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DOAS: Yesterday, Today, and Tomorrow

The preceding two chapters presented examples of the technological development and the scientific contributions of the DOAS technique. This final chapter will give a historical overview of this method in order to provide an outlook on the future of DOAS, with respect to both its further technological development, and upcoming scientific and monitoring applications. Following the approach taken throughout this book, we will distinguish between active DOAS, which employs artificial light sources, and passive DOAS, which uses sunlight.

12.1 Passive DOAS Applications

Figure 12.1 illustrates how, beginning with the measurements of total ozone in 1930s by Dobson through direct sunlight, the passive DOAS method has branched out in a multitude of different applications. Direct sun- or moonlight applications are quite rare at the present time. Among these, the most important are balloon borne DOAS measurements (Ferlemann et al., 1998; Harder et al., 1998), which have given important insights into the vertical distribution of trace gases such as NO_2 and BrO. A few direct moon measurements of photolabile species, such as NO_3, have also been reported. While not employed frequently in the past, direct sunlight observations have been revived through the occultation measurements of the SCIAMACHY (Scanning Imaging Spectrometer for Atmospheric Chartography) instrument.

The measurement of scattered sunlight, which was initiated by Noxon in 1975 by aiming his instrument at the zenith, led to a better understanding of both ozone and NO_2 in the stratosphere. Driven by the discovery of the Antarctic ozone hole in 1985, DOAS rapidly found its place as a key tool to study the halogen-catalysed ozone destruction mechanisms and the budget of nitrogen species. The measurements of BrO and OClO by Solomon et al. (1987b, 1989d) revealed that chlorine and bromine chemistry played a crucial role in the formation of the ozone hole. Followed by this success, variations

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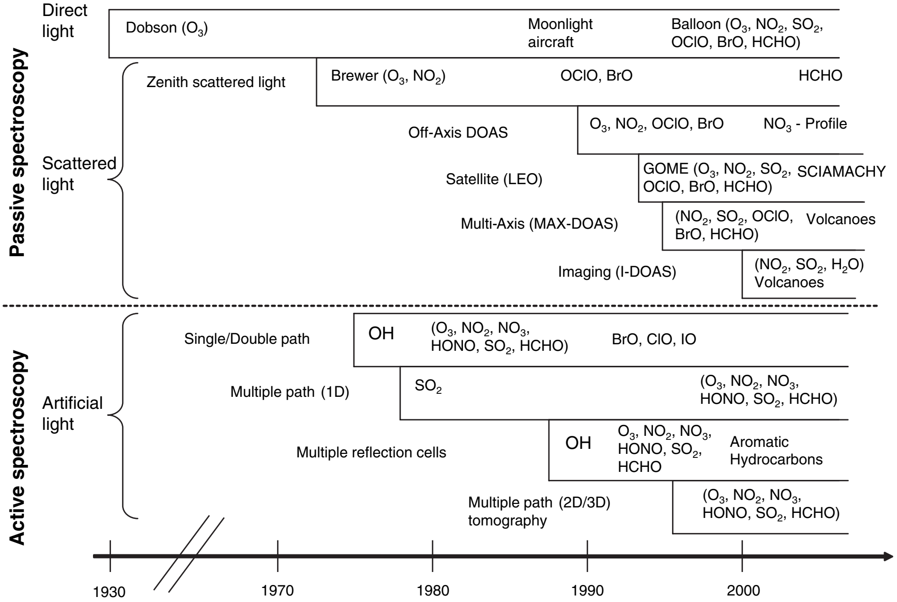

Fig. 12.1. Development of differential optical spectroscopy since 1930

of the zenith-light technique were developed by aiming the telescope to lower elevations and increasing the sensitivity, for example for NO_3 (e.g. Sanders et al., 1987). This advance culminated in the recent development of Multi-Axis DOAS, which uses multiple viewing angles. MAX-DOAS also expands the use of passive DOAS systems from mostly stratospheric applications, to the measurements of tropospheric trace gases.

One of the most exciting developments over the past decade was the expansion of DOAS to satellite-based measurements. With the launch of GOME (Global Ozone Monitoring Instrument) on board ERS-2 (Earth Research Satellite 2 by ESA) in 1995, a new era of DOAS measurements began. GOME's unique ability to measure multiple trace gases (despite its name only hinting ozone), such as O_3, NO_2, BrO, HCHO, and SO_2, on a global scale has expanded the scale of DOAS applications from local and regional applications, to global coverage. Moreover, for the first time species in the troposphere, and even in the boundary layer, can be routinely monitored from space. The next generation of satellite instruments, SCIAMACHY, was launched in 2002 and is now operational.

Passive DOAS techniques today encompass a wide variety of applications. Balloon-borne occultation experiments are used in the study of upper tropospheric and stratospheric chemistry and the validation of satellites. The measurement of NO_2 and other species using zenith-scattered sunlight is used in the monitoring of the stratosphere in the Network for the Detection of Stratospheric Change (NDSC) and the Global Atmospheric Watch (GAW) network.

Currently, most active efforts concentrate on the application of MAX-DOAS. A number of uses have emerged in recent years. In particular, the fact that MAX-DOAS instruments can be built small and inexpensively makes them ideal to use in remote and difficult to access areas, such as polar regions, volcanoes, and the ocean. Several applications have shown the value of this new method, for example to measure halogen oxides in the remote Arctic and Salt Lakes, measure NO_2 and BrO on board ships, and monitor emissions from volcanoes (Bobrowski et al., 2003). MAX-DOAS has become a powerful new method. While its applications show rapid growth, it is undergoing further refinement at this moment. Much of the effort of the DOAS community in recent years has also focused on the use of satellite borne DOAS instruments, in particular the GOME instrument.

The advances of passive DOAS over the past few years points to a number of developments that are likely to occur in the future. These developments are, in part, technical. However, a number of interesting applications are expected to emerge.

12.1.1 MAX-DOAS

The rapid development of MAX-DOAS over the past few years offers a large number of practical applications. A number of these applications have been demonstrated. Others are in the development phase, and some are currently just ideas that may or may not be developed. One of the most promising uses for MAX-DOAS is as an inexpensive and easy to use automatic technique to monitor both the level of air pollution, and the emissions from individual sources. One should, however, point out that, in contrast to current air pollution monitoring stations, MAX-DOAS leads to an altitude-averaged measurement in the lower atmosphere. This is, however, a tremendous advantage if one wants to monitor total levels of gases such as NO_2 or HCHO in the troposphere. Due to this averaging, MAX-DOAS measurements are only weakly influenced by local effects and/or small-scale transport phenomena. In addition, the monitoring of trace gas transport above the boundary layer is particularly helpful in the monitoring of long-rage pollution transport.

A recent example of the monitoring capabilities by MAX-DOAS is the remote measurement of SO_2 emitted from volcanoes. Small spectrometers have made it possible to develop miniaturised instruments that can easily be carried to volcano craters. Continuous measurements of SO_2 and other gases are often used in the monitoring of the state of a volcano, with the goal of predicting its next eruption. While few MAX-DOAS instruments are currently dedicated to this task, the advantages of these instruments make it likely that this will become a widespread application. A similar application that has thus far not been attempted is the monitoring of emissions from forest fires.

Another promising application of MAX-DOAS is the monitoring of pollutant emissions, both from industrial point sources, as well as from area sources such as traffic. Again, the path averaging capabilities of MAX-DOAS will allow the determination of the total emissions. It is, for example, straightforward to set up a DOAS system downwind of a power plant to monitor the composition of the plume at some distance from the smoke stack. Setting up an instrument close to a road or in a city will allow the measurement of averaged emissions from cars. Many other applications are possible.

12.1.2 Aerosol and Cloud Monitoring

While DOAS has primarily been used for the measurement of atmospheric trace gases, the ability to measure gases with constant mixing ratios in the atmosphere, i.e. O_2 and O_4, allows for new applications in cloud and aerosol monitoring. This technique has been applied in the study of radiative properties of clouds, and is based on the fact that aerosol scattering in the atmosphere changes the light path length, and thus the optical density of the O_2 and O_4 absorptions. Using radiative transfer calculations, one can therefore extract information about the vertical distribution of the aerosol and its optical properties.

12.1.3 Imaging DOAS

An expansion of the plume monitoring technique uses MAX-DOAS to quantitatively ‘visualise’ emission plumes. By using two-dimensional detectors, it is possible to acquire a one-dimensional (1D) spectral image of a plume. An additional fast scanning mirror then moves the horizontal viewing angle along the plume, resulting in a data-set of absorption spectra in a 2D field of viewing direction. This can then be converted into a trace gas concentration image with typically 100 × 100 pixels, clearly showing the plume of a specific trace gas. This truly ‘multiple-axis’ approach is a unique tool for the visualisation of trace gas distribution, and a large number of applications are conceivable.

12.1.4 Tomography

Another promising, application of MAX-DOAS, the testing of which has just begun, is the tomographic observation of 2D or 3D trace gas distributions. The basic idea here is to deploy many simple MAX-DOAS systems throughout an urban area. The instruments are then consecutively aimed in many different directions, so that viewing geometries cross at multiple locations (Frins et al., 2006). The tomographic analysis of these observations results in 2D or even 3D concentration fields that can, for example, be used to identify pollution sources, or to initialise regional air pollution models.

12.1.5 Satellite Instruments

One of the most exciting aspects of DOAS in recent years has been the success of the space-borne GOME instrument. Results from GOME have shown the usefulness of DOAS observations from space for many applications. The next step in this development was taken in 2002 with the launch of SCIAMACHY. While at the time of writing this book only examples of data have been available, the smaller ground-pixel size, the expansion of the useable wavelength range in the IR, and the ability to make limb and occultation measurements adds a new aspect to space-borne DOAS.

The most useful application for DOAS from space may be the continuous monitoring of tropospheric pollution levels from space which, like today's meteorological satellites, would provide maps of the 'chemical weather'. To achieve this goal, the time frequency of measurements over any point of earth has to be increased from every 1–3 days to perhaps every 2 h. One way in which this could be achieved would be the deployment of a number of smaller satellites in polar orbit that pass over any point on earth, following each other in a determined temporal pattern. Ultimately, one would wish to deploy DOAS instruments in geostationary orbit, which would allow the recording of the diurnal variation of the atmospheric composition. First proposals of such an instrument have been made. In summary, it is very likely that a network of 'chemical weather' satellites will available in the next two decades.

12.2 Active DOAS Applications

The first active DOAS instruments were developed in the 1970s as research tools for the measurements of various radicals, in particular OH. To develop systems capable of measuring O_3, NO_2, and SO_2, as well as NO_3 and HONO, the 'broadband' laser used in these initial systems was soon replaced by thermal light sources (e.g. Xe arc lamps), which give a much broader spectrum and are technologically simpler. These early instruments, which were based on opto-mechanical 'slotted disk' detectors, are the basis of most commercial air pollution monitoring instruments available today. In addition, the desire to fold the long light path in a small volume led to the development of multi-reflection DOAS systems. Improvements of the various active DOAS instruments were more subtle. The use of new photodiode array detectors, first for OH measurements in 1985, and later for broadband active DOAS in 1995, increased the measurement frequency and allowed the use of longer light paths, thus improving the detection limits. The introduction of the coaxial telescope/retroreflector set-up greatly simplified the deployment of the instruments in the field. In addition, the number of trace gases that are measured with DOAS has expanded over the past decade, and now includes all tropospheric halogen oxides and many aromatics.

12.2.1 New Trace Gases

The increase in the number of species measured by active DOAS has been driven in large part by the enhancement of detection limits and new applications for this technique. Despite these improvements, there is still about an order of magnitude in sensitivity to be gained in active DOAS applications. An extrapolation of the success in the past indicates that it is very likely that new trace gases will enter the pool of species that can be observed. Possible candidates for such species are, for example, polycyclic aromatics, and oxygenated hydrocarbons such as acrolein or ketones.

12.2.2 Infrared Measurements

A number of trace gases that play an important role in atmospheric chemistry and climate research, such as CH_4 and CO, absorb in the near infrared wavelength region. By expanding DOAS to longer wavelengths, new species can be measured, opening opportunities for new applications. It is well possible that more trace gases will be targeted in the near infrared wavelength region in the future.

12.2.3 Hydrocarbons

Possible target species in the near IR region between 1 and 2 µm, wavelength region are hydrocarbons. The overtone spectra of the C–H stretch are located in this spectral region, thus allowing the measurement of these compounds. While the absorption may be too small to allow for ambient monitoring, DOAS could be used for emission or fence-line monitoring (see below).

12.2.4 Air Pollution Monitoring

A number of commercial active DOAS instruments are available on the market to monitor pollutants such as O_3, SO_2, and NO_2. While some instruments have been employed by air quality agencies, the potential of DOAS for monitoring purposes has not been fully exploited. DOAS offers a number of advantages over other methods that are often not recognised. Due to the simultaneous measurement capability, one DOAS instrument can replace a whole set of instruments, which are individually dedicated to the measurement of O_3, SO_2, NO_2, or BTX. DOAS is an absolute method that does not need to be calibrated. The cost of calibrations is thus absent. DOAS instruments are also easy to run automatically, and remote control can be implemented. Finally, taking into account the legal implications of air quality measurements, DOAS measurements provide a ‘photograph’ of the chemical composition of the atmosphere which can be used as incontestable evidence in court.

12.2.5 BTX Monitoring

The measurement of the ambient concentrations of aromatic hydrocarbons, such as benzene, toluene, and xylenes, has not been extensively explored, and is a promising expansion of the pollution monitoring capabilities of DOAS.

Research applications have illustrated that, by overcoming challenges with overlaying O_2–O_2, and O_2–N_2 dimers, and O_3, the accurate measurement of a wide variety of aromatic hydrocarbons is possible. It should be noted that DOAS is, in contrast to most other techniques, able to distinguish different isomers of aromatic compounds.

12.2.6 Fence-Line Monitoring

A thus far unexplored application of DOAS is the monitoring of emissions downwind from large sources. This so-called fence-line monitoring is often difficult to achieve in a quantitative manner, since dilution will reduce the pollutant concentrations. In a long-path application, however, the integral over an entire plume can be measured, thus making the result less dependent on dilution. Active DOAS systems set up near such a source can thus provide continuous data on the total amount of a species emitted.

12.2.7 Tomography

Initial experiments have shown that DOAS can be used to make tomographic measurements. A set-up of a large number of active DOAS instruments with multiple crossing light beams, together with established tomographic methods, will allow the determination of 2D or even 3D concentration fields. This is a promising approach for pollution monitoring in urban areas, as well as in industrial complexes, that desire spatially resolved emission control. The installation of such a tomographic system would be challenging, since a large number of instruments and reflectors have to be deployed and maintained. The extensive effort in setting up the system would, however, be rewarded by the unique information that such a network would provide. It is thus only a question of time until a sponsor for such work can be found and DOAS tomography is implemented.

12.2.8 Range Resolved Technology/Broadband LIDAR

Another application that has not been extensively explored is the use of the DOAS approach in range resolved techniques, i.e. LIDAR. In contrast to classical LIDARs, which are based on one or multiple lasers, a DOAS LIDAR would require a high-intensity broadband light source that allows the detection of an entire spectrum. While the detection capabilities for time resolved measurements of the returning light are available with modern CCD detectors, a suitable light source has not yet been found. The ability to observe emissions, for example, of NO_x, with a high spatial resolution is, however, a very promising application, both for research and for monitoring purposes.

12.3 Development of the Underlying Technology

In the past, the advancement of DOAS has often gone hand in hand with the availability of new technology. For example, the multiplex advantage of new solid-state detectors, such as photodiode arrays, has reduced the noise in the spectroscopic detection, thus allowing for longer light paths in active DOAS applications, and shorter exposure times in passive DOAS measurements. The availability of inexpensive miniaturised spectrometers has made it possible to build small and light MAX-DOAS instruments that can be carried to a volcano crater for SO_2 monitoring. Many such examples can be found in the history of DOAS. It is thus valuable to speculate how new technology will influence the development of DOAS in the future.

12.3.1 New Light-Sources

Illumination technology in recent years has seen an increased use of light emitting diodes. Today they are, for example, used in traffic lights, and flash lights. Initial applications for home illumination are also becoming available. The high brightness of modern LEDs makes them a natural choice for DOAS applications. Advantages include the low power consumption, longevity, and high stability of these sources. Initial tests have shown that LED-based active DOAS instruments are feasible and the technical implementation is only a question of time.

Tunable diode lasers have also seen a rapid development over the past years. The introduction of the quantum cascade lasers, which can be operated at ambient temperatures, makes these systems easier to use and also less expensive. The scanning ability results in absorption spectra that can be analysed using DOAS techniques. The combination of TDLS and DOAS would open novel applications in the infrared wavelength region.

The development of a broadband LIDAR that is based on DOAS depends on the availability of suitable light sources. Further development of lasers, flash lamps, and other sources could provide such a source, making this exciting instrument possible.

12.3.2 New Detectors

The development of photodiode arrays, and more recently CCD and CMOS detectors, have considerably influenced DOAS. Both expensive high-quality and low-cost CCD detectors are available today. The development of this technology is, however, still advancing, and new detectors become available every year. In particular, for active DOAS, high capacity (large full well capacity) detectors are not yet available, thus limiting the use of these detectors mostly to passive DOAS applications. An increase readout speed would also be highly desirable.

DOAS has mostly been restricted to the UV and visible wavelength range. The upper wavelength limits were determined in the beginning by the availability of suitable photomultiplier tubes, and later by the bandgap limit of silicon used in photodiode arrays and CCDs. New semiconductor technology has led to the development of solid-state detector arrays based on gallium-arsenide that also work above wavelength of 1 μm. These detectors, which work similar to CCDs, open a new spectral window for DOAS. As the development of these detectors advances, DOAS will also expand its IR capabilities.

12.3.3 New Software

A goal for future DOAS applications is to further advance the automation of DOAS instruments. While advances have been made in the control of instruments and the long-term operation, improvements in the analysis software with respect to the fully automated extraction of trace gas concentrations from the absorption spectra, is needed. To reduce the need of initial manual spectral evaluation, and to simplify the process of data reduction, methods have to be found that automatically recognise changes in the atmosphere and the instrument, and provide corrections for these effects. In addition, algorithms for automatic quality control and improved error calculations are needed. These improvements will particularly benefit the use of DOAS as a monitoring technique, where ease of operation and reliability is a key component.

Advances in software development are also expected for MAX-DOAS applications. While radiative transfer models are available to interpret MAX-DOAS data, the algorithms to invert the observations in order to derive vertical profiles of trace gases are still under development. Within the next few years, one can expect considerable advancement in these methods.

12.3.4 Improved System Design

The design of DOAS instruments will proceed in two directions: First, the improvement of current detection limits and the expansion to new wavelength regions. Second, the development of smaller, more automated, and less expensive DOAS systems. The detection limits of current active DOAS instruments are about one order of magnitude above the physical limits imposed, by photon noise. There is thus great potential in improving these instruments to measure lower trace gas levels, improve the accuracy of the measurements, and expand the pool of observable species. While it is currently not clear how these instruments can be further improved, it is very likely that a breakthrough will be achieved during the next decade.

The development of miniaturised spectrometers has allowed the construction of smaller DOAS instruments. The lower power consumption of the systems also allows for operation in remote locations. It is expected that this trend will continue in the future and that DOAS instruments will decrease in size. The use of these systems in highly mobile platforms, such as cars, ships, and aircrafts, is thus on the horizon. The low price of these instruments also makes it very likely that the number of DOAS instruments will increase, and that observation networks will be established. This will most likely occur first with respect to the monitoring of volcanoes, but later expand to air pollution and emission monitoring. Ultimately, one can imagine that further miniaturised 'personal' DOAS instruments may become a tool for trace gas monitoring for the interested scientist and personnel working in air quality control.

There is little doubt that DOAS will be an increasingly valuable tool in our ongoing efforts to understand the atmosphere and the chemical and physical processes occurring in it.