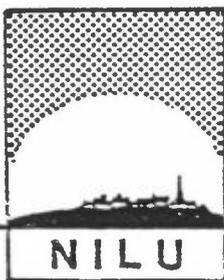


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MEASUREMENTS OF SULPHUR DIOXIDE IN THE PPB RANGE

S. Grochovsky



NORWEGIAN INSTITUTE FOR AIR RESEARCH

ROYAL NORWEGIAN COUNCIL FOR SCIENTIFIC AND INDUSTRIAL RESEARCH

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SUMMARY

The present report gives a detailed description of a coulometric instrument which can be used to measure very low sulphur dioxide concentrations in background air. The principles were tested by reconstructing a PW 9700 Philips monitor. For the measure system which is very stable, a sensitivity of $4 \mu\text{g SO}_2/\text{m}^3$ for a confidence level of 0.68 was obtained. This can be further improved.

MEASUREMENTS OF SULPHUR DIOXIDE IN THE PPB RANGE

The aim of the present study is to construct a coulometric instrument which can be used to measure sulphur dioxide concentrations in background air down to $1 \mu\text{g SO}_2/\text{m}^3$. In order to save time, it was decided to test the methods by reconstructing a PW 9700 Philips monitor. This instrument has a sensitivity of only $10\text{-}15 \mu\text{g SO}_2/\text{m}^3$, but it works on a coulometric principle. Most of the parts in this instrument could therefore be used in the new construction. It was decided to make only such changes that the original construction could be restored at any time.

In the following a technical description is given of the changes made and the test results.

1 MODIFICATIONS OF THE ELECTRONIC CIRCUIT

- a) The current generator for the electrolysis was substituted by a high intrinsic impedance source (Figure 1A).
- b) The output signal was increased by removing the resistive output voltage divider (Figure 1B).
- c) Introduction of a possibility for zero current compensation on the input resistor of the second amplifier (Figure 1B).

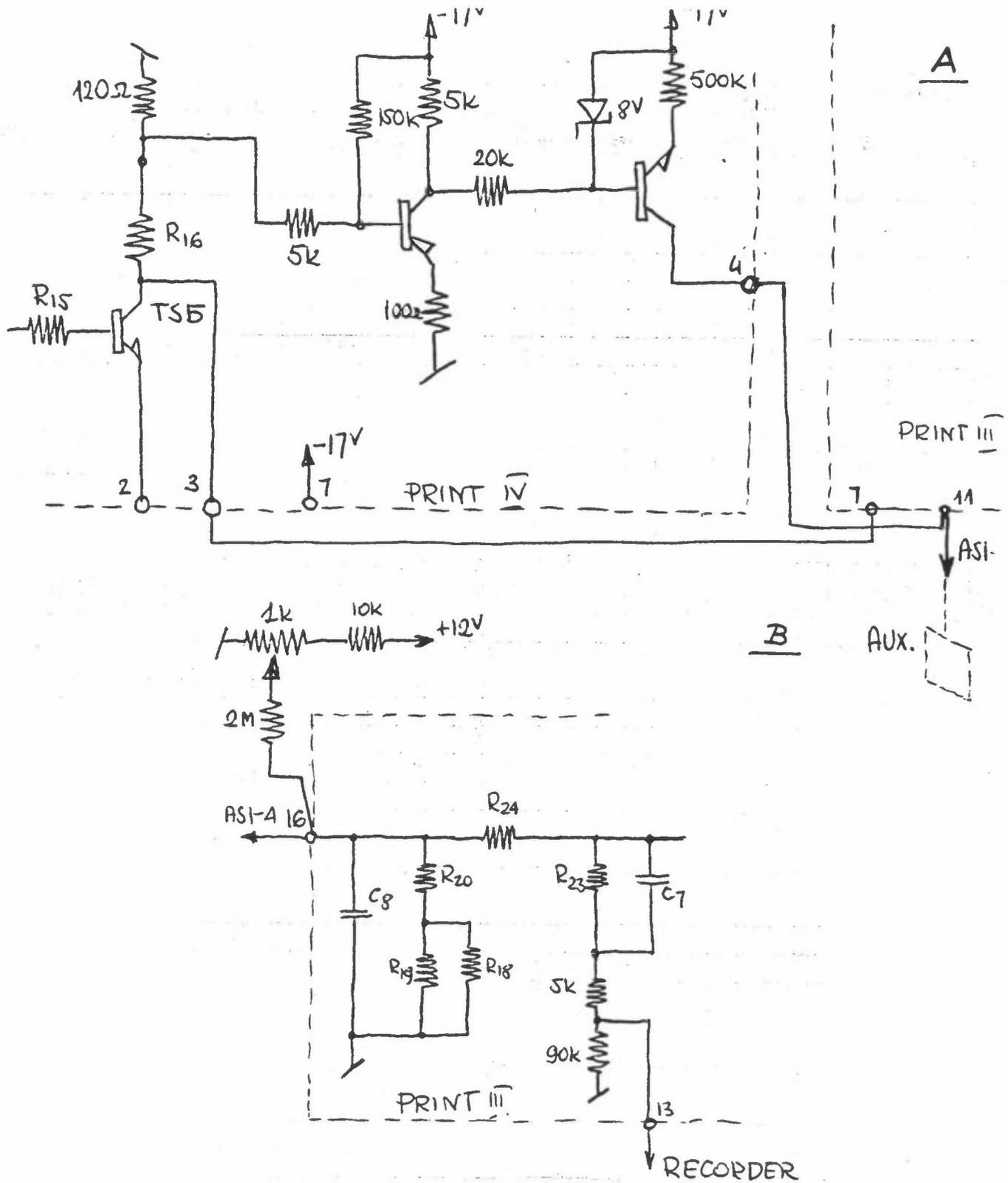


Figure 1: A. Modification of the current generator to increase the source impedance.

B. Modification of the amplifier output (voltage divider removed and zero current compensation possible).

2 MODIFICATIONS OF THE MECHANICAL CONSTRUCTION

- a) The communication orifice between the inner and outer vessel of the measuring cell had an internal diameter > 1 mm. This is too large and a new inner vessel for the measuring cell has been constructed (Figure 2).
- b) A more efficient filter was constructed for the sample intake (Figure 3A).
- c) An internal dust filter was added to the construction (Figure 3B).
- d) A new selective filter to remove ozon in the intake air was constructed (Figure 3C).

3 SPECIFICATION OF WORKING CONDITIONS FOR THE MONITOR

- a) Room temperature between $+ 10^0$ and $+ 25^0$ C.
- b) The length of the teflon tube between the sampling filter and the monitor must not exceed 150 cm.
- c) The sampling intake must be suitably located (no interference from building ventilation or other sources (chemical vapors, H_2S etc.), sufficient distance from other monitors generating enhanced concentrations of interfering gaseous components (ozone)).
- d) The sampler must not be exposed to mechanical shocks.

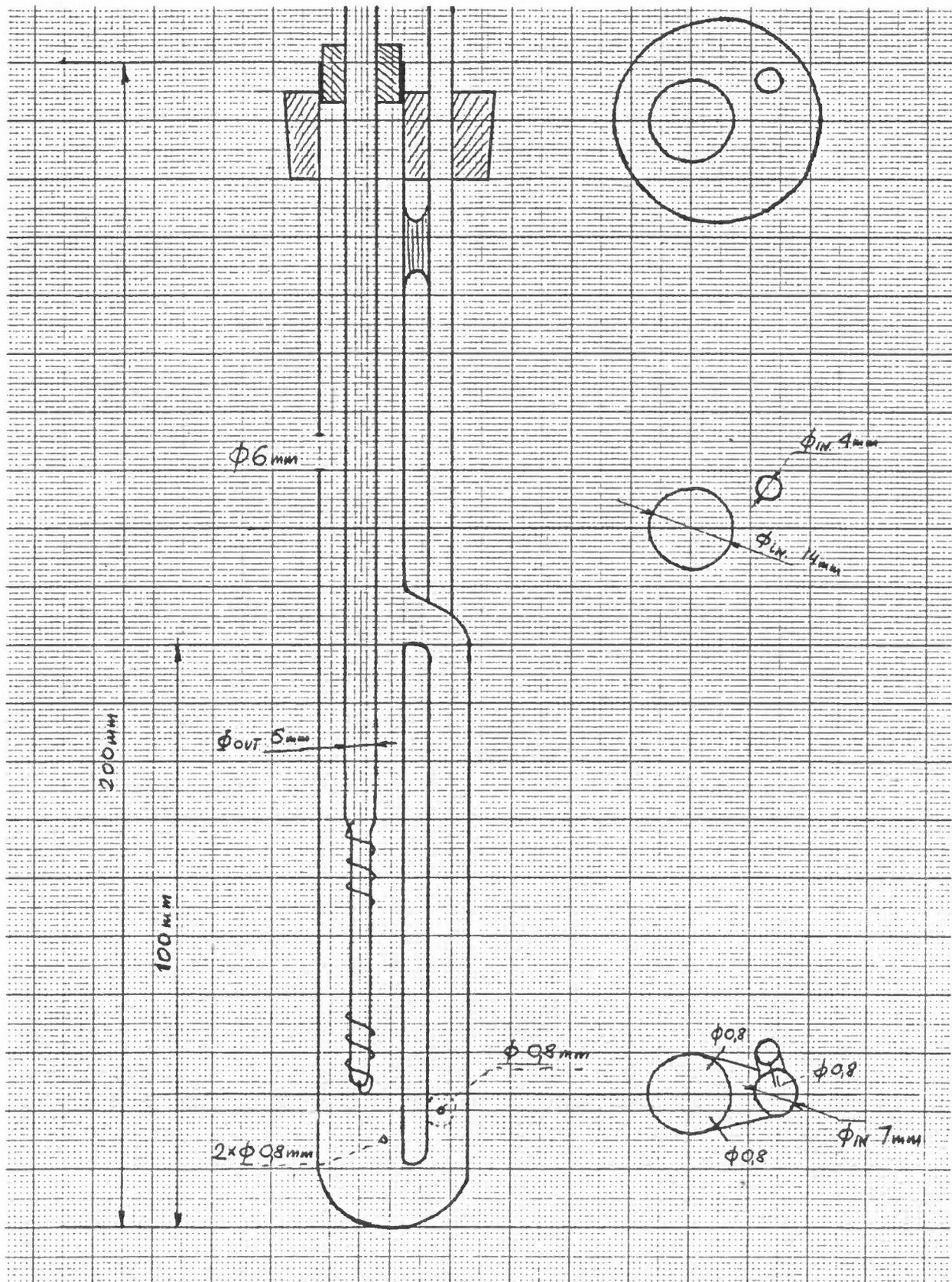
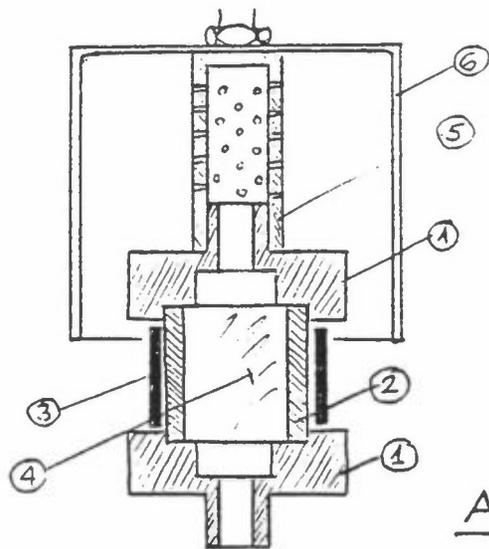


Figure 2: Modification of the inner reaction vessel.



SAMPLE DUST FILTER I (1:1)

1 - TEFLON

2 - GLASS

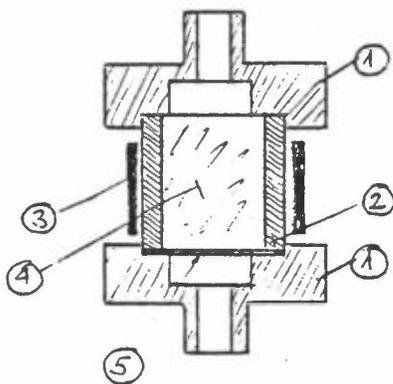
3 - HEATER 5W (110Ω)

4 - WOOL

5 - TEFLON

6 - PLASTIC CAP

A



INNER DUST FILTER (1:1)

1 - TEFLON

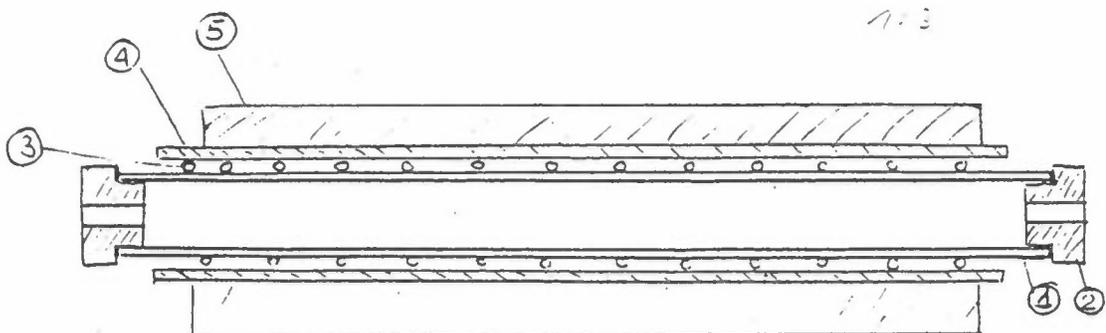
2 - GLASS

3 - HEATER 3W (180Ω)

4 - KVARC WOOL

5 - GLASS FIBRE FILTER

B



1. GLASS TUBE
2. TEFLON PLUGS
3. HEATER 45Ω (11W)
4. ASBEST CORD
5. THERMAL INSULATOR

C

(1:3)

Figure 3: A. Dust filter at sample intake.
 B. Construction of the internal dust filter.
 C. Heated glass tube to remove O_3 .

4 NOISE LEVEL EVALUATION

- a) Before the noise level can be evaluated, all transient processes must have reached equilibrium, and the vertical scale of the record must be calibrated (1 cm on the paper is equal to how many ppb or $\mu\text{g}/\text{m}^3$).
- b) The working conditions of the monitor must be kept constant during the period of examination (changes in main power supply, temperature, mechanical shocks, opening of the cover of the monitor, etc.).
- c) The tape recorder speed should be kept constant and
 $\geq 2 \text{ cm/h}$
- d) The mean noise amplitude should be $\geq 1 \text{ mm}$.
- e) The time required for the evaluation is $t \geq 12\text{h}$.
- f) If the difference between the mean noise amplitude at any concentration level and at zero level is less than 20%, the examination may be carried out at the zero level.
- g) Large and atypical amplitudes of noise may be neglected if the sum of their time occurrence does not exceed 0.1% of the total evaluation time t (see point e).
- h) Two lines are drawn on the recorder strip chartt strip (considering point g).
 First - for maximum zero signal
 second - for minimum zero signal
 The distance between these two lines should be calculated in ppb or $\mu\text{g}/\text{m}^3$.
- i) The distribution of the zero signal amplitude will be gaussian. Two times the standard deviation (2σ) is then equal to 68% of the valued determined under point h. This is our noise N expressed in ppb or $\mu\text{g}/\text{m}^3$. ($N \approx 2.6 = 0.68 d$)

k) The minimum signal which can be detected at a confidence level of 0.68 then becomes,

$$S = 2 N \text{ (ppb)}$$

5 EVALUATION OF THE LONG TERM ZERO FLUCTUATION

The minimum and maximum values of the mean zero level was determined as described under point 4 h). The difference between the two levels expressed in ppb is the long term zero fluctuation. The long term zero changes should show no tendency to increase or decrease. Otherwise, it means that the monitor is still in a transient stage.

Depending on the desired accuracy of measurements, the amplitude of the long term zero change determines the maximum time after which a new zero level has to be determined.

6 THE EFFICIENCY OF THE COULOMETRIC PROCESS

Generally, when the SO_2 passes through the measuring cell, the following process takes place:



Each molecule of SO_2 needs two electrons for its complete oxidation from S^{+IV} to S^{+VI} . Thus the equivalent weight of SO_2 is half the molecular weight (64/2). From the Faraday law follows

$$1 \text{ eq. w} = 96 \cdot 10^3 \text{ Cb}$$

$$1 \text{ Cb} = 0.33 \text{ mg SO}_2$$

This gives

$$1 \mu\text{A} \approx 1.2 \mu\text{g SO}_2/\text{h}$$

which is the general connection between the signal and the mass of gas in the coulometric process.

In the Philips monitor the sampling rate is 9 l/h of air. (this is controlled by a critical orifice). This means that a signal of 1 μA is obtained when the concentration of SO_2 in the ambient air is $130 \mu\text{g SO}_2/\text{m}^3$.

From the enclosed chart we find, (figure 4)

$$27 \mu\text{g SO}_2/\text{m}^3 = 15 \text{ steps} = 0.15 \mu\text{A}$$

Theoretically the output signal at this concentration of SO_2 should have been

$$27 \mu\text{g SO}_2/\text{m}^3 = 0.20 \mu\text{A}$$

This means the efficiency of the coulometric process in the measuring cell is

$$15/20 = 75\%.$$

This may be compared with data for the Novak-cell (Electrochemical measuring cell for SO_2 in ambient air - results from improvement step 2 - by Michael Oehme). From an electrochemical point of view the coulometric reaction with free iodine is identical to that of Br_2 in the Philips instrument. From Figure 3 in Oehme's paper we find that $45 \mu\text{g SO}_2/\text{m}^3$ gives an output signal from the cell of $1.9 \mu\text{A}$. In the Novak cell the air intake is 90 l/h. Thus, the cell receives $4 \mu\text{g SO}_2/\text{h}$. According to the Faraday law the output current then should be $3.3 \mu\text{A}$. Accordingly, the coulometric reaction efficiency is

$$1.9/3.3 = 60\%.$$

In each case the low reaction efficiency may be explained by an incomplete reaction between the SO_2 and the active agent, loss in the intake system or measuring cell by adsorption, or by side reactions.

To maintain stable working conditions of the cell, the free bromine concentration should not exceed 10^{-7} mol/l. It has been shown by measurement that the output air stream from the measuring cell is practically free from SO_2 .

It was also found that keeping the temperature constant, the efficiency factor of the cell does not change, when the SO_2 concentration is increased up to 5 mg/m^3 .

One straight forward way to increase the signal from the measuring system is to increase the air intake rate. However, in practice this may lead to additional problems such as,

- decreased efficiency of the cell
- increased noise
- increased evaporation rate of the electrolyte
- problems with the air sample intake
- problems with the sample pump and the flow rate stabilization

7 MEASUREMENTS OF THE LONG TERM ZERO FLUCTUATIONS

The monitor was switched on at 8 am. An example of the registration is given in Figure 4. (From strip chart A, not enclosed). After 24 hours stable conditions were obtained. All transient effects had disappeared. From this time the zero output was registered for 36 hours. During this run one small unit on the strip chart corresponded to $1.8 \text{ } \mu\text{g SO}_2/\text{m}^3$, and the data from strip chart A, showed that the long term zero level fluctuations did not exceed the value of one small unit, i.e. the mean value between the starting time and 36 hours will be

$$0.5 \times 1.8 = 0.9 \text{ } \mu\text{g SO}_2/\text{m}^3$$

As the short term zero fluctuations are statistically distributed, practically there will be no influence of long-term changes on the measurements, if the zero level is checked every 12 h.

8 SENSITIVITY MEASUREMENTS

The registrations on strip chart A showed no difference in the noise (short term) amplitude at zero and at $27 \mu\text{g SO}_2/\text{m}^3$ (see Figure 4). After stabilization, the noise amplitude of the instrument did not exceed ± 0.5 division. According to point 4 the noise of the zero level then becomes

$$2 \sigma = 0.68 \times 1 \times 1.8 = 1.2 \mu\text{g SO}_2/\text{m}^3.$$

Accordingly, the sensitivity becomes $2 \times 1.2 = 2.4 \mu\text{g SO}_2/\text{m}^3 = 0.9 \text{ ppb}$ for a confidence level of 0.68.

9 AMBIENT AIR MEASUREMENTS

In the first location (main ventilation room for the whole NILU building) vapors of ozone and ethylene produced by measuring instruments gave a strong negative signal (below zero level), regardless of whether the sample was taken from the room or from outside air.

After changing the location (distance from the first location about 20 m), ambient air concentrations were registered on strip chart B. The registrations showed a mean value of 10-20 $\mu\text{g}/\text{m}^3$ with accidental peaks as high as $60 \mu\text{g}/\text{m}^3$. Some times, during night (2100 - 0200) negative signals were also obtained (see Figure 5). Mean daily values determined by chemical analytical methods did not exceed $5 \mu\text{g}/\text{m}^3$. It was obvious that the monitor did not work correctly.

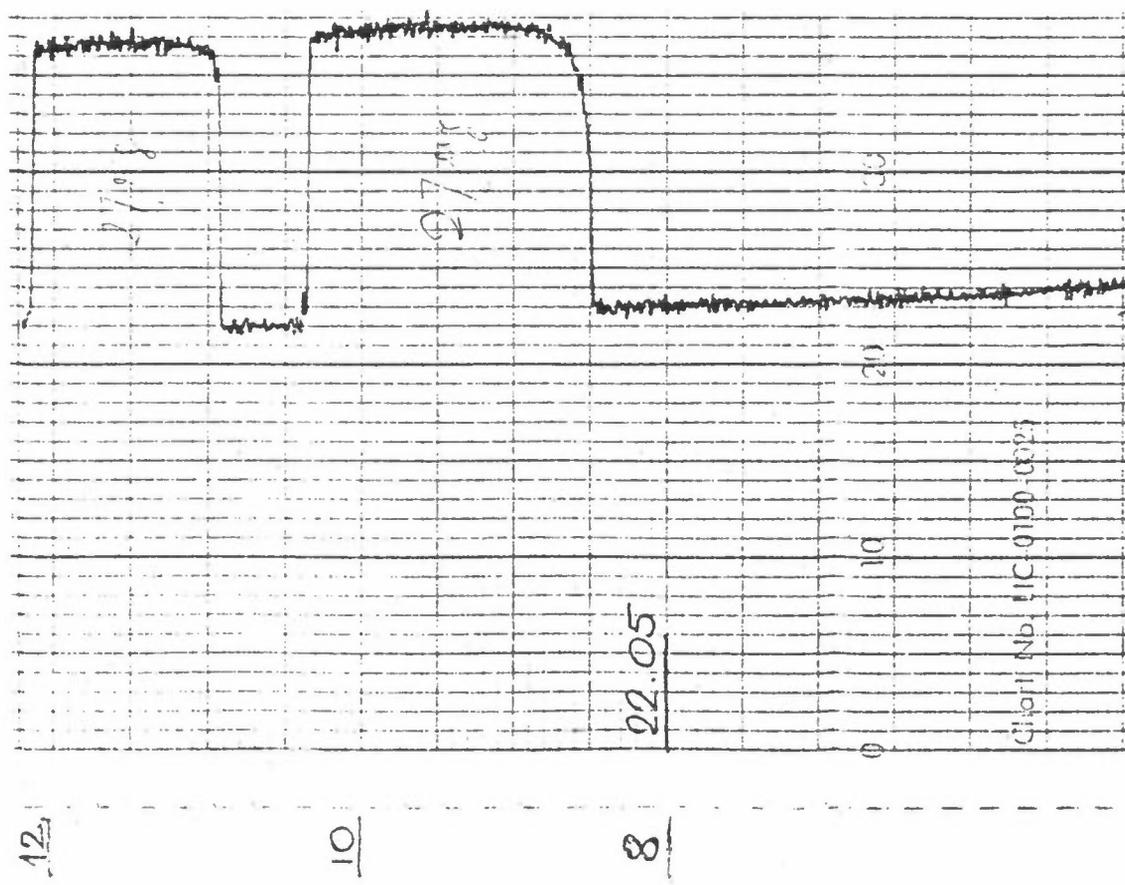


Figure 4: Noise level at zero and $27 \mu\text{g SO}_2/\text{m}^3$ after first improvement step.

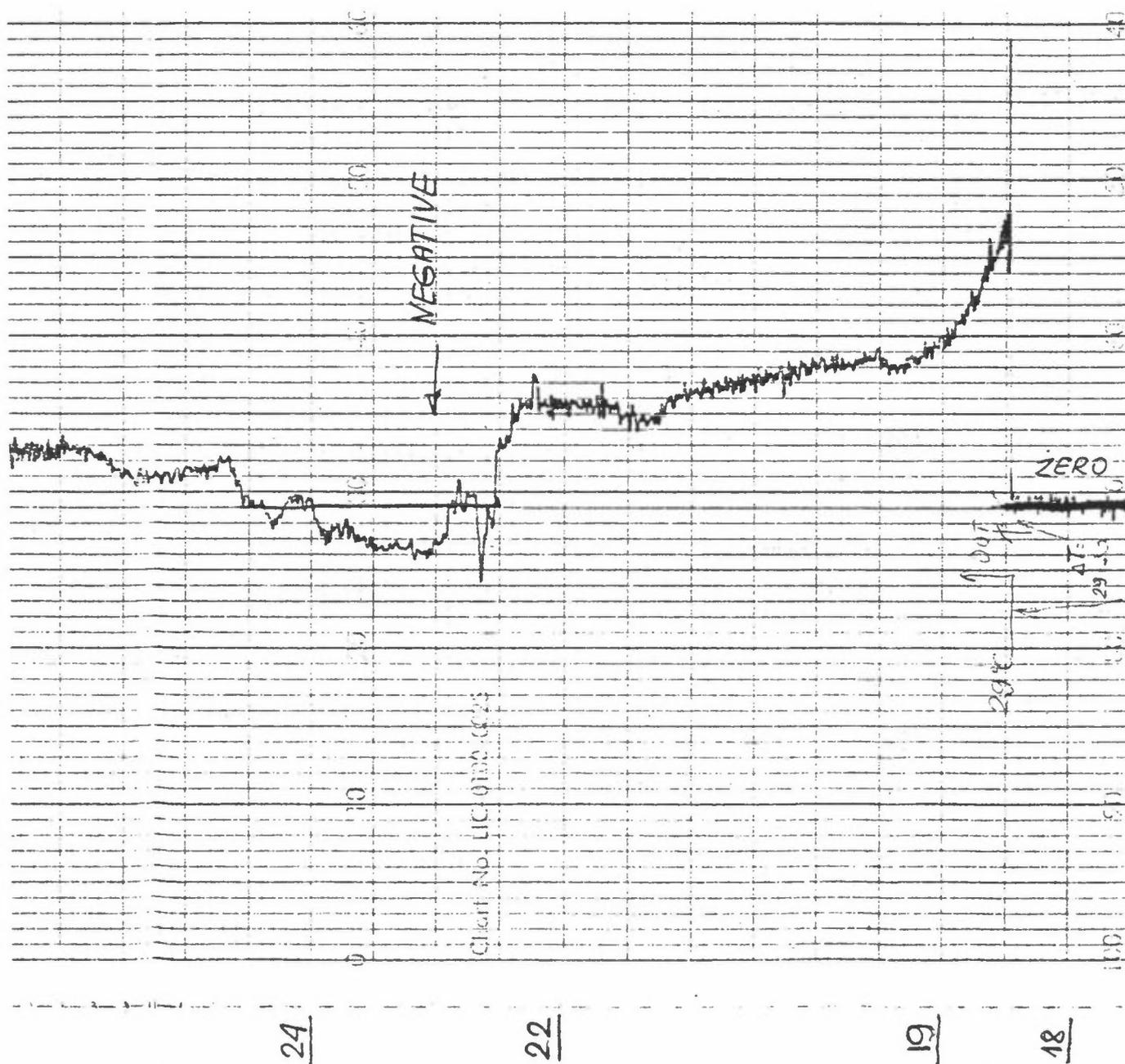


Figure 5: Negative signals obtained during night using the original Philips filter system.

10 INVESTIGATION OF THE SAMPLE INTAKE

The data from the experiments (see Figure 6) show that the materials used in the Philips filter housing (stainless steel coated with nylon), and in the NILU plastic filter holder, gave a positive monitor signal corresponding to 8-20 $\mu\text{g SO}_2/\text{m}^3$. The intensity of the signal increased with temperature. This interfering signal was all the time much greater than the SO_2 -signal, which means that the vapours from the filtering system initiate an unknown chemical reactions in the electrolyte (this is similar to the situation with acetone, see below). Such errors are not acceptable when the sensitivity of the system is to be 1 ppb.

Evidently, the sample intake must be built from materials which are inert to SO_2 and do not give off any kind of vapours which react in the measuring system. Accordingly, only glass and teflon was then used in the air intake. The best solution is to make the dust filtration in two steps, as mentioned in point 2.

11 CALIBRATION GAS SOURCES

The calibration and selectivity measurements required gas sources of SO_2 , of nitrogen oxides, and ozone with concentrations from several to some hundred ppb. When using the low concentration sources, the instrumental background must be very low. This means that special measures must be taken to clean properly the diluting air stream (clean air generator or special construction with char coal and particle filter) and the materials used.

The permeation rate from gas bottles with diaphragm and atmospheric pressure is practically constant at room temperature (+18 - +25⁰C). An exhausted Philips gas bottle was used as a low concentration SO_2 source. From chemical analysis the permeation rate of the bottle was determined to 13.5 $\mu\text{g}/\text{h}$. A

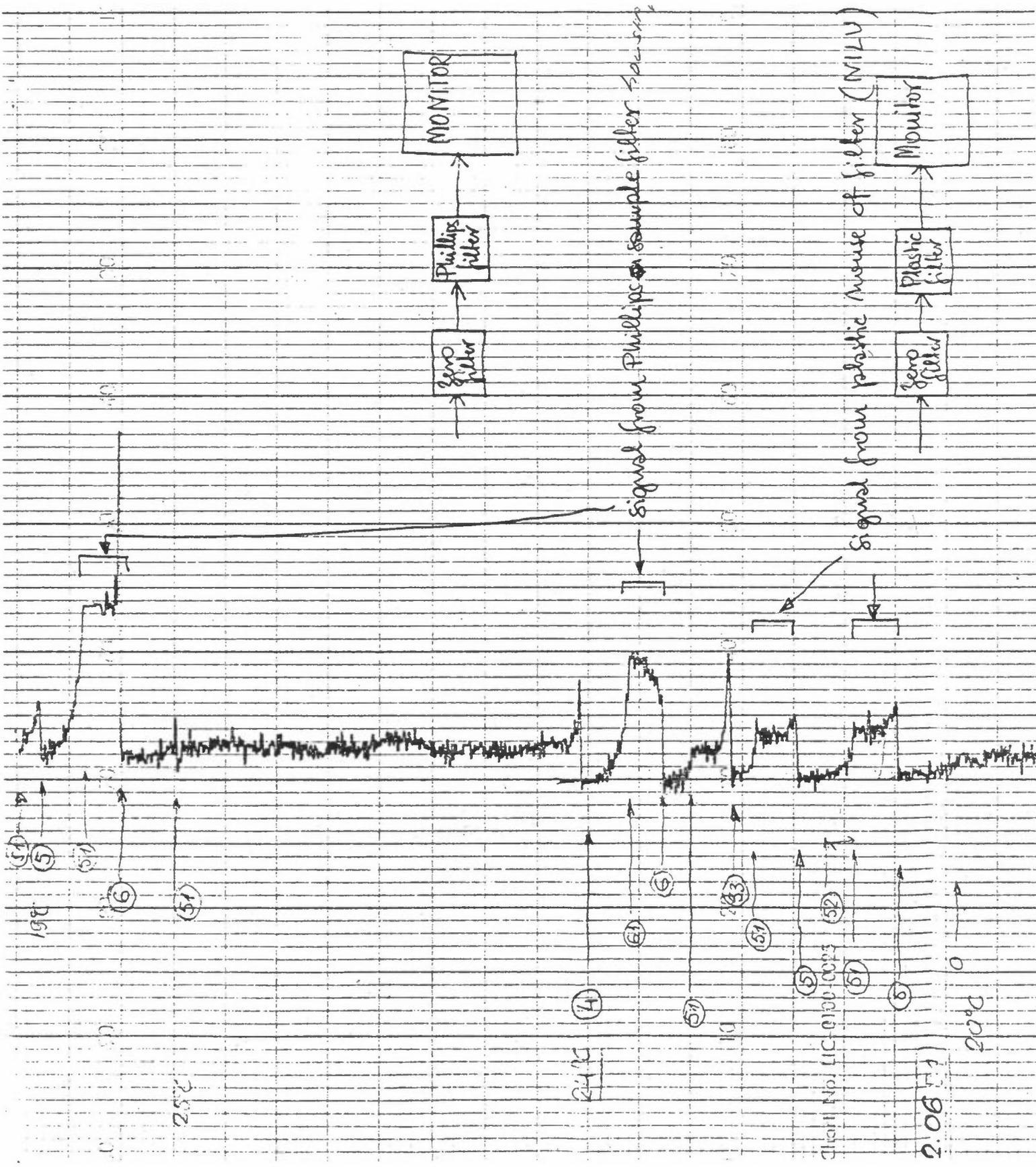


Figure 6: Interferences obtained from the original dust filter and from NILU filter holder.

concentration of $27 \mu\text{g SO}_2/\text{m}^3$ (9.6 ppb) was obtained with a diluting air stream as high as 500 l/h in the chamber. The quality of the dilution air was found to be good. No contaminants were detected at zero level from this source.

A liquid permeation tube ($2.5 \mu\text{g NO}_2/\text{min}$) from Instrument Calibration System Ltd was used as a NO_2 source. A diluting air stream of 1000 l/h gave a concentration of $150 \mu\text{g NO}_2/\text{m}^3$ (75 ppb) in the output decompression chamber.

The ozone generating part of a ML ozone monitor was used as a source for O_3 . The output concentration was 140 ppb.

12 SELECTIVITY MEASUREMENTS

O_3 is a strong oxidant and should therefore give a negative interference in the instrument. Philips also reports interference by NO_2 , all though NO_2 as a weak oxidant should not react with the Br^-/Br_2 system at all (at the working electrode potential used). Seven series of experiments were made in order to examine:

- the original Philips selective filter SF_1 (silver cartridge).
- a new selective filter SF_2 .

The silver content of the cartridge and the temperature of the filter were varied during the experiments. The general conclusions are as follows, (the records are on strip chart D, an example is given in Figure 7):

SO₂, silver cartridge out:

good response

SO₂, silver cartridge in :

new silver cartridge (purged in electric oven at 800⁰C)
retains all SO₂. After a few hours, the saturation process
is finished, and SO₂ passes through the silver cartridge.

After saturation, optimum transfer conditions through the
silver are obtained at temperatures between 80 and 200⁰C.

NO₂, silver cartridge out:

practically no response

NO₂, silver cartridge in :

negative response, amplitude increases with silver
temperature

O₃, silver cartridge out :

negative response decreases when temperature becomes
larger than 150⁰C

O₃, silver cartridge in :

practically no response

After mounting the selective filter SF₂ (see figure 3c) the
following situation was observed when the filter was kept at
200⁰C:

No response was observed for the following chemical vapours up
to 1 ppm tested: Methanol, benzene, toluen, cyclohexane,
n-hexane, isobutyl- methylketon.

A high positive response was observed for acetone vapours, and
the recovery time was very long (>40 minutes). This suggests
some unknown chemical reaction with the electrolyte and not a
coulometric reaction.

No response was found for NO₂. The NO₂ concentration was 1
ppm, and N₂ was used as a diluting gas. The mixture was
supplied from a bottle.

No response was observed for 140 ppb O₃.

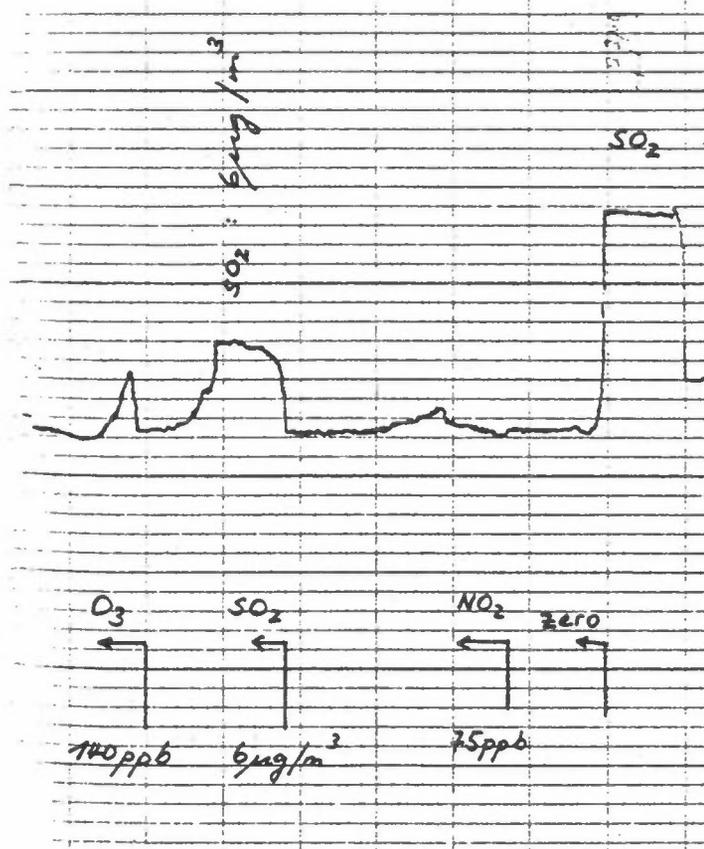


Figure 7: Influence of NO_2 (75 ppb) and O_3 (140 ppb) on zero-signal after mounting of the heated glásstube (see Figure 3C).

13 FINAL CONCLUSIONS

Of the halogens, iodine is most easily oxidized. Then comes bromine and chlorine. The system Br_2/Br^- does not respond to NO_2 , but ozone is a stronger oxidant and gives a negative response. The main role of the silver filter in the air intake is to retain any H_2S as silver sulphides. At higher temperatures silver also catalyses the decomposition of ozone. But, at the same time the silver also reacts in some unknown way with NO_2 . The result is a strong oxidizing reaction in the measuring cell. The reaction increases with temperature.

A main objective of the present work was to arrange the air intake in such a way that SO_2 passes to the cell, while O_3 and NO_2 are retained. More time and additional instrumentation will be needed in order to explain in detail the observed reactions.

The monitor with a modified air intake (silver wool removed) will be sensitive to H_2S . (Complete oxidation of H_2S from -2 to +6 releases 8 electrons. This means that at the same concentration the reaction of H_2S in the coulometric cell will be four times more sensitive than for SO_2 . However, the lifetime of H_2S in the atmosphere is extremely short due to its high reactivity. Significant concentrations of H_2S may be expected only close to emission sources.

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		OPPDRAGSGIVERS REF.	
OPPDRAGSGIVER (NAVN OG ADRESSE) NILU			
3 STIKKORD (å maks. 20 anslag) SO ₂ -monitor ppb-område luft			
REFERAT (maks. 300 anslag, 7 linjer) En kontinuerlig SO ₂ -monitor fra Philips ble modifisert. En nedre deteksjonsgrense på 1 µg SO ₂ /m ³ ble oppnådd ved et signal/støyforhold 2:1. Langtidsstabilitet og selektivitet mot NO ₂ og O ₃ ble undersøkt.			
TITLE See above			
ABSTRACT (max. 300 characters, 7 lines) A commercial continuous SO ₂ -monitor from Philips (based on a coulometric principle) was modified. A detection limit of 1 µg SO ₂ /m ³ (S/N 2:1) was obtained. Stability and selectivity aspects are discussed.			

* Kategorier: Åpen - kan bestilles fra NILU A
 Må bestilles gjennom oppdragsgiver B
 Kan ikke utleveres C