, or 20 x 1 configurations.

Figure 7-2 Possible viewing geometries for monitoring plume progression

Figure 7-3 Possible plume geometries suitable for monitoring broad areas, or tracking plumes as they are blown across the view of the instrument
With the spatial sampling available from additional geometries, the possibility to reconstruct detailed dimensions of an individual plume or the characteristics of the polluted urban canopy are available. Such capabilities are significantly enhanced through the use of two CMAX-DOAS systems running concurrently. For example, two systems, running a configuration of 1 zenith telescope, and an array of 10x2 off-axis views could sample the Leicester City centre as shown in Figure 7-5. Through the use of tomographic algorithms, information from all 40 off-axis telescopes could be used to reconstruct the shape and varying concentration of the polluted urban canopy with a time resolution of only a minute. Such a system could be totally autonomous, requiring only the installation of the two instruments, and the alteration of the existing CMAX-DOAS software to perform the DOAS analysis on the additional geometries.
The use of 2 concurrent systems with such broad azimuthal ranges would provide boundaries to the polluted boundary layer sampled by the other instrument. For example, with an easterly wind, the instrument to the east of the city centre would be able to measure the dimensions of the significant NO\textsubscript{2} concentrations, in the north-south dimension. These dimensions could then be used to refine the 4 km estimate currently used in calculations, to produce not only spatial information, but a much more absolute measure of concentration, as the length of absorption paths is more accurately quantified.
7.4 Final Conclusions

The CMAX-DOAS instrument developed in this work has proven a reliable tool for the measurement of Nitrogen Dioxide in both remote locations, and the urban environment. The unique capabilities of the instrument are ideally suited to the challenge of measuring heterogeneous and rapidly changing concentrations of Nitrogen Dioxide produced through anthropogenic activities. The current instrument has proven capable of producing valuable information on individual plumes and diurnal, weekly, and seasonal trends within Leicester. However, the true discovery of this work is the potential of the technique, with a second generation of instruments to be a significant tool to monitor an urban environment for air quality in real time. Such a tool would add considerable information to current automated monitoring networks which are constrained to ground-level information with modelled plume development.
Bibliography


Humfrey, C., L. Shuker, and P. Harrison, IEH Assessment on indoor air quality in the home., Leicester MRC Institute for Environment and Health, 1996.

IPCC, Climate Change 2001, the scientific basis, The Intergovernmental Panel on Climate Change, 2001.


