

Construction and Testing of a
Differential Optical Absorption
Spectrometer (DOAS) System

Diploma paper
by
Carsten Bohlen and Eva-Lotta Reinholds

LRAP-28 (1983)

Abstract

A long-path Differential Optical Absorption Spectroscopy (DOAS) system has been built and installed for the purpose of analyzing trace gas pollutants. In the DOAS system a xenon high-pressure lamp, situated 1-10 km away from the optical receiver, is used. The data acquisition system consists of a spectrometer, a rotating slotted disc and a signal averager. The concentrations, down to the ppt level, can be derived by subtracting reference spectra. Due to the high sampling frequency, noise due to atmospheric fluctuations will be eliminated and by averaging a large number of spectra a high signal-to-noise ratio can be obtained.

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0. Introduction

In the spring of 1982 it was decided to build and install an atmosphere monitoring system based on optical long-path differential absorption. The technique is called DOAS (Differential Optical Absorption Spectroscopy). It was first developed at the Institute for Atmospheric Chemistry (Institut für Atmosphärische Chemie) in Jülich, West Germany [2]. The method is of a bistatic nature. A powerful lamp is situated 1-10 km away from the data acquisition system (Fig. 0.1). The lamp is of xenon high-pressure type.

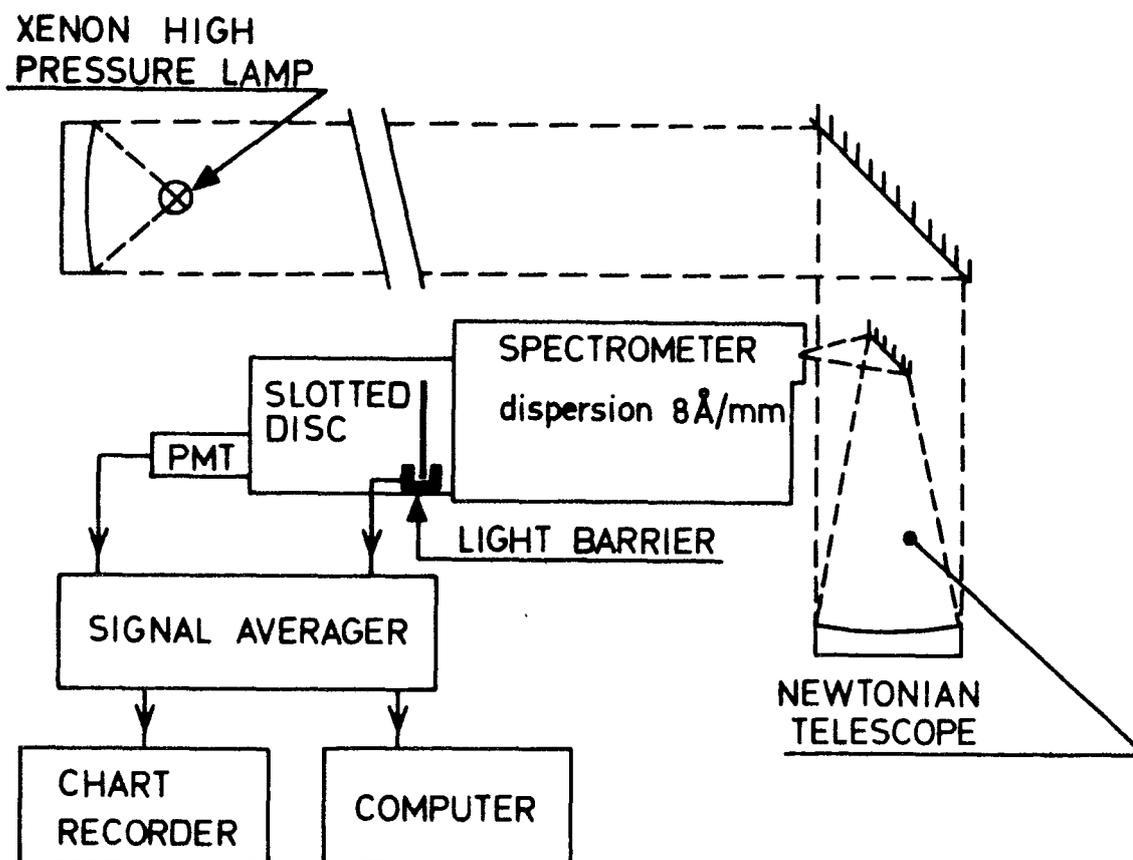


Fig. 0.1 The DOAS system

After the light is dispersed in a spectrometer, the spectrum is recorded using a unique method. This method will be described in Chapter 4. The main thing is that the spectra are recorded with a frequency well above that of the air fluctuations. This enables us to measure extremely low concentrations in the probed volume. The use of absorption spectroscopy has many advantages over sampling methods. First of all, we have real-time measurements, which can easily be used for warning systems. Secondly, we can analyze many different gases with one system. A tunable dye laser could of course also do the job, but it is 200 times more expensive than the xenon lamp. The practical limitations of DOAS as compared to differential

absorption lidar (DIAL) are the bistatic nature of the measurements (transmitter and receiver are physically separated) and the inability to perform range-resolved measurements. However, DOAS is more suitable for measurements of low concentrations. Using a single laser system it is hard to switch the laser frequencies of DIAL at sufficient speed, and because of this, the fluctuations of the atmosphere degrade the results.

1. Air Pollution

We will begin this survey of air pollution by defining what we mean by air pollution. Pollutants are all substances that alter the natural composition of the air, both natural and artificial, having a lasting effect on people, nature, animals or climate. The contaminants can be classified in many different ways, e.g. manmade - natural, organic - inorganic, but we choose to divide them into two groups, gaseous - particulate. Airborne particles can appear in both solid and liquid states and are either manmade (e.g. smoke or pesticides) or naturally occurring (e.g. dust or sea spray). However, our measurements will concentrate on gaseous contaminants. Air pollution in general is not really a new problem. Already in the seventeenth century people knew that there was a connection between respiratory diseases and foul air. The now so frequently used word smog, was invented in the nineteenth century. At the end of 1950's the pollution had reached such a level that effective work on how to reduce it began. In the future such work will be increasingly important because of the effects of pollution. The effects can be divided into seven main groups [1] :

1. Effects on health; e.g. bronchitis, asthma and perhaps even cancer of the lung.
2. Inconveniences like bad smells or hazy air.
3. Effects on animals and plants, where dangerous pollutants can enrich and stay in nature forever, e.g. DDT.
4. Effects on materials as experienced in the Mediterranean area, where many sculptures have been destroyed mainly due to sulphurdioxid (SO_2).
5. Climatological effects will appear with average temperature rising, resulting in partial melting of the polar ice caps.
6. Social effects when certain polluted areas will be less attractive to live in.
7. Economical effects which actually are the result of the six points above mentioned.

1.1 Gaseous Pollutants

Gases are not affected by gravitation as particles are and due to this fact they have a long residence time (defined as the time they can stay in the atmosphere). This is the reason why gases easily spread over very large distances. Under certain conditions, pollution from the US and Canada can be detected in Sweden, a distance of over 6000 km. The gases in the atmosphere are often transformed into other compounds or turn into liquids or solids. This happens in three main ways:

1. Photochemical reactions
2. Reactions in water droplets
3. Phase transitions

In these reactions, the gases can be transformed into all three states of matter. The cleansing of the atmosphere in the case of gases mainly occurs through wash-out, the process where gases form particles which are washed out by rain, and through rain-out, where the gases unite with clouds and then fall to earth with rain. If the transformed gases form liquids or solids they are cleansed either by the two ways mentioned above, through gravitational settling or through turbulent impaction (i.e. fine particles impact on surfaces by centrifugal action due to turbulence). Below we will now try to mention the most important pollutant gases in their primary form, i.e. we concentrate on what is emitted from the sources of pollution.

Sulphur dioxide (SO_2) is one of the most wellknown and studied pollutants. Main source is the combustion of fossil fuels, where most of the sulphur present in the fuel is oxidized to SO_2 . Other major sources include metallurgical, cement, petroleum refining and miscellaneous other chemical industries. Nature also contributes with SO_2 , mainly from volcanoes.

Sulphur dioxide in itself is not toxic except in high concentrations, but combined with other pollutants, there is a clear synergistic effect on the respiratory organs.

SO_2 can form sulphuric acid (H_2SO_4) through oxidation either by catalysis or by photoreactions. Sulphuric acid can cause considerable damage to plants, lakes and property. The acid can be neutralized in the air, forming solid sulphate particles. These aerosoles disperse the sunlight and cause a visual effect, seen as haze on summer days. In a longer perspective this might bring about a reduction of the average temperature of the earth.

Forty per cent of the sulphur dioxide produced in Sweden

originates from heating and electricity production and the rest from industries.

Carbon dioxide (CO_2) is also emitted through burning of fossil fuels. Over the last twenty years there has been an annual increase of the concentration of CO_2 by 0.6 ppm. This might lead to an overall increase of the temperature, because carbon dioxide transmits incoming short wave radiation but blocks the outgoing long wave radiation. This is known as the greenhouse effect. If the temperature increases, the water vapour content of the air will also increase, which will further speed up the greenhouse effect. This alteration of the climate might lead to problems of a global character, for instance the ices in the Polar areas will melt and raise the seawater level by several meters. This will happen if the temperature rises with approximately four degrees centigrade. The growing deforestation further increases the CO_2 concentration. The carbon dioxide pollution is a very serious problem because of its global nature and the difficulty of changing the conditions back to normal.

Carbon monoxide (CO), unlike CO_2 , is poisonous. It is bound to the haemoglobin of the blood and prevents the blood from transporting oxygen. CO mainly comes from motor vehicle emissions and is the result of incomplete combustion.

Nitrogen oxides (NO_x), where the x can be replaced with 1, 2 or 3, play an important role both near and far from the surface of the earth.

Nitric oxide (NO) is formed through $\text{N}_2 + \text{O}_2 \rightarrow 2\text{NO}$ and this reaction is favoured at high temperatures and needs a lot of oxygen.

Nitrogen dioxide (NO_2) is formed either through oxidation of NO or through the reaction $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$. The NO_2 gas is a very dangerous one, mainly for two reasons. Firstly, it is, unlike NO , very toxic. Already at concentrations as low as 100 ppb human health effects can be observed. Secondly, it produces other dangerous pollutants. If NO_2 is oxidized it forms nitric acid, which causes damages to lakes and to materials. Nitrogen dioxide can also be influenced by sunlight to produce an oxygen atom, which oxidizes and forms ozone (O_3), which is an important component in photochemical smog. O_3 is, apart from being toxic, the gas responsible for the major part of the damages caused to plants by air pollution. In the stratosphere,

nitrogen oxides, emitted by supersonic aircrafts, destroy ozone, which may lead to an increase of harmful UV light in the troposphere. This brings about a rise at the rate of human skin cancer.

Polyaromatic Hydrocarbons (PAH) are mainly emitted from motor vehicles, but the burning of wood and coal also plays an important role. PAH gases have varying properties and some of them are believed to be carcinogens. The analysis of PAH gases is very difficult, because they appear in extremely low concentrations. The material presented in this chapter is mainly from Ref. [1] .

1.2 Particulate Pollutants

In this diploma paper particles will be treated superficially, because the DOAS technique is not intended for analyzing particles. Particles are divided into large and small particles with the arbitrary division at 1.0 micrometer. Larger particles are usually formed through mechanical processes such as erosion, grinding, drilling etc. High temperature processes, like combustion, are the main sources for the smaller fraction. Generally, smaller particles are more dangerous than the larger ones because they can stay longer in the air and as a result of this they can be transported over very large distances. Smaller particles can also more easily get down into the respiratory organs and cause more damage [3] .

In Table 1.1 the sources and main sizes of the more common particulate pollutants are presented.

<i>Element</i>	<i>Main size</i>	<i>Main source</i>
<i>Sulphur</i>	<i>Small</i>	<i>Burning of coal and oil</i>
<i>Calcium</i>	<i>Large</i>	<i>Erosion</i>
<i>Chromium</i>	<i>Small</i>	<i>Metallurgical processes</i>
<i>Iron</i>	<i>Large</i>	<i>Erosion</i>
<i>Copper</i>	<i>Small</i>	<i>Metallurgical processes</i>
<i>Zinc</i>	<i>Both</i>	<i>Surface treatment, vulcanization</i>
<i>Bromine</i>	<i>Small</i>	<i>Motor vehicles</i>
<i>Mercury</i>	<i>Small</i>	<i>Droplets from burning of coal</i>
<i>Lead</i>	<i>Small</i>	<i>Motor vehicles, melting</i>

Table 1.1 Particulate pollutants, their main size and their main sources

2. Remote sensing of the atmosphere.

The field of remote sensing can be divided into two main areas, passive and active measurements. Whichever technique one chooses, it will be based upon the interaction between electromagnetic radiation and the molecules in the measurement volume. The frequency dependence of this interaction is characteristic for different substances. This means, that in order to analyse any results one must have access to accurate spectroscopic information on the substances one wishes to measure.

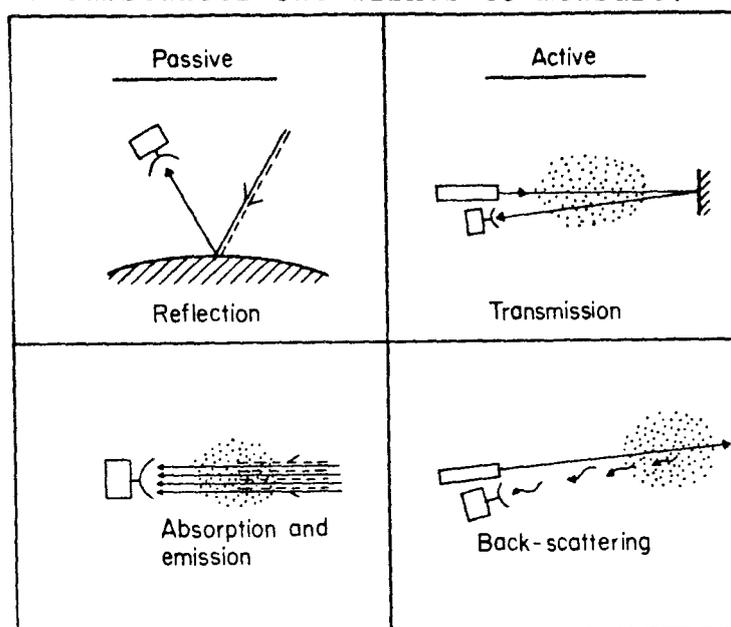


Fig. 2.1 Passive and active remote sensing techniques [4]

2.1 Passive techniques

In passive remote sensing measurements, the atmosphere is probed by analyzing the spectral distribution of the background radiation from e.g. the sun or the sky. The absorption of the background radiation at a number of frequencies is measured. The frequencies are chosen depending on what substances one wishes to measure. The missing or partially missing frequencies are used

as means of identification. The strength of the absorption lines determines the concentration of the absorbing gas according to the Beer-Lambert law:

$$I_t(\nu)/I_0(\nu) = \exp(-\sigma(\nu) \int_0^R N(r) dr)$$

$I_t(\nu)/I_0(\nu)$: transmitted intensity fraction

σ : absorption cross section

$N(r)$: concentration at the distance r

ν : frequency

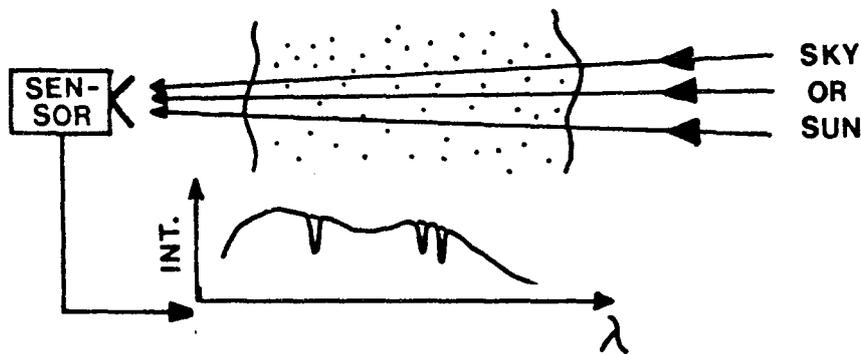


Fig. 2.2 Principle of passive remote sensing [5]

The presence of the factor $N(r)$ in the Beer-Lambert law suggests a problem since the distance r is not always known. Generally the presence of an atmospheric inversion layer can be used. Such a layer prevents the mixing of atmospheric layers. Thus the mean concentration of pollutions between the ground and the inversion-layer can be determined according to the modified Beer-Lambert law:

$$\ln(I_t(\nu)/I_0(\nu)) = -\sigma(\nu)NR$$

Passive techniques are not limited to absorption. Other features that can be utilized are IR and microwave emission from hot gases.

The sensor in Fig 2.2 could be based on different schemes, some of which are described below.

Dispersive spectrometers: Grating or prism spectrometers of suitable resolution can be used for a wavelength analysis of the incoming radiation. The spectrum is recorded with a photo electric device. One recording combination that is becoming increasingly important is an array-detector combined with a multichannel analyzer.

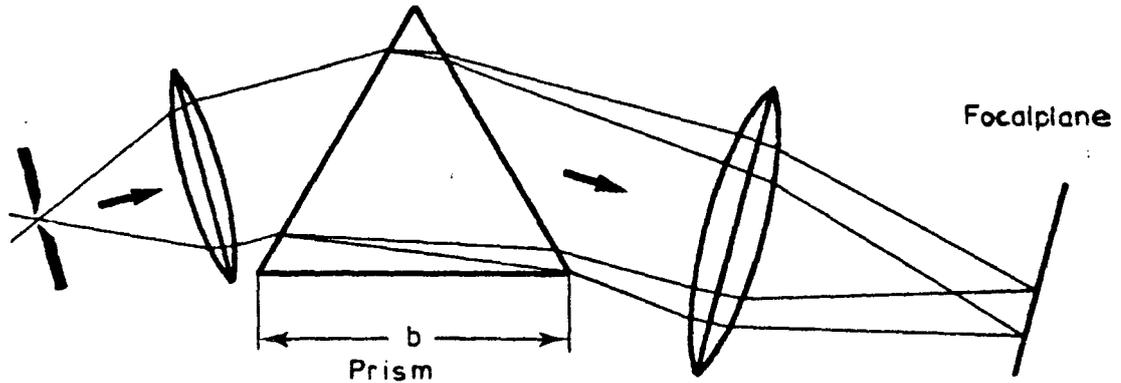


Fig. 2.3 Dispersive spectrometer [5]

Fourier spectrometers: The incoming light is divided into two perpendicular beams by a beam-splitter. The two beams are brought together again at the detector. The path length for one of the beams can be altered by moving a mirror. This introduces an optical path difference, and accordingly a variation of intensity at the detector. With the use of the Fourier transform the spectrum can be calculated.

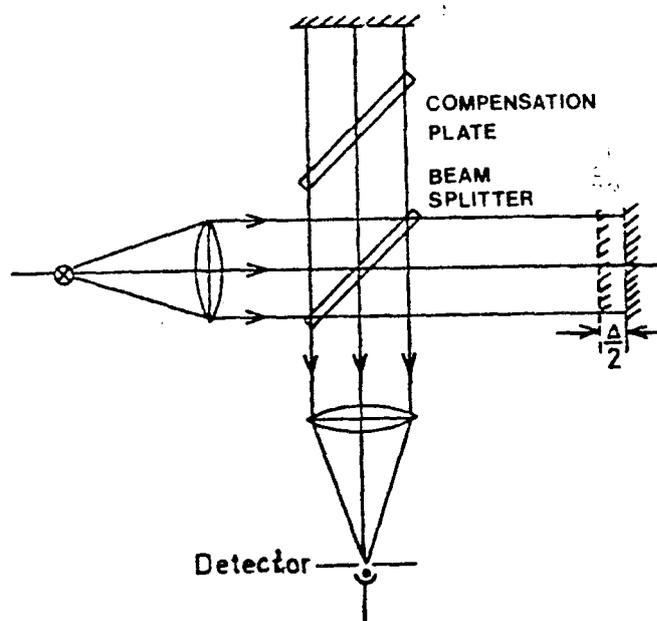


Fig. 2.4 Fourier spectrometer [4]

The Fourier spectrometer has one main advantage over the dispersive spectrometer. It records the whole spectrum simultaneously.

Correlation spectrometers: In a correlation spectrometer an absorption spectrum of the gas one wishes to investigate is stored. The spectrum of the incoming light is correlated with the stored spectrum. There are two types of correlation spectrometers

1. Dispersive correlation spectrometers
2. Gas correlation spectrometers

1. In a dispersive spectrometer, with photo electric recording, a metal mask perforated with the lines of a gas spectrum is vibrated in the focal plane. The AC component of the registered light is recorded. If the incoming light does not show the desired absorption lines no correlation is obtained. If the absorption lines exist the signal will show periodical changes.

2. In a gas correlation spectrometer the metal mask is exchanged for a gas cell containing a high concentration of the gas to be detected. The incident light is switched between this gas-filter and an empty cell. Since the gas cell completely absorbs the wavelengths characteristic of the gas, and the reference cell does not, an intensity difference will occur.

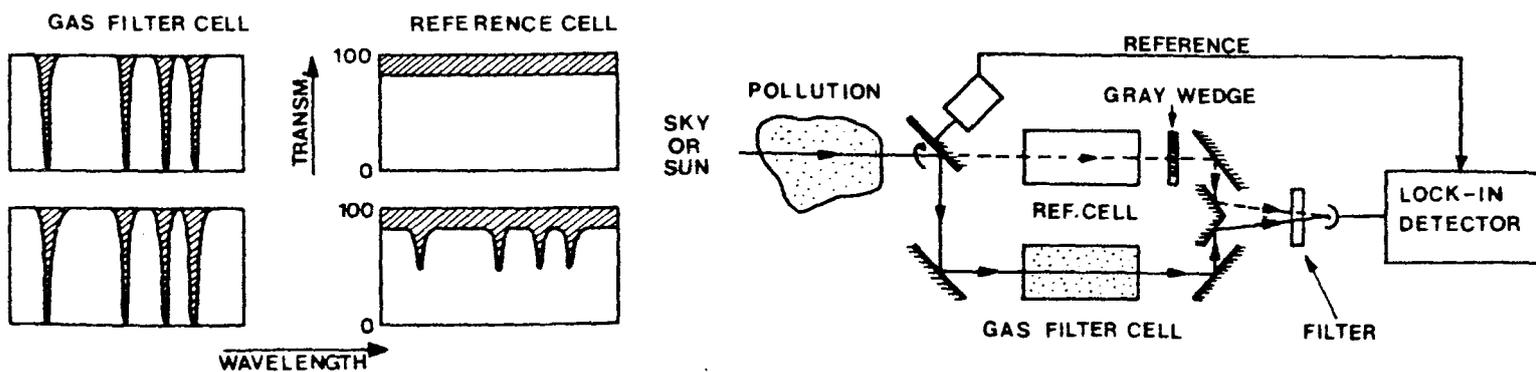


Fig. 2.5 Gas correlation spectrometer [5]

Optical heterodyne spectrometers: The incoming light is chopped and mixed with radiation from a local oscillator.

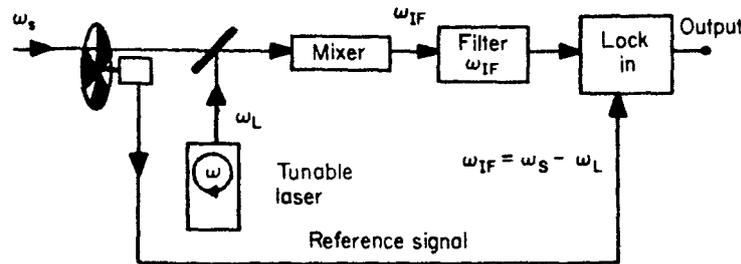


Fig. 2.6 Optical heterodyne spectrometer [4]

A narrow band filter of fixed frequency ω_{IF} defines the intermediate frequency of the receiver. This means that by sweeping the local oscillator frequency ω_L , the detected signal frequency ω_s will be swept. Consequently the spectrum will be recorded at the lock-in amplifier. In the IR region, the heterodyne technique yields a very high signal-to-noise ratio.

2.2 Active techniques

Equipment for active remote sensing transmits electromagnetic radiation into the probed area. The measured changes in this radiation are used to determine the contents of the air.

Long path absorption measurements: A continuous laser beam is directed towards a retroreflector. The distance can be up to 5 km.

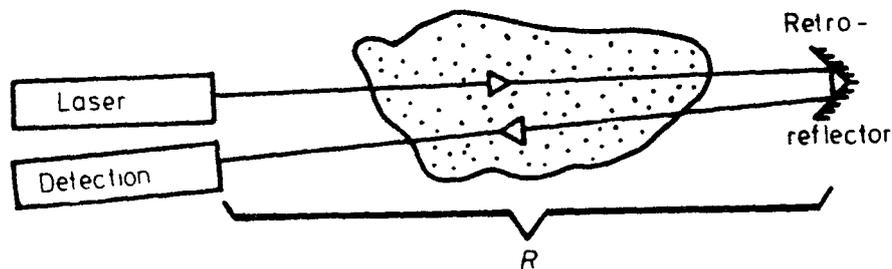


Fig. 2.7 Principle of long path absorption [4]

After reflection, the light is received by an optical telescope and detected. The mean concentration along the measuring path is given by a Beer-Lambert expression.

Since the emitted frequency can cause absorption in more than one molecular species, measurements must be made at more than one frequency. Actually, in order to determine n concentration values, measurements must be made at $n+1$ different frequencies. This means that the laser must be a tunable one.

Lidar measurements: The lidar (light detection and ranging) method bears a strong resemblance to radar methods.

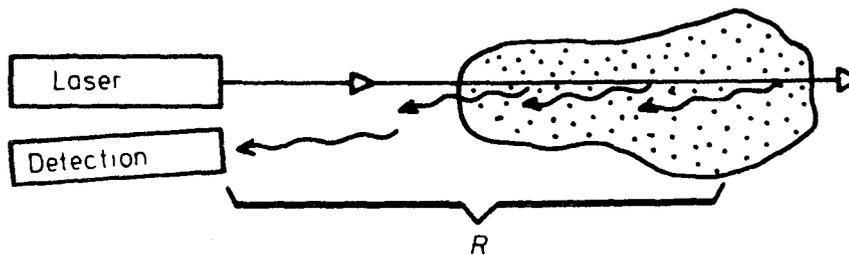


Fig. 2.8 Principle of lidar [4]

A short intense laser pulse is transmitted into the atmosphere. Light back-scattered in e.g. Mie scattering from particles is collected with an optical telescope. Light scattered at the distance R will reach the telescope with a time delay of $t=2R/c$, (c is the speed of light), after the transmission of the laser pulse. Through this time delay it is possible to achieve a range resolution. The laser pulse length Δt_p limits the resolution ΔR to $\Delta R = c\Delta t_p/2$. The range resolution can be further reduced e.g. in the case where the scattering process involves an upper state lifetime, such as in the case of fluorescence.

The power $P_v(R, \Delta R)$ received from the interval ΔR at the range R , is given by the general lidar equation.

$$P_v(R, \Delta R) = (CW\sigma_b N_b(R) \Delta R/R^2) \exp(-2 \int_0^R \sigma(v) N(r) dr)$$

C : system constant

W : transmitted pulse power

$N_b(R)$: density of scatterers

σ_b : back-scattering cross section

The exponential describes the attenuation of the beam and the backscattered light due to the absorption of molecules of density $N(r)$ and absorption cross section $\sigma(v)$. The product $\sigma_b N_b(R)$, which can be caused by different processes, determines the strength of the back-scattering.

Fluorescence: This process is particularly suitable for stratospheric measurements since quenching (radiationless deexcitations by collisions) does not occur.

Raman scattering: One important application of Raman scattering is measurements of water vapour content in the air, another is atmospheric temperature measurements.

Mie scattering: Mie scattering from particles yield very strong signals and thus particles from e.g. smoke-stacks can easily be detected.

3. Atmospheric chemistry.

The subject of atmospheric chemistry has assumed considerable importance in recent years because a number of the natural chemical cycles in the atmosphere may be particularly sensitive to perturbation by industrial and related activities. Two examples of this sensitivity are the possible decay of the stratospheric ozone layer and the photochemical smog, that appears in a number of cities today. As this is not intended to be a complete survey of the topic, we wish to limit ourselves to these two examples.

3.1 The ozone layer.

3.1.1 Screening from solar radiation.

The principal components of air, nitrogen and oxygen, strongly absorb the X-rays and very short wavelength ultraviolet radiation from the sun well above the stratosphere.

Ultraviolet radiation, up to 180 nm, is absorbed above the stratosphere by the Schumann-Runge bands of molecular oxygen. Only a little radiation below 190 nm enters the stratosphere. Between 190 and 242 nm solar radiation is removed more or less equally by stratospheric ozone and by molecular oxygen.

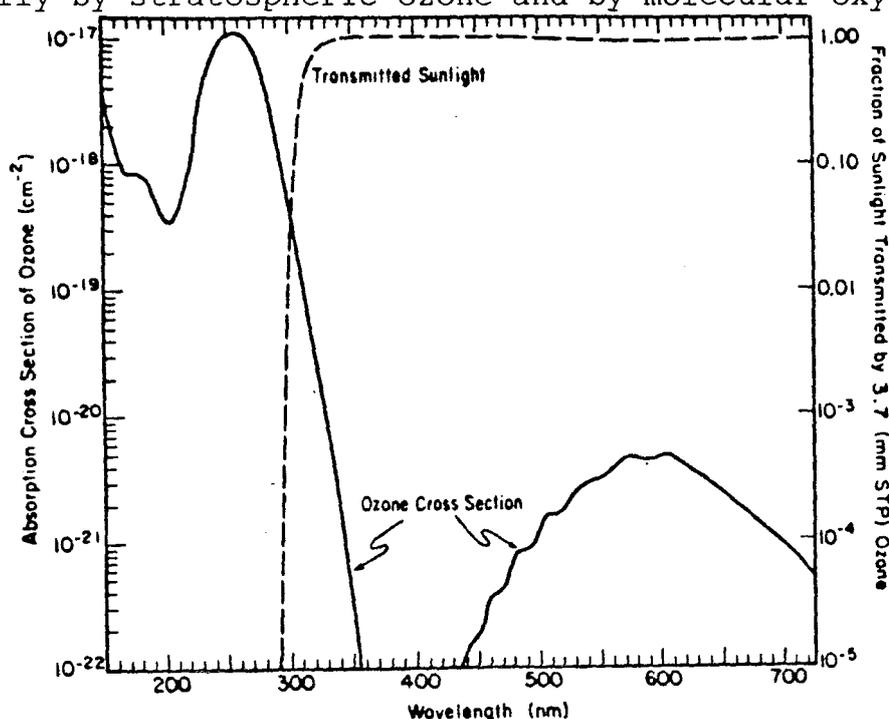


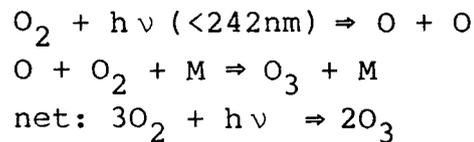
Fig. 3.1 Absorption cross section for ozone. The dashed line gives the fraction of solar radiation transmitted by 9.9×10^{18} molecules ozone per cubic centimeter [6].

The minimum in the ozone absorption spectrum plays a vital role in stratospheric photochemistry. This minimum allows some energetic ultraviolet radiation to reach the lower part of the stratosphere. Here it is absorbed by several relatively stable molecules that enter the stratosphere from the troposphere, i.e. nitrous oxides and chlorinated hydrocarbons.

Stratospheric ozone is the only effective absorber of solar radiation between 250 and 300 nm. This region is called the B-band of UV radiation. Biological DNA is very sensitive to this radiation.

3.1.2 Ozone formation.

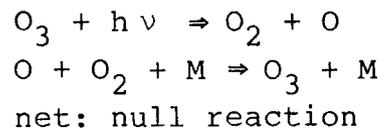
As oxygen absorbs solar ultraviolet radiation, ozone is formed.



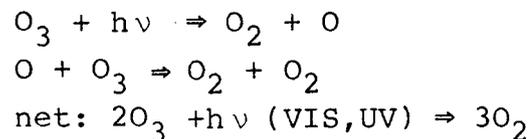
Here M is any molecule.

3.1.3 Ozone destruction.

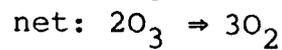
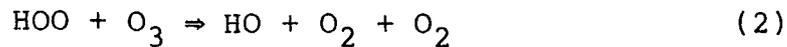
1. When ozone absorbs solar radiation, it forms oxygen atoms. However, this photolysis does not constitute real destruction of ozone since it is usually followed by reformation.



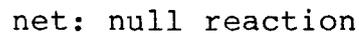
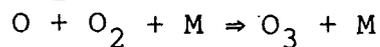
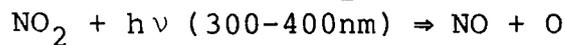
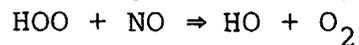
If the molecule M is not present, ozone is destroyed by ozone in the following reaction.



2. The free radicals derived from water, H, HO, HOO, destroy ozone. In the lower stratosphere there is a catalytic cycle that destroys ozone but not HO_x.



Step (1) is not always followed by (2), there may be a neutral cycle with respect to ozone formation or destruction.



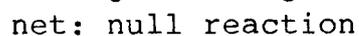
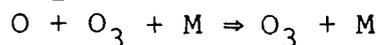
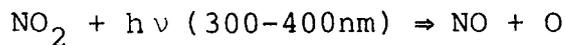
In the upper stratosphere another catalytic cycle destroys ozone.



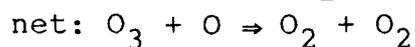
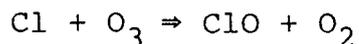
3. In the natural stratosphere the active oxides of nitrogen destroy ozone. In the middle stratosphere, the primary ozone formation region, the oxides of nitrogen destroy ozone by a catalytic cycle.



Step (3) is not always followed by (4). There is a competing neutral cycle.

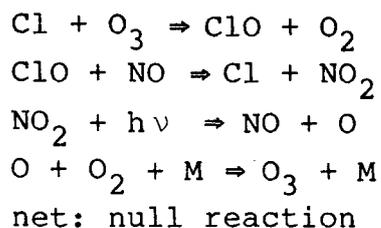


4. Free radicals based on chlorine are capable of destroying ozone in a catalytic cycle, parallel to the NO_x cycle.



As in the case of the NO_x-cycle there exists a competing

neutral cycle.



5. Less than one percent of the global production of ozone below an altitude of 45 km is transported into the troposphere and later destroyed at the ground.

Ozone destruction as percent of the global rate of ozone production below 45 km.

1. 20-30 percent
2. 10-20 -"-
3. 55-70 -"-
4. <1 -"-
5. <1 -"-

One can easily understand that the complicated equilibrium between ozone production and destruction is rather sensitive. The material presented in this chapter is mainly from Ref. [6].

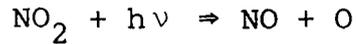
3.2 Smog.

The word smog can be defined in several ways. When it was coined it referred to a combination of coal smoke and fog. Later it was used to describe any dirty urban atmosphere.

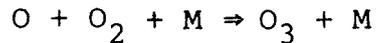
A unique type of dirty atmosphere was recognized in the late 1940's and early 1950's, it came to be known as photochemical smog. It can be defined as a type of air pollution, which owes many of its properties to the products of photochemical reactions involving the vapor of various organic substances, especially hydrocarbons, oxides of nitrogen and atmospheric oxygen. Occasionally, fog may also be involved in the formation of such smog.

Photochemical smog is particularly apparent in cities where coal is burned, there are some industries and large concentrations of automobiles. Smog in any given locality is generally a highly complex mixture of various pollutants, photochemically formed or otherwise. The intensity of photochemical smog is markedly influenced by meteorological conditions and geographical features. If a city is in a bowl defined by mountains or hills and an atmospheric inversion "clamps a lid" over the area, smog of any kind is apt to be intense.

Photochemical smog was first recognized in Los Angeles. Ozone in high concentrations (typically 0.2 part per million by volume, ppmv) was first detected. This ozone was formed photochemically from a mixture of oxides of nitrogen, hydrocarbon vapor and air. It was pointed out, that the reaction that initiated the ozone formation was almost certainly the photochemical decomposition of nitrogen dioxide.



The resulting oxygen radical reacts with atmospheric oxygen to form ozone. (M can be any molecule)



The chemistry of smog formation is very complicated, and it involves a number of reactions. Many radicals take part in these reactions. One main advantage of the DOAS technique is the capability to measure the low concentrations of these radicals. This provides a mean to further investigate the reactions involved .

4. Description of a DOAS system

4.1 Basic Physical Principles

The physical phenomenon we use in the DOAS technique is absorption, i.e. atoms will be excited and will emit the absorbed light in random directions. Let us assume we have a slice of the examined medium with a thickness of dx (Fig 4.1). We denote the change in the intensity of the light by dI , which gives us:

$$dI = -a I dx \quad (1)$$

where a is the coefficient of absorption, which varies with medium and wavelength.

The solution of Eq. (1) is $I = I_0 \exp(-a x)$. From this we can derive the trace gas concentration:

$$C = \log(I_0 / I) / (\epsilon L) \quad (2)$$

I_0 : light intensity without absorption from the gas

I : light intensity reduced due to absorption

ϵ : absorption coefficient of the gas

L : the length of the light path

With our method we cannot measure the intensity I_0 , but instead we estimate I_0' (Fig. 4.2), which gives us a slightly smaller absorption coefficient. We define $\log(I_0' / I)$ as the optical density i.e. the logarithm of the inverse of the transmittance. The difference between I_0 and I_0' is mainly due to absorption from other substances and scattering.

Fig. 4.1 Absorption of the examined medium

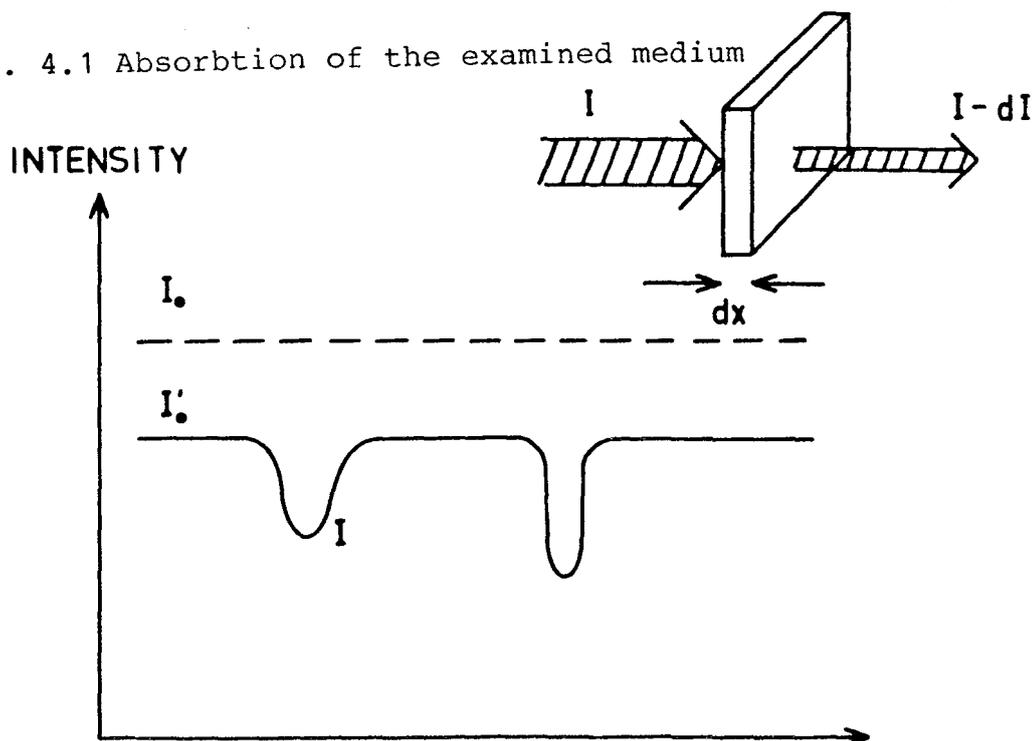


Fig. 4.2 Differential absorption spectroscopy WAVELENGTH

4.2 Light source

We use a xenon high pressure lamp (Osram XBO 450W). Because of the high pressure we get a relatively smooth spectrum due to pressure broadening of the spectral lines (Fig. 4.3).

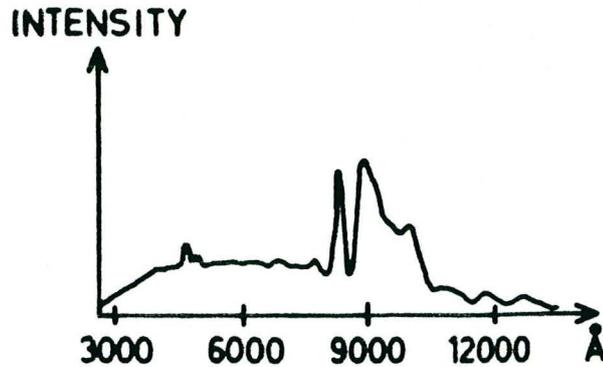


Fig. 4.3 Spectrum from xenon lamp [7]

The discharge lamp we chose has a power consumption of 450 W, and a burning time of 2000 hours. This burning time will decrease if the lamp is ignited often. The high power results in a lot of heat, which makes it necessary to divide the lamp housing with an inner wall. One part of the housing contains the lamp and the mirror and the other part all the electronics, which must be cooled with a fan. The lamp housing is equipped with a hatch (Fig 4.4).

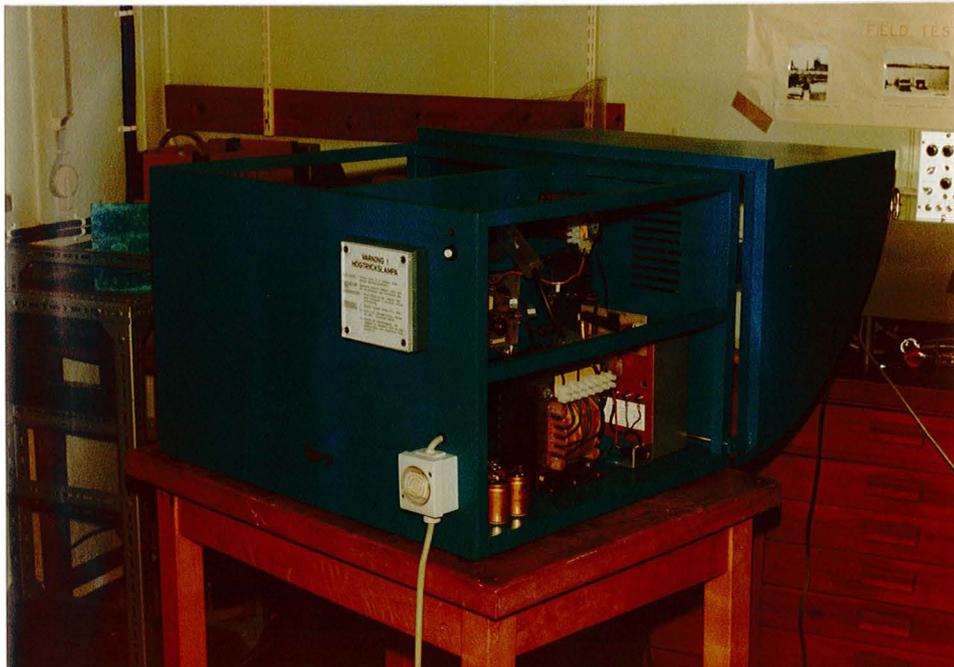


Fig. 4.4 Lamp housing

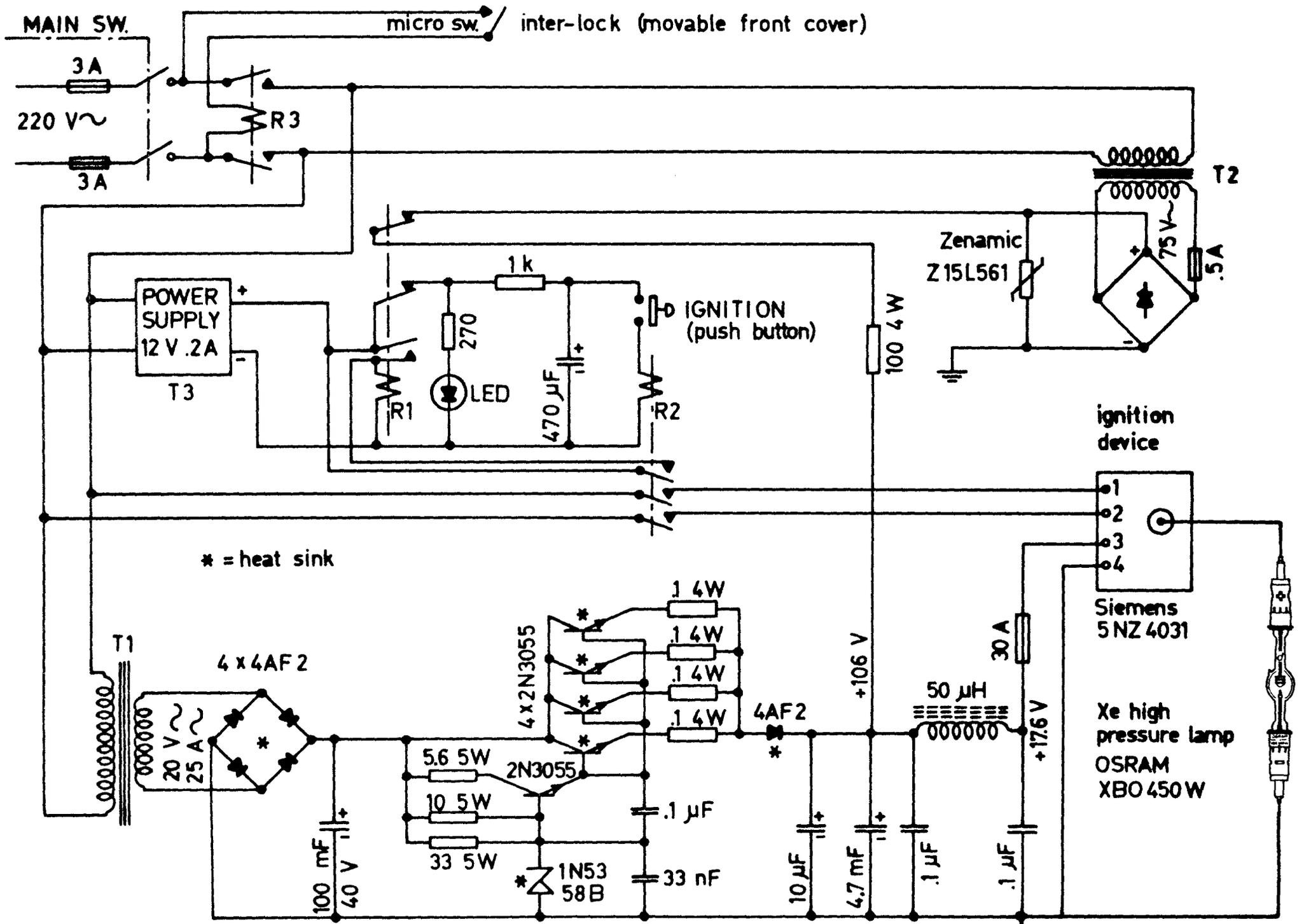


Fig. 4.5 Circuit diagram of the light source

When the hatch is closed, it affects a micro switch, which disables ignition. The hatch can be locked, which makes it possible to prevent involuntary ignition.

If the lamp is to ignite, it needs three different levels of voltages. When the button for ignition is pressed, the ignition device (Siemens 5NZ4031) will deliver a pulse of 38 kV with a duration of 0.4 sec. The relay R2 and the RC net (Fig. 4.5) determines the duration of the pulse. The lamp then needs a voltage of 106 V for a short while. The capacitor of 4.7 mF takes care of this. The voltage for the lamp will slowly decrease to 17.6 V producing a current of 25.0 A.

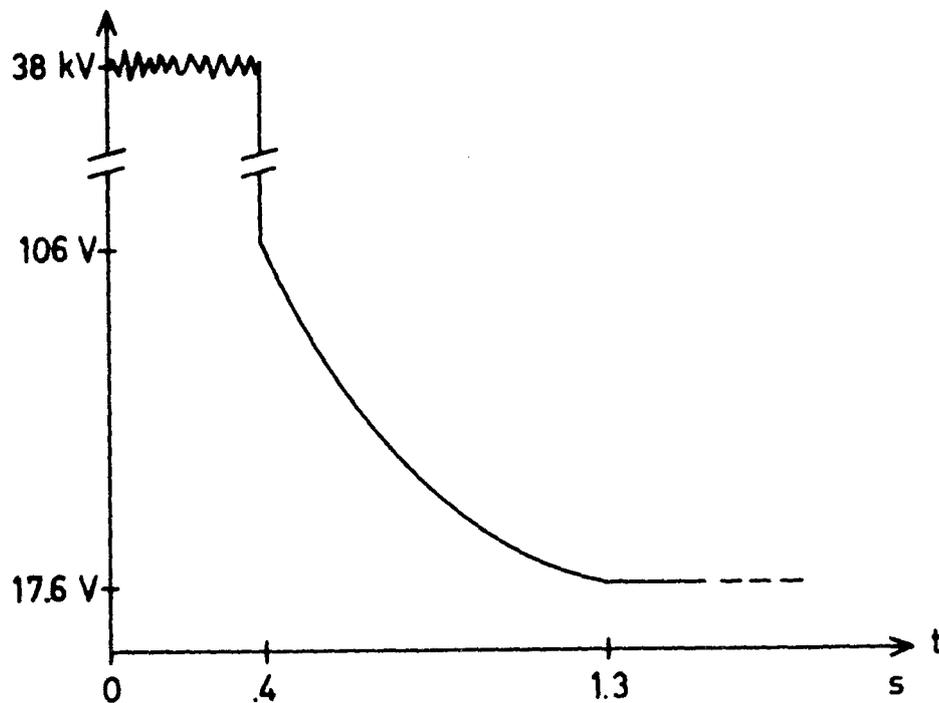


Fig. 4.6 The voltage supplied to the lamp, after the ignition button has been pressed

We measured the ripple factor of the emitted light to 0.8 per cent, which is an acceptable value.

In order to get a parallel light beam we placed the lamp in the focal point of a concave mirror. It has a diameter of 300 mm and a focal length of 270 mm. The mirror is coated with aluminum and a protective layer of SiO₂.

4.3 Safety precautions

The lamp is equipped with a protective plastic housing. Without this cover, the lamp must be handled with outmost care. If not, it is possible for the lamp to explode, due to the high pressure. It is therefore important to use a protective mask and gauntlets. When the lamp has been used, it must cool off for at least ten minutes before it can be removed. Another element of risk with the lamp is its large intensity and the emission of UV light, which might lead to eye and skin damages. Therefore looking directly into the lamp should be avoided and, if necessary, protective dark glasses should be used. If the lamp is used indoors the room should be well ventilated since ozone is formed close to the lamp.

These warnings and the way to operate the lamp are printed in Swedish on the back of the lamp housing.

Take care and always follow these instructions.

The procedure of ignition

1. Open the hatch and lock it.
2. Press the main switch and wait for one minute.
3. Press the button for ignition. If the lamp does not ignite, turn off the main switch and repeat from point two.

If the lamp has been operated, wait at least five minutes before reignition.

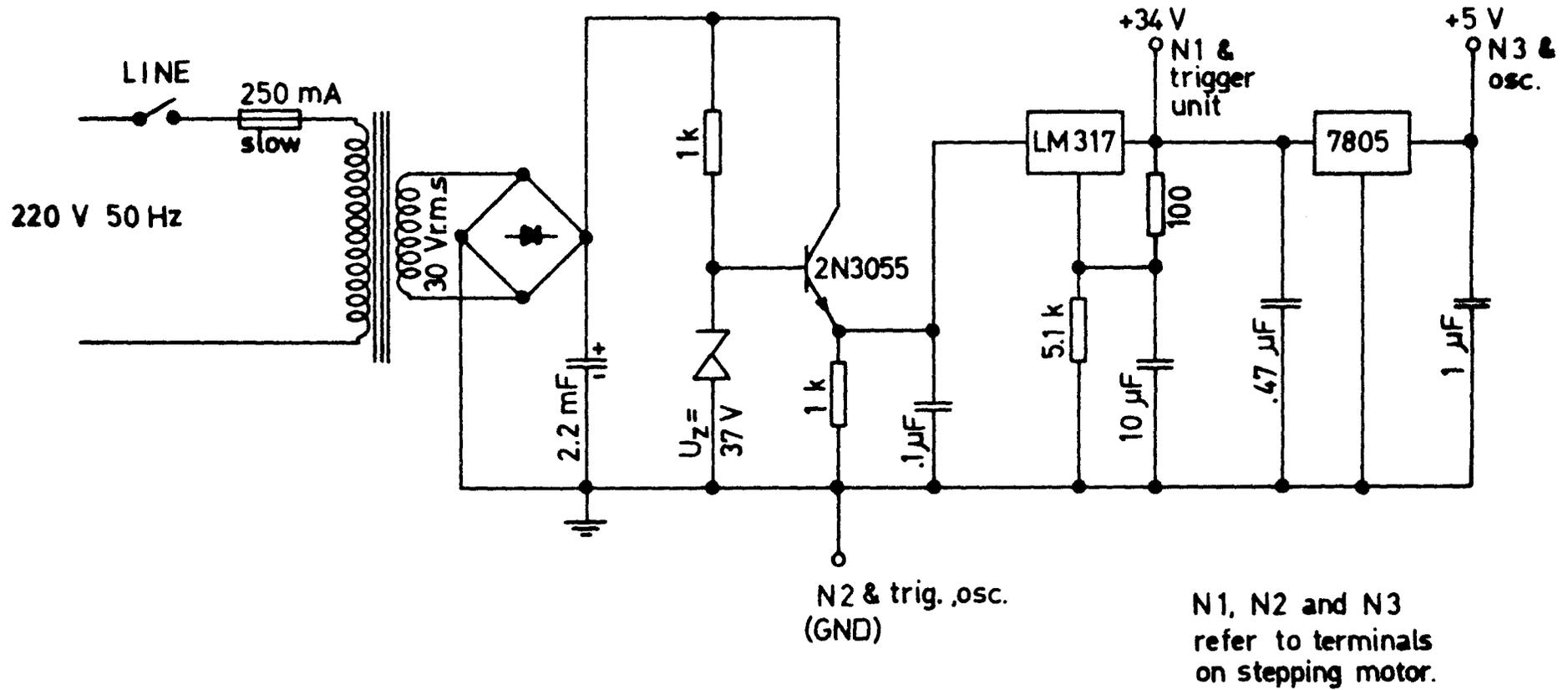


Fig. 4.7 Power supply to stepper motor and light barrier

4.4 Data acquisition system

When the light is received, it is first reflected with a plane first surface mirror onto a concave mirror with a focal length of 1000 mm. The refracted beam is focused via a small plane mirror (see Fig. 0.1). We use a Jobin Yvon HR 1000 spectrometer with a focal length of 1000 mm. It has a 92 HSM 212 grating (1200 grooves/mm), with a dispersion of 8 Å/mm and a spectral range of 1900–7000 Å.

Attached to the spectrometer is an assembly, which contains a rotating slotted disc, a cog belt, a stepper motor, a light barrier, a photomultiplier and a power supply (Fig. 4.7). The slotted disc is driven by a stepper motor (Philips 9904 115 23101) and a stepper drive unit. The motor gets step command pulses with a frequency of 263 Hz (Fig. 4.8) and gives the disc, via a cog belt, a rotation of 4.2 revolutions per second. The fluctuations of the rotation are less than 0.1 per cent.

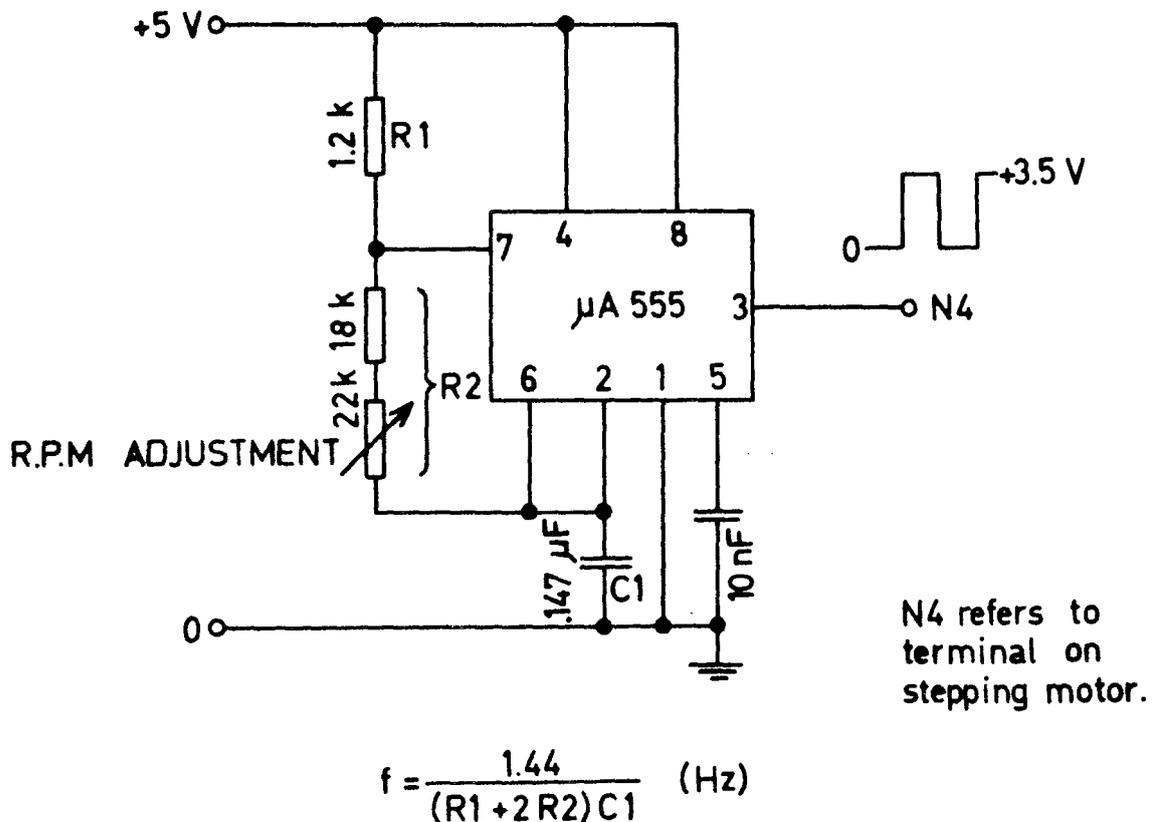


Fig. 4.8 Speed control circuit for stepper motor

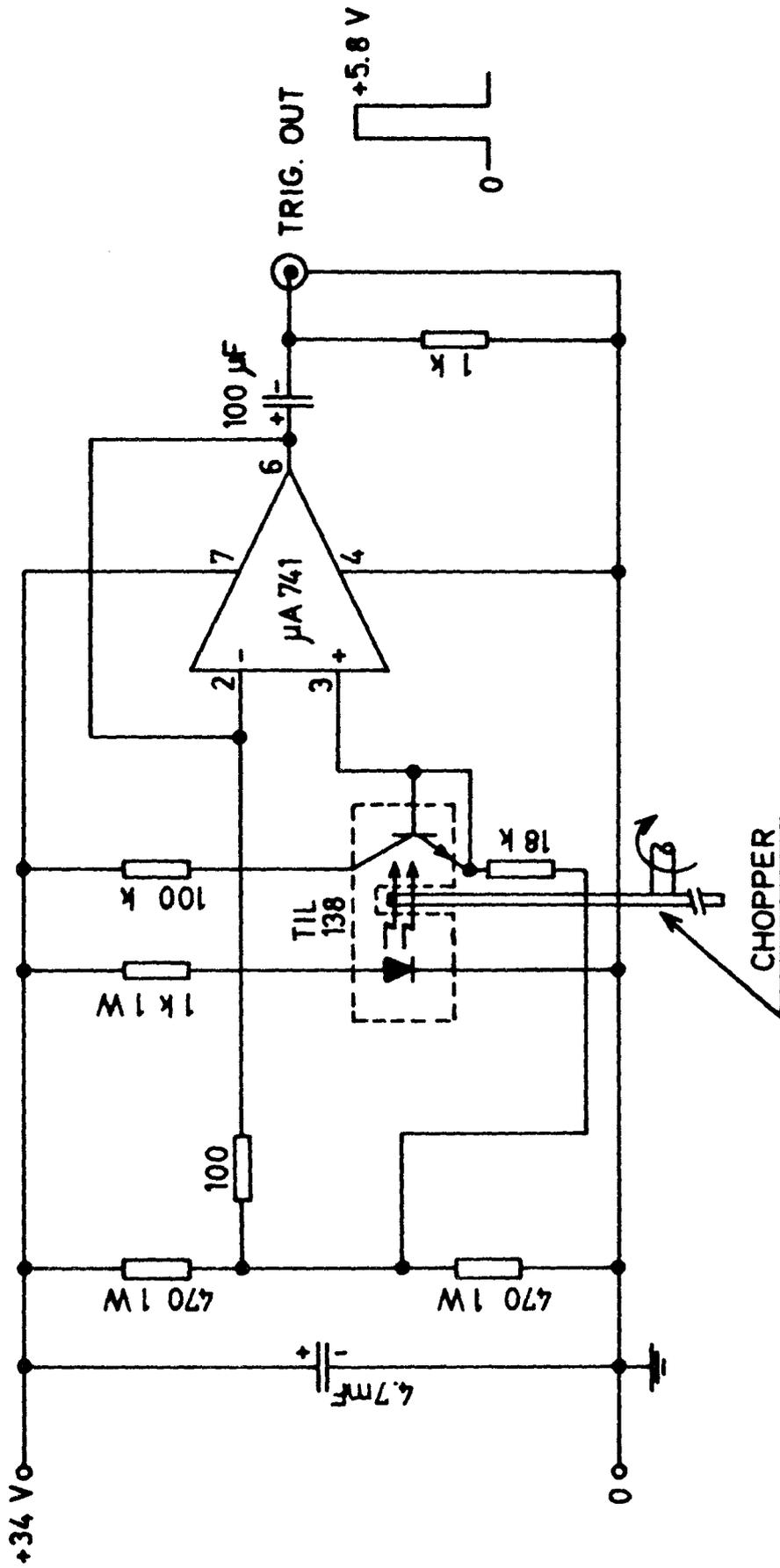


Fig. 4.9 The DOAS system's trigger unit.

The disc has a diameter of 200 mm and the width of the slits is 0.2 mm. The spacing between two consecutive slits is 35 mm. It takes 12.2 milliseconds for the next slit to appear.

The signal averager, described below, needs a trigger signal to start the sweep. This signal is accomplished with a light barrier (Texas TIL 138), which gives a positive pulse of 5.8 V when a slit appears (Fig. 4.9). The signal averager triggers on a positive rising edge.

The light, that passes through the slits, is recorded with a photomultiplier. We use an EMI 9558 QB tube, where Q stands for quartz window, which gives the tube extended UV response. The wavelength range is between 1750–8500 Å. The tube is fed with 1100 V and has an effective cathode diameter of 45 mm, well above the required 35 mm.

The signals from the photomultiplier are received by a signal averager unit. It consists of a main frame (Tracor TN 1710) and its plug-in units, signal averager (TN 1710-30) and pre amplifier (TN 1710-1). The main frame enables us to communicate with printers or with computers which we use for storing spectra on floppy discs. It also produces a possibility to add or subtract spectra, a necessity for our method. The signal averager starts its sweep when it gets a trigger signal and stores the signal from the photomultiplier into 1024 channels. The duration in each channel is called the dwell time, in our case set for 11 microseconds. We can choose two kinds of delay, post and pre delay. Post delay is the time the trigger is disabled after a completed scan. Pre delay is the time the unit waits, after a received trigger signal, to start the sweep. This delay is the only one we use and we have it set for 880 microseconds (Fig. 4.10).

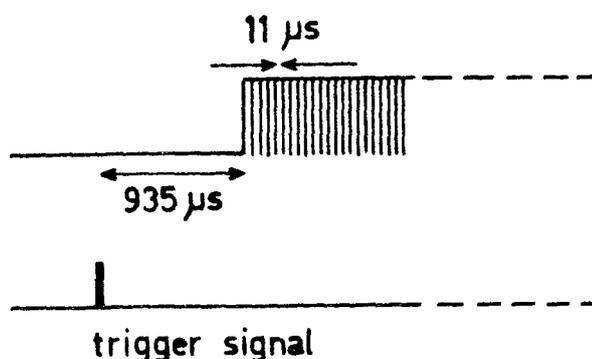


Fig. 4.10 Pre delay and dwell time

The duration of a scan is 12.1 milliseconds, which gives a maximum sampling frequency of 82 Hz. We use an effective data acquisition frequency of 79 Hz, enough to average out the ripple and atmospheric fluctuations. The signal averager also enables us to preset the total number of scans up to as much as 65 536 scans.

Another plug-in unit we use is a high voltage unit (TN 1710-10), which provides the photomultiplier with its required voltage. A new signal averager unit is now being developed in our department with all the features of the Tracor and some special applications as well [8] .

4.5 Detection limits.

Detection limits can be calculated according to Eq. 4.2, if the absorption coefficient, the length of the light path and the minimum detectable optical density are known. An increase of the light path does not always, as one would expect, decrease the detection limit since the noise also increases. This could in fact mean a increase of the detection limit.

In order to find an optimum light path, the light attenuation due to atmospheric absorption and Mie and Rayleigh scattering must be taken into account.

$$I_{\text{recieved}} = I_{\text{source}} \exp(-L/L_0)$$

L : absorption length due to the atmosphere

L₀ : light path length

The noise level of a photomultiplier is dependent on the number of photons received and thus proportional to the square root of the light intensity. This gives us a signal-to-noise ratio as a function of the light path length L :

$$S/N \approx L \exp(-L/2L_0)$$

The optimum light path length given by this relationship is $L=2L_0$. Table 4.1 gives the detection limits for a number of atmospheric trace constituents [2] .

Substance	Wavelength Range nm	Differential Absorbption, Coefficient ¹ cm ² /molec	at nm	Detection for 10 km Light Path ppt
SO ₂	200-230, 290-310	5.7 * 10 ⁻¹⁹	300	17
CS ₂	200-220, 320-340	4 * 10 ⁻²⁰		240
NO	215, 226	2.3 * 10 ⁻¹⁸	226	400 ²
NO ₂	330-500	1.0 * 10 ⁻¹⁹	363	100
NO ₃	623, 662	1.8 * 10 ⁻¹⁷	662	0.5
HNO ₂	330-380	4.2 * 10 ⁻¹⁹	354	20
O ₃	220-330	4.5 * 10 ⁻²¹	328	2100
HCHO	230-360	7.8 * 10 ⁻²⁰	340	120
OH	308	2 * 10 ⁻¹⁶ ³	308	0.05

¹0.3 nm spectral resolution

²1 km light path, minimum detectable optical density = 10⁻³

³0.003 nm spectral resolution

Table 4.1 Atmospheric Trace Components Observed by Differential Optical Spectroscopy [2]

4.6 Laboratory tests and measurements.

In order to evaluate any measurements, some characteristics of the DOAS system must be known.

One of these characteristics is the resolution. The dispersion of the spectrometer, 8 Å/mm, and the sensitive width of the photomultiplier, 35 mm, and the number of channels in the signal averager, 1024 channels, give us a resolution of 0.27 Å.

An experiment with a He-Ne laser, where the wavelength region of the spectrometer was swept, showed that the recorded spectrum covers 225 Å.

In reality the resolution is limited by the size of the largest of the spectrometer's entrance slit and the slits in the slotted disc. In our case this value is 0.2 mm, determined by the slits in the disc. This gives us a true maximum resolution of 1.6 Å. This maximum resolution is only obtained when the slit is in a vertical position. Whilst the slit passes across the spectrum the angle between the slit and the spectrum changes. This makes the resolution, ΔR , vary across the spectrum. (Fig. 4.11)

$$\Delta R = R(h \cos \alpha + d) / d \sin \alpha$$

R : resolution

h : height of the spectrum

d : width of the slit

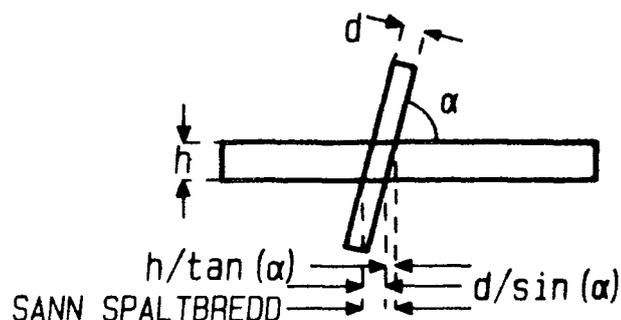


Fig 4.11 Geometry of the slits of the rotating disc.

When we combined our test results with some basic trigonometry it turned out that the angle varies between 86 and 94 degrees. The height of the spectrum is controlled by the entrance slit, in our case 1 mm. This means that the resolution at the edges of our spectra is 2.2 Å.

Another important characteristic of the DOAS system is the xenon lamp itself. Even though it is a high pressure lamp, the xenon lines are still distinguishable. We recorded the lamp spectrum using the system photomultiplier and spectrometer (Fig. 4.12). We covered the region between 1900 Å and 7000 Å. (For reference see paragraph 4.4) If we regard the fact that one measurement only will cover 225 Å, most of the fluctuations in the lamp's spectrum are too slow to be of any consequence. There is one exception to this, the region 4500-5000 Å can not be recommended for measurements since the xenon lines are very prominent here.

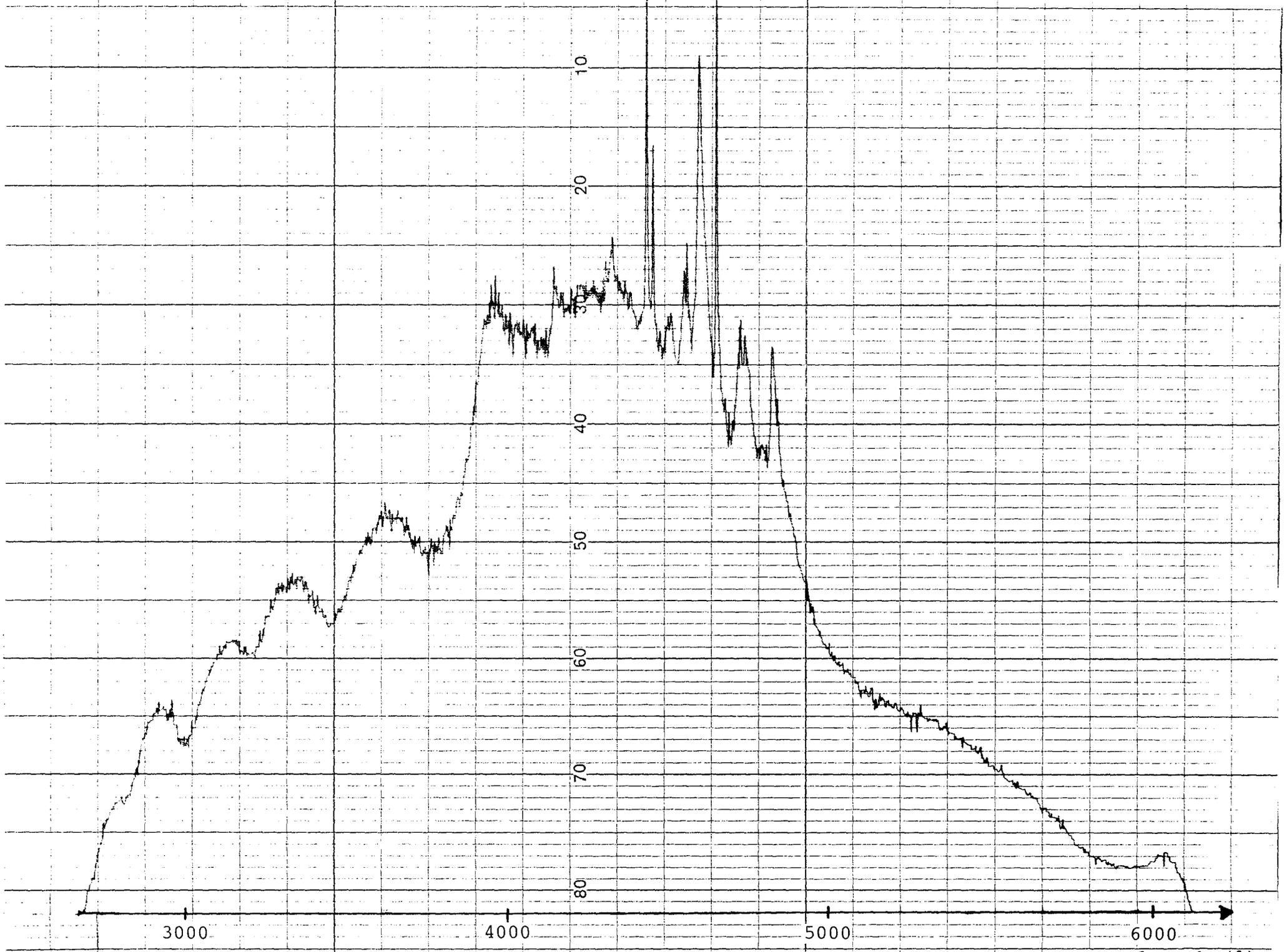


Fig. 4.12 The recorded xenon lamp spectrum.

Wavelength (Å)

We also performed an experiment using the xenon lamp and an interference filter (Fig. 4.13). The result showed, that the system worked as expected.

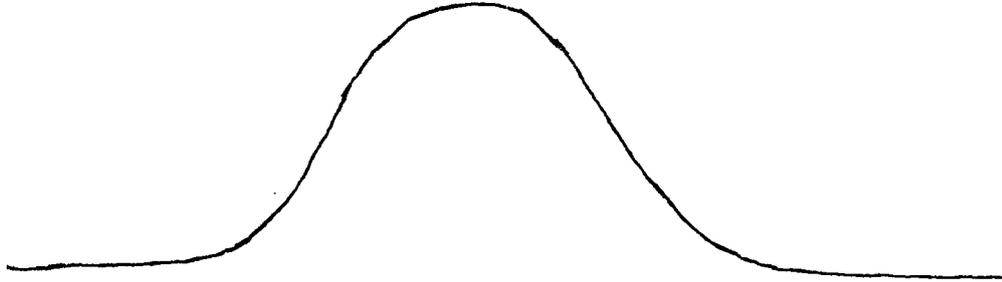


Fig. 4.13 Recording of the transmission profile an interference filter averaged over 1600 scans.

A test in order to calibrate our system was also performed. We used a monochromatic light source, a He-Ne laser. With a pre delay of 960 μ s and a dwell time in each channel of 12 μ s, the wavelength preset on the spectrometer corresponded to the contents in channel 449.

We also attempted to make measurements of gas constituents in the air, one measurement under laboratory conditions, the other under more realistic conditions.

In the first measurement an absorption cell containing mercury was placed in the light path. The cell was heated in order to evaporate the mercury. This spectrum was not recorded on the Tracor Northern signal averager, but on a signal averager built at this department [8] (Fig. 4.14).



Fig. 4.14 Mercury absorption spectrum averaged over 16000 scans. Recorded at 2530 Å. [8]

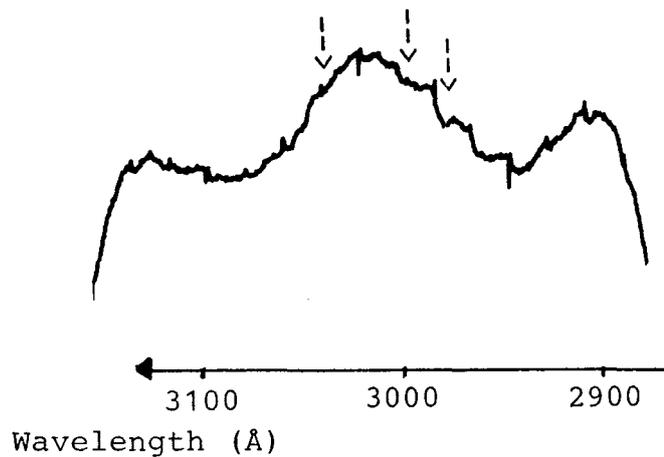


Fig. 4.15 Recorded spectrum at 3100 Å, averaged over 16000 scans. Arrows indicate SO₂ absorption.

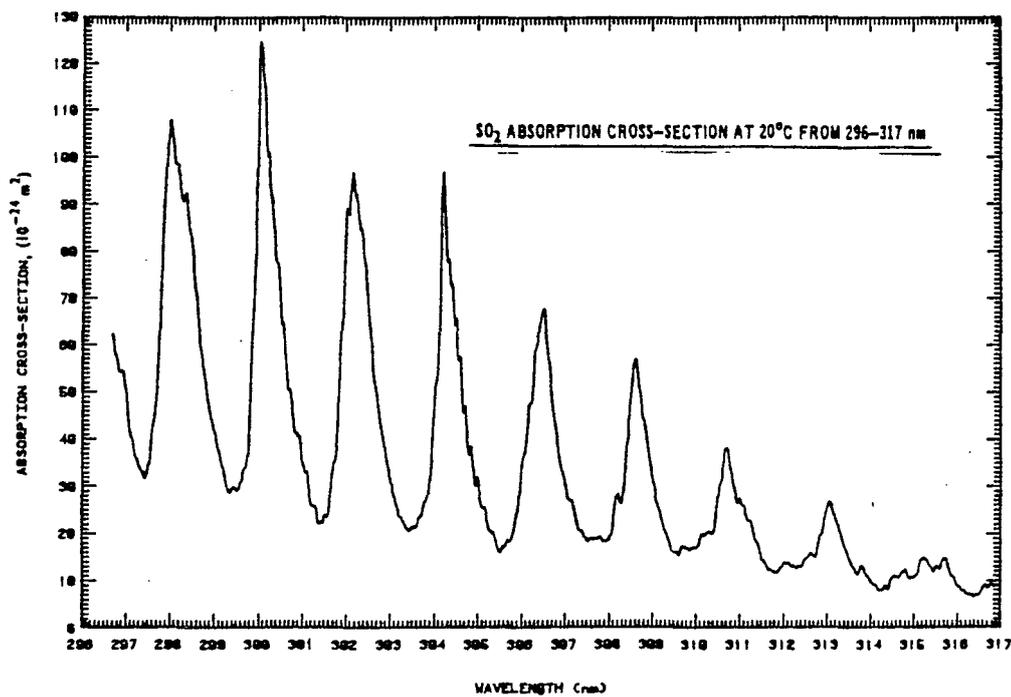


Fig. 4.16 SO₂ absorption spectrum [11].

The second measurement was an attempt to discover SO_2 in the air. The light path was 670 m and the signal was averaged over 16000 scans. Due to weather conditions and a bad signal-to-noise ratio, the spectrum was somewhat difficult to interpret. However, we feel that some correlation between the spectrum (Fig. 4.15) and the SO_2 absorption (Fig. 4.16) can be found. We have not tried to evaluate these spectra regarding concentration. The appropriate tools to perform such an evaluation will be developed at the department in a near future.

Acknowledgements

First of all we would like to thank the people at the Institute for Atmospheric Chemistry in Jülich, West Germany, who inspired us and helped us on our way.

The staff at Hotel Sparta deserves special thanks for letting us use their roof for our measurements

The authors are very grateful to everyone at the department of physics in Lund, they were always willing to help in our moments of need. We would especially like to thank Åke Bergquist for his help with the electronic part, Rolf Olofsson with the mechanic part and Carin Holmqvist with her help concerning the written part.

Last, but not least, we wish to thank our instructor, professor Sune Svanberg, because he always was a source of inspiration.

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