

F18 Atmospheric Trace Gases

20.11.95

Messprotokoll:

Christiane Stünker
Dunah Pross

* 1. Characterizing the instrumentation

1.1. Offset

exposure time: 1 ms

number of scans 10.000

mean offset value per pixel per scan:
in the range 437 - 504 nm

~~1,0663 · 10⁶~~ 208,47 counts
~~288,01~~ scan

1.2. Dark current

exposure time: 60 s

number of scans: 1

average number of counts per pixel per second: ~~277,52~~ 168,65 counts

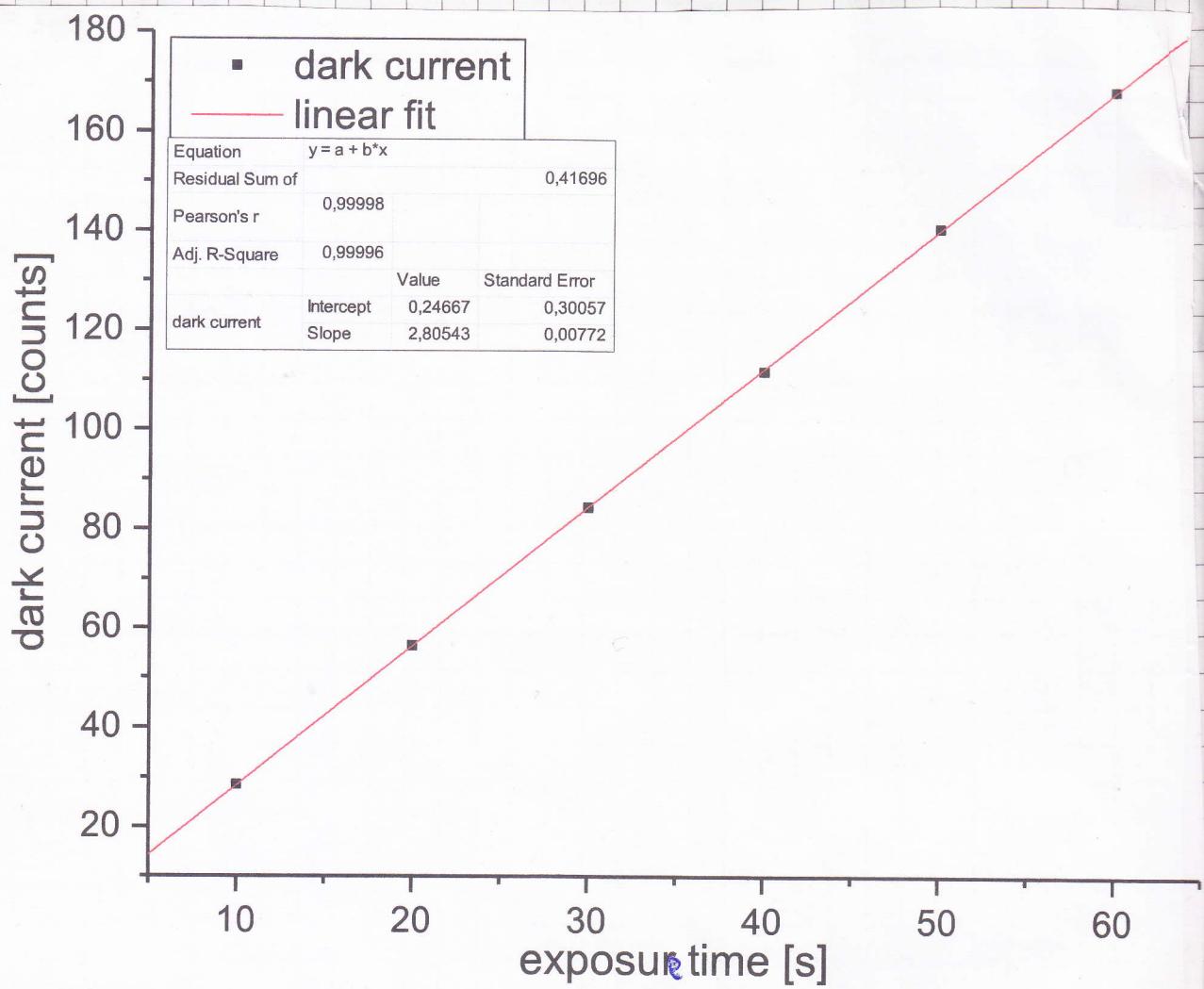
Table 1: Dark current scans for different exposure times (#scans = 1):

exposure time [s]	average number of counts per pixel per second [counts scan]
50	247,71
40	218,80
30	191,18
20	156,43
10	28,49

We do not need to correct the electronic offset, because it is very small in comparison to the Dark current. ($\frac{208,47}{10.000} < \frac{275,51}{1}$)

We have corrected the values for the electronic offset determined in part 1.1.

As can be seen in Diagram 1, the Dark current is not constant for different exposure times, but increases linearly.



Graph 1: Time dependance of dark current

1.3 Determining the instrument noise and total noise

Instrument noise:

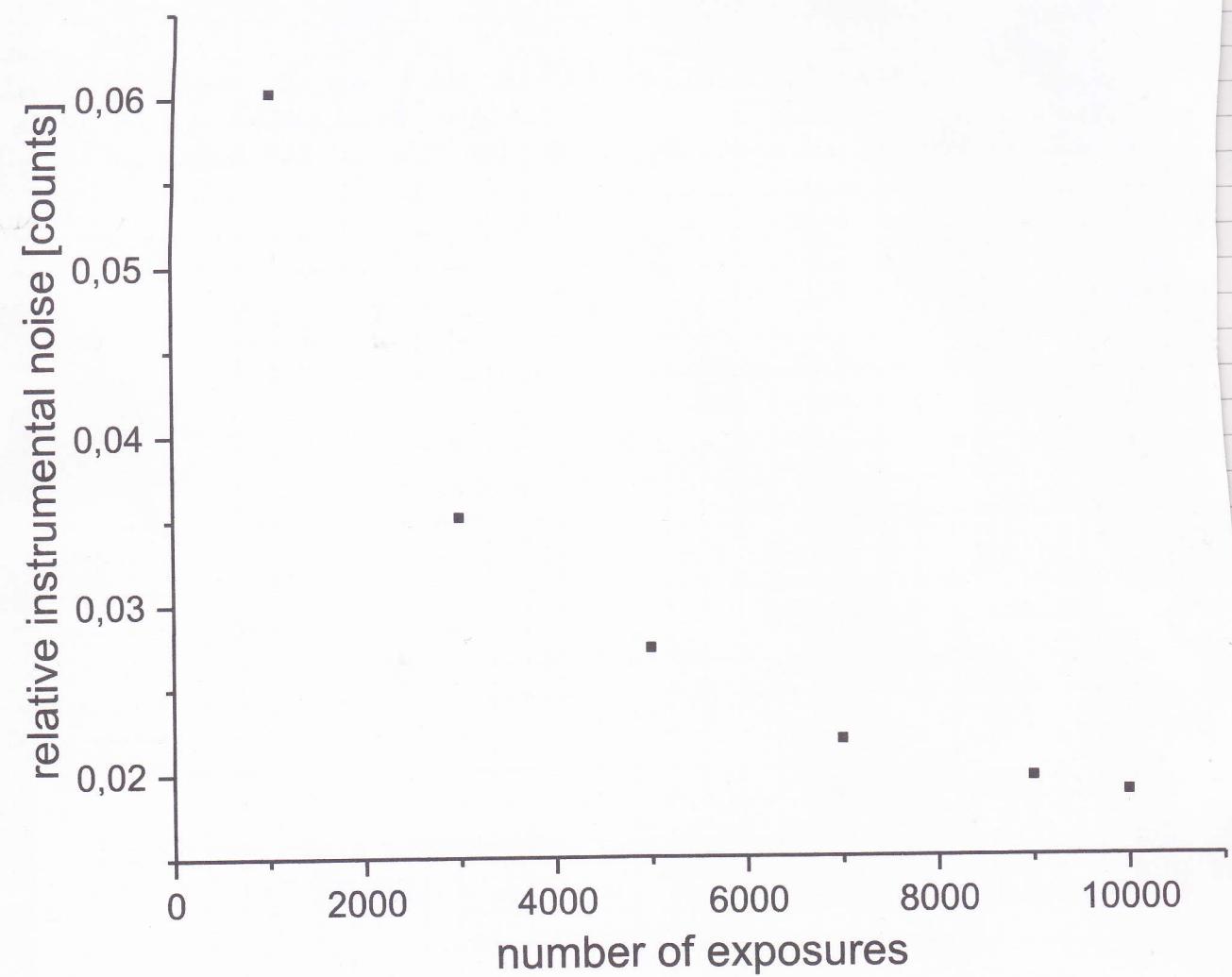
We measure ~~a second offset spectrum~~ with an exposure time of 1ms and 10.000 scans from ~~from one another~~ (offset_2.spz, offset_3.spz) which we subtract ~~the~~ ~~original offset spectrum~~. We then determine the standard

deviation to be $265,71 \frac{\text{counts}}{\text{scan}}$. The instrumental noise is $\sigma_i = \frac{1}{\sqrt{2}} \sigma_D = 187,89$ b2w. $\frac{0,060}{0,015} \frac{\text{counts}}{\text{scan}}$

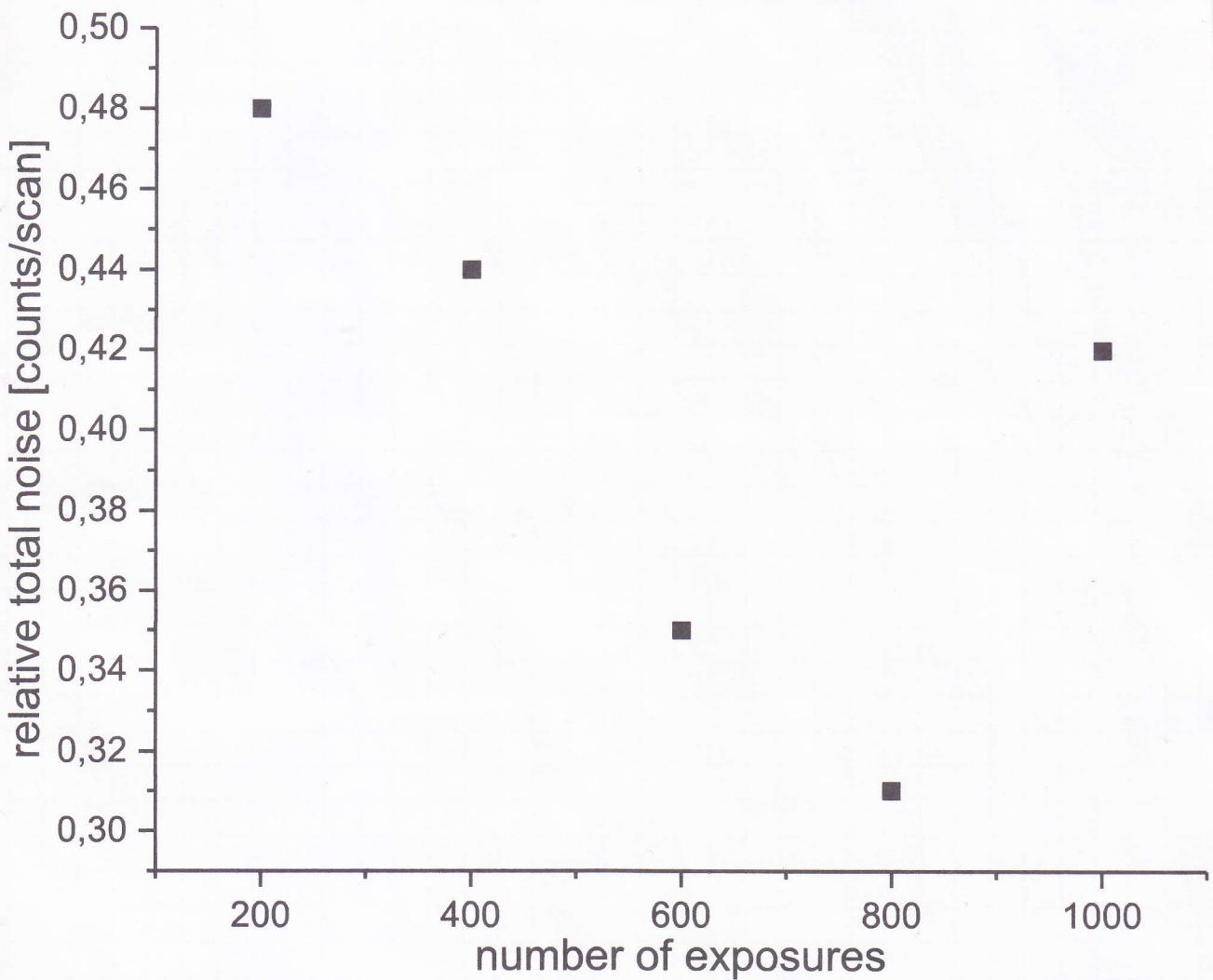
table 2: instrumental noise

exposure time [ms]	number of scans	standard deviation [counts]	instrumental noise [counts]	instrumental noise [counts]
1	9.000	250,53	177,15	0,060 - 0,035 0,01
1	7.000	217,58	153,85	0,035 - 0,027 0,02
1	5.000	193,60	136,90	0,027 - 0,020 0,03
1	3.000	169,28	105,56	0,022 - 0,020 0,03
1	1.000	85,31	85,31 - 60,32	0,020 - 0,019 0,01

Again we notice a linear dependency on the number of scans. See diagram 2. We notice an exponential decrease with a ~~rising~~ ~~rising~~



Graph 2: instrumental noise of the spektrometer



Graph 3: relative total noise of the spectrometer

Total noise:

To reach a saturation of 60%, we place the lenses on the optical way in a ~~the reach saturation at an intensity of 4.~~ manner that gives us a maximum pixel counts/pixel of 2222,4 (after correcting

\rightarrow for $N=1$, saturation = 54,26%)

offset and dark current) and adding a low pass filter due to irregularities in the lamp intensity.)

table 3: total noise

exposure time [ms]	number of scans	saturation	standard Deviation [counts]	absolute total noise [counts]	$T \ln(I/I_s)$	relative total noise [counts/scan]
40	1.000	0,05 %	345,15	583,58	4,16, 19	0,42
40	800	0,07 %	348,67	246,55	$-1,51 \cdot 10^{-5}$	0,31
40	600	0,03 %	295,66	209,06	$8,56 \cdot 10^{-6}$	0,35
40	400	0,14 %	247,58	175,07	$-2,39 \cdot 10^{-6}$	0,44
40	200	0,27 %	135,29	95,66	$-3,04 \cdot 10^{-6}$	0,48

1.4. Calibrating the spectrometer

table 4: mercury spectrum ($t_{\text{exp}} = 300 \text{ ms}$, $n_{\text{scan}} = 300$)

$\lambda [\text{nm}]$	FWHM [nm]	channel number	FWHM [chan. number]	$R = \frac{\lambda_{\text{max}}}{\Delta \lambda} = \frac{\lambda}{\text{FWHM}}$
435,89	0,77	1271,17	7,94	566,03
404,66	0,77	958,39	7,39	562,03
364,98	0,88	585,85	8,09	376,42
333,98	1,12	127,03	10,18	272,07
312,60				

We can see that the

optical resolution of the

spectrometer depends on the

wavelength and is therefore not cons.

table 5: wavelength calibration (Hg-lamp, $t_{\text{exp}} = 300 \text{ ms}$, $n_{\text{scan}} = 300$)

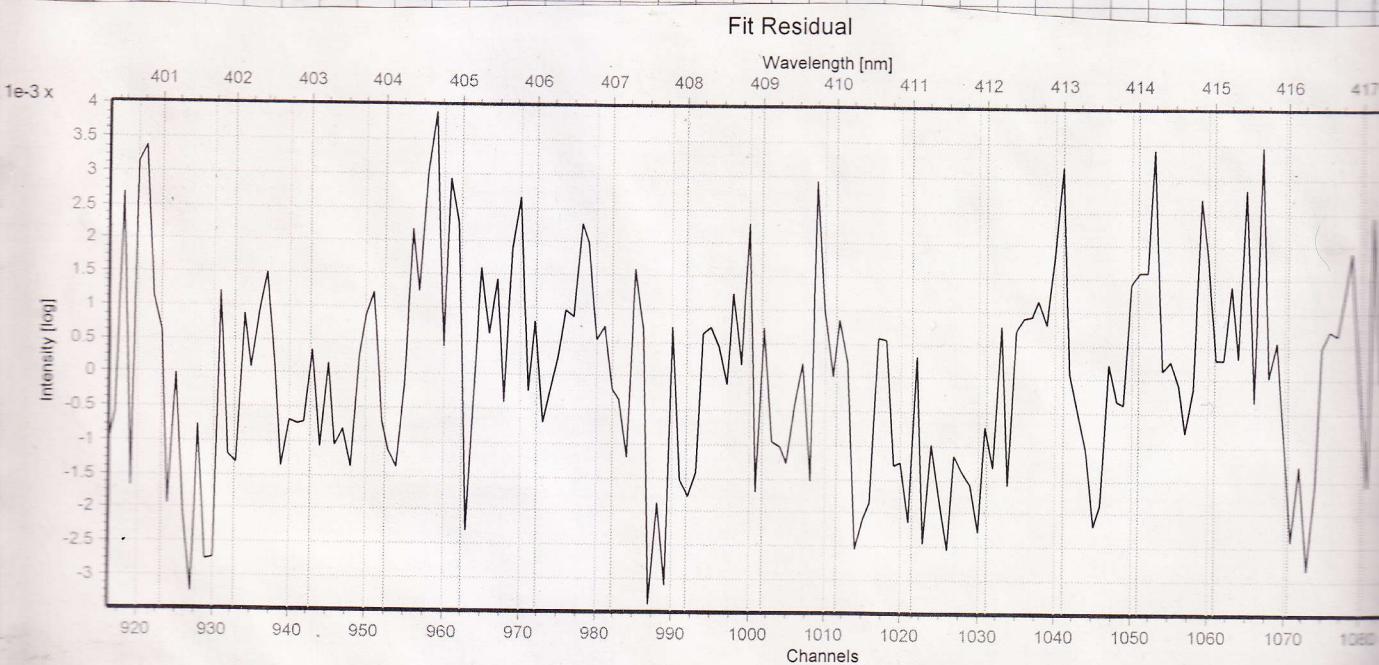
$\lambda [\text{nm}] (\text{meas.})$	channel number	$\lambda [\text{nm}] (\text{theo.})$
435,98 $\pm 0,03$	1271,17	435,84
404,66 $\pm 0,04$	958,36	404,66
333,95 $\pm 0,01$	309,82	334,15
301,87 $\pm 0,02$	36,70	302,15

$$\text{calibration coefficients: } C_0 = 297,73 \pm 0,02$$

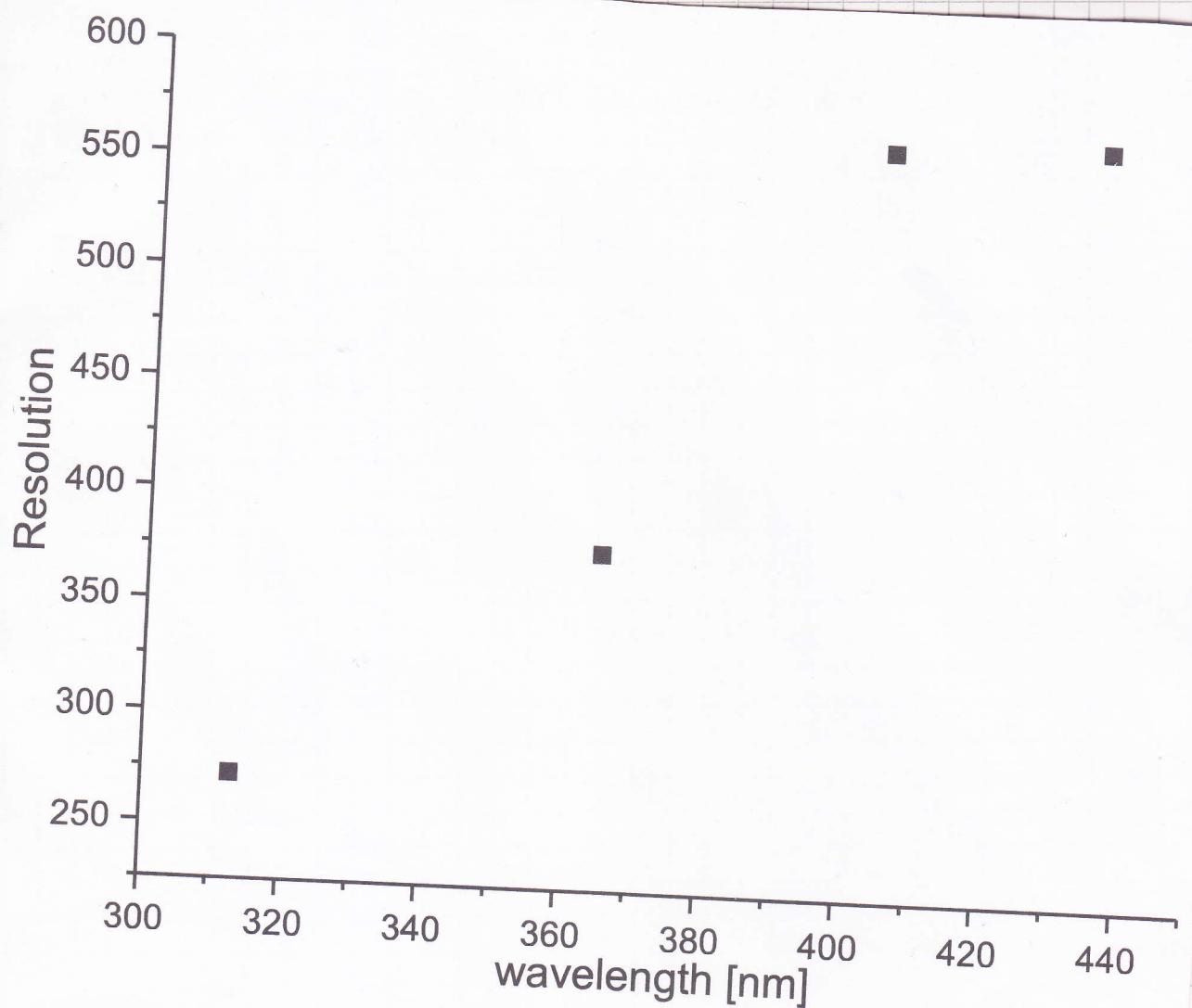
$$C_1 = 0,12047 \pm 0,00011$$

$$C_2 = (-0,9,2969 \pm 0,0805) \cdot 10^{-6}$$

Spectrometer wavelength resolution: 300 nm - 504 nm



Graph 5: Fit residuals



Graph 4: optical resolution of the spectrometer

2. Laboratory Measurements

2.1. Convolution of reference cross section

We convolute high-resolution reference cross section with our calibration to adapt them to our channel number of 2048 channels / 300 - 506 nm.

We do this for NO₂, O₃, O₂ and H₂O.

The effect of the convolution on the reference cross sections is that they get stretched or compressed.

2.2. Recording a spectrum of the NO₂ gas cell

We choose an exposure time of $\frac{100}{300}$ ms resulting in a saturation of $\frac{76,49}{76,23}$ for a single exposure. Varying the number of scans does not significantly change the saturation.

We choose as number of scans: $n_{\text{scan}} = 500$

With these settings we record the Hg-Spectrum once with and once without a tube of NO₂ in the light path.

In the spectrum with NO₂ the intensity was reduced by about a third (at the peak) and we notice that the Hg-Peaks lost intensity when NO₂ was added to the path. We can identify small irregularities due to the absorption caused by NO₂. The intensity was roughly halved.

2.3. Determining the NO₂ concentration in the gas cell

We take the optical density $\tau = \ln\left(\frac{I_0(\lambda)}{I(\lambda)}\right) = \sigma_{\text{NO}_2}(\lambda) \cdot g_{\text{NO}_2} \cdot L$

On this we perform a χ^2 -fit. (SCD is varied until χ^2 is minimized)

For the fit we chose a fit range of $\frac{400-420}{370-390}$ nm and a DOAS-polymer of the 4th order. The fit coefficient was $3,50 \cdot 10^{17} \pm 2,26 \cdot 10^{15}$, shift: $-0,00323 \pm 0,0105$, Squeeze: $1 \pm 0,000961$.

You can see the fit residual in Diagram 3.

$$L = (2 \pm 0,5) \text{ cm}, d = (2 \pm 0,05) \text{ cm}$$

$$g_{\text{NO}_2} = 3,50 \cdot 10^{17} \cdot \frac{1}{L} = 1,75 \cdot 10^{17} \frac{\text{mol}}{\text{cm}^3} = 1,75 \cdot 10^{17} \cdot \frac{1}{N_A} \frac{\text{mol}}{\text{cm}^3} \approx 2,31 \cdot 10^{17} \frac{\text{mol}}{\text{cm}^3}$$

$$V = \pi \left(\frac{d}{2}\right)^2 \cdot L = 6,28 \text{ cm}^3 = 6,28 \cdot 10^{-3} \text{ l}$$

$$n = g_{\text{NO}_2} \cdot V = 1,83 \cdot 10^{-6} \text{ mol} \stackrel{!}{=} 1,83 \cdot 10^{-6} \text{ m} \cdot 22,4 \text{ l} = 8,16 \cdot 10^{-8} \text{ l} = 8,16 \mu\text{l}$$

$$\Rightarrow 1,3 \cdot 10^5 \text{ ppm}$$

Fehlerrechnung:

$$\Delta s_{\text{NO}_2} = \sqrt{\left(\frac{\Delta \text{SCD}}{c}\right)^2 + \left(\frac{\Delta \text{CD}}{c^2} \cdot \Delta L\right)^2} \approx 4,52 \cdot 10^{-5} \frac{\text{mol}}{\text{cm}^3} \stackrel{!}{=} 7,51 \cdot 10^{-9} \frac{\text{mol}}{\text{cm}^3}$$

$$\Delta s_{\text{NO}_2} = \sqrt{(s_{\text{p}_{\text{NO}_2}} \cdot V)^2 + (s_{\text{NO}_2} \cdot \Delta V)^2} = \sqrt{(s_{\text{p}_{\text{NO}_2}} \cdot V)^2 + (s_{\text{NO}_2} \cdot \sqrt{(2d \cdot \Delta d \cdot L)^2 + (d^2 \cdot \Delta L)^2})^2} \stackrel{!}{=} 1,13 \cdot 10^{-4} \text{ mol}$$

$$\stackrel{!}{=} 2,84 \cdot 10^{-16} \text{ mol}$$

$$\stackrel{!}{=} 2,52 \cdot 10^{-6} \text{ l}$$

$$\stackrel{!}{=} 401,3 \text{ ppm}$$

$$\Rightarrow s_{\text{NO}_2} = (2,91 \pm 0,08) \cdot 10^{-7} \frac{\text{mol}}{\text{cm}^3}$$

$$n_{\text{NO}_2} = 1,3 \cdot (1,299 \pm 0,004) \cdot 10^5 \text{ ppm}$$

3. Atmospheric Measurements

3.1 Configuring the f.t. with single measurement

We took the day: 27.05.2017

~~→ midday / Spectra: 75650 655 626~~

~~→ evening Spectra:~~

~~midday~~

~~→ midday / ref. - Spectrum: 75626 11:25~~

~~with solar-zent.-angle: 28,05°~~

~~→ evening Spectrum: 75698 18:05~~

~~with solar-zent. angle 20,046°~~

Both spectra are corrected by the dark current and offset

Also the calibration is added.

- from ~~to~~ the reference spectrum the Ring-Spectrum is obtained
- the evening Spectrum is divided by the reference Spectrum and the logarithm is taken.
- selected wavelength ranges:

~~O₃: 330 - 340 nm~~

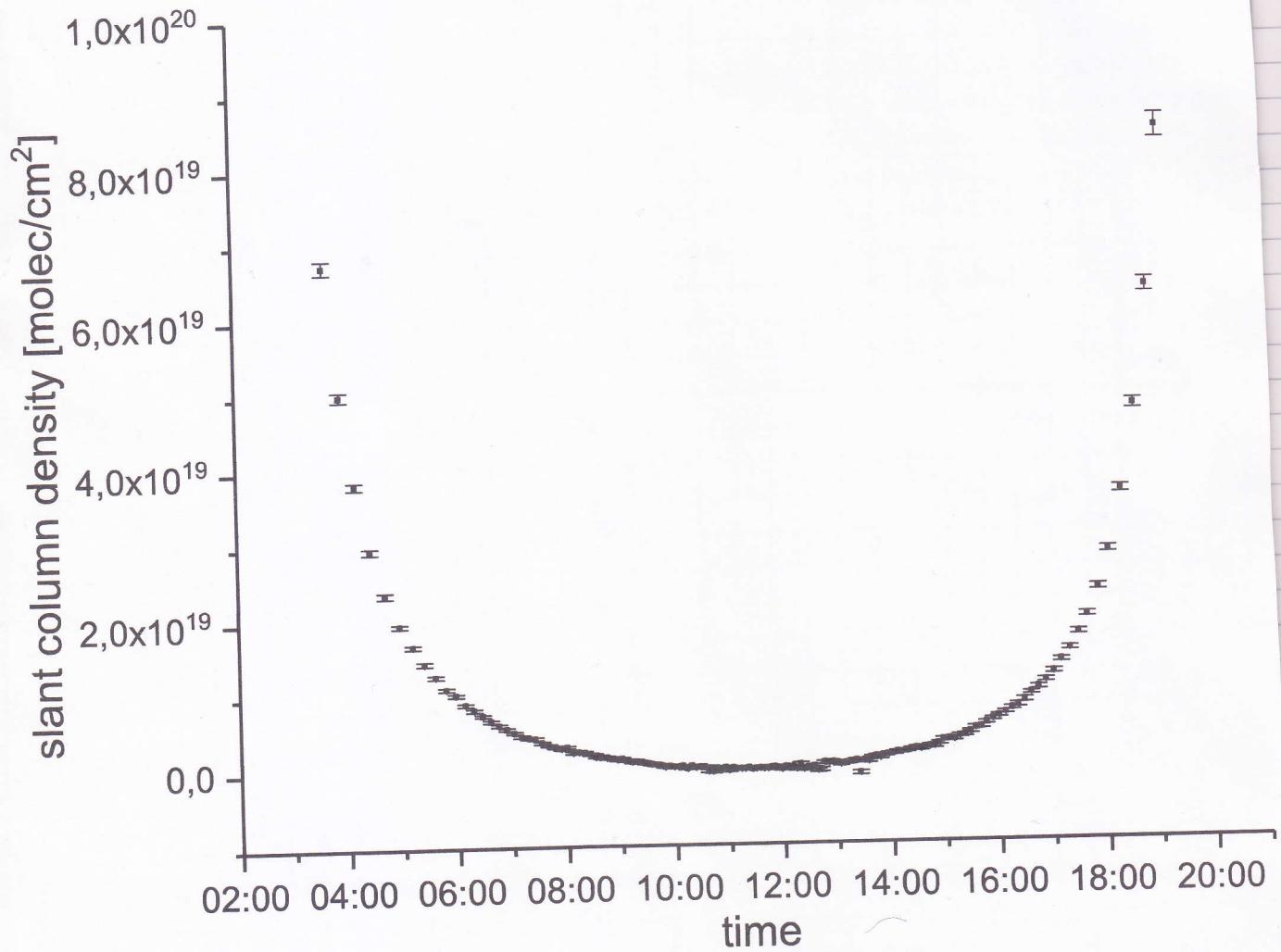
O₃: 337 - 353 nm

~~NO₂: 400 - 430 nm~~

NO₂: 492 - 417 nm

O₃: f.t. coeff: 2,83 · 10¹⁴ ± 4,15 · 10¹⁷

NO₂: f.t. coeff: 3,15 · 10¹⁶ ± 1,13 · 10¹⁵



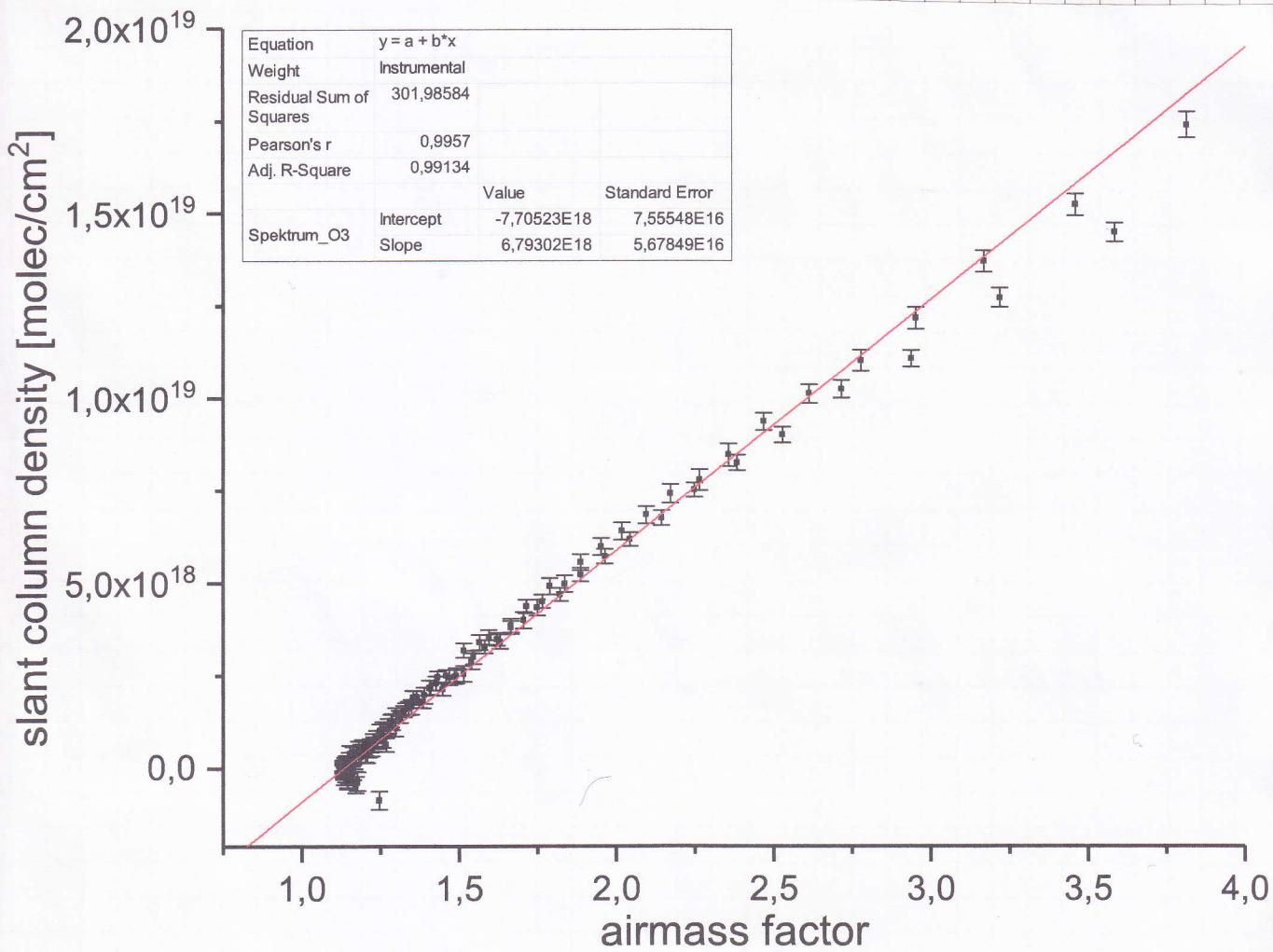
Graph 6: Time series of slant column density of ozone (O_3)

J.2 Automatet evaluation of entire day

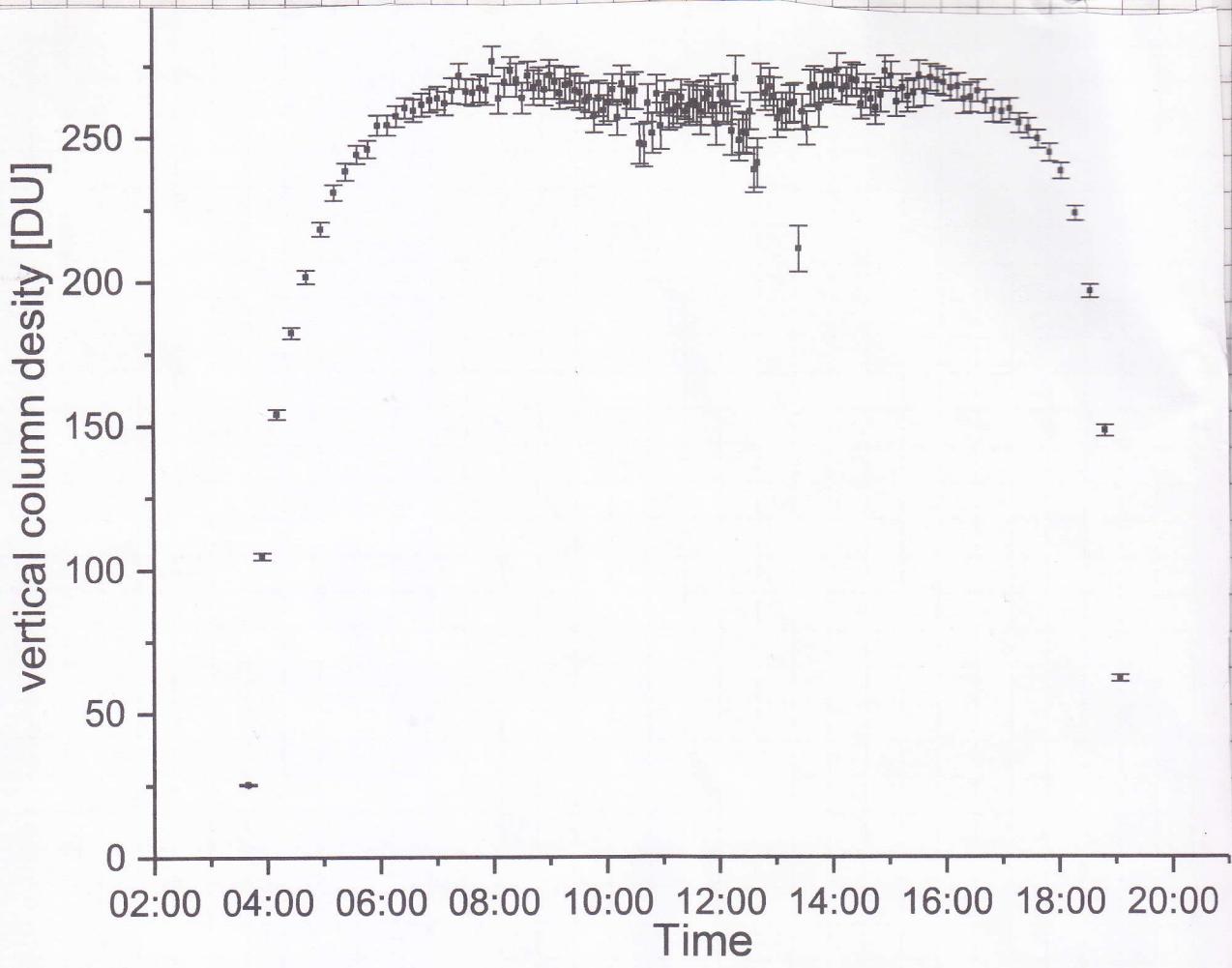
- used Files: 75538 - 75706

27.5.17

- es wurde ein Script für O₃ ~~entwickelt~~ ausgeführt und es ergeben sich die folgenden Plots



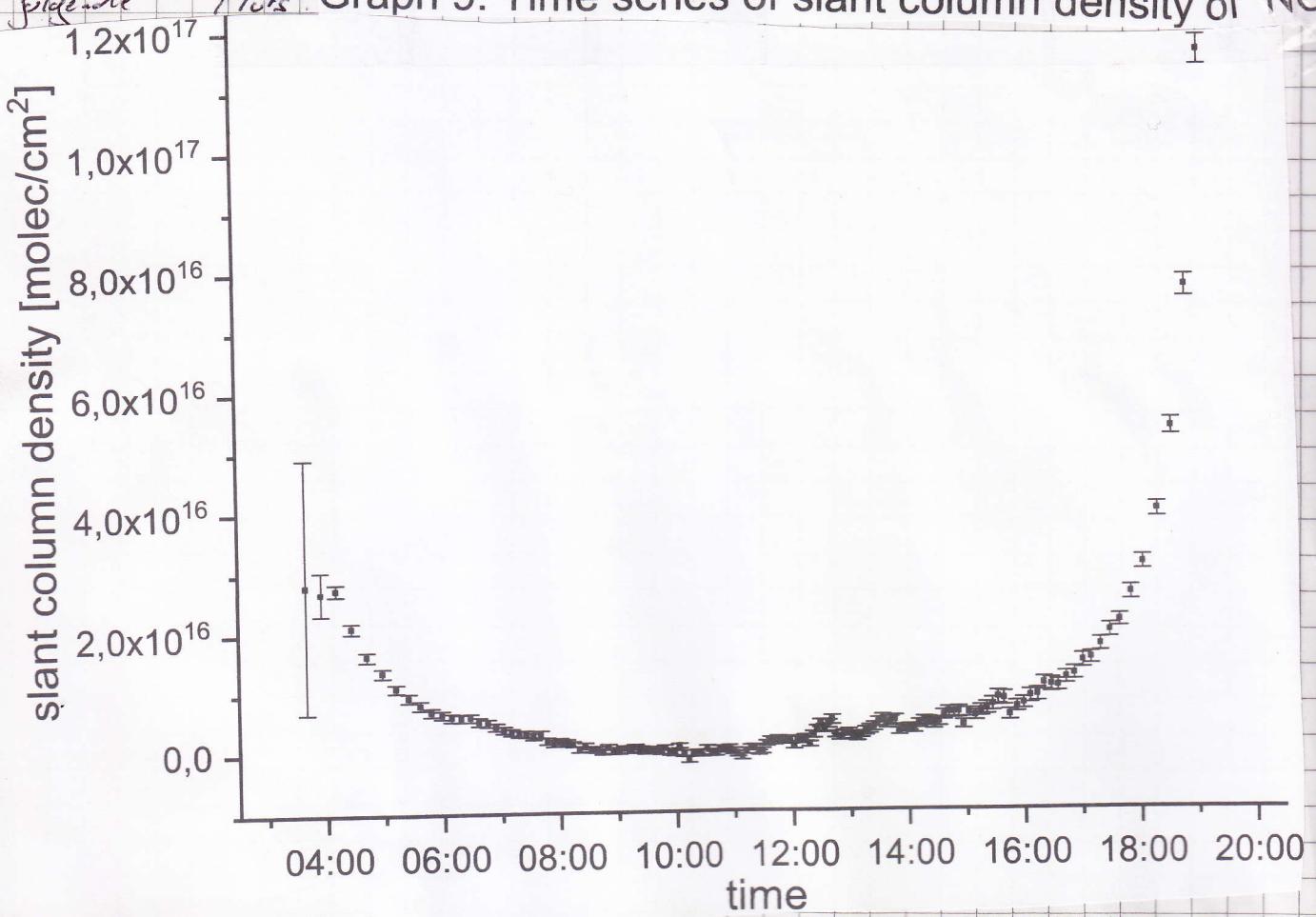
Graph 7: Langley plot of ozone (O₃)



Graph 8: Time series of vertical column density of ozone (O₃)

- gleicher Werte für NO_x abgefehlt, es entsteht.

gleiche Plots: Graph 9: Time series of slant column density of NO_x



7.4 Multi Axis DOAS

7.4.1 Recording light spectra

Settings: 7° : exp. Time: 250 ms
 exposures: 1000

12° : exp. Time: 500 ms
 exposures: 1000

30° : exp. Time: 500 ms
 exposures: 1000

four sets of Spectra were recorded

Set 1: 1:24 - 1:47 UTC

Set 2: 1:48 - 2:08

Set 3: 2:09

Set 4:

7.4.2 Max-DOAS evaluation

Set 1: 7° 13:23:40 UTC

$$\begin{aligned} O_3 &: (6,58 \pm 0,86) \cdot 10^{12} \frac{\text{mole}}{\text{cm}^2} & 197 - 282 \\ O_4 &: (4,78 \pm 0,09) \cdot 10^{43} \frac{\text{mole}}{\text{cm}^2} & 281 - 355 \\ NO_2 &: (6,44 \pm 0,18) \cdot 10^{16} \frac{\text{mole}}{\text{cm}^2} & 611 - 841 \end{aligned}$$

12° : 13:30:05 UTC

$$\begin{aligned} O_3 &: (0,26 \pm 0,032) \cdot 10^{12} \frac{\text{mole}}{\text{cm}^2} \\ O_4 &: (3,70 \pm 0,09) \cdot 10^{43} \frac{\text{mole}}{\text{cm}^2} \\ NO_2 &: (4,36 \pm 0,18) \cdot 10^{16} \frac{\text{mole}}{\text{cm}^2} \end{aligned}$$

Set 2: 7° : 13:48:02 UTC

$$\begin{aligned} O_3 &: (7,40 \pm 1,01) \cdot 10^{12} \frac{\text{mole}}{\text{cm}^2} \\ O_4 &: (5,19 \pm 0,10) \cdot 10^{43} \frac{\text{mole}}{\text{cm}^2} \\ NO_2 &: (8,72 \pm 0,19) \cdot 10^{16} \frac{\text{mole}}{\text{cm}^2} \end{aligned}$$

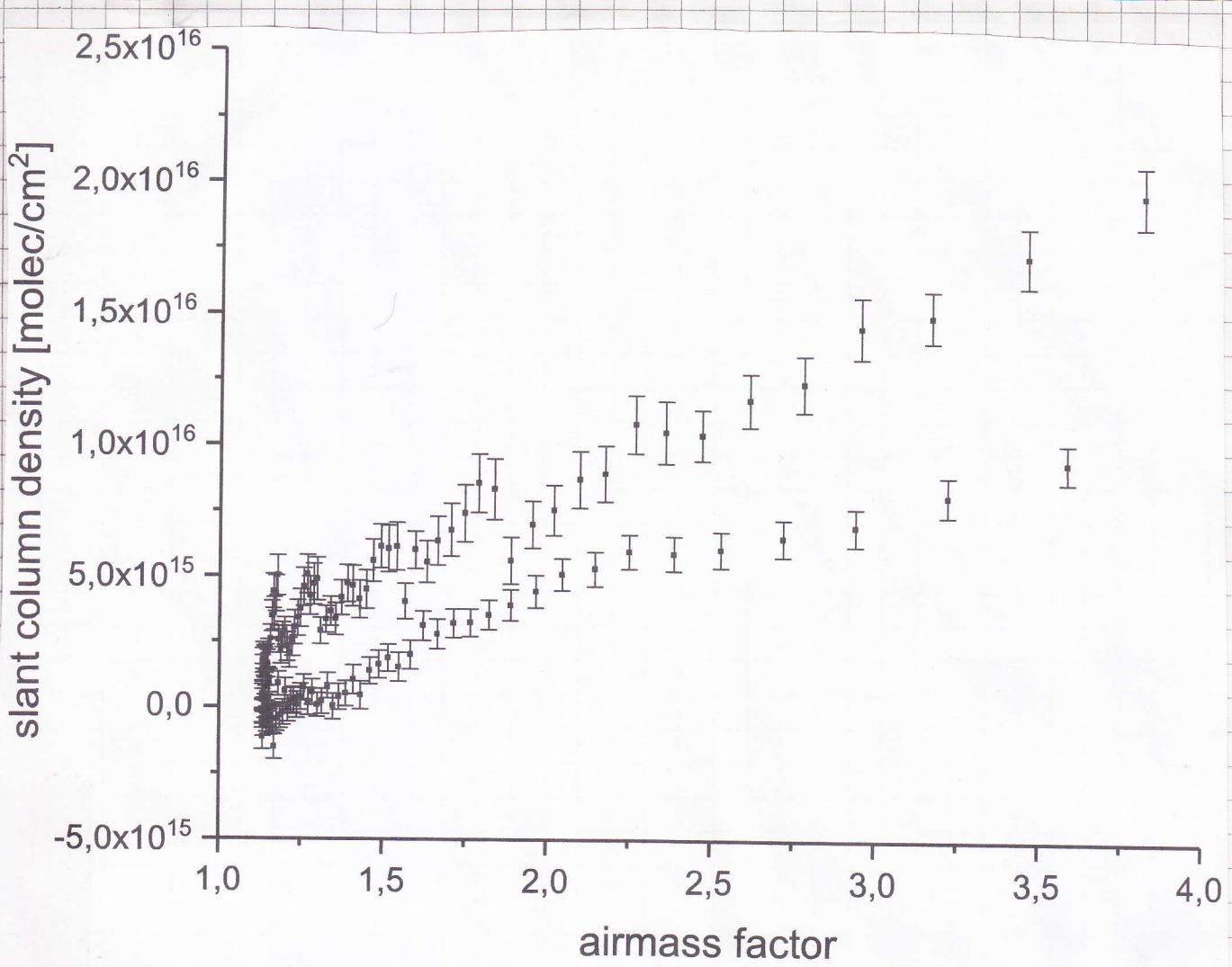
12°	13:53:06	0°C
O ₃	(7,98 ± 0,81) · 10 ¹⁷	mole/cm ²
O ₄	(3,89 ± 0,00) · 10 ⁴³	mole/cm ²
NO _x	(7,20 ± 0,17) · 10 ¹⁶	mole/cm ²

Set 3: 7°	14:08:28	
O ₃	(1,71 ± 0,21) · 10 ¹⁸	mole/cm ²
O ₄	(5,57 ± 0,12) · 10 ⁴³	mole/cm ²
NO _x	(1,02 ± 0,02) · 10 ¹⁷	mole/cm ²

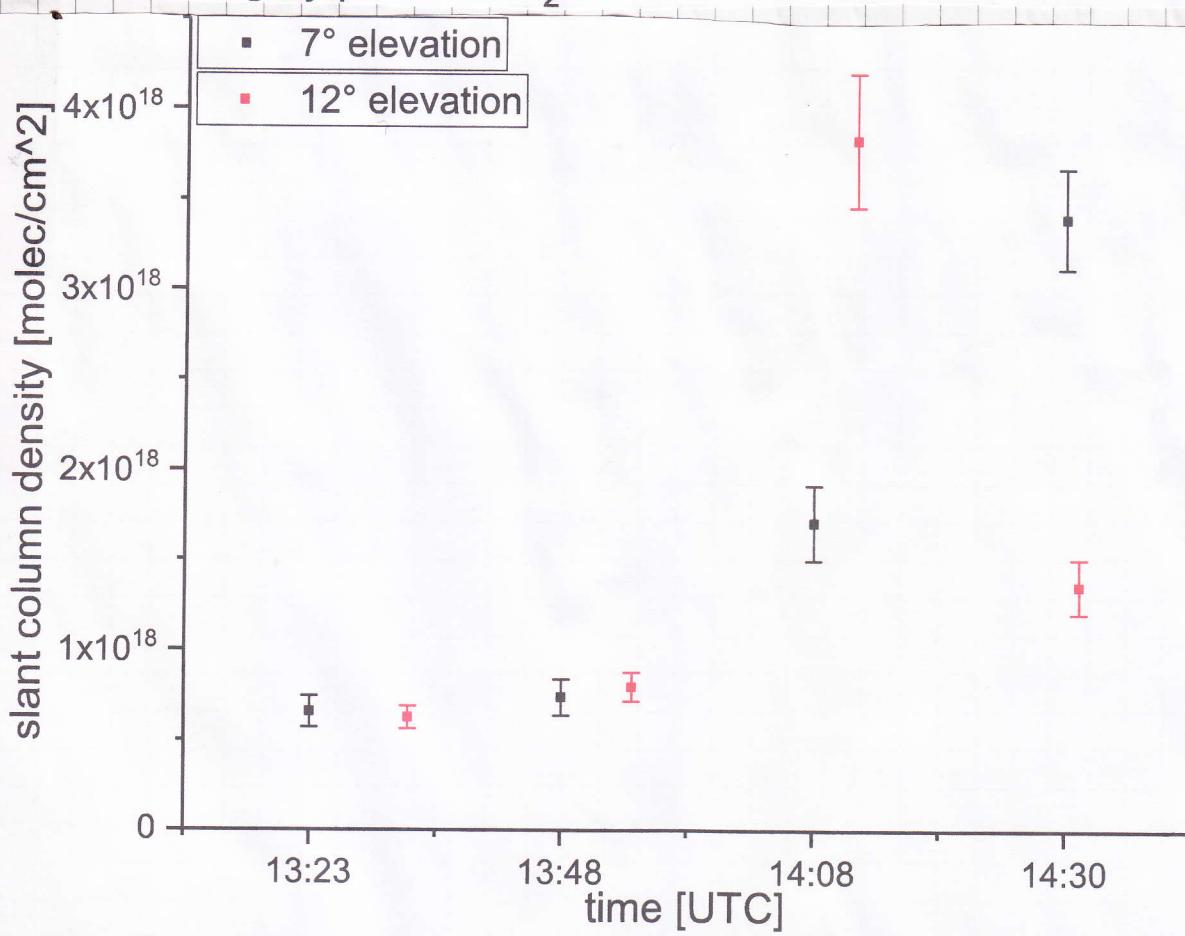
12°	14:13:25	
O ₃	(3,83 ± 0,17) · 10 ¹⁸	mole/cm ²
O ₄	(2,30 ± 0,35) · 10 ⁴³	mole/cm ²
NO _x	(7,23 ± 0,002) · 10 ¹⁶	

Set 4: 7°	14:15:20	14:20:54
O ₃	(3,40 ± 0,28) · 10 ¹⁸	mole/cm ²
O ₄	(5,54 ± 0,15) · 10 ⁴³	mole/cm ²
NO _x	(1,02 ± 0,03) · 10 ¹⁷	mole/cm ²

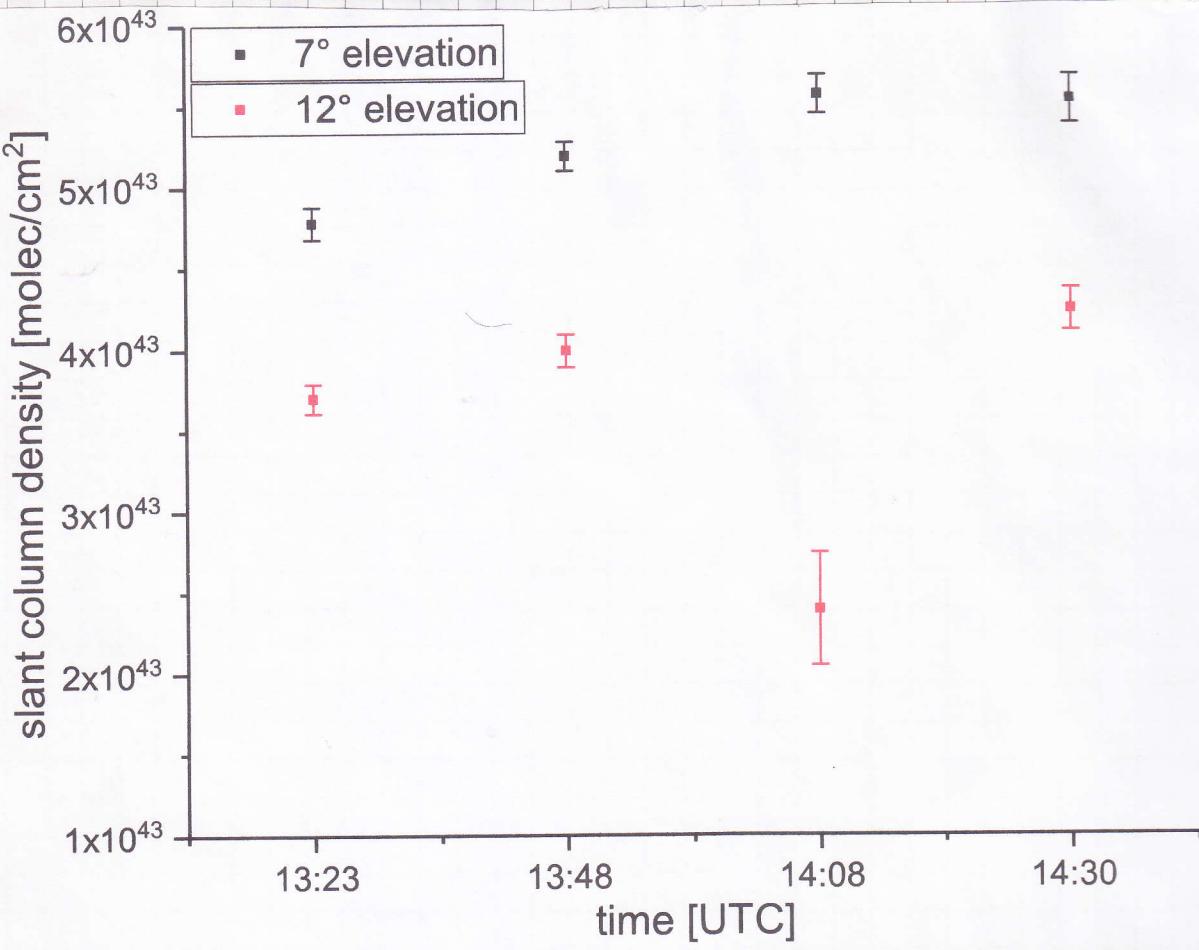
12°	14:35:07	
O ₃	(1,36 ± 0,15) · 10 ¹⁸	
O ₄	(4,24 ± 0,13) · 10 ⁴³	mole/cm ²
NO _x	(5,07 ± 0,28) · 10 ¹⁶	mole/cm ²



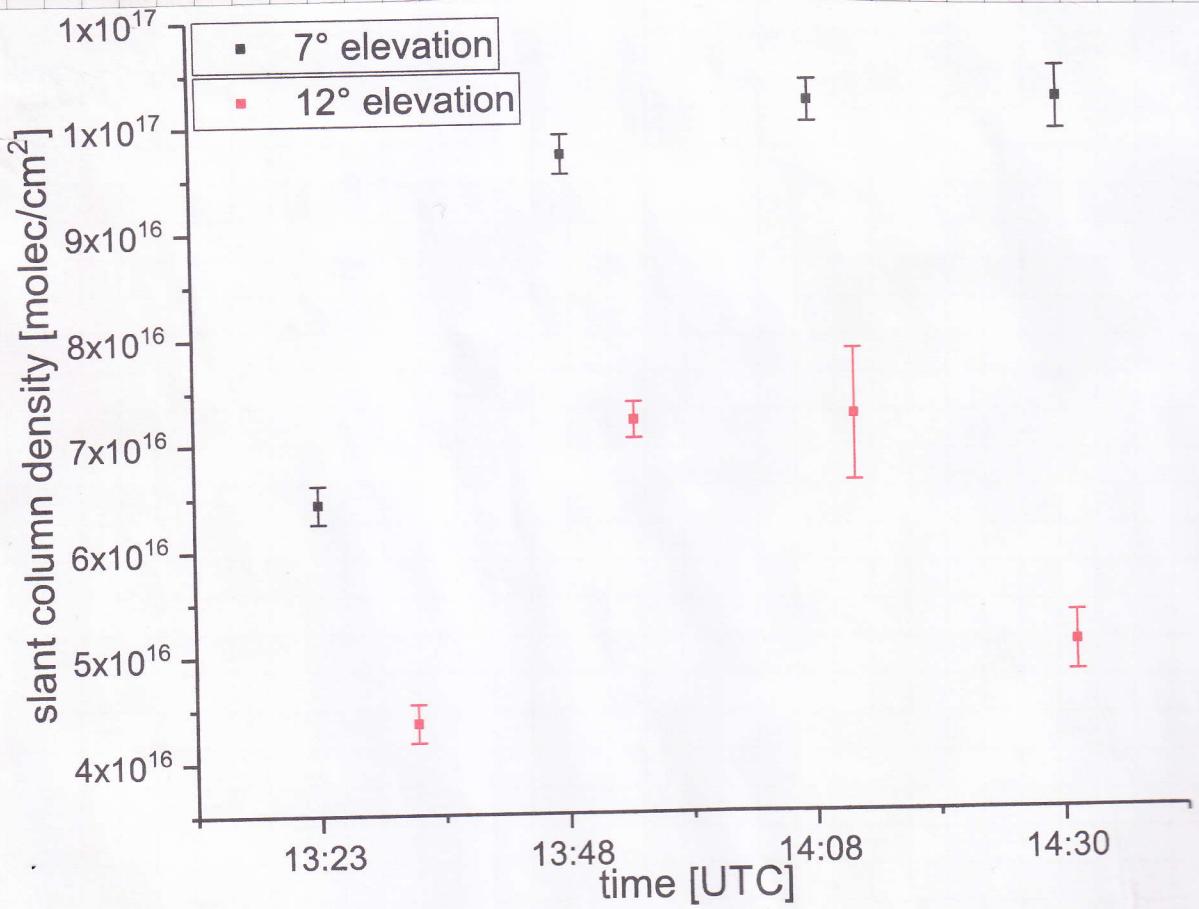
Graph 10: Langley plot of NO_2



Graph 11: slant column desity of O_3 with MaxDoas for two elevation angles



Graph 12: slant column desity of O_4 with MaxDoas for two elevation angles



Graph 13: slant column desity of NO_2 with MaxDoas for two elevation angles

Diskussion

During the course of this experiment, we measured the slant column densities of atmospheric trace gases and recorded their behaviour during the course of a day, as well as their distribution to troposphere and stratosphere.

We started by determining the instrumental offset, dark current, instrumental and total noise of the used spectrometer. All values measured with this spectrometer had to be corrected by these offset sources.

Comparing the instrumental and total noise, we can see that both decrease with an increasing number of exposures. The total noise is bigger than the instrumental noise.

Afterward we calibrate the wavelength output of the spectrometer by using a Hg-Lamp as reference. We also determine the optical resolution of the spectrometer and notice that it seems to be wave As discussed, this is due to dual lines wavelengths with a Resol wavelengths

We then started our actual mea:

mixing ratio in a glass cell. We did this in the laboratory using a halogen lamp (active DOAS). The NO_2 concentration could be determined to $p_{\text{NO}_2} = (2,91 \pm 0,08) \cdot 10^{-4} \text{ mol cm}^{-3}$ and the mixing ratio to $n_{\text{NO}_2} = (1,2994 \pm 0,0060) \cdot 10^5 \text{ ppm}$. This is a very high concentration of NO_2 , so high that we could actually see the brown gas with our bare eyes. To determine these values we used the fit function of the DOASIS program which gave us the slant column density. Furthermore the program plotted the fit residuals shown in graph 5. They give a measure for the quality of the fit and should be as small as possible. Ours were of the order 10^{-3} in most cases. They also show us if there are certain spots we want to exclude from our fit.

due to e.g.
dead pixels
in the CCD

We then DOAS me

measurmen^t we plot the slant column density for

almost constant for bigger
and decreasing for smaller

the NO_2 concentration and

mixing ratio in a glass cell. We did this in the laboratory using a halogen lamp (active DOAS). The NO_2 concentration could be determined to $p_{\text{NO}_2} = (2,91 \pm 0,08) \cdot 10^{-4} \text{ mol cm}^{-3}$ and the mixing ratio to $n_{\text{NO}_2} = (1,2994 \pm 0,0060) \cdot 10^5 \text{ ppm}$. This is a very high concentration of NO_2 , so high that we could actually see the brown gas with our bare eyes. To determine these values we used the fit function of the DOASIS program which gave us the slant column density. Furthermore the program plotted the fit residuals shown in graph 5. They give a measure for the quality of the fit and should be as small as possible. Ours were of the order 10^{-3} in most cases. They also show us if there are certain spots we want to exclude from our fit.

evaluation,
measurement was
done automatical-
ly ~~in the past~~
for our shows

a slight decrease during the day with a higher SCD at the early morning and in the evening. This makes sense, because sunlight during daytime splits the ozone. However, the two give us very accurate and reliable measurements for sunlight. The plot for

mainly light-path dependent!

very early and very late) don't always form but smaller SCDs.

Dewi & differential through measurement

less SCDs become very small. This can be explained by observe. While there is a constant more or less ozone in the stratosphere, NO_2 is usually the result of some kind of combustion process. This means that there is considerably more NO_2 in the air at weekdays and at times of high traffic. But we chose to observe a Saturday where traffic and industrial combustion were small, leading to small SCDs. Small peak in the plot can be explained by traffic, for example a truck passing by close to the measurement instruments.

Looking at the Langley plot of ozone, we see the expected linear form (for an AMF < 5). We can distinguish two lines close to each other. One represents the values taken in the morning and one representing the values in the evening. Through extrapolation from the Langley-Plot (for AMF values < 3.5), we determined the reference slant column density $SCD_{ref} = (7.71 \pm 0.08) \cdot 10^{-18} \frac{\text{ molec}}{\text{cm}^2}$. We also plotted the Langley-Plot for NO_2 which showed many fluctuations over the course of the day, because the NO_2 concentration experiences heavy and quick variations. (graph 10)

The vertical column density of ozone (graph 8a) shows a more or less constant plateau at about 275 DU which is only marginally smaller than the literature values acquired from <http://ozoneq.gsfc.nasa.gov> which are between 300-350 DU for Heidelberg. Our value might be too small due to the fact that it was a very sunny day and a lot of ozone was destroyed.

On the last day of the experiment we also did a MDT-PDOES measurement giving us information about the distribution of the gases in troposphere and stratosphere. The measurements for 7° elevation angle and 12° were almost

identical for ozone, implying that ozone can be found mostly in the stratosphere. (graph 11). In graph 12 we see the plot for O₃ which shows a gap between the T°- and the 10°-values, implying that O₃ can mostly be found in the troposphere. We see one point with a strong deviation of the others ~~which might~~ and a very big error. This might be caused by clouds or a measurement error. NO₂ shows a similar gap between T°- and 10°-values, meaning it can mostly be found in the troposphere.

General error sources which might have influenced all of our measurements are: Variations in light intensity, varying influences by traffic, too few measurement points for the Max-DOTS measures

andere Fehlerquellen:
Blickrichtung / Winkel
Filtereichweite

← Das ist ein sehr
kein Problem, ihr
hätt ja 1000x
jene Messpunkt
generieren / aufzubauen

Diskussion

During the course of this experiment, we measured the slant column densities of atmospheric trace gases and regarded their behaviour during the course of a day, as well as their distribution to troposphere and stratosphere.

We started by determining the instrumental offset, dark current, instrumental and total noise of the used spectrometer. All values measured with this spectrometer had to be corrected by these offset sources.

Comparing the instrumental and total noise, we can see that both decrease with an increasing number of exposures. The total noise is bigger than the instrumental noise.

Afterward we calibrate the wavelength output of the spectrometer by using a Hg-Lamp as reference. We also determine the optical resolution of the spectrometer and notice that it seems to be wavelength dependent being almost constant for bigger wavelengths with a resolution of roughly 560 and decreasing for smaller wavelengths.

We then started our actual measurements by determining the NO_2 concentration and mixing ratio in a glass cell. We did this in the laboratory using a halogen lamp (active DOAS). The NO_2 concentration could be determined to $p_{\text{NO}_2} = (2,91 \pm 0,08) \cdot 10^4 \frac{\text{mol}}{\text{cm}^3}$ and the mixing ratio to $n_{\text{NO}_2} = (1,2994 \pm 0,0040) \cdot 10^5 \text{ ppm}$. This is a very high concentration of NO_2 , so high that we could actually see the brown gas with our bare eyes. To determine these values we used the fit function of the DOASIS program which gave us the slant column density. Furthermore the program plotted the fit residuals shown in graph 5. They give a measure for the quality of the fit and should be as small as possible. Ours were of the order 10^{-3} in most cases. They also show us if there are certain spots we want to exclude from our fit.

We then made an automated measurement over the course of an entire day. Since the DOAS method needs sunlight, we chose a very sunny day, the 27.05.2017, for our measurement. We plot the slant column density for ozone and NO_2 . Ozone shows

a slight decrease during the day with a higher SCD at the early morning and in the evening. This makes sense, because the sunlight during daytime splits the ozone. However, the two extremes of the plot (very early and very late) don't give us very accurate information because at those times there wasn't enough sunlight. The plot for NO_2 has a similar form but smaller SCDs. During midday the NO_2 SCDs become very small. This can be explained through the day we chose to observe. While there is a constant more or less constant amount of ozone in the stratosphere, NO_2 is usually the result of some kind of combustion process. This means that there is considerably more NO_2 in the air at weekdays and at times of high traffic. But we chose to observe a Saturday where traffic and industrial combustion were small, leading to small SCDs. Small peak in the plot can be explained by traffic, for example a truck passing by close to the measurement instruments.

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