Investigation of the absorption cross-section of hydrogen sulphide in the ultraviolet region using a White cell

Diploma paper
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May 1988

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INTRODUCTION

Hydrogen sulphide, H_2S, is probably the most common natural discharge of sulphur into the atmosphere. It arises e.g. from subversion of biological material. A source of less consequence is from bacteria that, in anaerobe circumstances, reduce sulphate to H_2S (ref. 1). The subversion or deposition of H_2S from the atmosphere is not very well known. For research about this it would be advantageous if it was possible to measure the concentration of H_2S in the atmosphere in an easy way. This can maybe also give us a conclusion of how to decide about anthropogene contamination of other sulphur compounds, primarily sulphurdioxide.

Optical methods would probably be advantageous here. It is easy to send a light beam through the air, even at long distances. That makes it possible to measure a large area with just a few operations.

As a preparation of that, this diploma work is concentrated on obtaining the absorption cross-section of H_2S, primarily in the UV-region.

Why measure the absorption cross-section?

A powerful way of deciding the concentration of a substance is to look at the absorption of light. This depends of both the molecule density and the absorption cross-section.

The total absorption is predicted by Beer-Lamberts law. It states that the light intensity that passes a sample is

$$I = I_0 e^{-nl\sigma}$$

where I_0 is the entering light intensity, n is the concentration of the molecules, l is the distance the light travels through the sample of molecules and σ is the absorption cross-section.

$$\text{Thus the transmission } T = \frac{I}{I_0} = e^{-nl\sigma}$$

The structure of absorption spectra can vary a lot. It can have a smooth slope in a wide spectral region. Another possibility is many very narrow lines close together.

The spectrum of H_2S is more like the first one, at least in the region under 210 nm (ref. 2).

Two ways of measuring the concentration of a gas, e.g. a pollutant, in the air, are Differential Optic Absorption Spectroscopy (DOAS) (ref. 3) and Light Detecting And Ranging (LIDAR) (ref. 4). Both methods compare the amount of detected light at two spectrally very close wavelengths, where the gas, which is studied, have very different absorption cross-sections.

By looking at two different wavelengths, λ_1 and λ_2 with the according absorption cross-sections σ_1 and σ_2 respectively and comparing the light intensity for each wavelength, one obtain the ratio

$$\frac{I_1}{I_2} = \frac{I_{01}e^{-nl\sigma_1}}{I_{02}e^{-nl\sigma_2}} = \frac{I_{01}}{I_{02}} e^{-nl\Delta\sigma}$$

where $\Delta\sigma = \sigma_1 - \sigma_2$

$$\text{This gives} \quad -n\,l\,\Delta\sigma = \ln\frac{T_1}{T_2} \qquad \text{and} \quad n = \frac{\ln(T_2/T_1)}{l\,\Delta\sigma}$$

By knowing $\frac{I_1}{I_2}$, $\frac{I_{01}}{I_{02}}$, l and $\Delta\sigma$ one can predict n.

As the two wavelengths are very close together, it can be presumed that the cross-section is constant for all other substances. If there is some known difference of importance, caused by other constituents, such effects can be taken into account.

DOAS uses a broadband lamp. The light, that is collimated to an almost parallel beam, is, via a spectrometer, monitored by a detector further away. The distance is normally a few hundred meters. Then the concentration is calculated by comparing the recorded spectrum with a characteristic part of the known absorption spectrum.

In the LIDAR technique laser pulses are transmitted into the atmosphere. The laser can be a tunable one that is altered at two close, well defined wavelengths. Another possibility is a broadband laser where a spectrometer separates the two close laying wavelengths. The light is scattered in all directions by dust etc. in the air. At the same location as where the laser beam is sent out, a telescope collect backscattered light. Then the light intensity, for each wavelength, is monitored and the concentration is calculated by a computer.

DOAS is a cheaper system but it can just measure the average concentration along the distance. In LIDAR each pulse is partially scattered along its pass through the air. As the speed of light is known one can calculate the time the light uses to reach a particular point along the pass and to return to the receiver. By considering the signal strength as a function of this time, LIDAR yields the range-resolved concentration.

THE WHITE CELL

The absorption cross-section of a substance is dependent on some circumstances. If the total pressure is increased the absorption band is broadened around a resonance line. Even a high partial pressure can influence.

Accordingly, to obtain a cross-section, that is valid for low concentrations of the substance in the atmosphere, it is necessary to do the measurements at the same circumstances, i.e. at low partial pressure, similar to that expected in the air, and at a total pressure of about 1 bar. If the cross-section is low, this means that a long distance is needed to record the absorption with sufficient accuracy. It must be possible to detect concentration-dependent effects.

In a White cell (ref. 5) a long folded path is used. In a tube there are three mirrors (see fig. 3). Two, the inlet and outlet mirrors, are placed beside each other in the rear end, facing the front end. There is the third mirror, which is larger and facing the other two. All mirrors are spherical whith a radius of curvature equal to the distance between the mirrors in each end. It means that light which is focused at one mirror plane will be focused at the same mirror plane again. At the front end, there are two windows of fused silica for inlet and outlet of light. The large mirror is formed so that light entering through the windows can proceed to the smaller mirrors. By this arrangement it is possible to focus a light source at the plane of the large mirror so that the light proceeds to one of the small mirrors (inlet mirror). The inlet mirror is directed so this light will be reflected to (focused on) the large mirror. The large mirror is directed so its optical axis points at a position in the middle between the two small mirrors. It means that light from one of the small mirrors will be reflected to the other small mirror. The other small mirror (outlet mirror) is directed so this light will go either back to the large mirror, or out through the other window. If it goes back to the large mirror it will be reflected to the inlet mirror and then back to the large mirror. Then it returns to the outlet mirror and again either out, or back to the large mirror. The essential is that the light can travel several times, maybe hundreds, through the cell.

At the large mirror two dotted parallel lines will arise. The number of spots is dependent of the number of passes.

The cell used has a tube of pyrex. The flanges, on which the mirrors are mounted, are made of stainless steel. The distance between the flanges is defined by 4 invar rods, to reduce the length dependence of temperature. The pyrex tube is fixed by O-rings in the flanges, so it can slide to reduce thermal tensions. The mirrors are made of glass with a reflexion layer of aluminium, coated with magnesium fluoride. Each mirror in the cell is fastened by a spring and three micrometer screws, one for longitudinal positioning and one each for horisontal and vertical inclination. At the rear flange there is also a window where it is possible to see the spots at the large mirror. This construction makes the cell rather easy to tune in. At the front flange there are also two valves for gas inlet. The valves have 6 mm tube fittings. At the rear flange there is a larger valve for evacuation (see fig. 3).

SPECTROMETER

Two different spectrometers were used. Both were of Czerny-Turner construction, see fig. 1. The light is focused at the slit S, in a direction so that it proceeds to the inlet mirror, M_1. This mirror is spherical with a focal length equal to the distance S_1-M_1. It means that the light will be reflected into a parallel beam. M_1 is directed so the light proceeds to the turnable grating G, which will be illuminated by a wide, parallel beam. The wavelength is chosen by the angular position of G. A part of the diffracted light from G reaches the outlet mirror, M_2. This mirror, which also is spherical, has a focal length and a direction so that the light will be focused at the slit S_2. I.e., if S_1 and S_2 are of the same width, S_1 will, in a certain colour, be imaged at S_2 as the continuous line in fig. 1 shows.

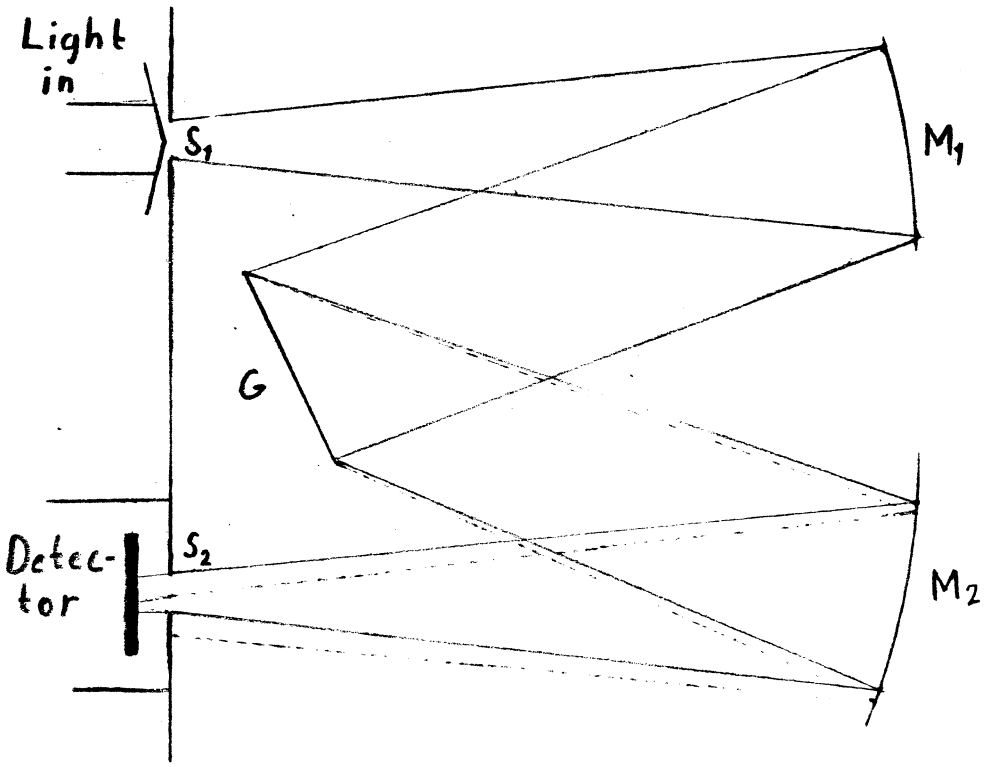


Figure 1. Principal outline of the beam paths in the spectropmeter: S_1 - inlet slit, M_1 - inlet mirror, G - grating, M_2 - outlet mirror, S_2 - outlet slit.

In other colours it will be imaged beside, like the dotted line in fig. 1 is showing. As the width of the slits are greater than zero, the colours will be overlapped. With increasing slit width, a greater range of colours will overlap that which fits perfectly. Outside the slit S_2 there is a detector (photomultiplier) which detects all light that exits from S_2. I.e. smaller slits give better resolution, on the contrary wider slits give better sensitivity. So for a given equipment it is impossible to increase both sensitivity and resolution. In order to get both good resolution and high sensitivity, it is necessary with a high light intensity per wavelength interval, in the spectral region that is to be studied. As this light must pass a small slit in a narrow angle, it also means high brightness (see appendix).

The spectrometer that was used first (A) was a Jobin Yvon HR 1000. This had a grating with about 1200 rules per mm, and a focal length of about 1 meter. The other one (B) is built at the department. It had about same focal length and its grating was possible to change. The grating that was used had 600 rules per mm.

Calibration of the spectrometer

The spectrometer has to be adjusted and, eventually, calibrated. To begin the adjustment of the spectrometer it is checked that the inlet slit is in the focus of the inlet mirror. The criterion for this is that the beam from the inlet mirror to the grating is parallel. If it is not parallel, different colours will be focused to the same point after the second mirror. The lamp was imaged on the inlet slit. As the lamp is powerful in the visible, it was easy to measure the beam by inserting a piece of paper in the beam. To adjust the slit was not so easy. By loosening a screw it was possible to move the element which contained the slit. As it just moves by hand, it was rather difficult get it in the right position. It would be easier if one could adjust it, in some way, by turning a screw. Adjusting the outlet slit, which is fastened and adjustable in the same way, is even hard to check. By removing the PMT and looking into the outlet slit it is possible to see the focus. A white lamp just gives rise to a "rainbow" and it is not easy to see when the "rainbow" has sharp lines. So it was necessary to use a spectral line source. But the accessible spectral lamps were so weak that it was not possible to see anything at all. Instead the PMT was mounted and the signal from it was maximized. Later a He-Ne laser was used (see chapter of fluorescence). It gave so much light in a very short spectral range, that it was possible to find the focus by eye.

After the spectrometer was adjusted, the resolution was tested by recording spectra from spectral lamps. Hg and Cd lamps with lamp bulbs of fused silica were used. These lamps have several lines in the spectral region between 200 nm and 300 nm, the region of interest in this work. The spectrometer (A) was possible to adjust to a resolution of about 0.1-0.2 nm. At the spectrometer (B), that had to be adjusted in the same way, a resolution of about 0.1 nm was reached.

The spectrometer (B) did not specify the wavelength directly on the display. Thus it had to be calibrated before use. For calibration the spectral lamps are used. The display shows a value that is related to the grating angle. The angle that corresponds to a particular wavelength in a particular order is possible to calculate. After that the correlation between the grating angle and the wavelength is calculated. The correlation between the grating angle and the display is calibrated.

Even the spectrometer (A) needs calibration to know how well the display agrees with the real wavelength.

The type (A) spectrometer worked in the first order. For type (B) it is possible to change the grating. A grating with a blaze of 2.5 μm was used. So it worked best around the 10th order in this spectral region. A high grating order means a better resolution. But when the wavelength λ is measured in order m, the wavelengths $m\lambda/n$ in order n are also measured; m and n are integers.

By using a filter, the wavelengths far away from λ were reduced. But because the width of the interference filter used, e.g. the 9th or 11th order also were recorded.

Another problem is the stray light. In the spectral region that is studied, the light source has very low intensity compared to e.g. the visible. It means that the stray light can be of the same magnitude as that light the grating is diffracting in the UV-C-region, another reason to use an interference filter. This filter has a maximum transmission of 23% at 227 nm (fig 2).

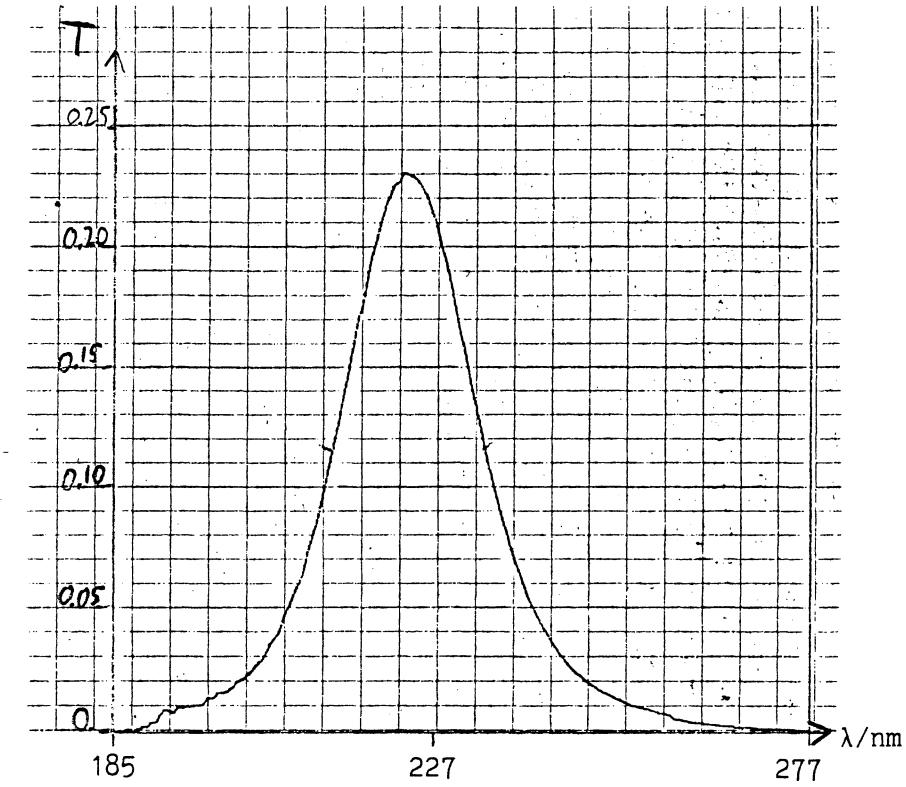
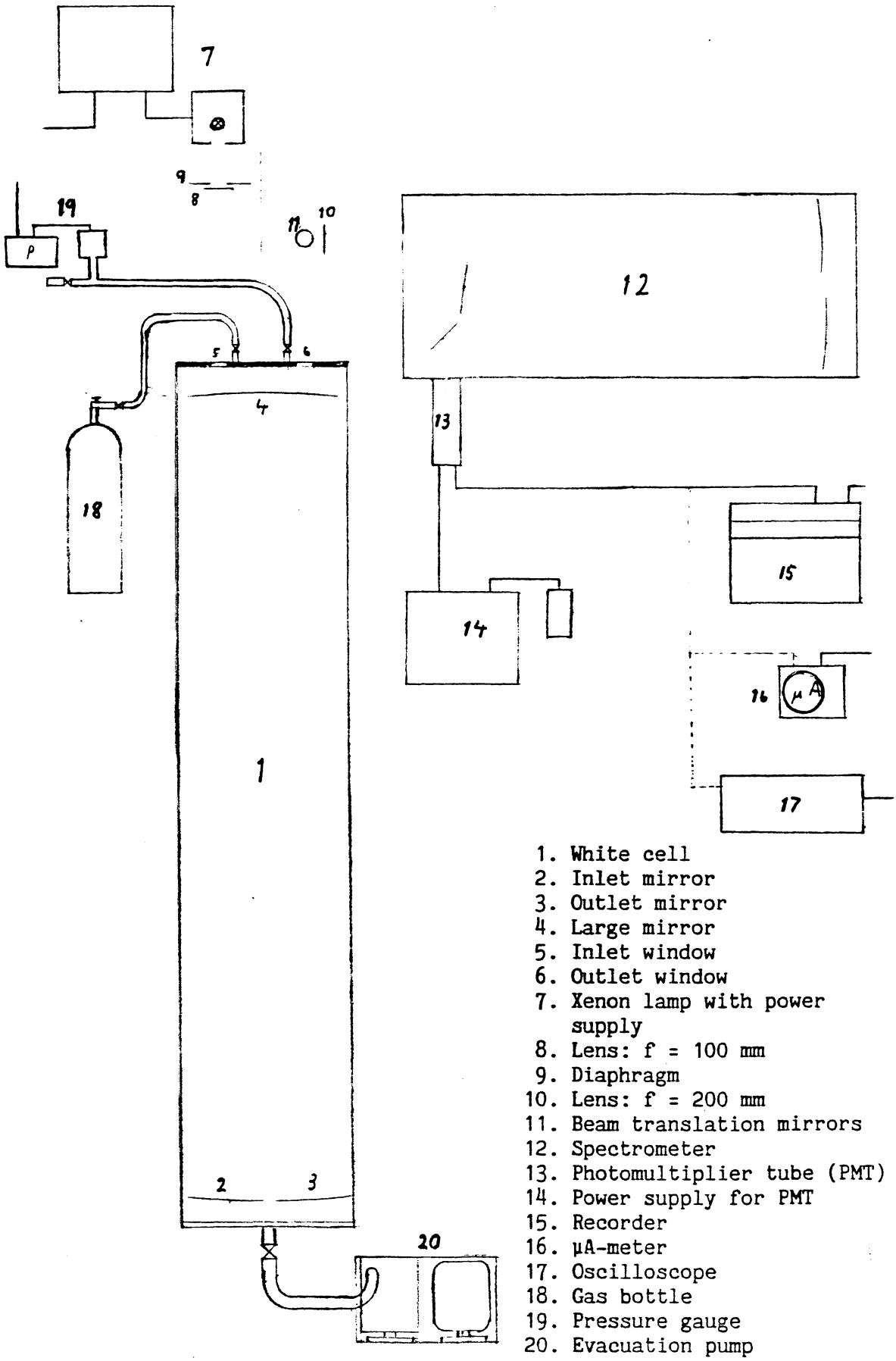


Fig. 2 Transmission of the interference filter.



1. White cell
2. Inlet mirror
3. Outlet mirror
4. Large mirror
5. Inlet window
6. Outlet window
7. Xenon lamp with power supply
8. Lens: f = 100 mm
9. Diaphragm
10. Lens: f = 200 mm
11. Beam translation mirrors
12. Spectrometer
13. Photomultiplier tube (PMT)
14. Power supply for PMT
15. Recorder
16. μA-meter
17. Oscilloscope
18. Gas bottle
19. Pressure gauge
20. Evacuation pump

Fig. 3 Arrangement for measurement of absorption cross-section

ARRANGEMENT

For performing accurate measurements, it is advantageous to use an amount of H_2S that gives an absorption of about 50%. This can be shown by using Beer-Lamberts law. The transmission is

$$T = \frac{I}{I_0} = e^{-nl\sigma}$$

This gives that $n\,l\,\sigma = -\ln T$ and $\sigma = -\ln T/(nl)$
The deviation is then

$$\frac{\Delta\sigma}{\sigma} = \left[\left[\frac{\Delta T}{T \ln T}\right]^2 + \left[\frac{\Delta l}{l}\right]^2 + \left[\frac{\Delta n}{n}\right]^2 \right]^{0.5}$$

So if ΔT is to have a small influence one shall maximize $(T \ln T)^2$ which yields $T = 1/e \approx 0.36$. However, ΔT can be dependent of the value of T, but if the transmission is very low or very high it will be very low accuracy.

The whole arrangement can be regarded as two parts. An optical part and a gas handling part.

Optical

The light source used is a 75 W Xe-high-pressure lamp. It has a continuous spectrum from about 200 nm into the IR region. The spectrum is rather smooth with some broad lines around 450 nm. The intensity increases with wavelength in the UV region. The lamp is imaged at the inlet window of the White cell, using a lens. This lens has a focal length of 100 mm and a diameter of 5 cm. The cell has an f-number of about 15. The light output from the cell is imaged at the inlet slit of the spectrometer, by another lens. This lens has a focal length of 200 mm and it is placed so that the magnification is about 0.5, according to the ratio of f-numbers (see appendix A). The spectrometer has an f-number of about 7. The inlet slit of the spectrometer is placed higher than the outlet window of the cell. To elevate the beam, two mirrors at an angle of 45 degrees to the vertical, were used. They are oriented so that the beams form a right angle in upper view. At the outlet slit of the spectrometer there is a detector.
The detector used was a photomultiplier, PMT. The signal from the PMT was led to either a recorder, a µA-meter or an oscilloscope. At the input of the recorder a small capacitor was connected to reduce the noise, without getting a too long time constant. The oscilloscope was just used as a voltmeter. Then the spectrometer was not scanned. It was possible to get better sensitivity by the oscilloscope than by the µA-meter. The cause is that the oscilloscope is possible to set at a measurement range so that the dark current is in the lower part of the screen. The oscilloscope had a large capacitor mounted at the input, to eliminate the fluctuations. As just one wavelength for the moment is measured, the long time constant does not matter.

Gas handling system

To evacuate the cell there is a pump connected to the large valve. At one of the small valves there is a gas bottle connected. At the other small valve there is a capacitive pressure gauge. The bottle contains nitrogen and about 1000 ppm H_2S. At the bottle there is a needle valve to make it possible to control the gas flux. If the pressure in the cell was changed and then changed back again to the original value, the adjustment of the optics was not influenced.

PRACTICAL WORK

White cell set-up

To know the distance the light travels through the White cell the number of spots at the large mirror is counted. With long distances the spots run into each other. But, while increasing the distance, each new spot passes the outlet window. That gives a signal from the PMT, if the spectrometer etc. is adjusted in a right way. By counting these signals, the number of spots is controlled. If the vertical inclination of the small mirrors is not well adjusted, the spots will "roll" when the outlet mirror gets inclined horizontally. Then the vertical inclination must be continuously adjusted, to control the horizontal inclination.

Achieving maximum light through the cell to the spectrometer

H_2S is practically without absorption above 300 nm. Under 200 nm the absorption by the oxygen makes the air practically opaque. This work is focused on the spectral region from 200 nm to 300 nm. Around 200 nm is the reflectance of the mirrors in the cell used, about 80-90 %. It means that after a few passages through the cell the lightpower is considerably reduced. After e.g. 20 passages (=19 mirror reflections), a reflectance of 90 % will reduce the light to less than 14 % of the light that entered through the cell. This is a reason why the light into (and through) the cell has to be maximized.

The brightness of the lamp combined with the f-number of the spectrometer limits the maximum brightness of focus at the spectrometers inlet slit. Good brightness is important because it shall be focused to the spectrometer through a small slit.

Several different arrangements were tried. At the lamp there is a reflector that could be used, but just using a lens resulted in more light. Probably the cause is that the reflector had a low reflectivity. All lenses used are made of fused silica. A disadvantage with lenses is that the focal length is dependent of the wavelength. It arises from the change of refraction index with wavelength. The difference from the visible region, where the basic adjustment can be done, to the UV-C-region, is rather significant. Table 1 shows how the refractive index in fused silica change from about 1.46 in the visible to more than 1.5 in UV-C (ref. 6). The lens formula

λ/nm	n
200.0	1.55051
265.2	1.50003
404.7	1.46962
546.1	1.46008
694.3	1.45542

Table 1. Refraction index of fused silica at some different wavelengths

$$\frac{1}{f} = (n-1)\left[\frac{1}{R_1} + \frac{1}{R_2}\right] \quad \text{or} \quad f = \frac{1}{n-1}\left[\frac{1}{R_1} + \frac{1}{R_2}\right]^{-1}$$

where f is focal length, n is refractive index, R is radii of curvature for each surface, defined positive for convex surface, shows how f depends of n. It is also shown in table 2. It is assumed that the marked f is for n = 1.46. It means that fine adjustments of the optics have to be done to optimizing the signal. I.e. the image from

n	1.46	1.50	1.55
f / mm	100 200	92 184	84 167

Table 2. The focal length at different refraction index, for the used lenses.

lamp to cell and from cell to spectrometer has to be optimized at the same time. This is a difficult job. A conclusion is to use as few lenses as possible, i.e. one between the lamp and the cell, and one between the cell and the spectrometer. That will also decrease the number of lens - air interfaces, of which each results in a loss of intensity. It can be shown that the essential limit is the f-number of the spectrometer (see appendix).

Lining up of the optics

The optics had to be lined up, step by step. In front of the cell a table with an adjustable height is placed. On the table there is an iron plate so it is possible to fasten magnetic bases. First the beam from the lamp to the mirror in the cell was lined up through the window via the lens. I.e. it is controlled that the lamp is focused just inside the window and that the light spot is at the middle of the inlet mirror. In order not to disturb the light spot by the reflected light from the outlet mirror, this mirror is adjusted so that the light is reflected to the wall of the cell, while the inlet light is lined up. I found it hard to see the light at the mirror without focusing it, so I prefered to have the lens inserted from the beginning.

Because of the reflector, there is also light that is not diverging from the lamp. This light will maybe pass the cell in an incontrollable way. A long distance between lamp and cell, will reduce this. The length is limited by the lens diameter.

When the light beam to the inlet mirror is in the right position, it is possible to adjust the mirrors in the cell so that the light beam is coming out through the other window (see the section "White cell set-up").

Then the light beam reaches the beam translation. The mirror arrangement that forms up the beam translation, makes it is easier to get the beam in a right position into the spectrometer, which can be lined up when the light gets out of the cell in a right way.

The light must pass the inlet slit of the spectrometer and proceed to the inlet mirror. While the spectrometer is adjusted the lens is inserted into the beam. This lens is adjusted so it focuses the beam at the inlet slit.

To make a fine adjustment, small slits are used at the spectrometer, which is set at a wavelength somewhere between 200 nm and 250 nm. The μA-meter is connected to the PMT. Then the mirrors in the cell are adjusted so that the PMT current is maximized. Now the beam reaches the inlet slit in the best way. Then the lens is moved in the direction of light proceeding and stopped when the PMT current is maximized. Now the light intensity at the inlet slit is maximized for the chosen wavelength.

Measurements

After the adjustment was finished it was possible to measure the light transmission. To check if the transmitted irradiance actually is reduced by absorption in the H_2S, the first measurement is done with the cell just filled with air. It was started with the shortest distance (8m) and longer distances later. It was possible to record spectra with a light path up to, at least, about 60 m in the cell.

By evacuating the cell it was checked to leaks. At the beginning the cell did leak. Especially the tubes were hard to get tight. All screws and nuts were checked, and fastened harder if they were too loose. As

a weld seam at the pressure gauge appeared to leak, a tightening paste was used.

To make a measurement of H_2S, some air of the cell was pumped out (about 10%) and it was filled up with the nitrogen-H_2S mix. The spectrometer was scanned while the signal is recorded. The signal was also led to the oscilloscope, used as a volt-meter. The latter gave better accuracy but it was not possible to scan during the measurements. The spectral region between 200 and 300 nm was in 2 or 3 scans, both with air-filled cell and with some H_2S in the cell. The spectrum was recorded with the oscilloscope with about 1 nm between each point.

A recording is given in table 3. The distance is 8 meters and the concentration is $2.49 \cdot 10^{21}$ molecules of H_2S per cubik metre.

$\frac{\lambda}{nm}$	I_0	I	T	$\frac{\sigma}{10^{-23}\ m^3}$	$\frac{\Delta\sigma}{\sigma}$
225	16.5	8	0.485	3.62	0.31
226	18.3	9	0.492	3.55	0.30
227	20.4	10	0.490	3.56	0.20
228	22.4	11.4	0.509	3.38	0.19
229	24.6	13.3	0.541	3.07	0.19
230	27.5	15.8	0.575	2.77	0.19
231	30.3	18	0.594	2.60	0.18
232	33.2	21.5	0.648	2.17	0.19
233	37	24.8	0.670	2.00	0.18
234	41.8	28.5	0.682	1.91	0.18
235	47.7	33.4	0.700	1.78	0.19
236	21	15.8	0.752	1.42	0.28
237	23.5	18.5	0.787	1.20	0.27
238	25.9	20.9	0.807	1.07	0.29
239	26.3	23.1	0.878	0.649	0.40
240	30	25.3	0.843	0.852	0.28

Table 3. Measureument of transmitted irradiancen, together with calculated transmission, cross-section and deviaton.

The cross section was calculated by using the Beer-Lambert law. The transmission for H_2S, σ, is calculated by comparing the transmitted irradiance through air, I_0 and through H_2S mixture, I. The ratio of these irradiances is

$$\frac{I}{I_0} = T = e^{-nl\sigma}$$

and $$\ln T = -n\ l\ \sigma$$

$$\text{This yields } \sigma = \frac{\ln (1/T)}{n\ l} = \frac{\ln (I_0/I)}{n\ l}$$

The accuracy is calculated by using the formula

$$\frac{\Delta\sigma}{\sigma} = \left|\frac{\Delta T}{T \ln T}\right| + \left|\frac{\Delta n}{n}\right|$$

where Δn is estimated to 10 % of n. ΔT is calculated by using that ΔI and ΔI_0 is between 0.4 and 1 unit (higher for lower values). Δl is very low, why it is not regarded.

CROSS-SECTION RESULTS

In the region above 225 nm the absorption cross section is just a smooth declining function (fig. 6, table 3). The slope is not large enough to be used for DOAS or LIDAR. Under 225 nm there was very little light. The whole signal of the PMT was small, even compared to the darkcurrent. Neither did it depend on wavelength, why it is presumable that it is just straylight.

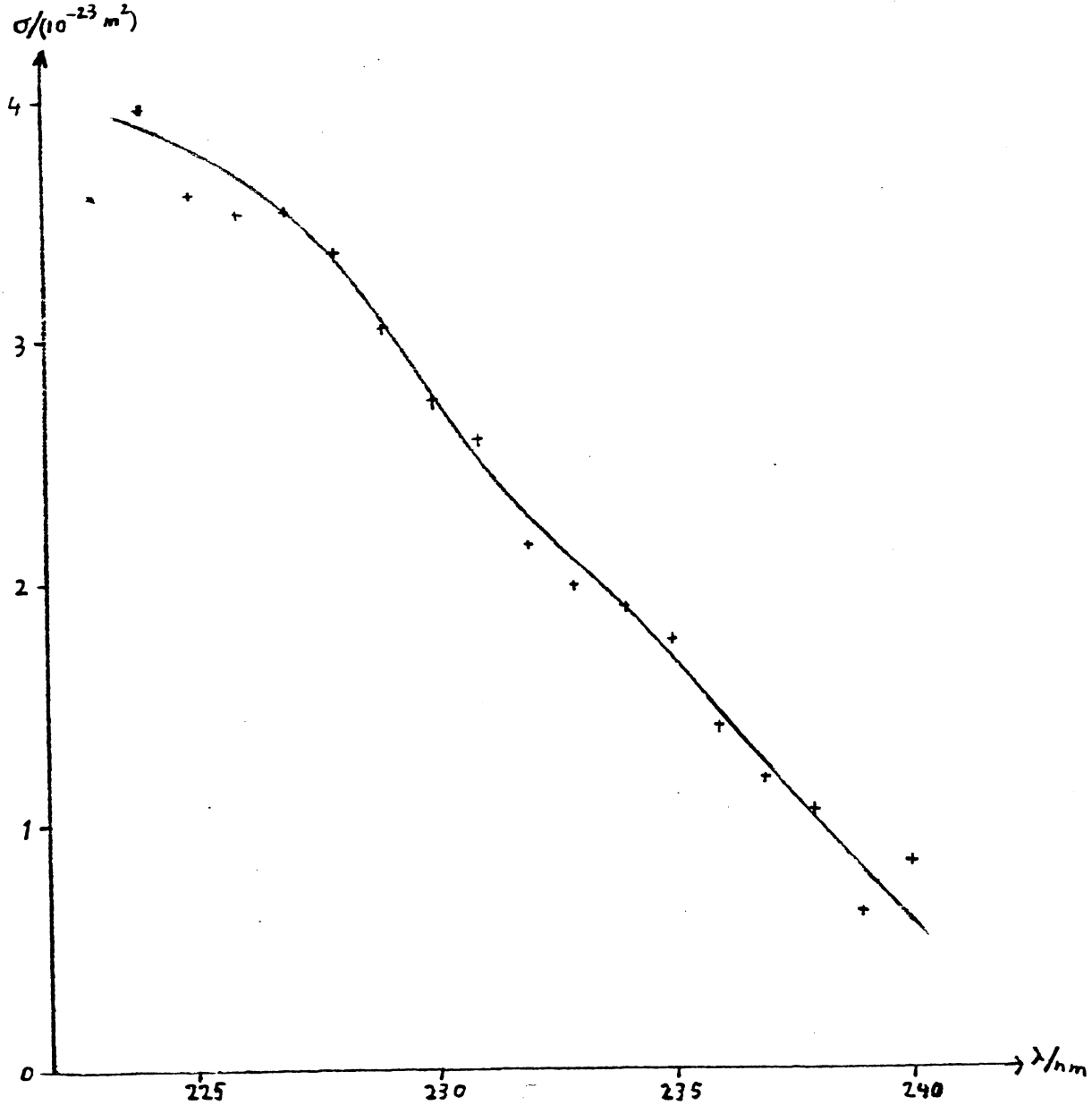


Fig. 6 The calculated absorption cross section for H_2S.

The structure of the spectrum is obtained by comparing the recorded transmission spectra through air and through gas mixture, contaning some H_2S (fig. 4 and 5). As both of the spectra are rather smooth, the conclusion is that the absorption spectrum for H_2S is rather smooth.

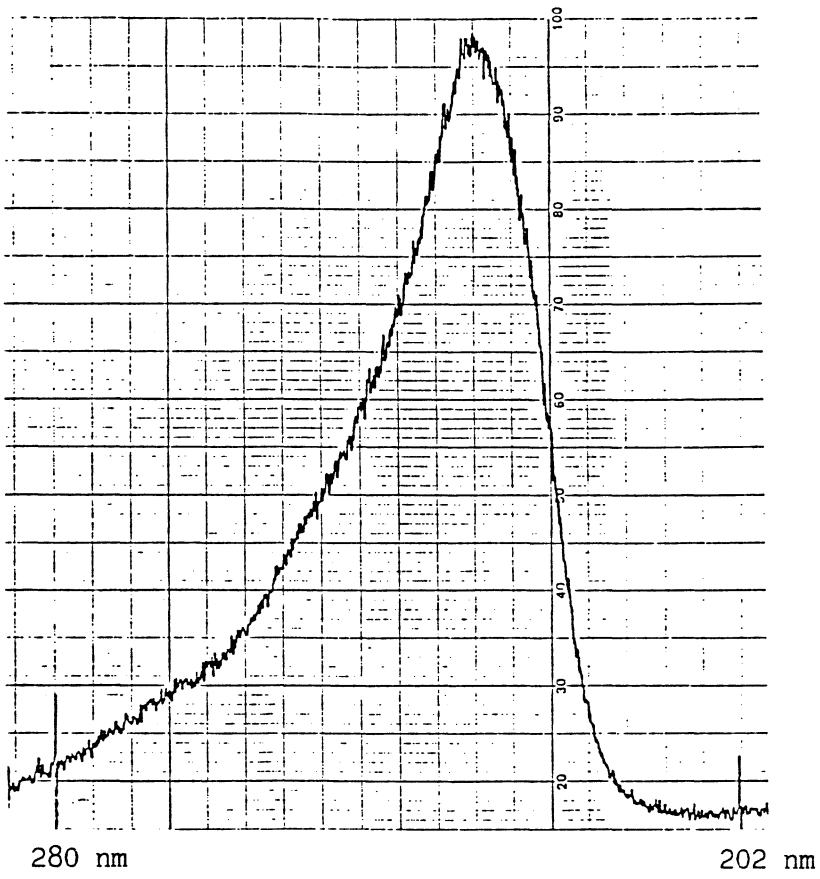


Fig. 4 Recording of the transmitted light through the cell, filled with air. The distance is 8 m.

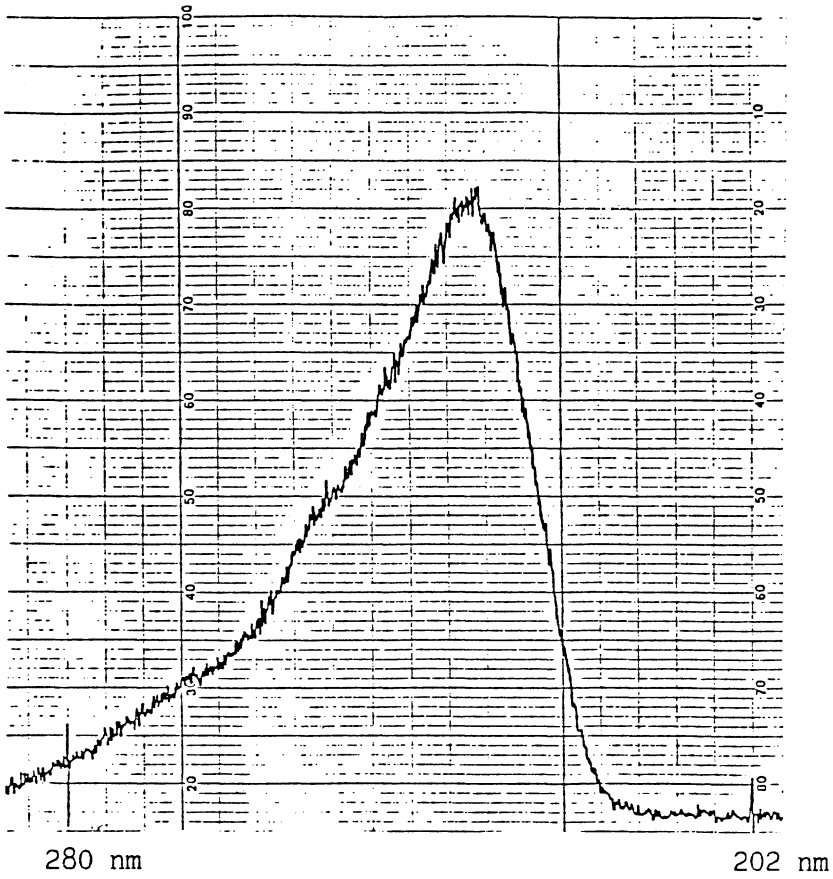


Fig. 5 Recording of the transmitted light through the cell of around 100 ppm H_2S. The distance is 8 m.

POINT MONITORING TEST

The White cell is also useful for point measurement of the atmosphere. This can be done by just blowing air through the cell and analyzing the spectra. Connected to a the DOAS system it would be a rather cheap system.

A commercial DOAS system, from OPSIS AB, was used here. It is built up with computer and spectrometer as one unit. The spectrometer is entirely controlled by the computer. The light reaches the spectrometer via an optical fiber.

To connect the cell to the DOAS system, an arrangment replacing the outlet window of the cell was constructed. This is a holder for an optic fiber. The outlet light is now focused at the fiber end. The fiber has a core diameter of 600 µm. The light spot is much larger than that. Thus, just a small fraction of the light is used.

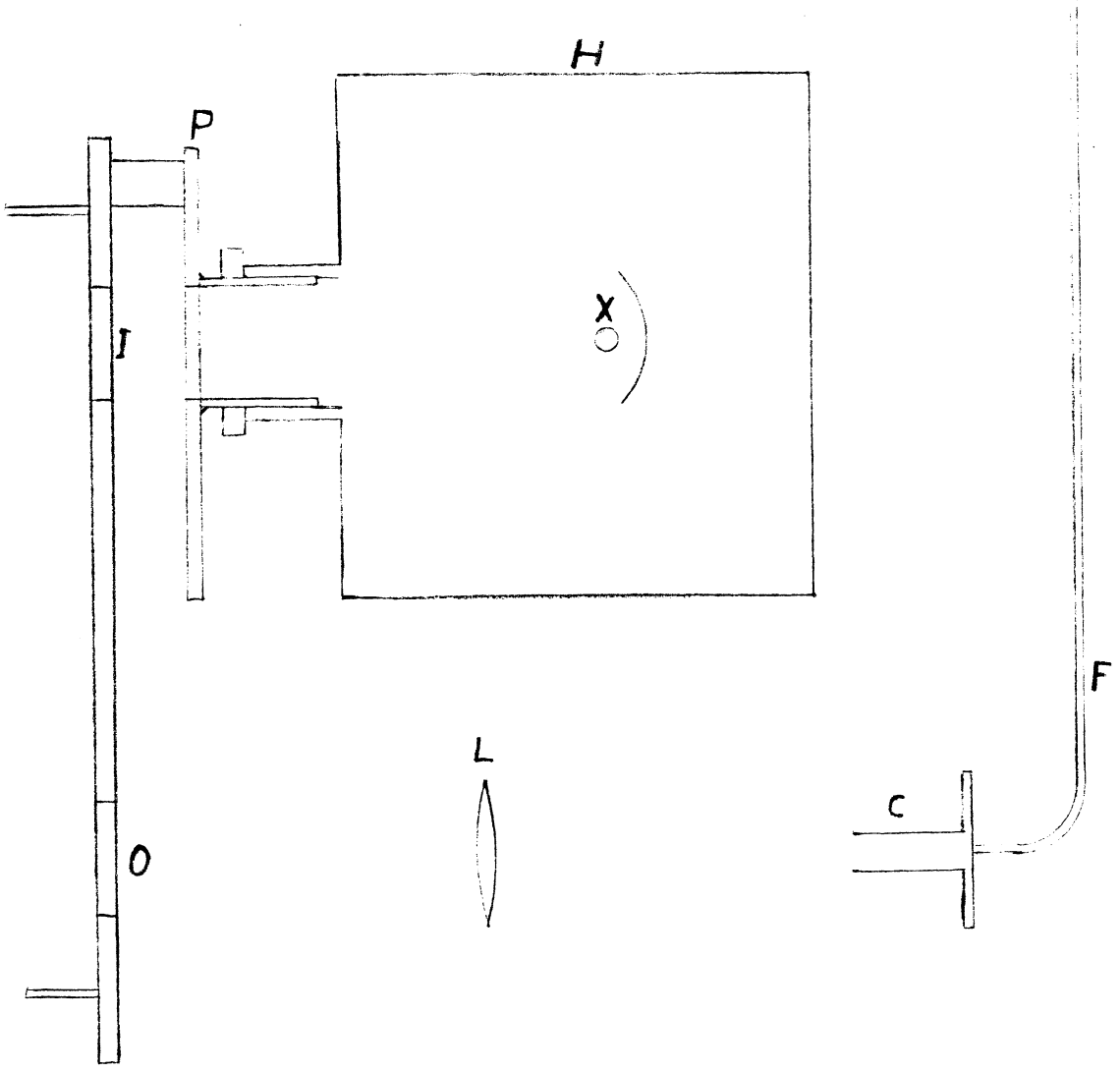


Fig. 7 Arrangement at Aspvreten The front end of the cell, is in the left part of the figure: I) Inlet window, O) Outlet window, X) Lamp, H) Lamphouse, F) Optic fiber, L) Lens, C) Fiber holder, P) Plate to hold the lamphouse

Here a lamp is used that is mounted directly on the front end of the cell. The reflector of this lamp is used instead of a lens. A special arrangement for mounting of the lamp was constructed by the workshop. This arrangement was first tested without connecting it to the DOAS system, just by looking if it was possible to see the light intesity change at the other end of the fiber. It was tested for different distances, and it was established that it was possible to see the light change, up to at least 144 meters through the cell.

To make it possible to blow air through the cell, a new valve was opened beside the lamp. This valve has about same size as that at the rear end.

After the adaptation of the cell it was transported to a research station at Aspvreten, run by the Swedish National Environment Protection Board, for further work. During transport, the cell was mounted at a table in a van. A possibility would be to keep the cell in the van. However, at Aspvreten the cell was dismounted and moved into the laboratory.

The cell was connected to the DOAS system by an optic fiber.

To blow air through the cell a vacuum cleaner was used in the beginning. Later another pump, that was made for longer running intervals, was used. The pump was connected to the valve at the backside. At the large valve at the front, a tube, with the other end outside the window of the house, was connected.

This system was tested to measure NO_2. At the first try it did not work so well. Instead of using the original system lenses were used and focused the light to the fibers end (see fig. 7). This arrangement was better, but still not satisfactory. The random errors were large, sometimes even larger than the monitored value.

Measurements where NO_2 was added to air was also studied. These measurements were compared with measurements by a chemiluminisence monitor, that is another point measurement system. A tube for getting gas to the chemiluminisence measurement system was inserted through one of the small valves.

The result is given in fig. 8. It shows that the two methods correlate well. DOAS shows about 10 % lower concentration, at least for concentrations of 300 - 400 $\mu g/m^3$. However, it does not show that this small relative deviation is maintained even for concentrations less than 100 $\mu g/m^3$. That can make the method rather unuseable for monitoring NO_2 in the air.

Chemiluminisence is measuring the total amount of nitrogen oxides and the amount of NO. The amount of NO_2 is then calculated as the difference of these quantities. Because of this even other compounds, such as N_2O_4 etc. are recorded as NO_2. That can be a reason for why chemiluminisence shows a higher value.

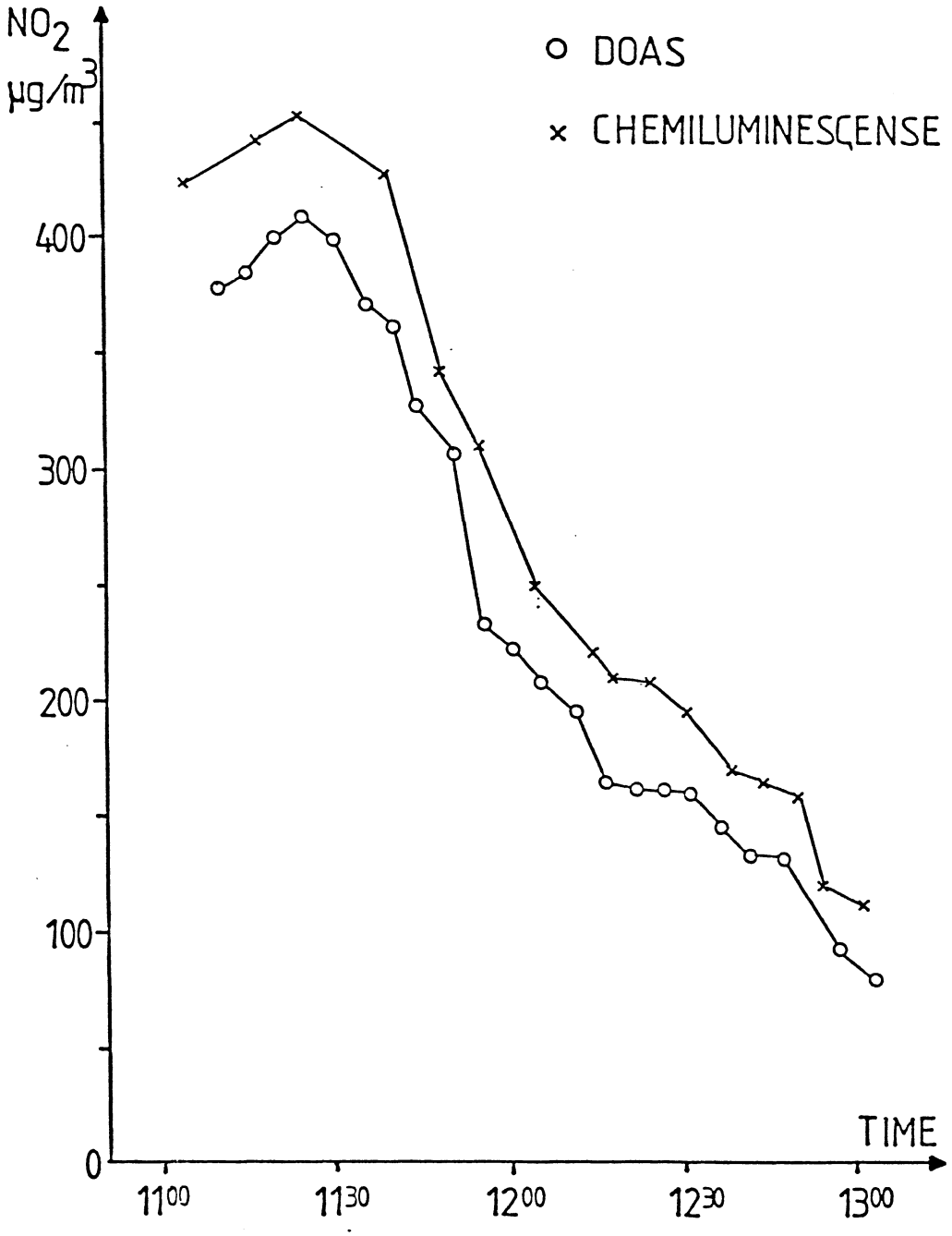


Fig. 8 NO_2 concentration monitored by chemiluminisence and DOAS respectively.

After the point monitoring test, the cell was mounted in the van and transported back to the physics department in Lund.

FLUORESCENCE MONITORING

In the absorption process the molecule is excited. The molecule normally is deexcited by collisions, thus producing heat. However, some molecules are still deexcited by light emission. The emmitting light is of longer wavelength than the exciting light. The light is emitted in any direction. The light is normally referred to as fluorescence. If the upper level has a long lifetime (more than a few ms) the emission is called phosphoresence.

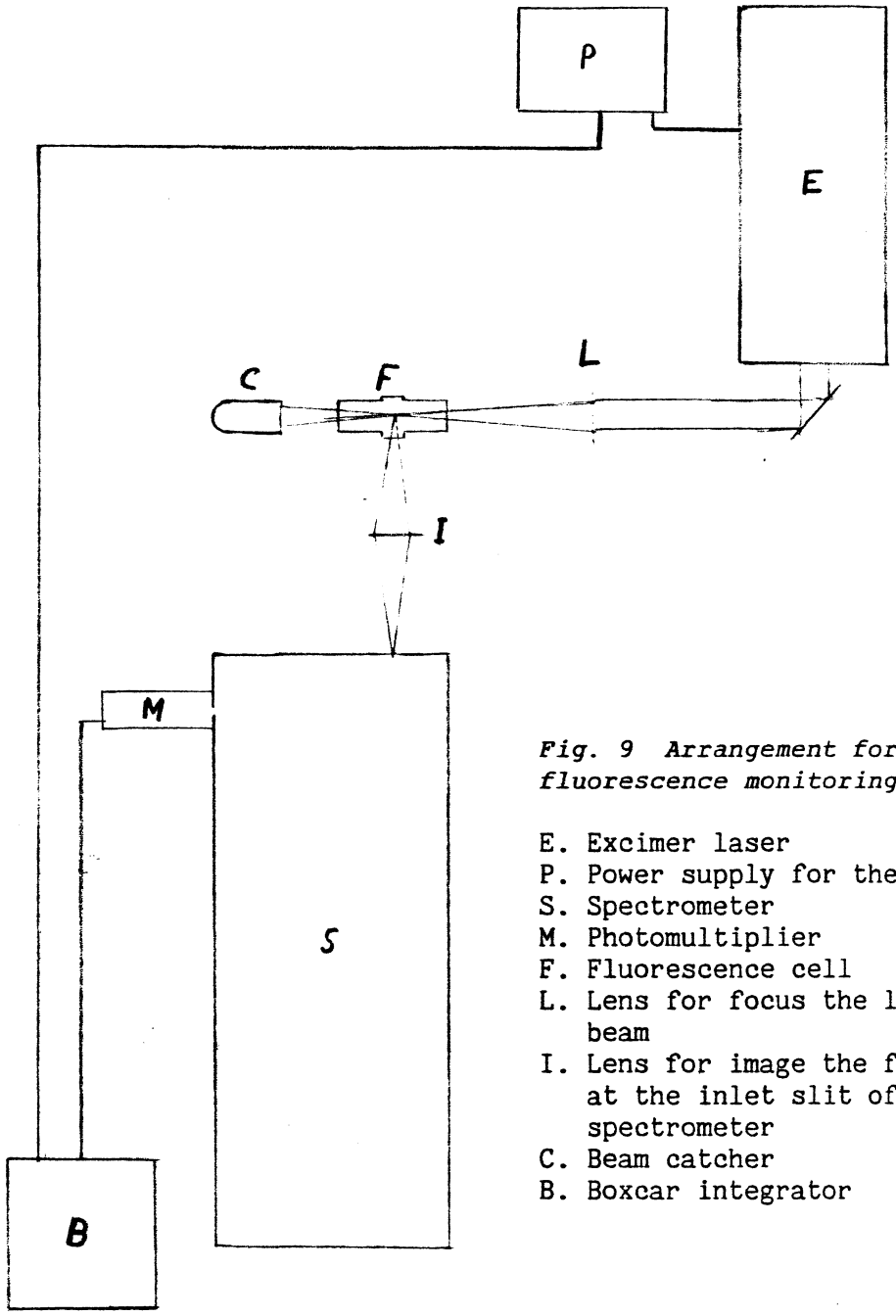


Fig. 9 Arrangement for fluorescence monitoring.

E. Excimer laser
P. Power supply for the laser
S. Spectrometer
M. Photomultiplier
F. Fluorescence cell
L. Lens for focus the laser beam
I. Lens for image the focus at the inlet slit of the spectrometer
C. Beam catcher
B. Boxcar integrator

Fluorescence can disturb the absorbance monitoring when a white lamp is used. As some traces of fluorescence were found in the measurements it was desirable to try to measure it. This requires a cell where it is possible to focus light from one direction and study the fluorescence in another direction. The emission is studied with a spectrometer. The spectrometer (A) that is described above was used. This time it was calibrated with a He-Ne laser.

First a Xe lamp was used to excite the H_2S, but it did not work well, probably because of low intensity. Instead an Ar-F-filled excimer-laser, with light of 193 nm, was used for exciting the H_2S.

To start the excimer laser, gas bottles containing the gases that should be used (Ar, F and He), had to be connected. As the laser had been used with chlorine mixture before, it had to be passivated first, i.e. it was filled up with fluorine gas mixture (according to instructions) for a while and was evacuated again. Then it was filled up with the recommended gas mixture and the laser was started. No emission occured at the first try. After it was tried a few times, the laser action lasted for a short while. For each new fillup it was a longer possible running time. A probable reason for these observations is gas adsorption at the vessel walls.

The H_2S was contained in a small cell with windows in 4 directions. The laser was focused into the cell so the light that was not absorbed, passed out through the exit window. By a third window the focus was imaged, in a right angle to the laser beam, at the inlet slit of the spectrometer. This laser was pulsed with a repetition rate of 10 Hz. As the fluorescence is fast, the light out will have a time dependence as the diagram below shows. The fluorescence arises just after the laser pulses. Because this the signal from the PMT was taken up by a boxcar.

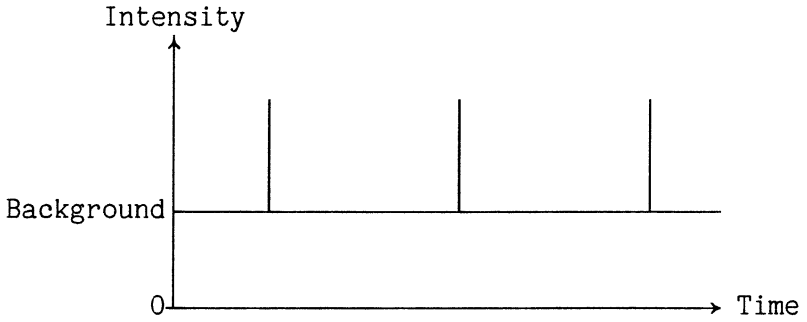


Fig. 10 Time dependence of light intensity.

Background radiation is almost unavoidable. Even scattered light from the laser contributes to the background light. Thermally emitted electrons at the chatode of the PMT are amplified and give rise to thermal noise. This can be reduced by cooling the PMT, e.g. to liquid nitrogen temperatures.

Boxcar integrator

A continuous measurement of a signal, like the one shown in figure 10, will not give much above the noise level. As it just is a short while after the pulses that there is a signal above the background, this is the only time when it is necessary to measure. That is what a boxcar integrator does. It needs a trigger pulse for each measurement and the delay and the time window can be selected.

An trigger signal from the excimer laser power supply is used as trigger pulse. This pulse comes some time before the laser pulse. By elastically scattered light, which was much more intense than the fluorescence light, it was possible to set the boxcar delay correctly. The boxcar was set to start measuring 3 µs after the triggerpulse. The time window was 5 µs.

When the boxcar is set to sample the weak signal, it gets overflowed by the intensive directly scattered light. It means that each time the spectrometer is set on a wavelength that is an order of the laser wavelength, i.e integer multiplyed with the laser wavelength, the boxcar gets overflowed. To make it possible to scan for a wider spectral region, a coloured glass filter (e.g. WG 280, fig. 11) was used.

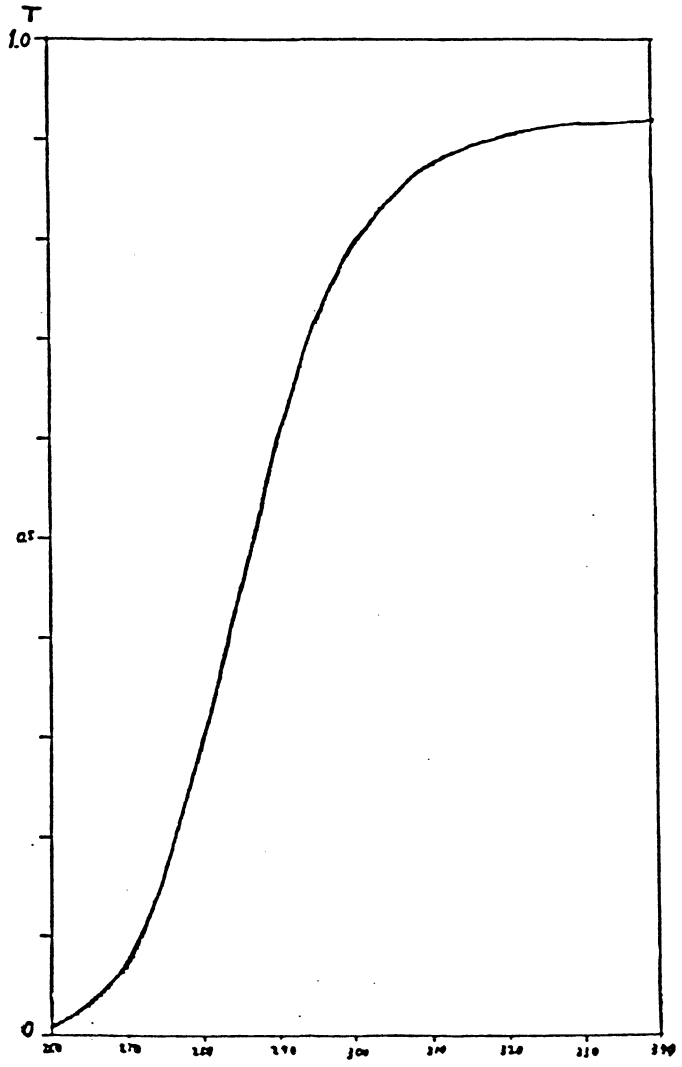


Fig 11 Transmission of the filter WG 280.

RESULTS OF THE FLUORESCENCE MEASUREMENTS

Figs. 12 and 13 show the fluorescence spectrum of the H_2S filled cell from 200 nm to about 780 nm. They show that there is some fluorescence in the spectral region up to about 470 nm. For the recording in figure 12 the filter WG 230 is used. That filter reduce well around the exciting light (193 nm), but not good enough to scan through higher orders of that wavelength.

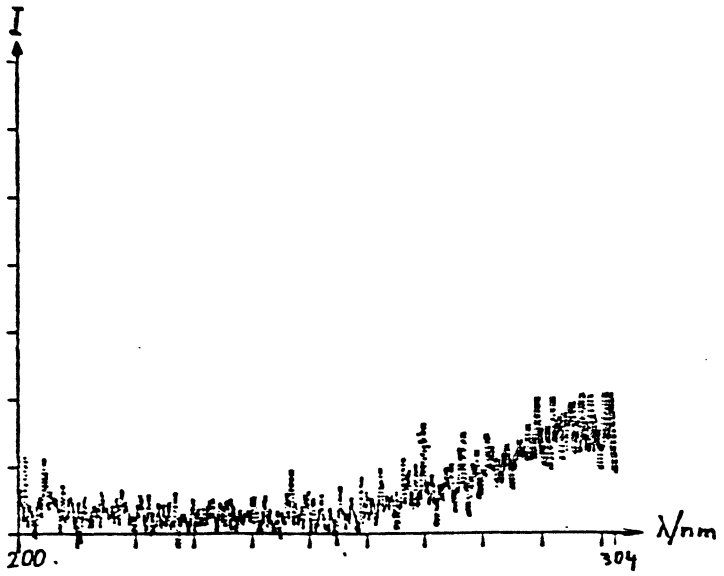


Fig. 12 Fluorescence spectrum from cell containing H_2S; 200 - 304 nm.

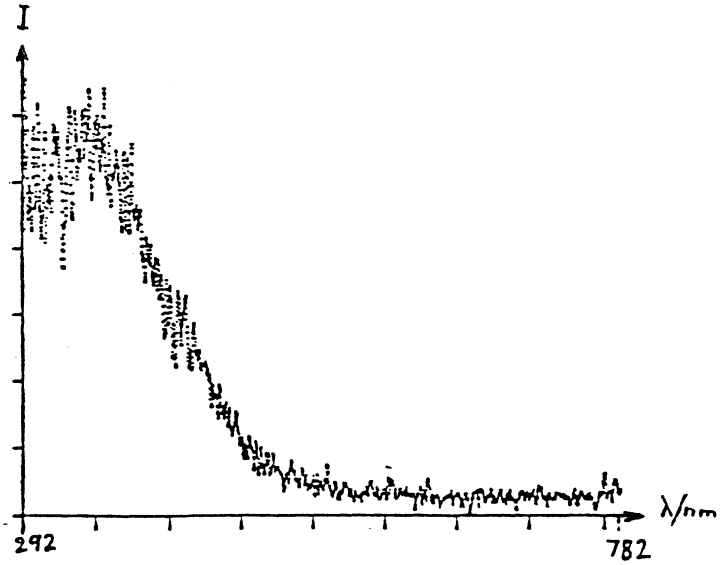


Fig. 13 Fluorescence spectrum from cell containing H_2S; 292 - 782 nm.

Fig. 14 shows the fluorescence spectra of the cell, filled with air, from 290 nm to 745 nm. For both of these recordings, the filter WG 280 was used. However, by comparing the figures 13 and 14 one can not see any significant difference. The figures 12, 13 and 14 have all the same scale for the intensity.

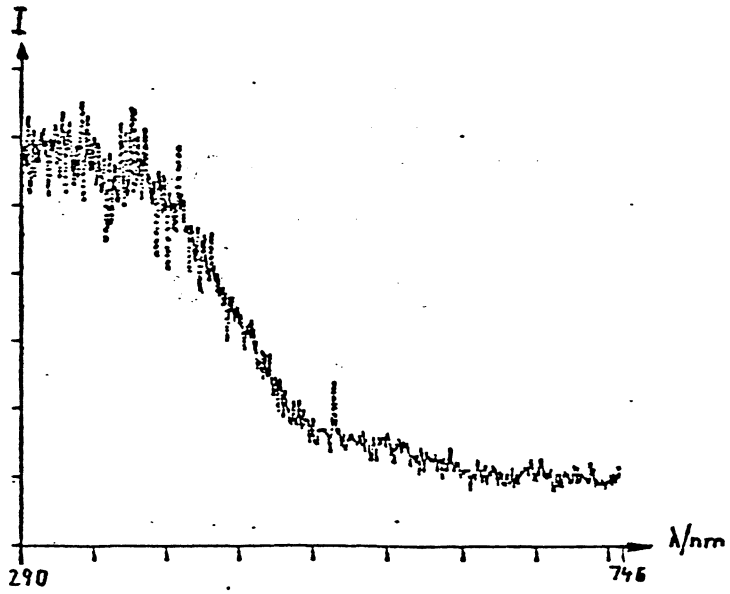


Fig. 14 Fluorescence spectrum from cell without H_2S; 290 - 746 nm.

Fluorescence spectra were also taken from air without using a cell. Figure 15 shows that the fluorescence does not arise from the air. The peaks arise from the first, second and third order of the exciting light (193 nm), since a filter was not used.

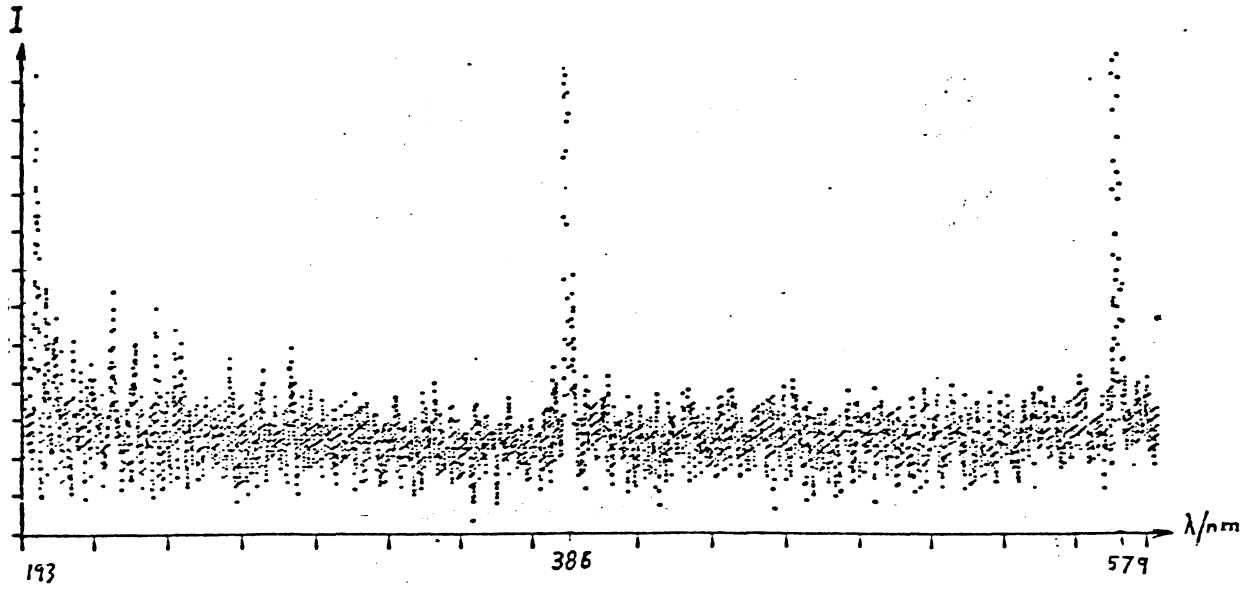


Fig. 15 Fluorescence spectrum without cell, 193-593 nm.

The observed fluorescence is probably from the cell windows. The conclusion is that fluorescence due to H_2S could not be observed in our set-up.

DISCUSSION

For DOAS and LIDAR it is not interesting to look at wavelengths shorter than about 200 nm, because the oxygen of the air has too much absorption for such wavelengths. In order to obtain a spectrum in the region of about 200 to 225 nm it is necessary to have more light through the measuring cell. (Others suggest that there is something interesting at about 218 nm, ref. 7) It can be done with a lamp that has better brightness per wavelength interval. A laser has that advantage. But it also has the advantage that it is not necessary to have a spectrometer to analyze the light.
A better spectrometer is also a possibility. The use of larger mirrors without changing the length of the spectrometer gives a lower (better) f-number. If the length is increased to the same degree it gives wider scale factor for the spectra, using the same f-number. That makes it possible to use wider slits. A better grating would improve the experiment. A higher rule density gives better resolution. The diffraction angle between different colours increases and more rules get illuminated, which makes the spectral lines sharper. A larger diffraction angle between different colours makes it possible to use wider slits instead of getting better resolution.

In the region of 225 nm to 240 nm the calculations are based on a measurement serie, recorded by oscilloscope (table 3).
The deviation due to the distance is not considered, because it is so small compared to the deviations due to the concentration and the transmission. The deviation due to concentration is lineary added to the remaining deviation, because it is the same error for all measurements here, why it must be regarded as a systematic deviation.
The deviation is less than 50 % and is partly even less than 25 %.
The error for wavelength is not considered, as it primarily is due to a lineary scale error on the spectrometer and to get the right spectra, it is just to move the scale.
Cross-sections that are calculated from the recordings that are given in the figures 4 and 5, does not deviate too much from the calculated cross-section in table 3 and figure 6. However, by using to different recordings, where the spectrometer is scanned between, yields less accuracy, because it is not sure that both transmitted irradiances are based on the same wavelength.

In order to perform accurate measurements, the transmission should be monitored when the cell is filled with pure nitrogen, to compare that with the transmission of H_2S and pure nitrogen. Else the high absorption of the oxygen will disturb the measurements. It is also possible that the H_2S will subverse in an uncontrollable way by the influence of the oxygen or humidity in the air.

The reason for traces of fluorescence being recorded can be fluorescence in the windows, lenses or mirrors of the equipment.
Another reason could be that there is something in the air, e.g. oxygen, that absorbs or scatter the light substantially in the spectral region. This absorption or scattering will decrease when the air gets replaced with nitrogen.

APPENDIX:

PREREQUISITES TO UTILIZE THE LIGHT SOURCE IN AN OPTIMUM WAY

It can be shown that the irradiance is, in some circumstances, only limited by the brightness of a light source and the f-number of the spectrometer. While the lens is large enough, the diameter that is used is $d=b/f_1$ where f_1 is the f-number of the cell and b is the distance between lens and cell. The light that is used is coming at that part of the lens. If the light power per st rad from the lamp is P the amount of light that is used is

$$p = \frac{P\ d^2}{a^2} = \frac{P\ b^2}{a^2\ f_1^{\ 2}}$$

where a is the distance between lamp and cell. But

$$a = \frac{1}{1/F - 1/b} = \frac{b\ F}{b - F}$$

where F is the focal length of the lens. The magnification M_1 from lamp to cell is

$$M_1 = \frac{b}{a} = \frac{b\ (b - F)}{b\ F} = \frac{b - F}{F}$$

If the surface of the lamp is S the surface of the image is

$$s = M_1^{\ 2} S = \left[\frac{b - F}{F}\right]^2 S$$

The light power at the image is

$$p = \frac{P\ d^2}{a^2} = \frac{P\ b^2}{a^2\ f_1^{\ 2}} = \frac{P\ b^2\ (b - F)^2}{f_1^{\ 2}\ b^2\ F^2} = \frac{P\ (b - F)^2}{f_1^{\ 2}\ F^2}$$

and the irradiance is

$$\frac{p}{s} = \frac{P\ (b - F)^2\ F^2}{f_1^{\ 2}\ F^2\ (b - F)^2\ S} = \frac{P}{f_1^{\ 2}\ S}$$

To use the entire f-number of the spectrometer, the magnification from cell to spectrometer should be

$$\frac{f_2}{f_1}$$

where f_2 is the f-number of the spectrometer.
It means that the irradiance at the inlet slit of the spectrometer is

$$\frac{P\ f_1^{\ 2}}{f_2^{\ 2}\ f_1^{\ 2}\ S} = \frac{P}{f_2^{\ 2}\ S}$$

if lenses etc are large enough.

ACKNOWLEDGEMENTS

I would like to thank all those persons, who, in different ways, have contributed to this diploma work.
Specially thanks are due to

- Göran Werner, who helped me with the mechanical constructions and the machining.

- OPSIS AB, that supplied with various pieces of equipment.

- Pedro Oyola of the Swedish National Environment Protection Board for letting me take part in the experiments at Aspvreten.

- My supervisor Anders Sunesson.

Finally I wish to thank all graduate students of the department of Physics, who have helped me with various questions.

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