Chapter 1
Air Pollution Monitoring Systems—Past–Present–Future

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Abstract Measurements of trace gas concentrations and other parameters like photolysis frequencies are a crucial tool for air pollution monitoring and the investigation of processes in the atmosphere. However, the determination of atmospheric trace gas concentrations constitutes a technological challenge, since extreme sensitivity (mixing ratios as low as 10^{-13}) is desired simultaneously with high specificity i.e. the molecule of interest usually must be detected in the presence of a large excess of other species. In addition, spatially resolved measurements are becoming increasingly important.

Today none of the existing measurement techniques meets all above requirements for trace gas measurements in the atmosphere. Therefore, a comprehensive arsenal of different techniques has been developed. Besides a large number of special techniques (like the ubiquitous short-path UV absorption for O_3 measurement) universal methods gain interest, due to their economy and relative ease of use. In particular, a single instrument can register a large number of different trace species.

The different types of requirements and the various techniques are discussed; special emphasis is given to spectroscopic methods, which play a large and growing role in atmospheric chemistry research. For instance, only spectroscopic methods allow remote sensing and spatially resolved determination of trace gas concentrations e.g. from space-borne platforms. Today many varieties of spectroscopic methods are in use (e.g. tunable diode laser- and Fourier-transform spectroscopy). The basic properties and recent applications of this technique are presented using differential optical absorption spectroscopy (DOAS) as an example. Future requirements and expected developments are discussed.

Keywords: Air pollution monitoring, trace gas, DOAS, spectroscopy, remote sensing

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1.1 Introduction

Measurements of trace gas and aerosol concentrations (and other quantities like the intensity of the radiation field in the atmosphere) are experimental prerequisites for pollution monitoring and the understanding of the underlying physicochemical processes in the earth's atmosphere (Roscoe and Clemitshaw 1997; Platt 1991, 1999; Clemitshaw 2004). At the same time the determination of trace gas concentrations in the atmosphere is a challenge for the analytical techniques employed in several respects.

First, the technique must be very sensitive to detect the species under consideration at ambient concentration levels. This can be a very demanding criterion, since, for instance, species present at mixing ratios ranging from as low as 0.1 ppt (1 ppt corresponds to a mixing ratio of 1 pmol of trace gas per mole of air or a mixing ratio of 10^{-12}, equivalent to about 2.4×10^7 molecules/cm^3) to several ppb (1 ppb corresponds to 1 nmol mol^{-1} or a mixing ratios of 10^{-9}) can still have a significant influence on the chemical processes in the atmosphere (Perner et al. 1987). Thus, detection limits from below 0.1 ppt up to the lower ppb-range are usually required, depending on the application.

Second, it is equally important for the measurement techniques to be specific, which means, that the result of the measurement of a particular species must neither be positively nor negatively influenced by any other trace species simultaneously present in the probed volume of air. Given the large number of different molecules present at the ppt and ppb level, even in clean air, this is not a trivial condition.

Third, the technique must allow sufficient precision and calibration to be feasible.

In most practical applications, there are other requirements, including spatial coverage, time resolution, properties like simplicity of design and use of the instruments, a capability of real-time operation (as opposed to taking samples for later analysis), and the possibility of unattended operation. Other factors to be considered are weight, portability, and dependence of the measurement on ambient conditions.

To date no single measurement technique can fulfil all the diverse requirements for trace gas measurements in the atmosphere. Therefore, specialised techniques or variants of techniques have been developed, which are tailored to the various measurement tasks occurring in atmospheric research, pollution control, and monitoring of atmospheric change:

1. Long-term observations are aimed at monitoring gradual changes in atmospheric parameters, e.g. its trace gas composition. Typical examples are

   - Trends of greenhouse gases like CO_2, CH_4, N_2O, or CFM's
   - Stratospheric ozone
   - Change of stratospheric chemistry (e.g. realised in the Network for the Detection of Atmospheric Composition Change, NDACC)
   - The temporal evolution in the abundance of species supplying halogens to the stratosphere (e.g. CFC-and HCFC-species)
   - Trend of the tropospheric ozone mixing ratio as routinely monitored by the Global Atmospheric Watch (GAW) programme.

In this context the so-called ‘operator dilemma’ should be noted: the measurement of a particular set of species over an extended period is frequently not considered a scientific challenge; on the other hand, the success of the data series hinges on the very careful execution of the measurements. Here the psychological side of the project may be as critical as the technology.

2. Regional and episodic studies seek to investigate causes, extent, and consequences of regional events like air pollution episodes or boundary layer ozone depletion events (Barrie et al. 1988). While routine monitoring is an issue many fundamental questions can only be investigated by observations made on a regional scale. Typical measurements tasks in this context are

   - Monitoring of air pollutants (like O_3, SO_2, NO, NO_2, hydrocarbons)
   - Investigation of urban plume evolution (e.g. with respect to O_3 formation downwind of source regions)
   - Mapping of continental plumes
   - Observation of the Antarctic Stratospheric Ozone Hole
   - Polar boundary-layer ozone loss events (the ‘tropospheric ozone hole’, (Platt and Lehrer 1997)

3. Investigation of fast in situ (photo) chemistry allows to neglect the effect of transport, in particular this is true for the following systems:

Free-radical (e.g. OH, HO_2, BrO) photochemistry, where the lifetime of the reactive species is of the order of seconds (OH: below 1 s, HO_2: from <1 s at high NO_X levels to ≈200 s at zero NO_X, BrO: ≈100 s).

‘Smog’-chamber (today frequently called reaction chamber or photoreactor) studies allow to suppress transport. However, care has to be taken to avoid artefacts which may arise from chemical processes at the chamber walls.

Today, atmospheric chemistry has a comprehensive arsenal of measurement techniques at its disposal; Table 1.1 gives an overview of the techniques available for a series of key species relevant for studies of atmospheric chemistry. Among a large number of specialised techniques (such as the gas-phase chemiluminescence detection of NO) universal techniques are of great interest, due to their relative simplicity and economy.

1.2 Measurement Techniques by Broad Categories

In this section we group the available techniques according to a series of broad criteria. According to the remarks above the degree of specialisation is of importance and we may distinguish between

- Specialised techniques, where one instrument measures a single species (‘box per species’)
- Universal techniques, where a single instrument can determine a large set of species

Examples for specialised techniques include gas-phase chemiluminescence detection of NO (Drummond et al. 1985) or short-path UV absorption detection of ozone using a

Table 1.1 Overview of species of relevance to atmospheric chemistry research and measurement techniques

Species	UV/ vis	FT-IR	TDLS (IR)	GC	MS (CIMS)	Fluorescence Chemoluminescence	Other
NO	O	O	O			+	
NO_2	+	O	+			+	MI-ESR[a]
NO_3	+						MI-ESR, LIF
HNO_2	+						Denuder
HNO_3		O	O				Denuder
OH	+				O		LIF
HO_2/RO_2			?		+		LIF, Ch. A[b]
H_2O_2		O	+			+	
O_3	+	O	O			O	Electrochemistry[c]
HCHO	+	O	+				Derivat.[d]
RCHO							Derivat.[d]
Alkanes				+			
Olefins				+	O		
Aromatic	+			+	O		
CO			O	+		+	
DMS				+			
SO_2	+		O			+	
N_2O			+	+			
CFC's		+		+			
HX[e]		+					Wet chemistry
XO[e]	+				O	+	
HOX[e]			?				

Symbols denote: well measurable (+), measurable (O), not measurable (empty field)
UV/vis UV/visible spectroscopy, FT-IR Fourier-transform IR Spectroscopy, TDLS tunable diode laser spectroscopy, GC gas chromatography, MS (CIMS) mass spectrometry (chemical ionisation mass spectrometry)
[a] Matrix isolation-electron spin resonance
[b] Chemical amplifier
[c] Electrochemical cell
[d] Derivatisation + HPLC
[e] X = Halogen atom (F, Cl, Br, I)

strong emission line of mercury near 253.7 nm (Proffitt and McLaughlin 1983). On the other hand, universal techniques include gas-chromatography or spectroscopic methods.

Another fundamental property of instruments is the spatial range of the measurements, usually expressed in terms of

- In situ measurements
- Remote sensing measurements

While in situ measurements come close to the ideal to determine trace gas concentrations at a 'point' in space, which is usually very close to the instrument, remote sensing techniques usually average the trace gas concentration over a relatively large volume of air, thus providing more representative measurements.

In addition remote sensing techniques allow observations from a (large) distance, perhaps as far as from a satellite instrument in the earth's orbit. Present remote sensing techniques always rely on the sensing of electromagnetic radiation, i.e. they are spectroscopic methods.

Further criteria are the capability of techniques to perform spatially resolved measurements:

- Volume integrated measurements
- Spatially resolved measurements

Also to be considered is the degree of redundancy in the measurements, i.e. the result of a measurement can be

- Just a number, i.e. the mixing ratio or concentration of a trace gas
- Redundant data, for instance the strength of several absorption lines

Examples of instruments belonging to either category include

- Gas-chromatography (universal technique, in situ, redundant data)
- Optical spectroscopy (universal technique, in situ and remote sensing, redundant data)
- Mass spectrometry (MS, redundant data)
- 'Any other (in situ) technique', where the most commonly employed principles include

Chemiluminescence (e.g. for the detection of NO or O_3, usually no redundant data)

Chemical amplifiers for the detection of peroxy radicals (Cantrell et al. 1993; Clemitshaw et al. 1997)
Electrochemical techniques
Matrix isolation–electron spin resonance (MI–ESR) (Mihelcic et al. 1985)
Derivatisation + HPLC (e.g. for the determination of carbonyls, (Lowe and Schmidt 1983)
Bubbler + wet chemistry or ion chromatography (IC), (in situ, usually no redundant data)

In this context, spectroscopic techniques are a promising variety: these techniques are highly sensitive, very specific, universally useable, provide absolute results, and have the potential for remote sensing. It is, therefore, not surprising, that spectroscopic techniques assume a unique role among the many methods, which are in use today. In the following section we will focus further on spectroscopic techniques.

1.3 Selection Criteria for Spectroscopic Air Monitoring Techniques

For a particular application, the selection of a specific spectroscopic technique will be based on the particular requirements as outlined above: which species are to be measured, is the simultaneous determination of several species with the same technique necessary, what is the required accuracy, time resolution, and spatial resolution? Also to be considered are logistic requirements like power consumption,

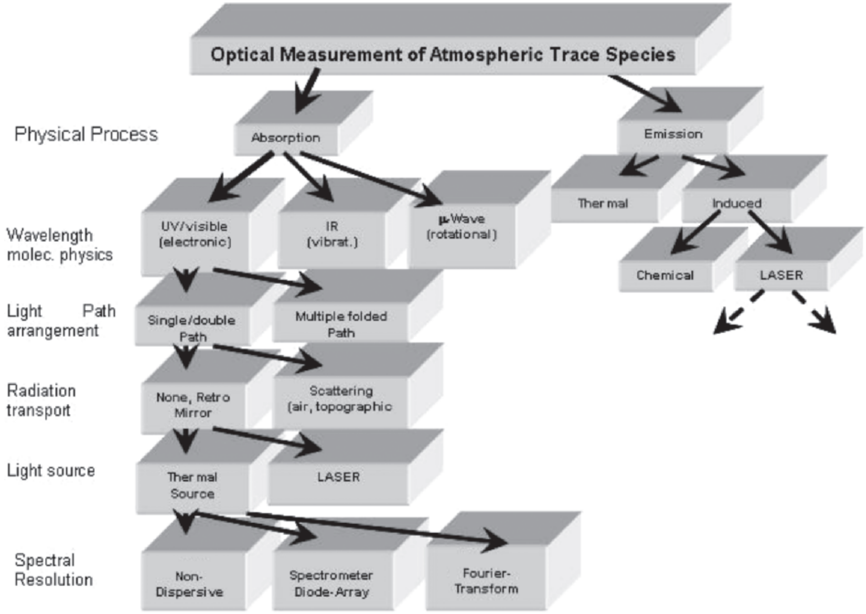

Fig. 1.1 Spectroscopic techniques are used in for the measurement of atmospheric trace species and parameters in a large number of variants. Shown here is a 'family tree' of spectroscopic techniques

mounting of light sources or retro-reflectors (see below), or accommodation of the instrument on mobile platform.

Important technical criteria of spectroscopic instruments are the wavelength region used (see Fig. 1.1), the physical principle (i.e. absorption- or emission spectroscopy), the arrangement of the light path, or the type of light source used. The following spectroscopic techniques are presently employed to measure atmospheric trace gases (see also Sigrist 1994; Clemitshaw 2004; Platt and Stutz 2007):

- Tunable diode laser spectroscopy (TDLS)
- Photo acoustic spectroscopy (PAS)
- Light detection and ranging (LIDAR)
- Differential absorption LIDAR (DIAL)
- Laser-induced fluorescence (LIF)
- Differential optical absorption spectroscopy (DOAS)
- Cavity-ringdown spectroscopy (CRDS)

1.4 The Principle of Absorption Spectroscopy

This universal spectroscopic technique makes use of the absorption of electromagnetic radiation by matter (Fig. 1.2). Quantitatively, the absorption of radiation is expressed by Lambert–Beers law:

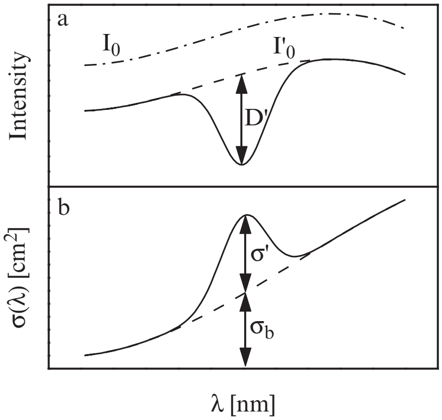

Fig. 1.2 DOAS principle: the trace gas concentrations are calculated (Stutz and Platt 1996) from the amplitude of absorption structures, e.g. from differences of the absorption in the centre of an absorption band (or line) and the spectral range between bands

$$I(\lambda) = I(\lambda) \cdot \exp\left(-S \cdot \sigma(\lambda)\right) \tag{1}$$

where $\sigma(\lambda)$ denotes the absorption cross section at the wavelength λ, $I_0(\lambda)$ is the initial intensity emitted by some suitable source of radiation, and $I(\lambda)$ is the radiation intensity after passing through a layer column density S of the trace gas (what is D in Eq. 1?)

$$S = \int_0^L c(s)\,ds = \bar{c} \cdot L \tag{2}$$

where the species to be measured is present at a concentration (or number density) $c(s)$, which may change along the light path (with $\bar{c}$ being the average) and thus vary with s, while L denotes the total length of the light path. The absorption cross section, $\sigma(\lambda)$ is a characteristic property of any species, it can be measured in the laboratory, while the determination of the light path length, L is usually trivial in the case of active instruments, but requires radiation transport calculations for passive measurements (Platt and Stutz 2007). Once those quantities are known the path averaged trace gas concentration $\bar{c}$ and/or the column density S can be calculated from the measured spectrum $I(\lambda)$ according to Eqs. 1 and 2. For measurements, where the light path is in the atmosphere there will be usually more than one absorbing species present, thus a more comprehensive description of atmospheric absorption can be expressed as

$$I(\lambda) = I(\lambda) \cdot \exp\left(-L\left[\sum_i \bar{c}_i \cdot \sigma(\lambda) + \sigma_{R0} \cdot \lambda^{-4} \cdot c_{air} + \sigma_{M0} \cdot \lambda^{-n} \cdot c_{aer}\right]\right) \tag{3}$$

The quantities $I(\lambda)$ and $I_0(\lambda)$ have the meaning as defined in Eq. 1, $\sigma_i(\lambda)$ and c_i denote the absorption cross-section and the concentration of the ith species, and c_{air} the concentration of air molecules (2.4×10^{19} cm^{-3} at 20°C, 1 atm). The expressions $\sigma_{\mathrm{R0}}(\lambda)\ \lambda^{-4}$ and $\sigma_{\mathrm{M0}}\ \lambda^{-n}$ describe the effective wavelength dependence of the Rayleigh- and Mie- extinction, respectively (with *n* in the range of 1–3, depending on the aerosol size distribution), while c_{aer} denotes the average aerosol number density. At long wavelengths, i.e. in the microwave or infrared spectroscopy, Rayleigh- and Mie- scattering from aerosol are usually of minor importance (however, Mie-scattering in clouds can play a role). However, scattering processes can not be neglected in the UV/visible part of the spectrum. Grouped by wavelength (see Fig. 1.1), the techniques can be categorised as follows:

1.4.1 Microwave Spectroscopy

This spectral range is presently not used for tropospheric measurements, due to the relatively large pressure broadening of the lines and would require measurements at reduced pressure. However, spectroscopy of thermally emitted microwave radiation is an established technology to study stratospheric ozone and ClO (DeZafra et al. 1995; Janssen 1993).

1.4.2 IR Spectroscopy

Infrared spectroscopy is a technique in use for several decades, initially developed for the detection of atmospheric CO_2 by non dispersive instruments (URAS). More modern instruments are based on Fourier transform techniques to measure HNO_3, CH_2O, HCOOH, H_2O_2, and many other species in km-path lengths multiple-reflection cells (Pitts et al. 1977; Tuazon et al. 1980; Galle et al. 1994). The sensitivity is in the low ppb-range. Thus these instruments appear to be best suited for studies of polluted air. The technique can be applied in two modes of operation: (1) active operation, where an artificial light source is used (Pitts et al. 1977; Tuazon et al. 1980) or (2) passive operation using the thermal emission from the trace gases under consideration (Fischer et al. 1983; Clarmann et al. 1995).

In recent years, tunable diode laser spectrometers (TDLS) were developed to become field-usable instruments, successfully employed to measure HNO_3, NO, NO_2, CH_2O, H_2O_2 at sub-ppb levels (Harris et al. 1989; Schiff et al. 1990; Sigrist 1994; Tittel et al. 2003; Clemitshaw 2004). In the usual arrangement, the merit of TDLS coupled to a multipass gas cell lies in the mobility and sensitivity of instrument allowing concentration measurements on board of ships and aircraft. Limitations are due to the need to operate at low pressures (in most applications),thus introducing possible losses at the walls of the closed measurementcell. Furthermore the present diode-laser technology still remains complex.

1.5 Differential UV/Visible Absorption Spectroscopy

In the ultraviolet and visible wavelength ranges, electronic transitions of the trace gas molecules (or atoms) are observed. Like the other absorption–spectroscopic techniques, DOAS makes use of the characteristic absorption features of trace gas molecules along a path of known length in the open atmosphere. Thereby the problem of determining the true intensity $I_o(\lambda)$, as would be received from the light source in the absence of any extinction is solved by measuring the ‘differential’ absorption. It is defined as the part of the total absorption of any molecule ‘rapidly’ varying with wavelength and is readily observable as will be shown below. Accordingly, the absorption cross section of a given molecule (numbered *i*) is split into two portions:

$$\sigma_i(\lambda) = \sigma_i'(\lambda) + \sigma_{i0}(\lambda) \tag{4}$$

Where σ_{i0} varies only ‘slowly’ (i.e. essentially monotonously) with the wavelength λ, for instance describing a general ‘slope’, (e.g. Rayleigh- and Mie- scattering) while $\sigma_i(\lambda)$ shows rapid variations with λ, for instance due to an absorption line (see Fig. 1.2). The meaning of ‘rapid’ and ‘slow’ variation of the absorption cross section as a function of wavelength is, of course, a question of the observed wavelength interval and the width of the absorption bands to be detected. After introduction of Eq. 4 into Eq. 3, we obtain

$$\begin{aligned} I(\lambda) = I(\lambda) \cdot \exp\left(-L\left[\sum_i \bar{c}_i \cdot \sigma'(\lambda)\right]\right) \\ \cdot \exp\left(-L\left[\sum_i \bar{c}_i \cdot \sigma_0(\lambda) + \varepsilon_R(\lambda) + \varepsilon_M(\lambda)\right]\right) \cdot A(\lambda) \end{aligned} \tag{5}$$

where the first exponential function describes the effect of the structured ‘differential’ absorption of trace species, while the second exponential constitutes the slowly varying absorption of atmospheric trace gases as well as the influence of Rayleigh- and Mie-scattering (described by the wavelength-dependent extinction coefficients ε_R and ε_M) and the (slowly) wavelength-dependent transmission of the optical system used (summarised in the attenuation factor $A[\lambda]$).

Atmospheric trace gas concentrations are then calculated from the first exponential term in Eq. 5 using least squares fitting procedures as outlined by (Stutz and Platt 1997; Platt and Stutz 1996). The second exponential in Eq. 5 describing rather continuous extinction is usually neglected. Obviously DOAS can only measure species with reasonably narrow absorption features. Thus continuous absorptions of trace gases will be neglected by DOAS. On the other hand, DOAS is insensitive to extinction processes, which vary only monotonously with wavelength, like Mie-scattering by aerosol-, dust- or haze particles. Likewise slow variations in the spectral intensity of the light source or in the transmission of the optical system (telescope, spectrometer etc.) are also essentially eliminated.

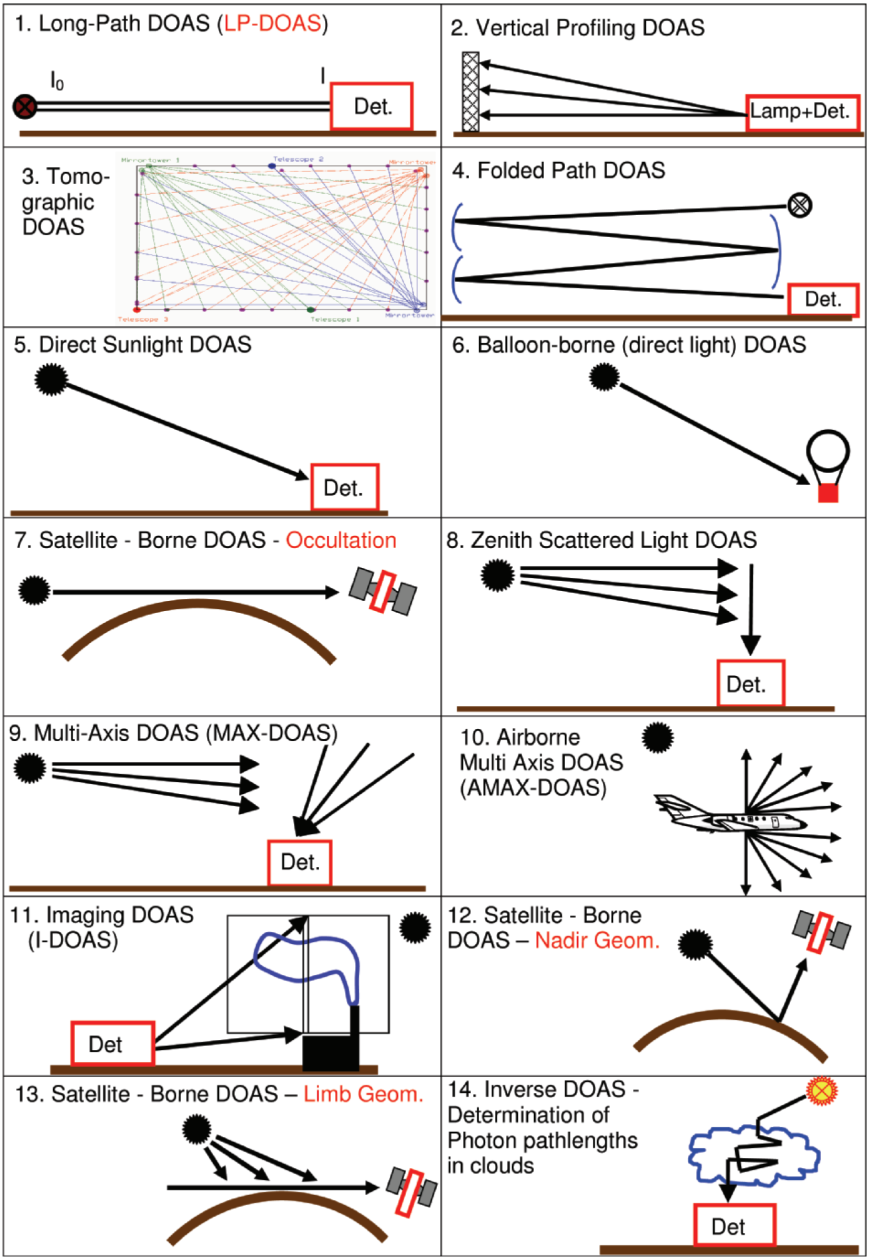

Fig. 1.3 The DOAS principle can be applied in a several light path arrangements and observation modes using artificial (arc lamps, incandescent lamps, or lasers, 1–4) as well as natural (sunlight or starlight; 5–14) light sources. Either the (light path averaged) trace gas concentration (1–4), the trace gas column density (5–13), or the length of the light path (e.g. in clouds, 14) can be determined

The DOAS principle (Platt 1994) has been applied in a wide variety of light path arrangements and observation modes as sketched in Fig. 1.3. The strength of DOAS lies in the absence of wall losses, good specificity, and the potential for real-time measurements. In particular, the first property makes spectroscopic techniques especially well suited for the detection of unstable species like OH radicals (Dorn et al. 1988; Brauers et al. 1996) or nitrate radicals (Platt et al. 1984; Platt and Janssen 1996; Allan et al. 1999).

Limitations of systems using a separate light source and receiving system are due to logistic requirements (the need for electric power at two sites separated by several kilometres, but in sight of each other) in the case of unfolded path arrangements (Fig. 1.3), also conditions of poor atmospheric visibility can make measurements with this technique difficult.

LIDAR techniques, on the other hand, combine the absence of wall losses and good specificity with fewer logistic requirements and the capability to make range-resolved measurements (while the above systems can only make point or path-averaged measurements). Unfortunately, this advantage is usually obtained at the expense of sensitivity.

1.6 Sample Applications of DOAS

DOAS applications encompass studies in urban air, measurements in rural areas, observations in the background troposphere as well as investigations of the distribution of stratospheric ozone and species leading to its destruction.

Using the DOAS technique, numerous new results of atmospheric chemistry could be obtained. For instance, the atmospheric concentration of several free radicals (such as OH, NO_3, BrO, and IO.) was determined. Further modern applications of the DOAS technique include the determination of the concentration of aromatic hydrocarbons and their degradation products in urban air (Etzkorn et al. 1999; Kurtenbach et al. 2002).

A growing field of DOAS application is the observation of trace gas concentration from space as implemented in the GOME instrument on ERS-2 (Burrows et al. 1999) and the SCIAMACHY sensor launched on ENVISAT in 2002 (Borrell et al. 2003). In addition, geometric light path lengths in clouds or haze could be determined (Noël et al. 1999).

An important early result obtained with DOAS was the first unambiguous detection of nitrous acid (HONO, [Perner and Platt 1979]) in urban air. Nitrous acid is produced from NO_2 and water at various types of surfaces. While many subsequent DOAS investigations confirmed that HONO levels rarely exceed 5% of the NO_2 it is, nevertheless, significant for atmospheric chemistry since its photolysis ($HONO + h\nu \rightarrow OH + NO$) leads to the production of OH radicals, which in turn initiate most chemical degradation process of air pollutants.

The detection of OH radicals presented a major challenge for DOAS for a long time, since (daytime) atmospheric OH levels are of the order of 10^6 molecules/cm^3 (roughly 0.04 ppt). After early attempts (Perner et al. 1976) steady progress is being made (Platt et al. 1988; Dorn et al. 1988, 1996; Brauers et al. 1996).

Another radical species, the nitrate radical (NO_3,) was also discovered in the troposphere (Platt et al. 1980; Noxon et al. 1980; Allan et al. 1999) by DOAS techniques. Nitrate radicals (NO_3) are formed via oxidation of NO_2 by ozone ($NO_2 + O_3 \rightarrow NO_3 + O_2$). The nitrate radical is a strong oxidant initiating the degradation of many (unsaturated) hydrocarbons. Some of the oxidation products lead to the formation of organic peroxy- and HO_2 radicals, which in turn can yield OH radicals. Since the formation of NO_3 does not require sunlight, this OH source will also be active at night time.

Among the first indications for the involvement of chlorine species in the formation of the Antarctic ozone hole was the detection of OClO by ZSL-DOAS (Solomon et al. 1987). Also BrO could since be detected in stratospheric air (Solomon et al. 1989; Wahner et al. 1990; Richter et al. 1998; Otten et al. 1998).

Recently reactive halogen species could also be found in the troposphere: bromine monoxide (BrO) and ClO (Platt and Hausmann 1994; Tuckermann et al. 1997; Stutz et al. 2002), IO (Alicke et al. 1998; Allan et al. 2000; Saiz-Lopez et al. 2004) by using ground-based DOAS systems with artificial light sources.

The distribution of stratospheric BrO (Richter et al. 1998; Hegels et al. 1998) was mapped by satellite-borne DOAS (GOME instrument). However, also successful detection and mapping of tropospheric species by GOME was demonstrated in the cases of NO_2 (Leue et al. 1998; Richter and Burrows 2002; Beirle 2004), CH_2O, SO_2 (Eisinger and Burrows 1998; Khokhar et al. 2005), and BrO (Richter et al. 1998; Wagner and Platt 1998). Like in the stratosphere, halogen monoxide radicals lead to very efficient, catalytic ozone destruction. A very spectacular phenomenon caused by BrO (and possibly ClO) is the complete, episodic destruction of boundary layer ozone during polar spring (the ‘polar tropospheric ozone hole’) (Platt and Lehrer 1997). In addition the ability to map the global NO_2 distribution allows determining human activities (e.g. industrial and traffic related) as well as the extent of biomass burning. A sample distribution of tropospheric NO_2 is shown in Fig. 1.4.

By ‘reversing’ the usual DOAS approach (i.e. instead determining an unknown trace gas concentration at known light path length *L*, an unknown *L* is derived from the absorption of an absorber with known concentration) the average lengths of photon paths in clouds (see Fig. 1.3-1.4) could be determined by making use of the known concentrations of oxygen (O_2)-, tropospheric ozone-, or oxygen dimers $(O_2)_2$ (Erle et al. 1995; Wagner et al. 1998). By analysing the absorption of individual rotational lines (e.g. of the O_2 a-band around 765 nm) it is possible to infer not only the average photon-path length in clouds but also

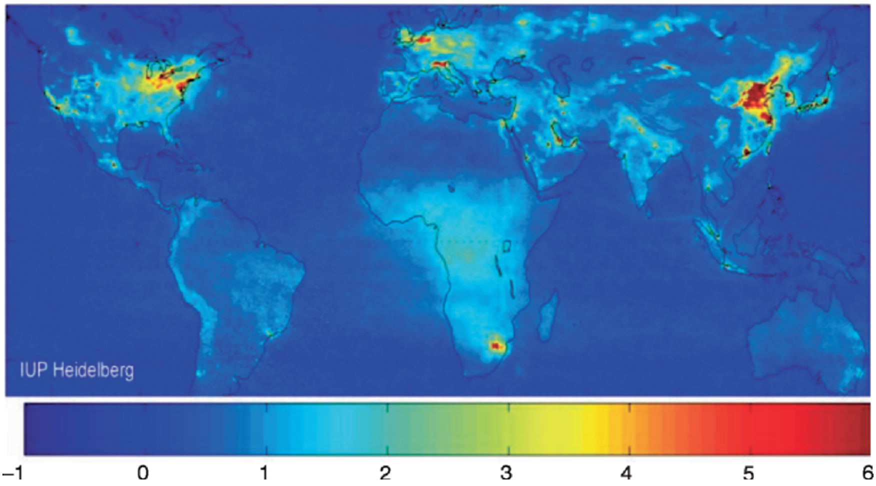

Fig. 1.4 The global NO_2 distribution (in units of 10^{15} molecules/cm^2), determined by the (SCIAMACHY) on the ENVISAT satellite. The data represent the tropospheric fraction of the total NO_2-column only, they are averaged over the period of Jan 2003–June 2004 (Beirle 2004). The industrial centres in Europe, North America, and Asia are clearly visible. Biomass burning plumes in equatorial America and Africa are less pronounced in the yearly average, but show up clearly in the 'burning seasons'

moments of its distribution (Pfeilsticker et al. 1998). These data give new insight into the internal structure and properties of the radiation field inside clouds.

1.7 Measurement Techniques: Tomorrow

At this point in time, it is interesting to speculate about the future of the measurement techniques. This can be approached from two directions: (1) by extrapolation, i.e. by extending present trends in instrumental design and development and (2) starting from the opposite direction by analysing the measurement requirements that might arise in future atmospheric chemistry research. Following the first approach evolutionary improvements are likely:

1. What can we expect?

Miniaturisation of instrumentation is a foreseeable trend, in particular in the electronics for the instruments, but we will also see applications of micromechanical devices, which are presently being developed. Further trends include:

Wider application of gas-chromatography (quadrupole) mass-spectrometry (GC–MS)

The following are the improvements in optical spectroscopy:

- Innovative passive DOAS spectrometers (e.g. multi axis-DOAS, MAX-DOAS [Hönninger et al. 2004]) or topographic target light scattering DOAS, ToTaL-DOAS (Frins et al. 2006)
- More compact DOAS instruments
- Application of tomographic techniques to determine the spatial distribution of trace gases (Hashmonay et al. 1999; Hartl et al. 2006; Pundt et al. 2005)
- Long-path infrared spectroscopy (LP-IR)
- Application of TDLS (mid-IR, near IR, UV for OH?)
- 'White light' LIDAR (South et al. 1998)
- Miniaturised, automated gas-chromatographs

2. What do we actually need (future requirements)?

Future research will require the study of new species with more compact, more universal instruments, which can be more readily calibrated. In particular, the measurement techniques for many free radicals are still not satisfactory (e.g. for RO_2 radicals or halogen radicals) or too difficult to use for routine measurements. In addition, modern chemistry—transport models cannot be tested because there are simply no techniques to observe the two- and three-dimensional distributions of trace gases on regional- or global scales. Thus a short list of requirements would include

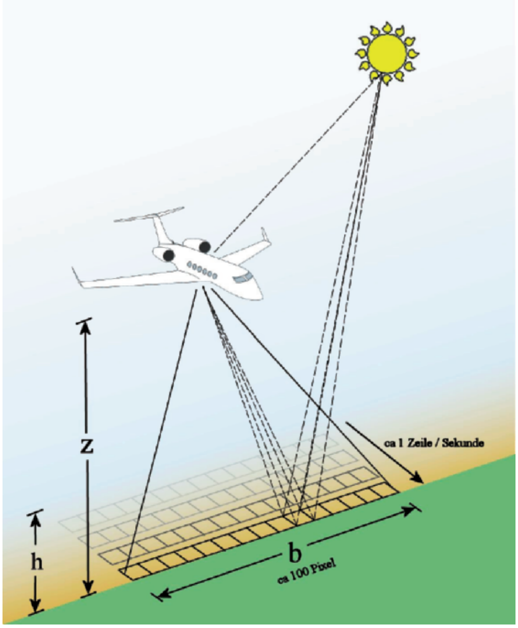

Fig. 1.5 Determination of 2D trace gas column density distributions (e.g. of NO_2, SO_2, CH_2O) in 'stripes' (≈10 km width) along the flight track

- Techniques for continuous hydrocarbon (VOC) measurements
- Instruments allowing detection of NO at mixing ratios <1 ppt
- Simple ozone monitoring instruments
- Simple sensors for the free radicals RO_2, HO_2, and OH.
- Techniques for the determination of the isotopic composition (with respect to e.g. $^{18}O/^{16}O$, D/H, $^{14}C/^{12}C$) of trace gases at ambient levels
- Measurement techniques for the sub-ppt detection of reactive halogen species (X, XO, OXO, HOX, where X = Cl, Br, I)
- Techniques that allow the mapping of two- and three-dimensional distributions of trace gases at high spatial resolution.
- Remote sensing (satellite-based) instruments which allow the global observation of trace gas distributions

In summary at present it can be said that the future development of atmospheric monitoring and research will to a large extent depend on the progress in instrumentation development. The recent years largely saw much evolutionary development but also new principles. (e.g. CRDS or MAX-DOAS).

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