5

Measurement Techniques for Atmospheric Trace Gas Concentrations and Other Parameters

Our knowledge about the physical and chemical processes in the atmosphere relies to a large extent on measurements of relevant parameters like temperature or ozone mixing ratio throughout the atmosphere. For instance, the 'meteorological parameters' such as temperature, humidity, pressure, radiation intensities, or wind speed and direction have routinely been measured in the atmosphere. In this book, we focus on measurements of trace gas concentrations and quantities related to chemical processes in the atmosphere, including the intensity of the radiation field. These are the experimental prerequisites for understanding the physico-chemical processes in the earth's atmosphere. In addition, measurements are made in model atmospheres, e.g. smog chambers or environmental chambers. As the name 'trace constituents' suggests, the species to be investigated here are present at minute quantities only (see Chap. 2). Therefore, the determination of trace gas concentrations in the atmosphere constitutes a challenge for the analytical techniques employed. In summary, measurements of atmospheric parameters are done for a variety of purposes:

- Weather forecast and climatological studies
- Meteorological research
- Climate studies
- Pollution control
- Monitoring of the state of atmosphere
- Atmospheric chemistry research

In recent years, the term 'chemical weather' was coined to encompass information on the trace gas composition of, say, air pollutants of the atmosphere.

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5.1 History of Measurement Techniques

After the discovery of a strong, characteristic smell near electric discharges by van Marum in 1785 and the identification and naming of ozone by Christian Friedrich Schönbein in 1839, this species was one of the first atmospheric trace gases to be investigated. An earlier technique relied on the use of 'Schönbein Paper' (Schönbein, 1840), a paper impregnated with iodide (e.g. KI) and starch. Upon exposure to the ambient air and hence to the ozone dispersed in it, the following reactions produced a blue colour:

$$2\,H^+ + 2\ I + O_3 \rightarrow I_2 + O_2 + H_2O \tag{R5.1}$$

$$I_2 + \text{starch} \rightarrow \text{blue colour} \tag{R5.2}$$

Together with a suitable colour scale, semi-quantitative measurements could be made. Later, it turned out that the amount of blue colour strongly depends on relative humidity and wind speed, and so these relatively large data set from the 19th century could not be used for quantitative studies.

These problems were avoided by another technique, which was also introduced during the 19th century. Here, air is bubbled through an arsenite-containing solution, which is oxidised to arsenate (Volz and Kley, 1988):

$$O_3 + AsO_3^{3-} \xrightarrow{I^-/I_2} O_2 + AsO_4^{3-}. \tag{R5.3}$$

Measurements near Paris during 19th century (1876–1910) [the so-called Montsouris series (Albert-Levy, 1886)] allowed Volz and Kley (1988) to reconstruct the much lower pre-industrial ozone content of the troposphere.

Besides the 'wet chemical' techniques, optical absorption spectroscopy was very closely linked to early research on atmospheric composition. For instance, Alfred Cornu in 1878 (Cornu, 1879) and Sir Walter Noel Hartley (Hartley, 1880) showed that a sharp drop in solar intensity below 300 nm was due to atmospheric ozone. This was later used by several researchers to determine the atmospheric O_3 column density (Fabry, 1913; Dobson and Harrison, 1926 (see also Chap. 6); Roscoe and Clemitshaw, 1997).

5.2 The Role of Measurements in Atmospheric Chemistry

As mentioned earlier, measurements of atmospheric parameters can serve the goal of coming to a better understanding of our atmospheric environment; however, this can be done in quite a number of different ways. They can be characterised by the time scale of measurements, i.e. there may be specialised 'measurement campaigns' aimed at investigating certain phenomena or 'long-term studies' to follow the evolution of chemical changes. In addition, we might look at the spatial scale of investigation, there may be interest in local, regional or global scale phenomena. Apart from measurements made primarily for scientific purposes, a large number of measurements of atmospheric trace gases are made every day to document the pollution level of our atmosphere and to alert the public of extreme pollution events. In trying to group the measurement efforts, we could use the following criteria:

5.2.1 Long-term Observations

There is great interest in changes in the composition of our atmospheric environment. Some well-known examples include the rise of CO_2 mixing ratio directly observed since the 1950s (e.g. Keeling et al., 1970). Since then, many other trace gases were followed, e.g. chlorofluorocarbon species (CFMs), methane, or the thickness of the stratospheric ozone layer (i.e. the total atmospheric O_3 column density).

Therefore, long-term observations are frequently aimed at monitoring gradual changes in the trace gas composition of atmosphere. They include observations of:

- trends in stratospheric ozone
- change of stratospheric chemistry, e.g. as realised in the Network for the Detection of Stratospheric Change, (NDSC)
- evolution of species supplying halogens to the stratosphere (e.g. CFC and HCFC species)
- trend of the tropospheric ozone mixing ratio (Global Atmospheric Watch, GAW)
- trends of greenhouse gases (CO_2, CH_4, or N_2O)
- trends of gases indicating the atmospheric oxidation capacity (i.e. the ability of the atmosphere to remove trace gases). For instance, ozone, CH_3CCl_3 and ^{14}CO are monitored for this purpose.

In this context, the ‘operator dilemma’ should be noted. The measurement of a given set of species with the same technique over an extended period of time is frequently not considered a scientific challenge; on the other hand, the success of the data series hinges on the very careful conduction of measurements. Here, the psychological side of the project may be as important as the technological aspects.

5.2.2 Regional and Episodic Studies

Regional and episodic studies seek to investigate the causes, extent, and consequences of air pollution. While routine monitoring is an issue, many fundamental questions can be investigated only by observations made on a regional scale. Typical measurement 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)
- Study of continental plumes
- Observation of the Antarctic Stratospheric Ozone Hole
- Investigation of polar boundary-layer ozone loss events (the 'tropospheric ozone hole') (Platt and Lehrer, 1995)

5.2.3 Investigation of Fast in-situ (Photo)Chemistry

Studies in 'Smog'-Chambers (frequently called 'Reaction Chambers' or 'Photo-Reactors') allow the suppression of transport processes; thus, the effect of chemistry alone can be investigated. In fact, the phenomenon of tropospheric ozone formation was observed in smog-chambers long before the chemical mechanism (see Chap. 2) was discovered. The main disadvantage of smog chambers is the presence of surfaces; thus, care should be taken to avoid artefacts that may arise from chemical processes at the chamber walls. In order to minimise these problems, very large smog chambers with volumes exceeding $100\,m^3$ were recently built; these facilities offer surface/volume ratios below $1\,m^{-1}$. However, investigation of fast (time scale of seconds) in-situ chemical and photochemical processes (see Sect. 2.5) in the open atmosphere allows us to largely neglect the effect of transport, since transport takes place only at longer time scales. Thus, it is possible to study the chemical processes directly in the atmosphere. In particular, this is true for free radical (OH/HO_2) photochemistry, where the lifetime of the reactive species is on the order of seconds.

5.3 Requirements for Measurement Techniques

Useful measurement techniques for atmospheric trace species should fulfill two main requirements. First, they must be sufficiently sensitive to detect the species under consideration at their ambient concentration levels. This can be a very demanding criterion; for instance, species present at mixing ratios ranging from as low as 0.1 ppt (mixing ratio of 10^{-13}, equivalent to about 2×10^6 molecules/cm^3) to several parts per billion (ppb) (1 ppb corresponds to a mixing ratio of 10^{-9}) can have a significant influence on the chemical processes in the atmosphere (Logan et al., 1981; Perner et al., 1987a). Thus, detection limits from below 0.1 ppt up to the ppb range are required, depending on the application.

Second, it is equally important for measurement techniques to be specific (or selective), which means that the result of the measurement of a particular species must be neither 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 ppt and ppb levels, even in clean air (see Chap. 2), this is also not a trivial condition.

In practice, there are further desirable properties of a measurement technique, including simplicity of design and use of instruments. In addition, the capability of real-time operation (as opposed to taking samples for later analysis) and the possibility of unattended operations are issues. Further considerations are weight, portability, and dependence of the measurements on ambient conditions. To date, no single measurement technique can – even nearly – fulfill all the diverse requirements for trace gas measurements in the atmosphere. Therefore, many different techniques have been developed (e.g. Clemitshaw, 2004).

5.4 Grouping Measurement Techniques in Categories

An important criterion of the available techniques is, therefore, the degree of specialisation; for instance, there are instruments for the measurement of a single species or parameter (like the thermometer that can measure only the temperature). Simply speaking, we distinguish between specialised techniques ('box per species techniques') and universal techniques capable of determining many parameters with a single instrument.

Another fundamental property of instruments is their ability to make **in-situ** or **remote sensing** measurements. While in-situ measurements come close to the ideal to determine trace gas concentrations in a 'spot' in space that is usually very close to the instrument, remote sensing techniques allow measurements from a large distance, perhaps as far as from a satellite instrument in the earth's orbit. On the other hand, remote sensing instruments usually average the trace gas concentrations over a large volume of air. Remote sensing techniques always rely on the sensing of electro-magnetic radiation, i.e. they are spectroscopic methods.

To date, a large variety of measurement techniques for atmospheric trace gases (and other atmospheric parameters) have been developed. A few examples of instruments belonging to either category include:

- Gas chromatography (GC, universal technique, in-situ)
- Optical spectroscopy (universal technique, in-situ, remote sensing)
- Mass spectrometry (MS, universal technique, in-situ)
- Chemiluminescence (e.g. for the detection of NO or O_3)
- Chemical amplifiers for the detection of peroxy radicals (e.g. Cantrell et al., 1984, 1993; Clemitshaw et al., 1997)
- Photoacoustic detection (e.g. Sigrist, 1994b)
- Electrochemical techniques
- Matrix isolation – electron spin resonance (MI-ESR) (e.g. Mihelcic et al., 1985)
- Derivatisation – HPLC or Hantzsch reaction (e.g. for determination of CH_2O) (Fung and Grosjean, 1981; Nash, 1953)

- ‘Bubbler’ combined with wet chemistry, colorimetry (e.g. West and Gaeke, 1956; Saltzman, 1954), or ion-chromatography (IC)

In this context, spectroscopic techniques are a powerful variety. These techniques are highly sensitive, very specific, universally usable, give absolute results, and have the potential for remote sensing. It is, therefore, not surprising that spectroscopic techniques assume a unique role among many other

Table 5.1. Overview of species of relevance to atmospheric chemistry research and measurement techniques

Species	UV/vis	FT-IR	TDLS (IR)	GC	MS (CIMS)	Fluoresc. Chemolum.	Other
NO	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	Electroch.[c]
HCHO	+	O	+				Derivat.[d]
RCHO							Derivat.[d]
Alkanes				+			
Olefines				+	O		
Aromatic	+			+	O		
CO				+		+	
DMS				+			
SO_2	+					+	
N_2O			+	+			
CFC’s		+		+			
HX[e]		+					Wet. Chem.
XO[e]	+				O	+	
HOX[e]			?				

Symbols denote: well measurable(+), measurable(O), not measurable (empty field).

Abbreviations: UV/vis, UV/visible absorption spectroscopy; FT-IR, Fourier-Transform IR Spectroscopy; TDLS, tunable diode laser spectroscopy; GC, gas chromatography; MS (CIMS), mass spectrometry (Chemical Ionisation MS).

[a] Matrix isolation – electron-spin-resonance.

[b] Chemical amplifier.

[c] Electrochemical cell.

[d] Derivatisation + HPLC.

[e] X = halogen atom (F, Cl, Br, I).

methods that are in use today. In this chapter, we will, therefore, have a closer look at spectroscopic techniques.

Today, atmospheric chemistry has a comprehensive arsenal of measurement techniques at its disposal, Table 5.1 gives an overview of popular trace gas measurement techniques for a series of key species relevant for studies of atmospheric chemistry. Among a large number of specialised techniques (like the gas-phase chemoluminescence detection of NO), universal techniques are of great interest due to their relative simplicity – a single (though perhaps relatively complicated by itself) instrument can measure a large range of species – these techniques have gained interest.

5.4.1 In-situ Versus Remote Sensing Techniques

Remote sensing techniques allow detection of the properties of an object from a distance. Using these techniques, the trace gas composition in atmosphere can be measured at a point that is remote from the probing instrument. Examples are LIDAR instruments (see Sects. 5.7.3 to 5.7.5) and observations of trace gas distributions from space. In fact, most DOAS applications constitute a remote detection of trace gases. In contrast to that, in-situ instrumentation measures trace gas concentrations (or other parameters) at a particular location – ideally at a point in space. There are a series of applications where localised measurements are very desirable, e.g. the determination of strong spatial gradients. Since many trace gases have a strong vertical gradient close to the ground, the observation of these gradients requires measurements that are localised at least in one (vertical) dimension. It should be noted, however, that in-situ measurements frequently require relatively long integration times, i.e. they average the concentration over a period (t_m) of time. As a consequence, they will average over the distance d_m given by:

$$d_m = t_m \cdot v_w,$$

where v_w denotes the wind speed.

Thus, an integration time of 5 min at $2\,\mathrm{m\,s^{-1}}$ wind speed already translates to a spatial average of $d_m = 600\,\mathrm{m}$.

5.5 Experimental Evidence for the Presence of Radicals in the Atmosphere

As an example of the combination of measurements by different technologies to solve a difficult problem in atmospheric chemistry, we briefly discuss both direct and indirect evidence for the presence of free radicals in the atmosphere.

Direct detection of free radicals has proven notoriously difficult because of the high reactivity and low concentration of these species in the atmosphere. For instance, although OH-initiated reaction chains are central to our understanding of atmospheric chemistry (see Sect. 2.4), direct experimental verification of this theory took a long time. From the suggestion of the central role of OH in the degradation of trace gases and ozone formation (see Chap. 2) in the early 1970s, it took more than a decade before the first reliable direct observations of atmospheric OH became available (see Table 5.2c). Only during the last decade have tropospheric OH measurements of very high quality been reported (e.g. Dorn et al., 1996; Hofzumahaus et al., 1996; Brauers et al., 1996; Platt et al., 2002; Bloss et al., 2003; Holland et al., 2003; see also Table 5.2). Although these data match the model predictions, they do not yet constitute a data set that covers all the conditions of the atmosphere. On the other hand, there has been a substantial amount of indirect evidence for the

Table 5.2. Evidence for the presence of OH radicals in the troposphere

Evidence	Literature (not intended to be complete)
Indirect	
Photochemical ozone formation	e.g. Crutzen, 1974
Pattern of VOC – degradation	e.g. Calvert, 1976
NO_X – dependence of peroxide formation	Tremmel et al., 1993
Global budgets of CO, ^{14}CO, CH_3CCl_3	Volz et al., 1981; Brenninkmeijer et al., 1992; Prinn et al., 1987
Semi-direct	
Detection by Chemical Ionisation Mass-Spectrometry	Eisele and Tanner, 1991; Eisele et al., 1994, 1996; Berresheim et al., 2000
Detection by in-situ oxidation of ^{14}CO	Campbell et al., 1979; Felton et al., 1990
Direct	
Long-Path Differential Optical Absorption Spectroscopy (DOAS) in the UV	Perner et al., 1976, 1987b; Platt et al., 1988; Mount and Eisele, 1992; Mount, 1992; Dorn et al., 1996; Brandenburger et al., 1998
Laser-Induced Fluorescence (LIF)	Hard et al., 1992, 1995; Holland et al., 1995, 1998, 2003; Hofzumahaus et al., 1996, 1998; Brauers et al., 1996; Dorn et al., 1996; Brune et al., 1995, 1998; Creasey et al., 1997; Hausmann et al., 1997; Carslaw et al., 1999; George et al., 1999; Kanaya et al., 2000, 2001; Heard and Pilling 2003; Hard et al., 2002; Bloss et al., 2003; Holland et al., 2003

presence of OH radicals in the atmosphere. In addition, a number of techniques were developed that, while not identifying the OH molecule directly, gave very good and quantitative measure for OH abundance [like CO, ^{14}CO (Volz et al., 1981; Brenninkmeijer et al., 1992), CH_3Cl (e.g. Prinn et al. 1987)]. In the following section, these methods shall be referred to as semi-direct. Table 5.2 summarises the available evidence for the presence of OH radicals in the troposphere. Today it can be concluded that, although direct, unequivocal identification of these species in the atmosphere can only be performed in a few cases; there is an enormous amount of indirect evidence of their presence. Thus, the central importance of HO_X for atmospheric chemistry can be assumed to be proven beyond reasonable doubt.

In the case of peroxy radicals, the situation is less satisfactory. To date, there are very few direct measurements of HO_2 and some other peroxy radicals by matrix isolation – electron spin resonance detection (see Table 5.3). Infrared spectroscopic detection of HO_2 has not yet been achieved in the troposphere. On the other hand, there are techniques for indirect

Table 5.3. Evidence for the presence of HO_2/RO_2 radicals in the troposphere

Evidence	Literature (not intended to be complete)
Indirect	
Ozone formation	Crutzen, 1974
Pattern of H_2O_2 (org. peroxide) formation	Tremmel et al., 1993
Change in the Leighton Ratio ('Missing oxidant')	Parrish et al., 1986
Semi-direct	
OH–LIF after titration by NO	Hard et al., 1995; Brune et al., 1995, 1998; George et al., 1999; Creasey et al., 1997; Kanaya et al., 2000; Hofzumahaus et al., 1996; Holland et al., 2003; Bloss et al., 2003
Chemical Amplifier (ROX-Box) Measurements	Stedman and Cantrell, 1981; Cantrell et al., 1984, 1993; Hastie et al., 1991; Monks et al., 1996; Clemitshaw et al., 1997; Carslaw et al., 1997; Perner et al., 1999; Mihelcic et al., 2003
Direct	
Matrix-Isolation Electron-Spin-Resonance Detection	Mihelcic et al., 1985, 1993, 2003
Tuneable Diode-Laser Spectroscopy (TDLS)	Werle et al., 1991

detection of HO_2 available that rely on the conversion to OH via reaction with NO (Table 5.3). Hydroxyl radicals can then be detected by the well-developed LIF technique. Another widely used 'semi direct' technique employs a chemical amplifier (ROX-Box) to convert NO added to the sampled airflow into NO_2. Although this basically simple technique appears to have severe limitations, it has been demonstrated that it can be used to investigate the tropospheric HO_X system, especially in clean air (e.g. Cantrell et al. 1984; Monks et al., 1996).

The first direct detection of NO_3 radicals (by DOAS) in the troposphere dates back to 1979 (see Table 5.4), but the idea of considerable influence of NO_3 on tropospheric chemical cycles only slowly gained acceptance. Since there appears to be no simple way to derive the global (or regional) average NO_3 concentration, this quantity has to be determined from long-term measurement series, which have recently begun (e.g. Heintz et al., 1996; Plane and Nien 1991]. Again, there is considerable indirect evidence for the importance of NO_3 radical reactions in the troposphere; these include (1) the lack of seasonal dependence of the NO_Y deposition (e.g. Calvert et al., 1985), suggesting

Table 5.4. Evidence for the presence of NO_3 radicals in the troposphere

Evidence	Literature (not intended to be complete)
Indirect	
Seasonal variation of the NO_Y deposition	Calvert et al., 1985
Night-time observation of RO_2 formation	Platt et al., 1990; Mihelcic et al., 1985; Gölz et al., 1997
Night-time degradation pattern of VOCs	Penkett et al., 1993
Semi-direct	
Conversion to NO + chemoluminescence	-
Direct	
Differential Long-Path Absorption Spectroscopy (LP-DOAS)	Noxon, et al., 1980; Noxon, 1983; Platt et al., 1979, 1981, 1984; Plane and Nien, 1991; Heintz et al., 1996; Aliwell and Jones, 1998; Allan et al., 1999, 2000; Martinez et al., 2000; Geyer et al., 2001, 2002, 2003
Cavity Ringdown Spectroscopy	King et al., 2000; Brown et al., 2001–2003
Matrix-Isolation Electron-Spin-Resonance Detection	Mihelcic et al., 1985, 1993, 2003
Laser-Induced Fluorescence (LIF)	Wood et al., 2003; Matsumoto et al., 2005

non-photochemical NO_X–NO_Y conversion via NO_3–N_2O_5 during winter; (2) observation of night-time radical formation (e.g. Mihelcic et al., 1993; Gölz et al., 2001); (3) degradation patterns of hydrocarbons (Penkett et al., 1993), details are discussed in Sect. 2.6.

Recently, a substantial amount of direct and indirect evidence has been accumulated for the presence of halogen atoms and halogen oxide radicals in certain parts of the troposphere (e.g. Wayne et al., 1991; Platt and Hönninger, 2003; see also Table 5.5). For instance, the degradation pattern of hydrocarbons, in particular in the Arctic as well as at remote mid-latitude areas, points to a noticeable role of Cl and Br atoms in the oxidation capacity of the troposphere. In addition, the events of ozone loss on extended areas in the polar

Table 5.5. Evidence for the presence of halogen radicals in the troposphere

Evidence	Literature (not intended to be complete)
Indirect	
'Hydrocarbon clock' observations (Cl, Br-atoms),	Solberg et al., 1996; Jobson et al., 1994; Rudolph et al., 1999; Singh et al., 1996; Wingenter et al., 1996; Ramacher et al., 1997, 1999; Röckmann et al., 1999; Platt et al., 2004
Sudden loss of ozone in the (polar) boundary layer	e.g. Barrie et al., 1988; Platt and Lehrer, 1996
Semi-direct	
Atomic fluorescence after titration by NO (BrO, ClO)	Toohey et al., 1996
Chemical Amplifier (ROX-Box) measurements	Perner et al., 1999
Direct	
Differential Long-Path Absorption Spectroscopy (LP-DOAS), detection of BrO, ClO, IO, OIO	Hausmann and Platt, 1994; Unold, 1995; Tuckermann et al., 1997; Platt and Lehrer, 1996; Kreher et al., 1997; Hegels et al., 1998; Wagner and Platt, 1998; Richter et al., 1998; Martínez et al., 1999; Alicke et al., 1999; Allan et al., 2000, 2001; Wittrock et al., 2000a; Frieß et al., 2001; Wagner et al., 2001; Matveev et al., 2001; Leser et al., 2002; Stutz et al., 2002; Hönninger and Platt, 2002, v. Roozendael et al., 2002; Pundt et al., 2002; Bobrowski et al., 2003; Hollwedel et al., 2004; Hönninger et al., 2004b,c; Frieß et al. 2004a; Saiz-Lopez, 2004a,b; Bobrowski, 2005; Zingler and Platt, 2005

boundary layer are best explained by BrO- and ClO-catalysed ozone destruction (e.g. Barrie and Platt, 1997), as discussed in Sect. 2.9.

In summary, we have a considerable body of indirect as well as direct evidence for the presence of several types of free radicals in the atmosphere.

5.6 Spectroscopic Techniques

To date, no single measurement technique can – even nearly – fulfill all the requirements; therefore, in a particular application the selection of a technique will be based on the specific requirements: What species are to be measured? Is simultaneous determination of several species necessary? What is the required accuracy, time resolution, and spatial resolution? Other aspects to be considered are logistic requirements like power consumption, mounting of light sources or retro-reflectors (see below), or accommodation of the instrument on mobile platforms.

Spectroscopic techniques can be broadly divided, on one hand, into methods relying on absorption of radiation directed to the sample from some source, or, on the other hand, into spectroscopic analysis of radiation emitted by the sample itself. Further divisions can be made according to the wavelength range used and thus the kind of internal state of the sample molecules the radiation interacts with. Figure 5.1 illustrates these different categories by giving a 'family tree' of spectroscopic techniques. In this section we give a brief overview of some spectroscopic techniques used to analyse atmospheric composition.

5.6.1 Microwave Spectroscopy

Spectroscopy in the microwave and sub-mm wavelength range can, in principle, be used in active and passive configurations. To our knowledge, no detection of atmospheric gases with active microwave instruments (i.e. with instruments employing their own radiation sources) has been made. However, the measurements of atmospheric parameters (clouds, precipitation, and turbulence) with RADAR techniques are common.

Passive measurements of stratospheric species by microwave and sub-mm wave emission are state of the art (e.g. Janssen, 1993). This technique registers the thermal emission due to rotational transitions of the atmospheric molecules. For instance, the ClO-molecule radiates at $\nu_o = 649.448\,\text{GHz}$, corresponding to 0.46 mm wavelength ($18_{1/2} \rightarrow 17_{1/2}$ transition of ^{35}ClO), but HOCl is also detectable by this technique. The line width is dominated by collisional (pressure) broadening, which by far dominates over Doppler-broadening ($\Delta\nu_D/\nu_0 \approx v_{\text{molec}}/c \approx 10^{-6}$), as described in Sect. 3.6. While this strong variation in line width with pressure, and thus altitude of the absorbing molecule, allows the retrieval of vertical profiles from a thorough analysis of the recorded

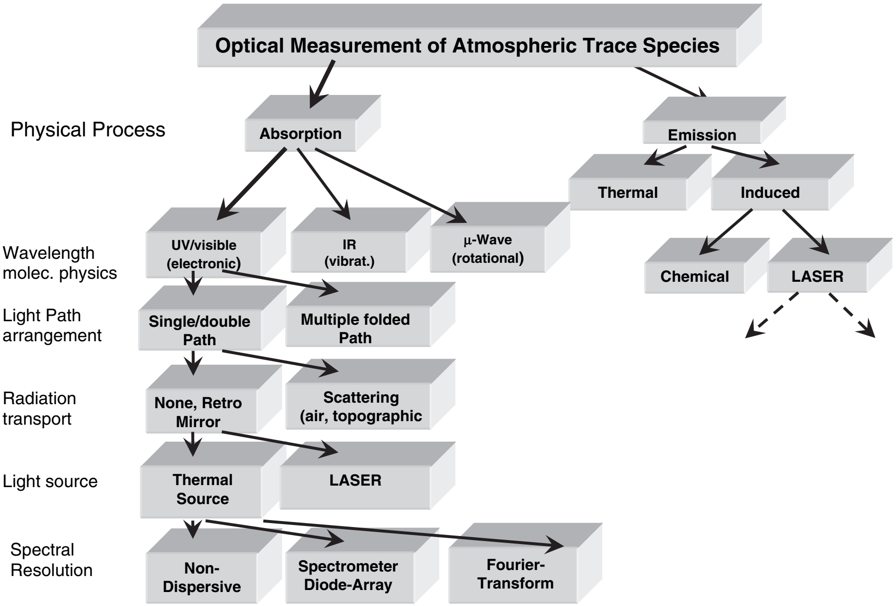

Fig. 5.1. 'Family tree' of spectroscopic measurement techniques for atmospheric trace species. Absorption spectroscopy can be categorised by the type of light source – natural (e.g. sunlight) or artificial (e.g. incandescent-, arc lamps, or lasers), the arrangement of the absorption path, the method of obtaining spectral information (non-dispersive, dispersive techniques, type of spectrometer, etc.), or other characteristics of the particular technique

line shape, it also limits the detection sensitivity at an atmospheric pressure exceeding a few mbars. Thus, for ClO, the best sensitivity is reached in the upper stratosphere, while detection at lower stratospheric or even tropospheric altitudes (i.e. below about 15–25 km) is usually difficult (e.g. Janssen, 1993; Klein et al., 2002; Livesey et al., 2003). The microwave and sub-mm wavelength range is presently not used for measurements in the troposphere; due to the relatively large pressure broadening of the lines, it would probably require measurements at reduced pressure.

5.6.2 IR Spectroscopy

IR spectroscopy has been in use for several decades, and was initially developed for the detection of atmospheric CO_2 by non-dispersive instruments ['Ultra-Rot AbSorption' (German for 'ultra-red absorption'), URAS]. More modern instruments are based on Fourier transform (FT) techniques to measure HNO_3, CH_2O, HCOOH, H_2O_2, and many other species on km path length multiple-reflection cells (e.g. Pitts et al., 1977; Tuazon et al., 1980). The sensitivity is in the low ppb range; thus, those instruments appear to be best suited for studies of polluted air. The technique has been applied in three modes of operation:

1. Active operation, where an artificial broadband light source, usually a thermal radiator, is used (Pitts et al., 1977; Tuazon et al., 1980; Galle et al., 1994).
2. Active operation, where a tuneable diode laser serves as light source. During the last two decades, tunable diode laser spectrometers (TDLS) have been developed as field-usable instruments, which were successfully used to measure HNO_3, NO, NO_2, CH_2O, H_2O_2 and other species at sub-ppb levels (e.g. Harris et al., 1989; Schiff et al., 1990; see also Sect. 5.7.1).
3. Passive operation using thermal emission from the trace gases under consideration. A particular example is the Michelson Interferometer for Passive Atmospheric Sounding (MIPAS) (Fischer, 1993; Fischer and Oelhaff, 1996; Notholt et al., 1997).

5.6.3 UV/Visible Absorption Spectroscopy

At ambient temperatures, thermal emission of UV/visible radiation is completely negligible; nevertheless, active and passive arrangements can be used, the latter technique relying on radiation from naturally hot objects, e.g. the sun.

The most common optical arrangement is shown in Fig. 6.1; the light source and the receiving system are typically separated by several kilometres. UV/visible absorption spectroscopy can be used in both ‘active’ and ‘passive’ modes; in the active mode, an artificial light source (see Chap. 6) provides the radiation, while in the passive mode natural light sources, usually the sun or stars, act as source of radiation. The strength of these techniques lies in good specificity, the potential for real-time measurements, and the absence of wall losses. In particular, the first property makes spectroscopic techniques more suitable for the detection of unstable species like OH radicals or nitrate radicals (see Chap. 10). Limitations in the systems using a separated light source and receiving system are due to logistic requirements (the need for electric power at two sites several kilometres apart, but in sight of each other) in the case of unfolded path arrangements; in addition, conditions of poor atmospheric visibility (see Sect. 4.7) can make measurements with this technique difficult.

LIDAR techniques, on the other hand, combine the absence of wall losses and the good specificity with somewhat smaller logistic requirements and the capability to make range-resolved measurements. In contrast to LIDAR, most of the above systems can only make point or path-averaged measurements. Unfortunately, this advantage of LIDAR is usually obtained at the expense of reduced sensitivity (see Sect. 5.7.3).

5.7 Selection Criteria for Spectroscopic Techniques

The important technical criteria of spectroscopic instruments are the wavelength region used (see Fig. 5.1), the physical principle (i.e. absorption or emission spectroscopy), the arrangement of the light path (path in the open atmosphere or enclosed – frequently folded – path), or the type of light source used. The following techniques are presently employed to measure atmospheric trace gases:

- Tunable Diode Laser Spectroscopy (TDLS)
- Photo Acoustic Spectroscopy (PAS)
- Light Detection And Ranging (LIDAR)
- Differential Absorption LIDAR (DIAL)
- Laser-Induced Fluorescence (LIF)
- Cavity-Ringdown Spectroscopy (CRD)
- Mask Correlation Spectroscopy
- Differential Optical Absorption Spectroscopy (DOAS)

While, in principle, most techniques (i.e. TDLS, LIDAR, DIAL, LIF, and DOAS) allow light paths (or sensitive volumina, in the case of LIF) in the open atmosphere, some techniques lend themselves more to enclosed light paths.

5.7.1 Tuneable Diode Laser Spectroscopy (TDLS)

The idea of tunable diode laser spectroscopy is to use a narrow-band, frequency-variable laser source to scan a suitable trace gas absorption structure. This type of laser can be frequency tuned e.g. by varying the diode current. In practice, a sawtooth-like waveform of the laser current results essentially in a linear scan across a certain spectral interval, typically a small fraction of a wave number. Thus, in principle, no further wavelength selective elements are required. Early applications relied on lead–salt (Harris et al., 1989; Schiff et al., 1990; Sigrist, 1994) diode lasers operating in the mid-infrared (about 3–30 μm), thus covering the fundamental vibrations of many molecules of atmospheric interest. The disadvantages of lead–salt diode lasers are their limited commercial availability and the requirement for cooling to temperatures around (and frequently below) the boiling point of liquid nitrogen. While diode lasers are very compact and low power-consuming devices, the need for liquid nitrogen cooling or closed cycle He-coolers and vacuum thermal insulation, in practice, offsets these advantages. In recent years, further development of tuneable diode lasers yielded devices operating around room temperature in the near IR (about 1.6–2 μm); here communication laser diodes operating at room temperatures are available, which allow very compact and lightweight instruments (e.g. Durry et al., 1999; Gurlit et al., 2005). On the other hand, in the near IR, typically weaker overtone-bands are available. In addition, recently, quantum cascade lasers became available, which can generate narrow band emission even in the mid-IR (e.g. Kosterev and Tittel, 2002; Jimenez et al., 2004).

During the last two decades, TDLS became field-usable instruments, and were successfully used to measure HNO_3, NO, NO_2, CH_2O, and H_2O_2 at sub-ppb levels (Harris et al., 1989; Schiff et al., 1990). In the usual arrangement coupled to a multiple reflection cell, the strength of TDLS lies in the mobility of the instrument, allowing measurements on board ships and airplanes, combined with high sensitivity. The limitations are due to the necessity to operate under low pressure (in many applications), thus introducing possible losses at the walls of the closed measurement cells. Moreover, at present, diode-laser technology is still quite complex. Therefore, the development of laser diodes is in demand, and diodes are mainly developed for applications where a mass market is seen (CD players, fibre optical communication, etc.). While the developments in the latter areas are quite impressive, diodes optimised for spectroscopic purposes, especially in the visible and ultraviolet spectral ranges, are still difficult to obtain.

5.7.2 Photo Acoustic Spectroscopy (PAS)

Photo Acoustic Spectroscopy is based on the detection of the pressure change occurring as a consequence of the temperature rise due to the energy absorbed by trace gas molecules illuminated by radiation at suitable frequency. Obviously, the absorption of radiation by atmospheric trace gases is very minute, thus giving rise to only small temperature and pressure changes. On the other hand, extremely sensitive devices for detecting periodic atmospheric pressure changes are available in the form of microphones for the detection of sound waves (e.g. Sigrist, 1994).

Thus, a typical PAS instrument consists of an intensity-modulated light source – usually a laser – illuminating the interior of a cell (e.g. a tube of a few millimetres of inner diameter and a fraction of a meter length) equipped with a microphone ‘listening’ to the periodic pressure changes occurring at the frequency of the modulation. The weak signal is sometimes enhanced by tuning the modulation frequency to an acoustic resonance of the absorption cell, leading to a signal increase by the ‘quality factor’ Q of the acoustic resonator (Sigrist, 1994).

Note that photoacoustic detectors directly measure the difference $I_0 - I$ (approximately proportional to $D \cdot I_0$ and thus the trace gas concentration) rather than determining I and I_0 separately.

5.7.3 Light Detection And Ranging (LIDAR)

The term LIDAR was coined to resemble the well-known RADAR (RAdiowave Detection And Ranging) (e.g. Rothe et al., 1974; Hinkley, 1976; Svanberg, 1992; Sigrist, 1994). In principle, short pulses of a strong, collimated light source, typically a pulsed laser, are emitted into the atmosphere. By analysing the temporal evolution of the intensity backscattered from the atmosphere, the spatial distribution of scattering and extinction along the direction of the emitted (and received) radiation can be deduced, as illustrated in Fig. 5.2.

The distance from which the radiation intensity (under consideration) is scattered back is given by:

$$R = \frac{c \cdot t}{2} \, ,$$

where c is the speed of light, and t is time (after emission of the laser pulse) at which the signal reaches the detector.

The general LIDAR equation is:

$$\begin{aligned} E\left(\lambda, R, \Delta R\right) = K \cdot E_0 \cdot c_S(R)\, \sigma_{SR} \frac{\Delta R}{R^2} \cdot \\ \times \exp\left(-2 \int\limits_0^R \left[\sigma_A\left(r\right) \cdot c_A\left(r\right) + \sigma_S\left(r\right) \cdot c_S\left(r\right)\right]\, dr\right), \quad (5.1) \end{aligned}$$

with the following meanings to the terms:

$E(\lambda, R, \Delta R)$ denotes radiation energy received from a volume of air between R, $R + \Delta R$;
ΔR is the distance interval to be averaged over (corresponds to $\Delta t = \frac{2\Delta R}{c}$);
K is a constant of the system (describes the influence and size of the receiving system);
E_0 is the radiation energy emitted by the laser;
$c_s(R)$is the concentration of backscattering centres (molecules, aerosol particles);
σ_{SR} is the backscatter cross-section;
σ_A is the absorption cross-section (aerosol or gas);
$c_A(R)$ is the concentration of the absorbers (i.e. gas molecules);
σ_S is the total scattering cross-section (note that $\sigma_S \neq \sigma_{RS}$!).

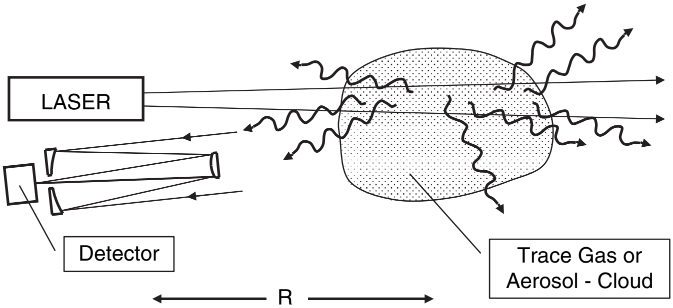

Fig. 5.2. The principle of the LIDAR technique

It is worth noting that the returned LIDAR signal is proportional to R^{-2}, while the returned RADAR signal varies with R^{-4}. This is due to the fact that the scattering volume increases with R^2, while in the case of RADAR the object (e.g. an airplane) is of constant size, and thus both the transmitted signal arriving at the target and the returned signal reaching the receiver decrease proportional to R^{-2}.

The LIDAR techniques combine the absence of wall losses with the unique capability to make range-resolved measurements along the line of sight. In contrast to that, the systems discussed earlier can only make point measurements or path-averaged measurements. In the form described up to this point, LIDAR systems have been successfully used to map aerosol distributions. There are, however, two central problems with LIDAR systems:

1. The signal [see (5.1)] depends on backscattering as well as on total scattering (or extinction) properties of the atmosphere, which are (in the case of Mie scattering) difficult to separate (the ratio $\sigma_\mathrm{S}/\sigma_\mathrm{SR}$ is usually unknown and must be estimated from a-priori information unless the Raman–LIDAR technology is used).
2. The backscattered signal is usually very weak, and thus even when high-energy lasers are used, only a relatively small number of photons is received. Therefore, the above advantages are usually obtained at the expense of high sensitivity.

5.7.4 Differential Absorption LIDAR (DIAL)

In order to measure the distribution of trace gases, at least two different wavelengths are required (in contrast to the 'ordinary' (= aerosol-)LIDAR) (Svanberg, 1992; Sigrist, 1994). The DIAL equation is obtained by dividing two general LIDAR equations (5.1) for two different wavelengths λ_1 and λ_2, respectively:

$$\frac{E(\lambda_2, R)}{E(\lambda_1, R)} = \exp\left(-2\left(\sigma_A(\lambda_2) - \sigma_A(\lambda_1)\right) \cdot \int_0^R c_A(r)\, dr\right). \tag{5.2}$$

Thereby it is assumed that σ_SR and σ_S are the same for λ_1 and λ_2, respectively. This assumption appears justified as long as $\Delta\lambda = \lambda_2 - \lambda_1$ is sufficiently small (a few nanometres). Obviously, the two wavelengths are chosen so that (while their difference is as small as possible) the difference in the absorption cross-sections $\Delta\sigma = \sigma_\mathrm{A}(\lambda_2) - \sigma_\mathrm{A}(\lambda_1)$ is as large as possible, i.e. one wavelength is at the centre of an absorption line, the other besides the line.

5.7.5 White Light LIDAR

Recently, suggestions and first experiments of two varieties of the LIDAR technique were made using broadband 'white light' sources in conjunction with wavelength dispersing detectors making use of the DOAS principle, see Sect. 5.7.9. If these techniques prove viable, they could combine the advantages of LIDAR and DOAS. Presently, there are two approaches:

1. A LIDAR principle that combines the differential UV-visible absorption spectroscopy and the classical LIDAR technique. The novel element of the system is the use of an imaging spectrometer in conjunction with a two-dimensional CCD detector array to simultaneously spectrally and temporally resolve backscattered radiation. The 'white' light (i.e. broadband radiation) required for this LIDAR approach is provided either by a flash-lamp or a broadband dye laser (of 10–20 nm full width at half maximum tuneable across the UV-visible spectral region). Thus, simultaneous range-resolved measurement of multiple molecular species is possible by the DOAS technique. A first application demonstrated absorption studies in the spectral regions where NO_3 and H_2O absorb using both elastic and inelastic (Raman) backscattered radiation (Povey et al., 1998; South et al., 1998). In addition, the technique has applicability for a wide range of molecules, including O_3, NO_2, and other spectrally structured absorbers, and for atmospheric temperature sounding, which may be derived from either rotational Raman return or temperature-dependent absorptions such as those of O_2.
2. In this approach, ultra-short (femtosecond) laser pulses produce a 'beam' of white light in the atmosphere, which can then be observed with a separate wavelength-dispersing detector system. Atmospheric constituents will leave their spectroscopic fingerprint on the distance between the 'beam' and the detector, which can then be detected by DOAS techniques (e.g. Rairoux et al., 2000; Kasparian et al., 2003).

5.7.6 Laser-Induced Fluorescence (LIF)

Laser-Induced Fluorescence is a very sensitive and specific technique for the detection of atmospheric trace gases. It relies on the excitation of trace gas molecules by absorption of (laser) radiation, the frequency of which corresponds to a suitable transition from the molecule's ground state to an (electronic) excited state, see Figure 3.6. The number of fluorescence photons detected is then proportional to the atmospheric trace gas concentration.

A central problem with LIF is the separation of Rayleigh scattered exciting radiation from the fluorescence signal. While Rayleigh scattering cross-sections of air molecules (i.e. O_2 and N_2) are typically six to eight orders of magnitude smaller than trace gas absorption cross-sections, typical trace gas mixing ratios are 10^{-12} to 10^{-9}. Combined with the fact that fluorescence efficiencies can be orders of magnitude below unity, scattered excitation radiation must be suppressed by many orders of magnitude. Several techniques have been developed to achieve this goal, which include:

1. Excitation at higher (vibrational) levels above the excited state in which fluorescence can be observed. The detected wavelengths (red) are thus shifted from the excitation wavelength, and can be separated by suitable filters (wavelength filtering).
2. Use of short laser pulses for excitation. The fluorescence signal can be recorded after the excitation signal has decayed and thus separated. This technique frequently requires low pressure in order to avoid too rapid a decay of the fluorescence signal by collision quenching and hence its denomination 'temporal' or 'baric' filtering (Hard et al., 1979).

Other potential problems in the technique are photochemical formation of species to be detected by excitation radiation [e.g. OH by O_3 photolysis (Ortgies et al., 1980; Davis et al., 1981; Shirinzadeh et al., 1987)], or saturation of the transition under consideration. In addition, absolute calibration from 'first principles' has been found to be extremely difficult (e.g. Hofzumahaus et al., 1996, 1998; Holland et al., 2003), and so experimental calibration is necessary (e.g. Hofzumahaus et al., 1996, 1997, 1998; Schultz et al., 1995).

5.7.7 Cavity-Ringdown (CRDS) and Cavity Enhanced Spectroscopy (CEAS)

Cavity-Ringdown and Cavity Enhanced Spectroscopy are relatively new techniques that make use of the effect of atmospheric absorbers on the quality of a usually passive optical resonator (a 'cavity'), see also Sect. 7.8.3 (e.g. Paldus and Zare, 1999; Brown, 2003). After initially exciting the resonator with a laser and then switching off the laser, the decay (or 'ringdown') of the resonator is observed, which is influenced by the extinction of light due to trace gases present in the resonator cavity. Alternatively, if excited with continuous radiation, the resonator will exhibit certain attenuation, which can be monitored. The energy loss per 'round trip' of the radiation in an optical resonator with no absorber is given by the reflectivity of the two mirrors, see Sect. 7.8.3. In the case of very weak absorbers, the quality, Q, of the cavity is only determined by mirror reflectivity, $\mathrm{R_M}$, which can reach 0.9999; thus, effective light path lengths on the order of many kilometres can be reached under favourable conditions with resonator lengths below 1 m. On the other hand, in some respects, the limitations of CRDS are similar to the limitations of DOAS in that the effective light path will be limited by visibility. CRDS has been developed into a useful tool for laboratory measurements; several measurements in the atmosphere, mostly of NO_3 radicals, were reported (e.g. King et al., 2000; Ball and Jones, 2003; Brown et al., 2001–2003; Simpson 2003; Ball et al., 2004).

5.7.8 Mask Correlation Spectroscopy (COSPEC)

Mass Correlation Spectroscopy was originally conceived as a tool for oil exploration by the detection of atmospheric iodine (I_2) vapour, which was assumed to be frequently associated with oil deposits. The fundamental idea of COSPEC is to analyse the absorption features (i.e. absorption bands) of atmospheric constituents imprinted on scattered sunlight. In modern nomenclature, it is a ‘passive’ instrument (see Chap. 6). The instrument allowed some degree of remote sensing of atmospheric trace gases. While the original idea of I_2-vapour detection did not prove practical, other applications were found quickly, which included the observation of tropospheric column densities of SO_2 and NO_2 in industrial emission (e.g. Giovanelli et al., 1979; Beilke et al., 1981; Redemann Fischer, 1985) or volcanic plumes (Hoff, 1992).

The COSPEC instrument was originally designed in 1960s (Barringer et al., 1970; Davies, 1970; Davies et al., 1975); it uses an innovative opto-mechanical correlator (e.g. Davies, 1970; Millan and Hoff, 1977; Millan, 1972, 1978, 1980) to identify and quantify the spectra of atmospheric trace gases. In this way, a remarkably compact and reliable instrument could be built, since spectral recognition of the molecules to be measured was done by special opto-mechanics (Fig. 5.3) with relatively simple electronics and without a computer. Since neither fast-scanning, multi-channel detectors nor powerful computers were available at that time, the mask correlation technique was an attractive way to measure total columns.

By making the instrument mobile and horizontally traversing emission plumes, a total integrated concentration cross-section of the plumes can be obtained (Giovanelli et al., 1979). After multiplication with the concentration weighted wind component perpendicular to the cross-section, the total emission from the source (e.g. in $\mathrm{kg\,s^{-1}}$) can be deduced.

For around 30 years, the COSPEC instrument has been the principal tool for remote surveillance of volcanic plumes. Although it was not originally designed for volcanological research, it had a major impact on the discipline, not only in volcano monitoring and eruption forecasting but also in estimating the global contribution of volcanic volatiles to the atmosphere (e.g. Weibring et al., 1998). By allowing the measurements of SO_2 and NO_2 flux in airborne plumes, it has fulfilled a vital role in the management of many volcanic crises, notably at Pinatubo in 1991 (Hoff, 1992), and recently at Soufrière Hills Volcano. The COSPEC instrument was a major technological innovation at its time, but is now outdated in several important respects. Problematic aspects of its concept are interferences from other gases, non-linearity, solar Fraunhofer lines, polarisation effects, and multiple scattering in aerosol and clouds. In particular, each compound to be measured required its individual mask, and the system is sensitive to wavelength shifts due to mechanical distortions and temperature variations.

5.7.9 Differential Optical Absorption Spectroscopy (DOAS)

As will be described in detail in the following chapters, the central idea of DOAS is to make use of structured absorption of many trace gases of atmospheric interest while ignoring the rather ‘smooth’ extinction features due to

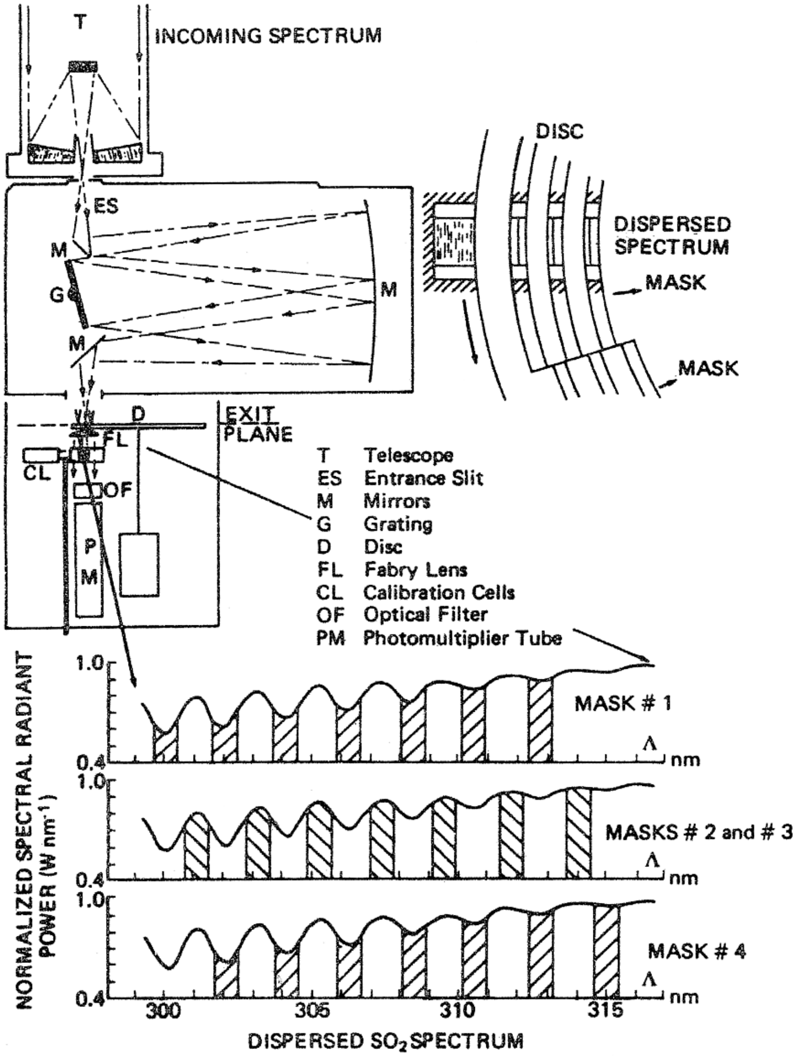

Fig. 5.3. The principle of a COSPEC instrument (from Barringer et al., 1970)

aerosol or instrumental effects. The DOAS principle and its technical realisation builds on some of the earlier developments, superseding them in many respects and supplementing other spectroscopic techniques (e.g. Platt and Perner, 1980; Platt, 1994, 2000; Plane and Smith, 1995; Roscoe and Clemitshaw, 1997; Russwurm, 1999; Finlayson-Pitts and Pitts, 2000; Clemitshaw, 2004).