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INVESTIGATION OF THE KOH
IMPREGNATED FILTER METHOD FOR SO₂
SAMPLING

BY

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SUMMARY

The need for a more sensitive method for the determination of low concentrations of sulphur dioxide (SO₂) at Norwegian background stations, led to the present investigation of potassium hydroxide (KOH) impregnated filters for sampling of SO₂. This method had previously been used by NILU and several other groups in aircraft sampling with short sampling periods.

The two main parts of the investigation deal with the laboratory experiments and the field evaluation of the absorption efficiency of the impregnated filters, for sampling periods of up to several days. The report also describes the sampling equipment and the analytical procedures for the developed method.

Preliminary field measurements had shown that impregnated filters gave somewhat lower concentrations (with 7.5 µekv KOH/cm²) than the hydrogen peroxide absorption (OECD) method. This occurred under conditions where the loading of the filters never exceeded 40% of their theoretical sorption capacity for SO₂.

The laboratory experiments conducted at different relative humidities, face velocities and KOH densities, showed that filters with 15 µekv KOH/cm² have capacity to sample 15-20 µg SO₂/m³ air for 24 hours, with an efficiency close to 100%, at a face velocity of about 45 cm/s and relative humidities higher than 20%. Tests conducted at less than 5% relative humidity showed that the addition of glycerol to the KOH solution markedly increased the absorption capacity of the filter at such low humidities.

Field measurements always showed quite high correlations between the impregnated filter method and the hydrogen peroxide absorption method. However, the KOH impregnated filters sometimes showed

less than 100% absorption compared to the bubbler method. This might be due to very low ambient temperatures (down to -25°C) or to desorption of SO_2 from the filters, when changes in the ambient SO_2 concentrations occur. The addition of glycerol to filters placed indoors gave almost full absorption for 24 hours at relative humidities down to about 3-4% at a face velocity of 1.8 cm/s and a concentration of about $45 \mu\text{g SO}_2/\text{m}^3$.

The investigation has shown that for the SO_2 levels and climatic conditions usually found at Norwegian background stations, the impregnated filter method has a satisfactory absorption efficiency. The method has a much lower detection limit than the hydrogen peroxide (OECD) method, and allows concentrations down to $0.2 \mu\text{g SO}_2/\text{m}^3$ to be measured accurately.

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INVESTIGATION OF THE KOH IMPREGNATED FILTER METHOD
FOR SO₂ SAMPLING

1 INTRODUCTION

Alkaline impregnated filters for absorption of SO₂ for air sampling purposes was first described by Huygen (1963). Several authors have reported the use of such filters for aircraft sampling (Johnson and Atkins, 1975; Flyger and Fenger, 1976; Lusic et al., 1977; Semb, 1978). Some of these authors and others (Anda and Heggen, 1973; Lewin and Zachau-Christiansen, 1977) have studied the collection efficiency of filters impregnated with potassium hydroxide (KOH) at various relative humidities and filter face velocities. They all report satisfactory efficiencies at relative humidities higher than about 30%. Filter face velocities up to 80 cm/s have been used in some of the tests.

The use of impregnated filters could be expected to give the necessary increase in the sensitivity for SO₂ measurements since the volume rate of air sampled could be increased at least tenfold compared to the widely used absorption solution (hydrogen peroxide) method. This would be true if the collected SO₂ could be effectively extracted as sulphate from the filters in a reasonably small volume of water. The latter has not been a problem, and for the Thorin method the treatment of the resulting solution with a cation exchange resin for removing the potassium ions and neutralizing the solution has also worked quite well.

Aircraft sampling using impregnated filters has usually been performed at a high flow rate and during quite short sampling periods (max 1 hour), giving relatively small sample volumes. It was then considered important to verify the reportedly high collection efficiency of the impregnated filters also for exposure times extending to 24 hours under varying temperature and relative humidity conditions, as also suggested by Lusic et al. (1977).

Some laboratory and field evaluations were performed to investigate these questions. The results of these experiments are described in this report.

2 INTRODUCTORY FIELD EVALUATION

Tests using KOH impregnated filters (Whatman 40) for 24-h sampling of SO₂ were conducted at the background station Birkenes in Southern Norway during several months in 1975-77. The impregnation solution strength was about 7.5 µeqv/cm² of filter area, corresponding to a theoretical SO₂ capacity of about 240 µg SO₂/cm². Although the SO₂ loading on the filters never exceeded 40% of the theoretical SO₂ capacity, the tests indicated that the collection efficiency was not satisfactory as compared with the hydrogen peroxide absorption solution method. The impregnated filters gave on the average an SO₂ concentration of some 80 percent of that measured with the hydrogen peroxide method. This difference was not restricted to the lower range of SO₂ concentrations where the less sensitive hydrogen peroxide method was likely to systematically overestimate the concentration.

The same tendency appeared in the results of intercalibration tests conducted in Finland during the spring of 1977 (Lättilä et al., 1977) and the winter of 1978 (Ruoho et al., 1979). During the spring 1977 the impregnation solution strength was 7.5 µeqv/cm², and the SO₂ loading on the filters varied up to 50% of theoretical maximum, with a mean value of about 16%. In the winter 1978 tests, the impregnation strength was increased to 15 µeqv/cm², and the SO₂ loading varied between 19% and 75%.

3 DESIGN OF TESTING AND SAMPLING EQUIPMENT

The presently used equipment for impregnated filter sampling at NILU has been developed concurrently with the laboratory and field tests done in the period 1975-78.

The main design criteria were:

- sampling rate sufficiently high to determine accurately typical background SO₂ concentrations in Norway,
- operation of the impregnated filter at ambient temperature and humidity conditions.

The latter criteria seemed necessary, as the work by Lewin (1975) has shown clearly the poor absorption efficiency of KOH impregnated paper filters at low relative humidities (<30%). Such low relative humidities would be expected to occur at the filter surface especially during winter conditions, if the filter were to be placed inside a shelter at room temperature.

The sampling equipment basically consists of an air intake with the filter holder placed inside it, a dry gas meter, and a diaphragm pump. The equipment operates semi-manually, with a timer starting and stopping the sampling at preset times of the day.

The filter holder holds two filters in series. A prefilter prevents aerosol particles from reaching the impregnated filter, which is placed immediately after the prefilter with a separating screen between them.

The sampling equipment, with minor design variations, has been tested in the laboratory and at the field test station at NILU intermittantly since the autumn of 1976, at Birkenes field station continuously from the same time (except for the period May 1977 - May 1978), and by the Finnish Meteorological Institute (a simplified version) in the spring of 1977 and winter of 1978.

The testing has lead to the following improvements and modifications since the first test model:

- the filter holder was changed from "in-line" to "open face", as the tube entrance sometimes caused problems. During cold winter periods with high relative humidity ice formed

at the entrance of and inside the holder and at the prefilter surface.

- the filter holder was modified to include a separating screen between filters, as when glycerol was added to the impregnating solution, the prefilter rear side was impregnated to some degree by the solution of the impregnated filter.
- the air intake was modified slightly due to changes in the prefabricated parts used.

A schematic drawing of the equipment is shown in Figure 3.1. The present design of air intake, filter holder and control unit is shown in Figures 3.2 and 3.3.

3.1 Air intake

The function of the air intake is to provide a shelter for the filter holder such that neither precipitation nor sunshine will influence the sampling efficiency.

To prevent radiative heat from sunshine to heat the air surrounding the filter holder (this would reduce the relative humidity at the filter surface), the intake is provided with an insulating layer of polyurethane foam (approx. 1 cm thick) as well as a outside coating of aluminium foil. Laboratory tests at NILU have shown that a design similar to the one shown in Figure 3.2 prevents the temperature inside the intake to differ by more than 1°C from the ambient temperature on sunny midsummer days at Lillestrøm.

The present shape of the air intake, together with the air flow rate, does not prevent the wind speed to influence the upper cut-off diameter of the aspirated particles. With the present design, the air speed vertically through the intake opening is approximately 5.5 cm/s. An indication of the influence of the wind speed upon the sampling efficiency of the air intake is given by the results of wind tunnel tests done by Steen and Johansson (1975).

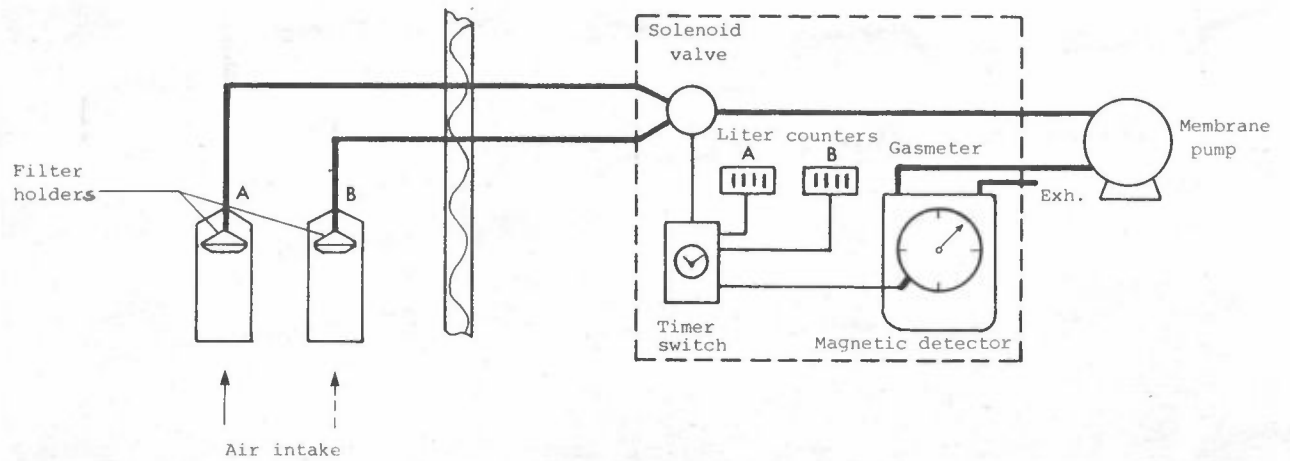


Figure 3.1: Schematic drawing of equipment for impregnated filter sampling.

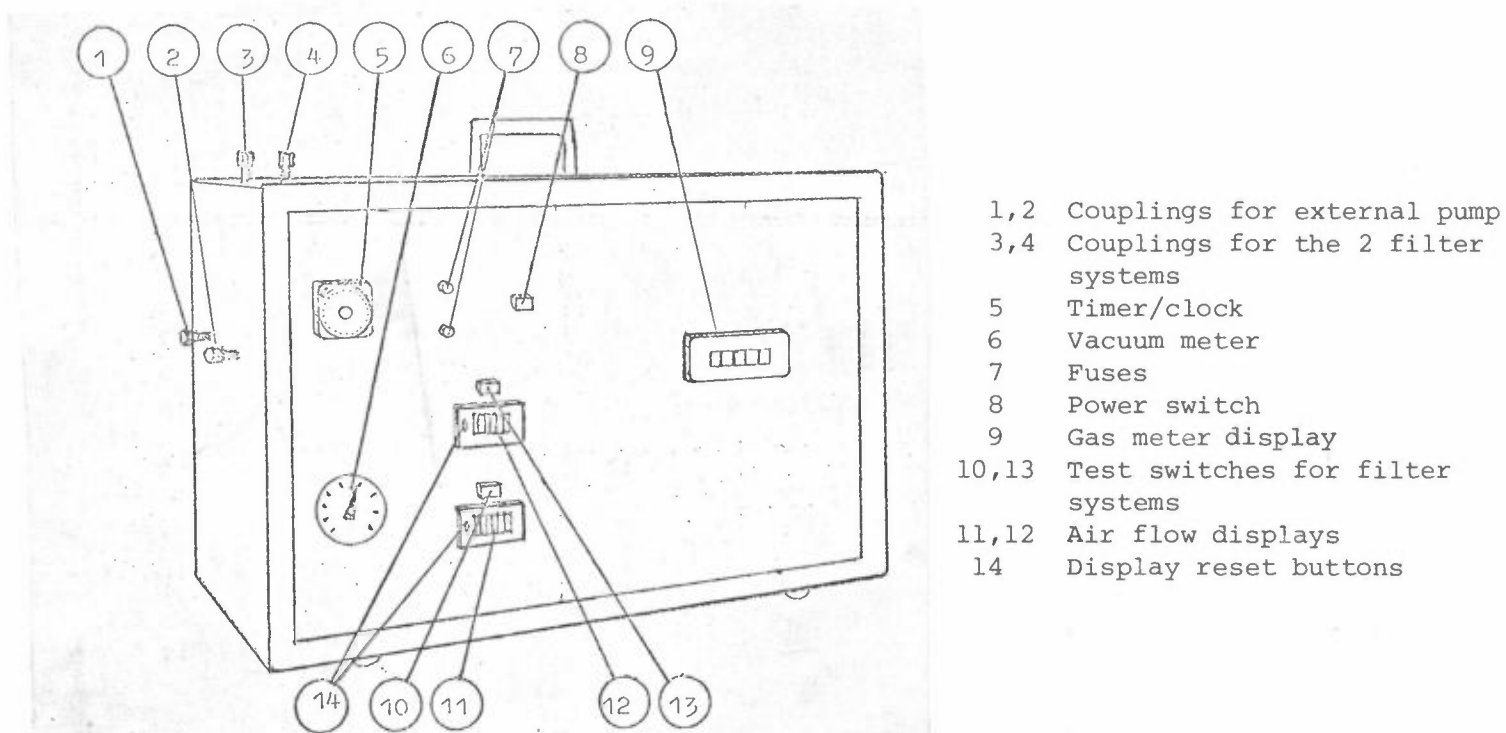


Figure 3.2: Present design of sampler control unit.

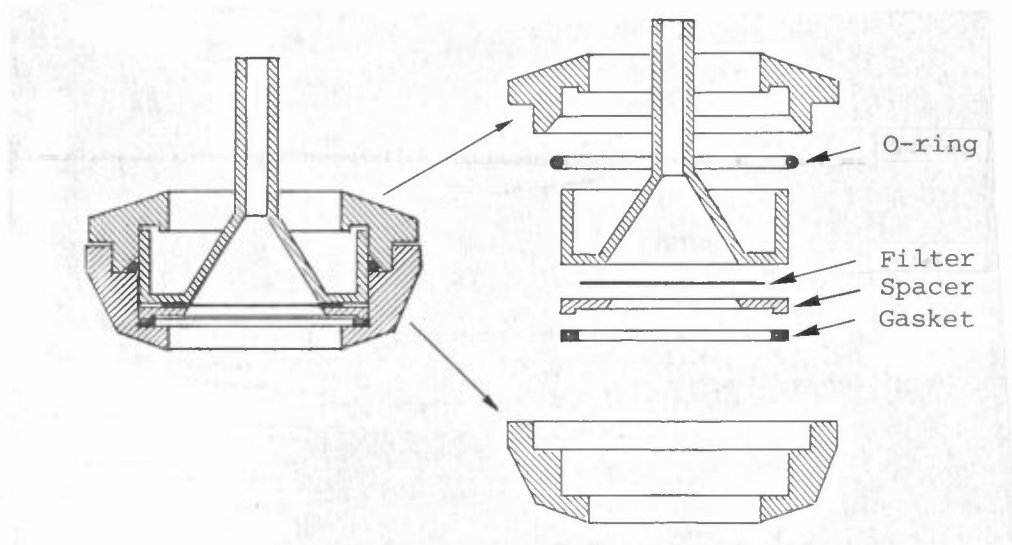
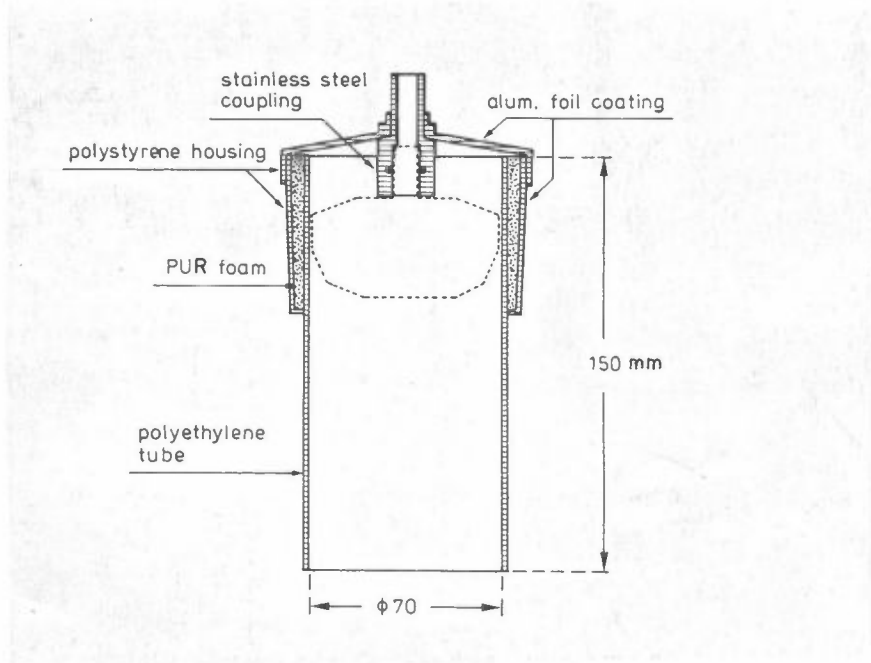


Figure 3.3: Air intake and filter holder designs.

3.2 Filter holder

The filter holder is made from polyethylene. It is an open-face filter holder with an effective opening diameter of 25 mm. A polypropylene screen (Propyltex 140-105 μm) provides the separation between the prefilter and the impregnated filter.

3.3 Control unit

It is an advantage for background station operation that the station attendant would not be required to be at the station at an exact time each day to change samples. The present sampling equipment therefore includes a double air intake unit, and the control switches the air flow from one air intake/filter holder unit to the other at a preset time of the day. This is done by means of two magnetic valves and a timer.

A magnetic detector detects each revolution of the gas meter, and two electronic counters, connected to the timer, provide a reading of the total air flow of each sample.

3.4 Pump

A diaphragm vacuum pump has a relatively low power requirement, and an acceptable noise level. At present a Gast pump, model DOA-121 BG is used. It pulls an air flow of approximately 12-13 l/min through two Whatman 40 cellulose fiber filters.

4 LABORATORY EXPERIMENTS

Laboratory investigations of the efficiency of KOH-impregnated filters for absorption of sulphur dioxide have been previously carried out by Lewin (1975), and Lewin and Zachau-Christiansen (1976).

After a 30-min. sampling period, with variable conditions of temperature and humidity, the absorption efficiency of Whatman 41 (W41) filters impregnated with $17 \mu\text{eqv}/\text{cm}^2$ was found to be:

- better than 95% for relative humidities above 20% (at 25°C), but dropping off rapidly at lower humidities;
- acceptable for SO_2 loadings up to about 50% of the theoretical;
- a function of relative humidity rather than absolute humidity, in the temperature range $-10^\circ\text{C} < T < 25^\circ\text{C}$.

Use of the impregnated filter method for determination of SO_2 at background sampling stations, as within the EMEP network, would normally require that the sampling period is extended to 24h. In addition, relative humidities below 20% at the filter surface may occur under extreme conditions. It was therefore desirable to ascertain the sampling efficiency under 24-h sampling exposures, and at the same time to investigate possibilities of improving the absorption efficiency under conditions of low relative humidity. The experiments were designed to evaluate the absorption efficiency of KOH impregnated filters as a function of:

- sampling time and SO_2 loading,
- KOH concentration of the impregnating solution,
- a glycerol additive.

4.1 Experimental setup

The experiments were conducted by aspirating SO_2 containing air through cellulose fiber filters (Whatman 40) impregnated with varying amounts of KOH and glycerol. Filters of 42 and 50 mm diameters were used with effective exposed filter areas of 25 mm

or 42 mm respectively. The SO₂ in the sample air was provided by a permeation tube system.

The relative humidity conditions of the tests were produced by letting the sample air pass through a climatic test chamber or a deep freeze. The relative humidity of the sample air was calculated from the dew point measurements inside the climatic chamber, or by the temperature in the deep freeze (assuming 100 percent saturation), and by the temperature at the impregnated filter, which was kept at room temperature.

The characteristic test parameters of the two series of tests are shown in Table 4.1.

Table 4.1: Characteristic parameters of test series.

	Series I	Series II
Air flow rate, l/min	≈ 1.5	12-13
Face velocity at filter, cm/s	≈ 1.8	≈ 42
SO ₂ concentration, µg/m ³	≈ 380	≈ 46

The purpose of series I was to investigate the effect of the concentration of the KOH solution and of a glycerol additive on the absorption efficiency as a function of time and SO₂ loading. During this series, the penetration of SO₂ through the filter was monitored by means of an electrochemical cell (Novak, 1965) giving a continuous record of the SO₂ concentration.

The purpose of series II was to run similar tests with sampling parameters close to those of the impregnated filter method proposed for the EMEP network.

The experimental setups of the tests are shown in Figure 4.1.

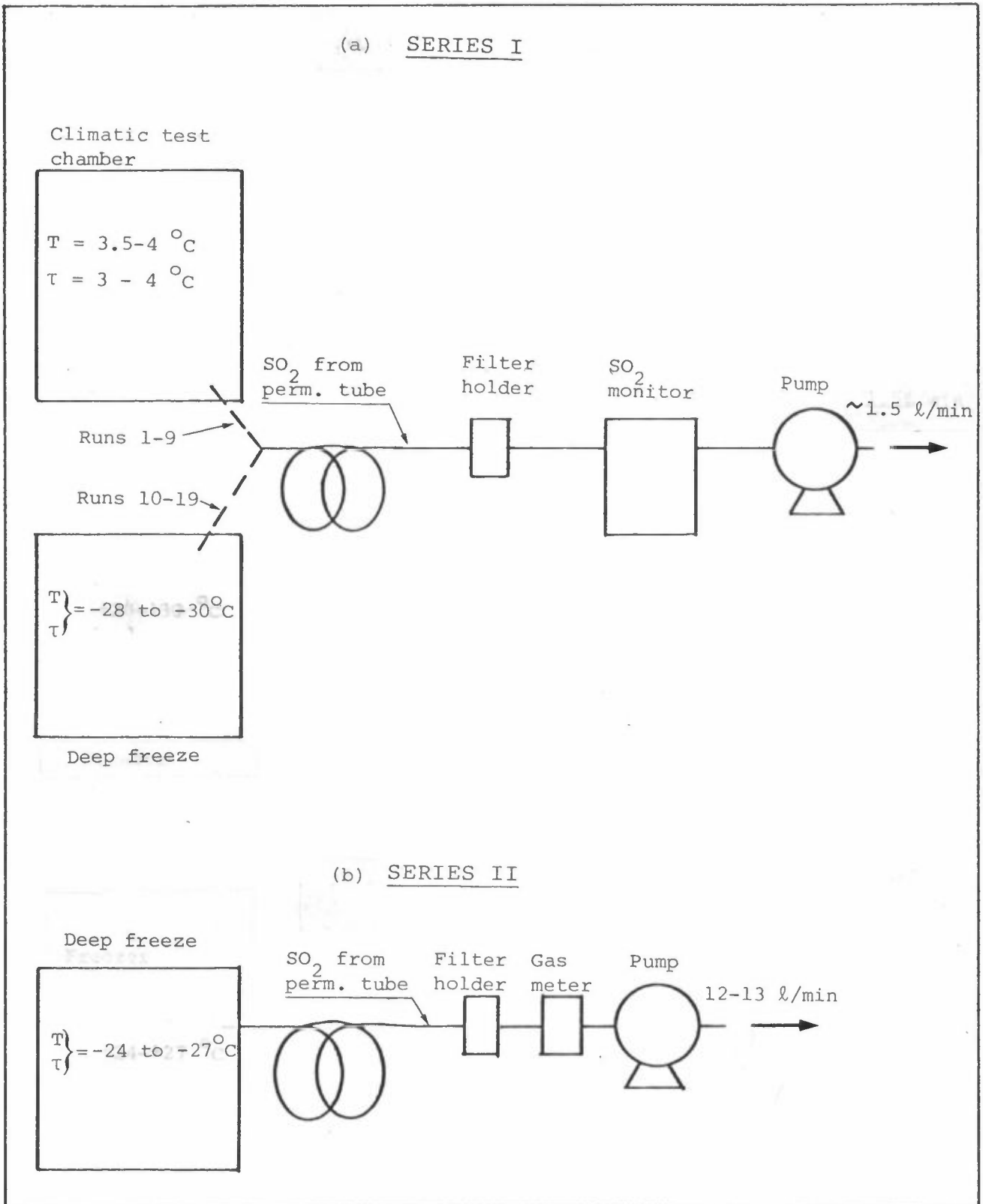


Figure 4.1: Schematics of experimental setups.

4.2 Analytical procedures

4.2.1 Filter impregnation

Solutions of different concentrations of KOH and glycerol were made by dissolving analytical grade KOH (containing less than 0.01% of sulphate) in distilled water. A given volume of glycerol (analytical grade) was then added. The concentrations of glycerol are expressed in percent by volume.

The filters were placed horizontally on polyethylene screw caps, and the impregnation solution added dropwise with a micropipette. An amount of about 15 μl per cm^2 filter area wetted the whole surface. For a 0.5N KOH solution, this corresponds to about 7.5 $\mu\text{eqv KOH}/\text{cm}^2$, and a theoretical absorption capacity of about 240 $\mu\text{g SO}_2/\text{cm}^2$, or 3.8 $\mu\text{eqv SO}_2/\text{cm}^2$. The filters were dried overnight at room temperature in a drying chamber with silica gel. After drying, the impregnated filters were stored in air-tight polyethylene bags.

4.2.2 Analysis of SO₂

After SO₂ sampling the filters were placed in polyethylene beakers. A measured volume of distilled water was added together with two drops of 30% hydrogenperoxide to oxidize all the absorbed SO₂ to SO₄²⁻. After being left overnight, about 10 mg of a cation exchange resin in acid form (Dowex 50) were added, and the beaker was swirled for a few seconds to remove potassium ions and neutralize the solution. The resulting solution was then analysed for sulphate with the automated Thorin method (Henriksen and Bergman Paulsen, 1974; NILU 1977).

4.3 Results and discussion

4.3.1 Absorption efficiency of 7.5 $\mu\text{eqv KOH/cm}^2$ impregnated filters as a function of time at various humidity conditions. Effect of a glycerol additive (face velocity 1.8 cm/s)

Figure 4.2 shows the penetration of SO_2 through W40 filters under the following conditions:

Impregnation solution : 0.5 N KOH ($15 \mu\text{l/cm}^2$) with/without glycerol
Sample flow : 1.5 l/min
 SO_2 -concentration : $380 \mu\text{g/m}^3$
Face velocity : 1.8 cm/s
Relative humidity : 10-30%
Prefilter (Whatman 40) in front of impregnated filter, unless noted otherwise.
 SO_2 loading after 24 hours of exposure: $\approx 25\%$.

The SO_2 loading is the ratio of the total amount of SO_2 the filter has been exposed to at the end of the test to the theoretical absorption capacity of the total amount of KOH added to the filter.

A 10% SO_2 loading is equivalent to approximately $24 \mu\text{g SO}_2$ per cm^2 of exposed filter area, when the impregnation is $7.5 \mu\text{eqv KOH/cm}^2$.

Figure 4.2 illustrates the following results, valid for a $7.5 \mu\text{eqv/cm}^2$ impregnation strength:

- at 20-30% relative humidity (RH) the impregnated filters have an acceptable absorption efficiency for 8-15 h exposure. After 8-15 hours of exposure a breakthrough of SO_2 occurs, resulting in an SO_2 loss that increases with time. The breakthrough occurs at an SO_2 loading of approximately 10-15%. The total loss for 24h exposures may then reach at least 15% (Tests 1, 2, 5).

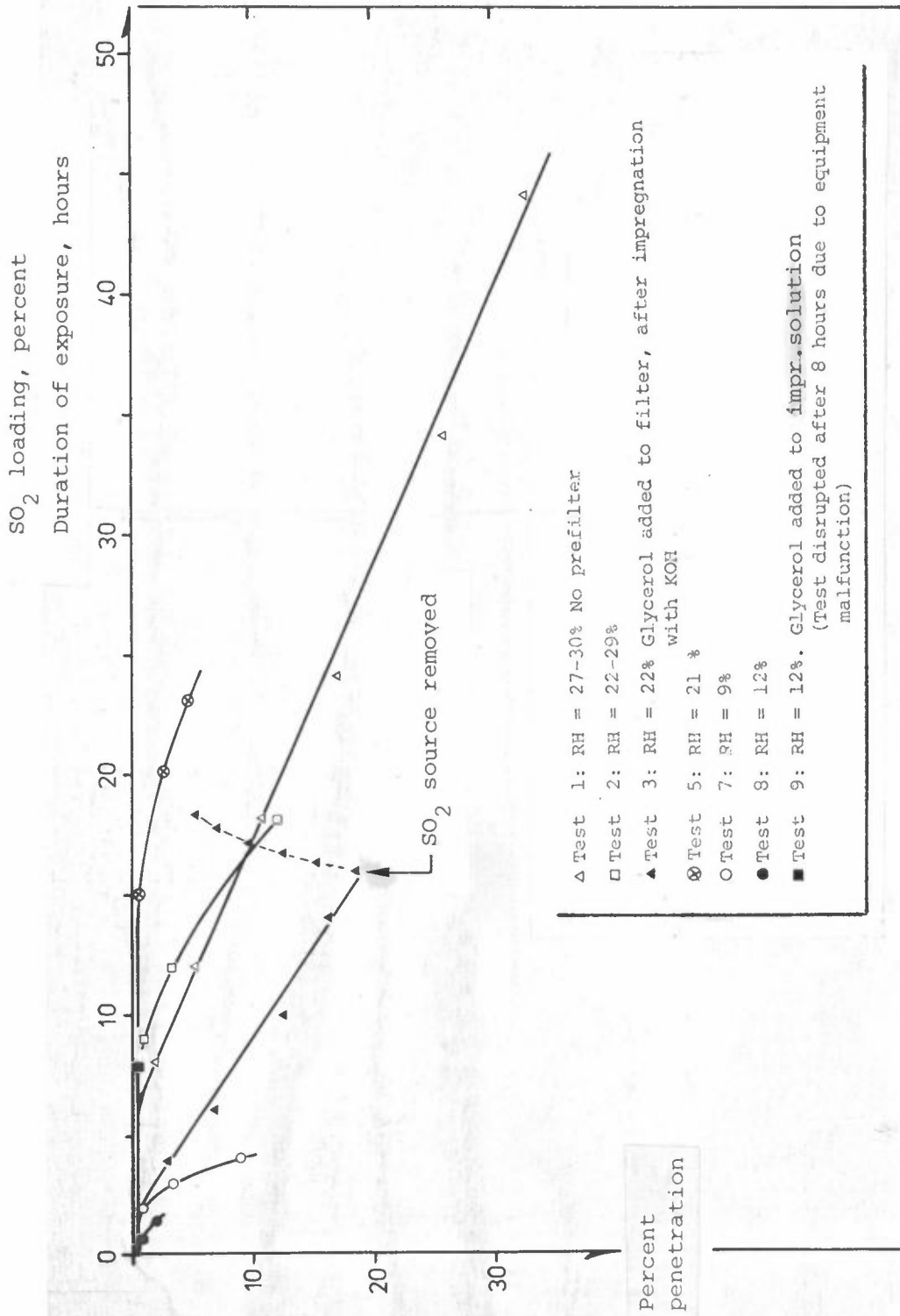


Figure 4.2: SO₂ penetration through KOH impregnated Whatman 40 filters (7.5 μeq/cm²) at 10-30% relative humidity. (Dotted line (Test 3) shows apparent release of SO₂, relative to exposure concentration, after removal of SO₂ source from the sample air.)

- At 10% RH the breakthrough occurs after 1-2 hours, corresponding to a 1-2% SO₂ loading. The total loss for 24h exposures is then large (Tests 7,8).
- at 20-30% RH the adding of glycerol to the filter surface, after KOH impregnation, did not improve the absorption efficiency (Test 3). At 12% RH, however, Test 9 indicated that the adding of glycerol to the KOH solution before filter impregnation has a very marked effect, and gives complete absorption for at least 8 hours under the stated test conditions.
- KOH impregnated filters may give off some SO₂ previously absorbed, as shown by Test 3. The SO₂ source was then removed after 16 hours of exposure. Such apparent desorption was also observed during another test on a filter with no glycerol added to the KOH solution.

These results substantiate the findings of Lewin (1975), namely that absorption is complete for short time (30 minutes) exposures at 20-30% relative humidity, and close to complete at 10% RH, using 17 $\mu\text{eqv KOH}/\text{cm}^2$. The tests described here show that a breakthrough occurs after a certain SO₂ loading is reached, depending upon the relative humidity. The resultant SO₂ loss for 24h exposure with 7.5 $\mu\text{eqv KOH}/\text{cm}^2$ is significant even at 20-30% relative humidity, when the SO₂ exposure increases beyond a SO₂ loading of 20%.

The tests with glycerol additives indicated that the method of adding glycerol to the filter is important. For test 3, glycerol was added to the filter after KOH impregnation. For test 9, glycerol was added to the solution before impregnation. No further investigation of this effect was made. In all later tests the latter method of glycerol addition was used.

4.3.2 Absorption efficiency as a function of impregnation strength (face velocity 1.8 cm/s)

Table 4.2 shows the exposure time and SO₂ loading before penetration of SO₂ occurs at various KOH concentrations, at relative humidities of 20-30%.

Table 4.2: Tests of penetration of SO₂ through KOH impregnated filters (W40) at 20-30% RH as a function of impregnation strength.

KOH conc. μeqv/cm ²	Exposure time before penetration is detected hours	SO ₂ loading at time of breakthrough	
		μg/cm ²	percent
7.5	8-15	24-36	≈ 10-15 (test 1,2,5)
15	70-80	170-192	≈ 35-40 (test 6)
30	> 140	> 340	> 35 (test 4)

It is seen that at 20-30% RH and under the stated test conditions, a 15 μeqv/cm² impregnation strength is sufficient for complete absorption for 2-3 days of exposure to a high SO₂ concentration (≈3-400 μg/m³, 1.8 cm/s).

This is in agreement with the results obtained by Lewin (1975), who reported full absorption for up to 50% SO₂ loadings on Whatman 41 filter impregnated with 17 μeqv KOH/cm² for filter face velocities up to 70 cm/s.

The results indicate that the SO₂ loading at breakthrough increases much more rapid than linearly with the impregnation strength. A doubling from 7.5 to 15 μeqv/cm² results in a 6-fold increase in the SO₂ amount absorbed by the filter before breakthrough occurs, corresponding to a 3-fold increase in the SO₂ loading before breakthrough.

4.3.3 Effect of KOH/glycerol concentration on absorption efficiency (face velocity 1.8 cm/s)

A series of tests were done at a relative humidity of 3-4% at approximately 23°C. Figure 4.3 shows the effect of different concentrations of KOH and glycerol on the SO₂ penetration. The effect of adding glycerol to the KOH solution is pronounced at this low relative humidity. The SO₂ loading before break-through increases from 0.3% for 7.5 µeqv/cm² without glycerol to 10-16% for 7.5 µeqv/cm² with 10 vol% glycerol, and to >35% at 15 µeqv/cm² with 20 vol% glycerol added. Test results are given in Table 4.3.

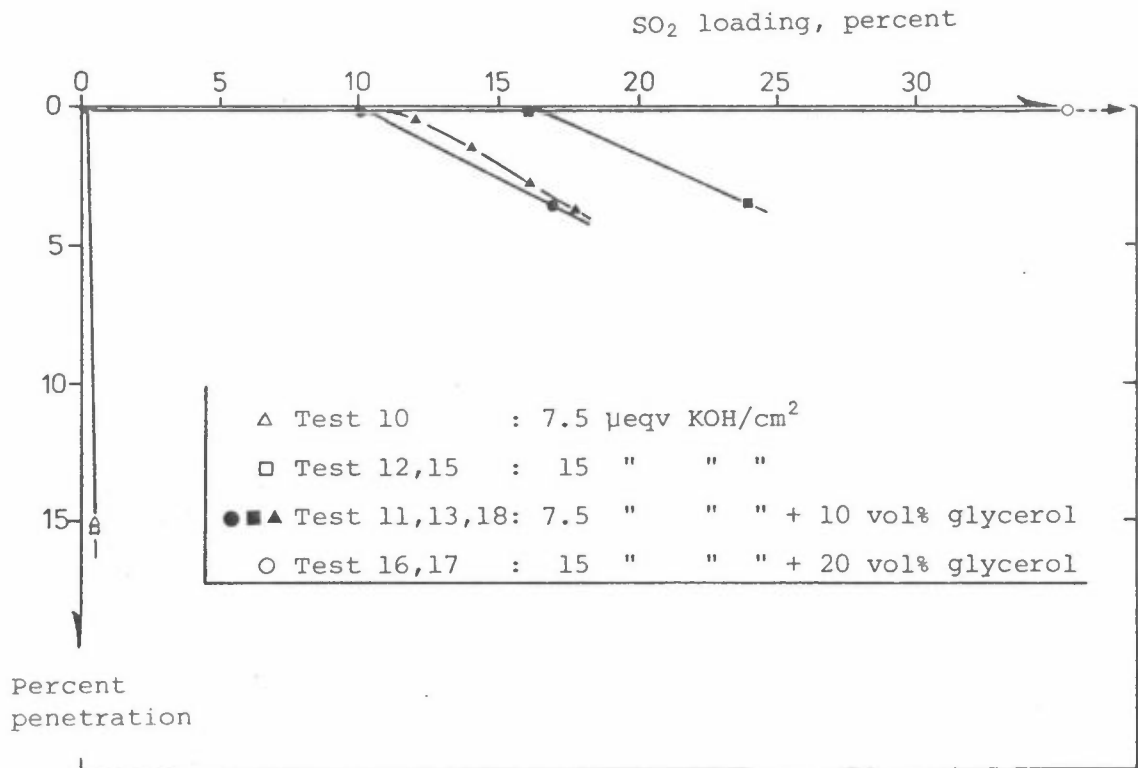


Figure 4.3: SO₂ penetration through impregnated Whatman 40 filters as a function of time and impregnating solution, at a 3-4% RH.

Table 4.3: Penetration results at 3-4% RH.

TEST PARAMETERS			RESULTS		
	KOH conc. ($\mu\text{eqv}/\text{cm}^2$)	Glycerol vol%	Time before penetration hours	SO ₂ loading at penetration time percent	$\mu\text{eqv}/\text{cm}^2$
Test 10	7.5	0	0.3	0.3	0.01
" 12	15	0	0.3	0.15	0.01
" 15	15	0	0.3	0.15	0.01
" 11	7.5	10	10	10	0.38
" 13	7.5	10	16	16	0.60
" 18	7.5	10	10	10	0.38
" 16	15	20	> 70	> 35	2.7
" 17	15	20	>120	> 60	4.5

4.3.4 Absorption efficiency for long-term exposures at 12-13 l/min and low relative humidities.

These series of tests were conducted with the setup shown in Figure 4.1(b). The characteristic parameters were as follows:

Impregnation solution: 1.0 N KOH + 20 vol% glycerol (15 $\mu\text{l}/\text{cm}^2$)

Sample flow : 12-13 l/min

Face velocity : \approx 45 cm/s

SO₂ concentration : \approx 46 $\mu\text{g}/\text{m}^3$

Relative humidity : 2.5-5.5%

A prefilter (Whatman 40) was placed in front of the impregnated filter.

The filters were exposed to SO₂ for periods ranging between approximately 6 hours and 44 hours, corresponding to an SO₂ loading range of 9-64%.

The results of the tests are shown in Table 4.4. They indicate that at a flow rate of 12-13 l/min, and a SO₂ concentration of 46 µg/m³ the absorption efficiency of filters impregnated with 15 µeqv/cm² and 20 vol% glycerol is acceptable for exposure times of at least 24 hours at relative humidities down to 2-3%. This corresponds to an SO₂ loading of approximately 35%. For 43 hours of exposure, or approximately 64% SO₂ loading the total absorption efficiency drops to below 80%.

Table 4.4: Absorption efficiency of Whatman 40 filters impregnated with 15 µeqv KOH/cm² and 20 vol% glycerol for long-term exposures under low relative humidity conditions.

Test parameters		SO ₂ loading at breakthrough		Retained percent (approx.)
Exposure duration hrs	Relative humidity percent	per-cent	µeqv/cm ²	
5.75	3	8	0.63	100
11.75	3	17	1.25	94
24	3-5	35	2.7	100
24	3	35	2.7	97
43.5	4	64	4.8	76

4.3.5 Conclusions

The tests conducted with a face velocity of 1.8 cm/s and at 20-30% relative humidity showed that penetration of SO₂ through the KOH impregnated filters occurred at a certain loading of SO₂. With an impregnation of 7.5 µeqv KOH/cm², the breakthrough occurred at a loading of about 0.5 µeqv SO₂/cm², or about 15% of theoretical capacity. A two-fold increase to 15 µeqv KOH/cm² gave breakthrough at about 3 µeqv SO₂/cm², i.e. a 6-fold increase, corresponding to about 35-40% of theoretical capacity.

Thus, 15 $\mu\text{eqv KOH/cm}^2$ filters have a capacity to sample 3-400 $\mu\text{g SO}_2/\text{m}^3$ air for 24 hours at a face velocity of about 2 cm/s, or 15-20 $\mu\text{g SO}_2/\text{m}^3$ air at a face velocity of about 45 cm/s. The results indicate that a further increase of the impregnation strength would increase the absorption capacity considerably.

The tests conducted at less than 5% relative humidity showed that at such humidities KOH impregnated filters have a very low capacity to absorb SO_2 . The addition of glycerol to the KOH solution markedly increases the capacity of the filter at such low humidities. With an impregnation solution of 15 $\mu\text{eqv KOH/cm}^2$ and 20% v/v glycerol added, the filters showed complete absorption at SO_2 loadings up to and beyond 35%. This result was obtained both with filter face velocities of 1.8 cm/s and 45 cm/s. The results indicate that adding glycerol to the solution would increase the SO_2 loading before penetration occurs also for relative humidities higher than 5%.

5 FIELD EVALUATION

The field experiments mentioned in Section 2 indicated a less than satisfactory absorption efficiency of the 7.5 $\mu\text{eqv KOH/cm}^2$ impregnated filters for 24 h sampling and about 45 cm/s face velocity. Further parallel sampling experiments in 1978 were designed to evaluate methods of improving the filter collection efficiency, using higher concentrations of KOH in the impregnating solution with and without glycerol added. In the winter of 1979, an impregnated filter sampler as described in Section 3 was operated continuous at a background station in parallel with a sampler using H_2O_2 absorption solution (OECD method). In the fall of 1979, an intercomparison test with samplers of different makes was carried out at the NILU test site.

5.1 Field evaluation at NILU test site, 1978

5.1.1 Effect of KOH concentration

For a two-week period in February 1978 the following sampling systems for SO₂ were run in parallel:

SO ₂ collection	Location	Flow	
		l/min	cm/s
A: H ₂ O ₂ solution (0.3%)	Indoor	2.5	-
B: Impr.filter (7.5 µeqv KOH/cm ²)	Outdoor	12.5	45
C: Impr.filter (15 µeqv KOH/cm ²)	Outdoor	12.5	45
D: Impr.filter (7.5 µeqv KOH/cm ²)	Indoor	2.5	9
E: Impr.filter (15 µeqv KOH/cm ²) + 20% v/v glycerol)	Indoor	2.5	9

Samplers D and E had backup bubblers (H₂O₂ solution) to trap any penetrating SO₂.

Table 5.1 summarizes the average air quality and climatic parameters for this test period.

Table 5.1: Characteristic test parameters for sampler comparisons at NILU's test site.

Period	Average SO ₂ conc., µg/m ³ (OECD method)	Ambient conditions		-Indoor conditions	
		Temp, °C	RH, %	Temp, °C	RH, %
9-15.2.78	9	- 8 -- 25	65-85	17-23	10-20
16-22.2.78	45	- 1 -- 26	45-90	20-28	5-10

The two weeks provided a large range of SO₂ concentrations. Both weeks were generally cold with night temperatures below -25°C. The daytime temperatures were high during the second week due to sunny weather. The relative humidity then dropped to 45%, compared to a minimum of 65% during the first week. The sunny weather also gave higher temperatures and lower relative humidities indoors during the second week.

Thus, the relative humidity of the outdoor air was within the range where the laboratory tests have shown satisfactory absorption efficiency of cellulose fiber filters impregnated with 15 µeqv KOH/cm². The absorption efficiency has not been tested, however, at quite so low temperatures as occurred at nighttime during this study.

The indoor conditions were within the ranges where filters impregnated with 15 µeqv KOH/cm² and glycerol absorbed satisfactory. Based on the results of laboratory tests and on the field test conditions, one would therefore expect that samplers C and E would have close to 100% absorption efficiency.

Table 5.2 gives the concentrations and absorption efficiencies of the various systems, relative to system A (OECD method), for relatively low (week 1) and relatively high (week 2) SO₂ concentrations.

Table 5.2: Results of field test (24 hours periods) at NILU's test site 9-23.2.1978.

Sampling System Period	SO ₂ concentration, µg SO ₂ /m ³				D			E		
	A H ₂ O ₂ bubbler room cond.	B Impr.filter 7.5 µeqv KOH/cm ² amb. cond.	C Impr.filter 15 µeqv KOH/cm ² amb. cond.	Impr.filter 7.5 µeqv KOH/cm ² room cond.	Impr.filter 7.5 µeqv KOH/cm ² room cond.	back up bubbler	total	Impr.filter 15 µeqv KOH/cm ² 20 vol % glycerol room cond.	back up bubbler	total
9-10.2	10	9	15	6	6		12	8	1	9
10-11.2	10	10	10	4	4		8	9	1	10
11-12.2	8	8	7	7	2		9	9	1	10
12-13.2	7	5	5	4	1		5	7	1	8
13-14.2	5	4	3	2	1		3	4	1	5
14-15.2	7	8	7	3	3		6	9	1	10
15-16.2	16	15	21	5	14		19	28	1	29
16-17.2	46	7	29	4	39		43	45	2	47
17-18.2	48	12	40	5	42		47	45	1	46
18-19.2	37	20	29	5	26		31	37	1	38
19-20.2	58	20	49	6	45		51	56	1	57
20-21.2	45	32	37	7	35		42	42	1	43
21-22.2	36	27	32	8	24		32	36	1	37
22-23.2	9	6	7	4	6		10	12	1	13
Mean										
9-15.2	9	8.4	9.7	4.5	4.4		8.9	10.6	1.0	11.6
% abs.		93	108	50	49		99	118	11	129
16-22.2	45	19.7	36	5.8	35.2		41.0	43.5	1.2	44.7
% abs		44	80	13	78		91	96.7	2.7	99.4

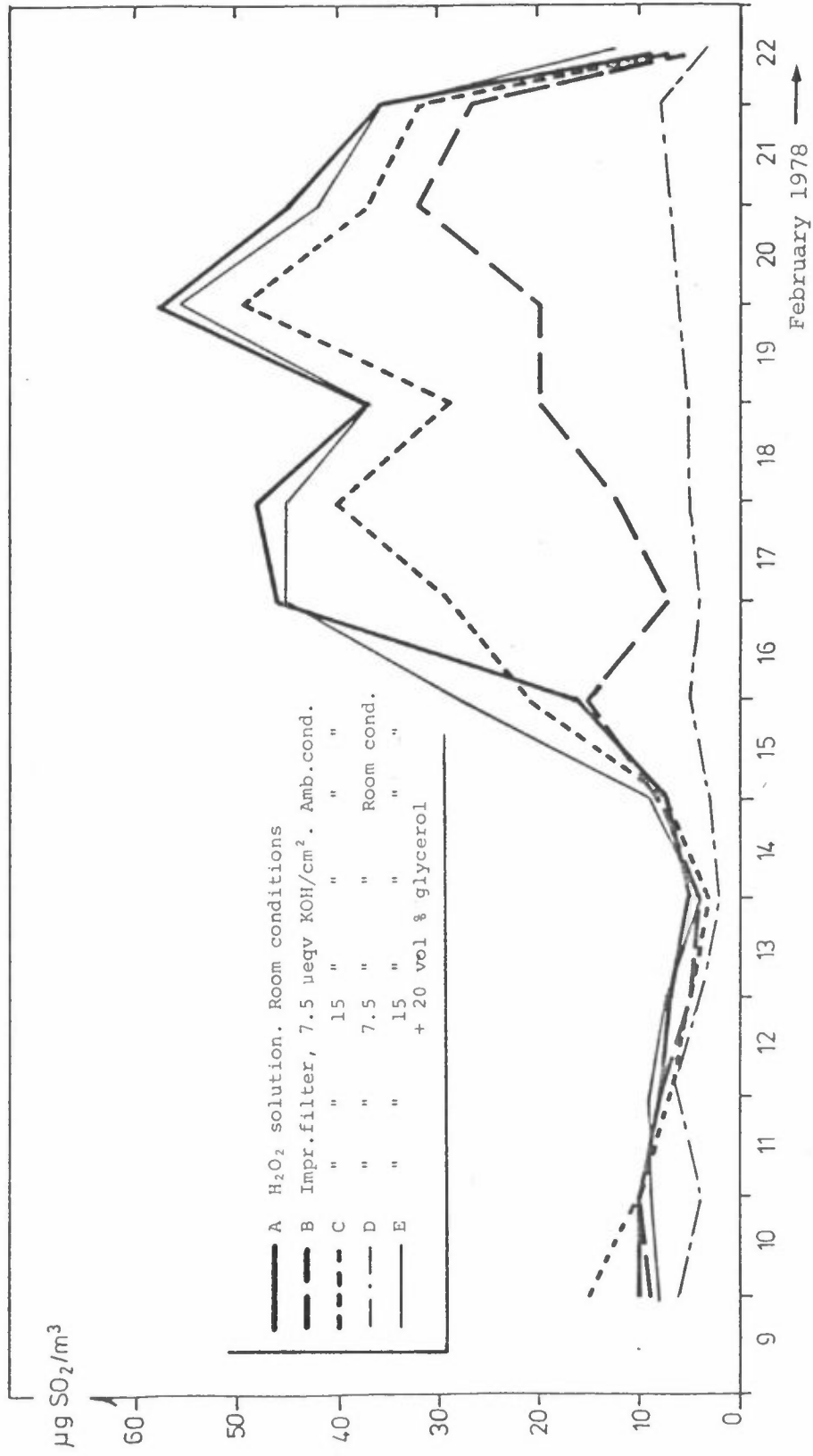


Figure 5.1: SO₂ concentrations measured with various sampling systems at NILU's test site.

Figure 5.1 gives the concentrations of SO₂ collected by the various sampling systems. It shows that system B, C and E performed satisfactory relative to the reference method, A, during the first period with low SO₂ concentrations. In the second period only system E performed well. The impregnated filters at ambient conditions showed significantly less than 100% absorption efficiency. System D performed quite poorly, especially with high SO₂ concentrations.

The results of this field test are thus not entirely in agreement with the laboratory test results described in Section 4.

7.5 µeqv KOH/cm² filters at ambient conditions, system B

The ambient relative humidity was within the range where laboratory tests gave close to 100% absorption up to 10% SO₂ loading, and a total loss of 10-15% at about 25% SO₂ loading. The field test showed, on the average, 93% absorption at 14% loading (9 µg SO₂/cm³), and 44% absorption at 69% loading (45 µg SO₂/m³). This low absorption efficiency may be due to a higher face velocity in the field test (42 cm/s) than in the laboratory test (1.8 cm/s), although the results of the short term exposures at Risø (Lewin 1975) indicated that the absorption efficiency was not affected by face velocity changes up to 70 cm/s. It may also be due to the low temperatures. Lewin (1975) had tested the absorption efficiency only down to -10°C and the laboratory tests at NILU were conducted at room temperatures.

15 µeqv KOH/cm², filter placed at ambient conditions, sampler C.

This system gave, on the average, full absorption at 7% SO₂ loading and 80% at 35% loading. The laboratory tests gave full absorption up to a loading of 35-40%. The discrepancy may also here be explained by face velocity or temperature effects.

7.5 $\mu\text{eqv KOH}/\text{cm}^2$, filters placed at room conditions, system D

The laboratory tests indicated an unacceptably low absorption efficiency for this system at 10-20% relative humidity. The field test confirmed this, but the absorption efficiency was even lower than expected.

15 $\mu\text{eqv KOH}/\text{cm}^2$ + 20% glycerol, filters placed at room conditions, system E

The laboratory tests indicated acceptable performance of this system for relative humidities above 3-4%. The field test confirmed the laboratory test results, and gave complete absorption at 9 $\mu\text{g SO}_2/\text{m}^3$ (1.5% loading), and close to full absorption ($\approx 97\%$) at 45 $\mu\text{g SO}_2/\text{m}^3$ (7.5% loading).

5.1.2 Effect of a glycerol additive

During a two-week period in October - November 1978, two parallel sampling systems were used to test the effect of a glycerol additive, when the filters were placed outdoor and the flow was 12.5 l/min. These systems were run in parallel with the OECD method. The ambient temperatures ranged from -3 to $+18^\circ\text{C}$, and relative humidities from 31 to 98%.

Table 5.3 gives the SO₂ concentrations found in the various systems.

Table 5.3: Results of field test at NILU's test site 19.10-10.11.1978.

SO₂ concentration, µg SO₂/m³

Sampling system Period	A H ₂ O ₂ absorption room cond.	B Impr.filter 15 µeqv KOH/cm ² + 20 vol % glyce- rol amb. cond.	C Impr.filter 15 µeqv KOH/cm ² amb.cond.
19-20.10	13.6	12.0	11.4
20-23.10*	8.6	7.0	7.0
23-24.10	15.4	14.4	13.6
24-25.10	6.4	5.2	5.0
25-27.10**	8.4	5.4	5.4
27-30.10*	11.8	9.6	10.2
30-31.10	6.2	7.6	8.2
31.10-1.11	17.0	20.6	22.0
1-2.11	9.4	11.8	12.0
2-3.11	8.4	10.2	11.0
3-6.11*	8.6	9.6	10.2
6-7.11	12.2	11.0	10.0
7-8.11	5.4	5.0	6.0
8-9.11	9.2	7.8	5.0
9-10.11	9.4	7.6	6.8
Mean	10.0	9.7	9.6

* 72-hour sampling

** 48-hour sampling

The results show that the addition of glycerol does not improve absorption efficiency significantly for the given set of ambient conditions, and for SO₂ loadings below about 17%. They also show that at such loadings the absorption efficiency of the impregnated filters is almost 100%, compared to the H₂O₂ method. This is in agreement with the results of the first part of the test period in February 1978, when the average SO₂ concentration was 9 µg/m³, and with the laboratory experiments.

During the October-November tests, the SO₂ concentration never approached the high level of the last week in February. Thus it was not possible to ascertain any positive effect of glycerol at high SO₂ loadings where the impregnated filter showed only 80% efficiency in the absence of glycerol.

Further experiments during this test period clearly showed that the prefilter (Whatman 40) has to be kept from contacting the impregnated filter, if glycerol is added to the solution. If not, some of the SO₂ may be absorbed on the prefilter, which will then be "impregnated" to some degree on its back side. Without glycerol added to the solution, the SO₂ "loss" to the prefilter in absence of a separating screen is of little importance, unless the relative humidity is high enough to actually wet the prefilter.

5.2 Field evaluation at a background station in Southern Norway, January-February 1979

Since the middle of January 1979 the impregnated filter sampling system has been tested at the regional station Birkenes, in South Norway, in parallel with the OECD (H₂O₂ solution) method.

The filters were impregnated with 15 µeqv KOH/cm² solution. No separating screen was used between prefilter and impregnated filter on this occasion.

The six-week long period gave the following mean SO₂ concentrations:

H ₂ O ₂ (OECD) method, 9 cm/s	8.6 µg SO ₂ /m ³
Impr.filter method, 15 µeqv/cm ² , 45 cm/s	7.7 " "

Thus, the apparent absorption efficiency of the impregnated filters (15 µeqv KOH/cm² and no separating screen) was approximately 90%, relative to the OECD method, at an average SO₂ loading of about 6%.

A regression analysis of the data is presented in Section 5.3, together with data from earlier test periods.

5.3 Regression analysis

Table 5.4 presents results of a linear regression analysis performed on data pairs from the various tests.

Table 5.4: Results of regression analyses on SO₂ concentrations from parallel sampling with KOH impregnated filters and the H₂O₂ absorption method.

	Linear regression/correlation y = ax+b			SO ₂ mean		SO ₂ range (impr.filter)	
	a	b(μg/m ³)	r	x(μg/m ³)	y(μg/m ³)	μg/m ³	% loading
<u>February 1978</u>							
x: 15μe/cm ² , no glycerol							
y: H ₂ O ₂							
9-15.2	0.41	4.6	0.90	9.7	9.0	3-15	2.5-11
15-23.2	1.23	0.77	0.94	36	45	7-49	6 -37
<u>Oct-Nov 1978</u>							
x: 15μe/cm ² , no glycerol	0.61	4.1	0.80	9.6	10.0	5-22	4 -17
y: H ₂ O ₂							
x: 15 μe/cm ² , 20% glycerol	0.73	3.0	0.88	9.7	10.0	5-21	4 -16
y: H ₂ O ₂							
x: 15μe/cm ² , 20% glycerol	1.05	-0.6	0.97	9.7	9.6	5-22	4 -17
y: 15μe/cm ² , no glycerol							
<u>Jan-Feb 1979</u>							
x: 15μe/cm ² , no glycerol	0.82	2.3	0.91	7.7	8.6	0.2-34	<25
y: H ₂ O ₂							

The analyses show fairly high correlation coefficients generally in the range 0.80-0.97. They also show in most cases for the range 0.8-4.6 $\mu\text{g}/\text{m}^3$ a fairly substantial, positive offset (line intercept b) of the H_2O_2 method.

The regression coefficient a has values from less than 1.0 to larger than 1.0. In the low SO_2 range (<25% SO_2 loading on the filter), it is less than 1.0, in the range 0.41-0.82. Still, the H_2O_2 method gives a higher mean SO_2 concentration than the KOH method (except for 9-15.2.78) due to the positive offset of the H_2O_2 method.

In the higher SO_2 range (period 15-22.2.78) the offset is small, and a is 1.23. This indicates that the KOH method is less than 100% effective in this range. The table shows that the SO_2 loading in this period approached 37%, still within the range where laboratory tests showed complete absorption.

There is a high correlation, $r = 0.97$, between KOH impregnated filters with and without glycerol, with a regression coefficient of 1.05.

5.4 Intercalibration test at NILU test site 1979

The field tests before and during 1978 indicated discrepancies between the impregnated filter method and the H_2O_2 solution absorption method. An intercalibration test was carried out in 1979, in order to establish the relationship between those two methods at the low SO_2 concentrations that normally occur at background stations in Scandinavia.

5.4.1 Sampling program

During the period 25.10-24.12.1979 the following samplers from Denmark (D), Sweden (S), and Norway (N) were run in parallel at NILUS test site in Lillestrøm.

<u>Sampler</u>	<u>SO₂ collection</u>	<u>Flow</u>		<u>Filter</u>
		l/min	cm/s	
S	H ₂ O ₂ solution (0.3%)	15	-	-
N1	H ₂ O ₂ solution (0.3%)	2	-	-
N2	Impr. filter (15 µeqv KOH/cm ²)	14	48	Whatman 40
N3	" " "	14	48	" "
D	Impr. filter (17 µeqv KOH/cm ²)	35	42	Whatman 41

A total of 41 parallel samples were obtained, with most samples representing 24h sampling periods, starting at 0900 hours. The ambient temperatures varied between +7°C and -21°C, and the relative humidities between 30% and 100%.

5.4.2 Analytical procedures

H₂O₂ solution. The absorption solution was an ≈ 0.5% H₂O₂ solution acidified with HClO₄ to pH 4.5. In the N1 sampler, 180 ml polyethylene bubblers contained 100 ml each of this solution. During sampling, part of the solution evaporated. Approximately 70 ml were left after 24 hours of sampling. In the S glass frit bubbler, a glass cylinder contained 100 ml of the solution. The amount of solution in the cylinder was automatically kept at a constant level.

Impregnation of filters. The Whatman 40 filters for the N2 and N3 samplers were prepared as described in Section 4.2. The filters for the D sampler were first submerged into 0.5 N KOH solution and then dried.

SO₂ analysis. The H₂O₂ solutions from the N1 and S samplers were analysed by the Thorin method. The impregnated filters from D, N2 and N3 samplers were treated and analysed as described in Section 4.2.

5.4.3 Results and discussion

The SO₂ concentration varied within the range 2-40 µg SO₂/m³, with a mean value of about 14 µg SO₂/m³. The samplers gave the mean concentrations listed below.

Sampler	Mean SO ₂ conc.	SO ₂ loading %	
		mean	max
S (H ₂ O ₂)	14.1 µg/m ³	-	-
N1 (")	14.2 "	-	-
N2 (Imp. filter)	13.6 "	≈ 12	≈ 45
N3 (Impr. filter)	13.4 "	≈ 12	≈ 45
D (Impr. filter)	12.7 "	≈ 10	≈ 46

Very good agreement is apparent between the two H₂O₂ samplers, and between the two identical impregnated filter samplers (N2 and N3). It also appears that the mean concentrations given by the impregnated filters are somewhat lower than those from the H₂O₂ samplers.

Figure 5.2 shows plots of the relationship between pairs of samplers. Sampler N1 is chosen as the reference sampler. The figure also shows results from linear regression analyses.

The correlation coefficients for the four sampler pairs exceeded 0.97. The regression coefficients are close to 1.0, except for sampler pair D/N1, for which it is 0.92. The zero offset of the N1 sampler varies between -0.8 µg SO₂/m³ and + 0.4 µg SO₂/m³.

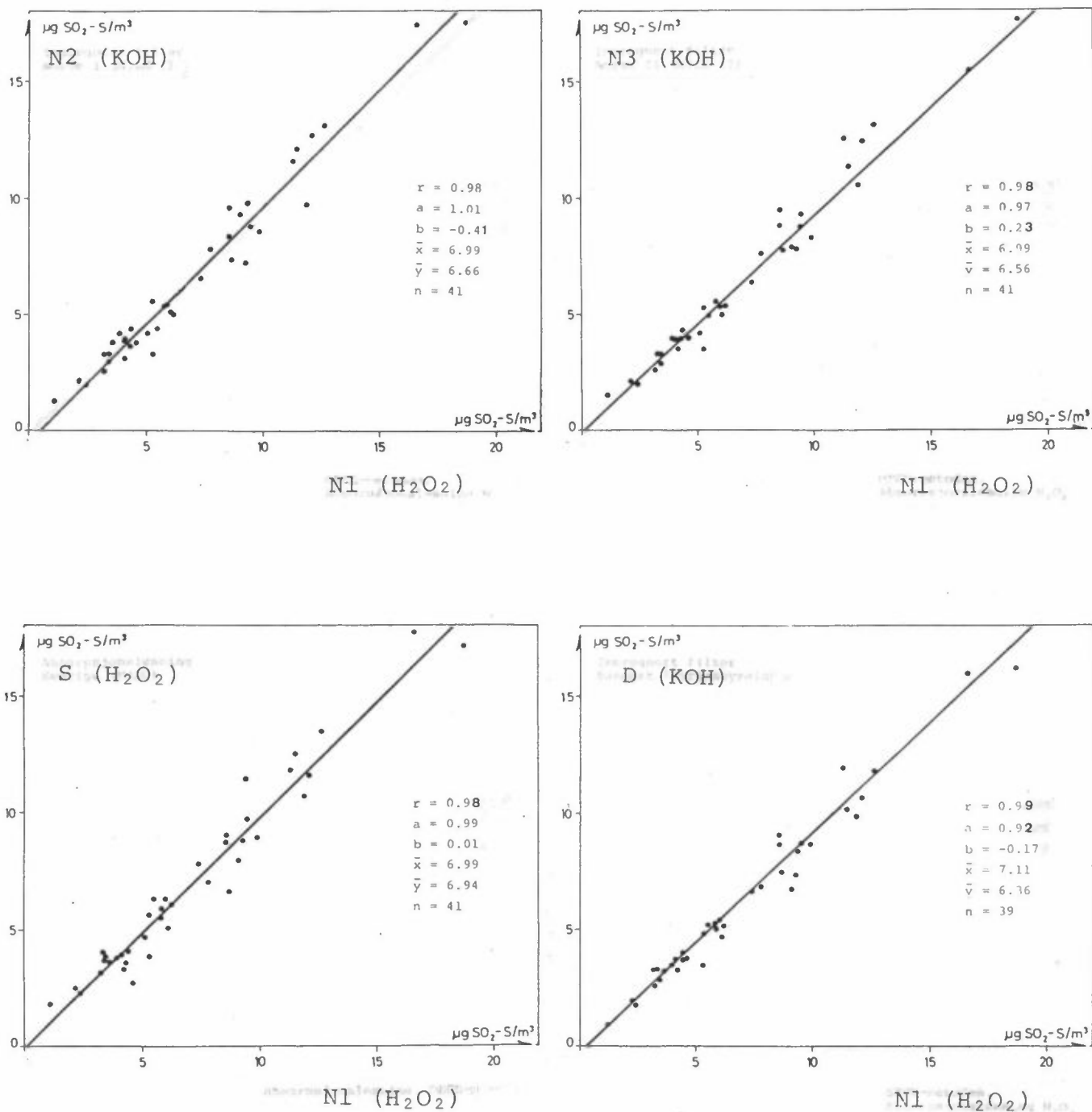


Figure 5.2: Results of regression analysis (linear) of sampler pairs N2/N1, N3/N1, S/N1 and D/N1. NILU test site 25.10-24.12.1979.

It can be concluded that the samplers gave results that are well correlated, but the impregnated filter samplers gave concentrations somewhat lower than the H₂O₂ absorption method.

The plots indicate no apparent change in the regressions for the lower and higher SO₂ concentration ranges.

5.5 Conclusions on field tests

When impregnated filter samplers, similar to the type described in Section 3, are tested in parallel with the H₂O₂ method, the data pairs always show a quite high correlation coefficient, within the range 0.80-0.99 for all the tests reported here.

Filters impregnated with 15 µeqv KOH/cm², and exposed for 24 hours, something show less than 100% absorption for SO₂ loadings down to somewhat less than about 35%. During the field tests, the relative humidity was always within the range 30-100%. For such humidities, the laboratory tests showed 100% absorption up to about 35% SO₂ loading. The field test in February 1978 indicated about 80% absorption efficiency, relative to the H₂O₂ method, at about 35% SO₂ loading and full absorption at about 7% loading. The field test in October-December 1979 indicated an absorption efficiency of about 100% for one type of sampler, and about 92% for another type of sampler at an average SO₂ loading of 10-12%.

Considering the high correlation between the methods, the impregnated filter method performs acceptably, relative to the H₂O₂ method. The somewhat lower absorption efficiency in the field than that obtained in the laboratory might be due to the very low ambient temperatures (down to about -25°C) encountered during some of the field tests. In laboratory tests, the method has not been studied at temperatures below -10°C. Laboratory tests also suggested that some desorption from the filter may take place,

when the SO₂ concentration is abruptly reduced. In the field, the SO₂ concentration may change considerably during the 24 hour sampling period used. This may lead to some desorption that will reduce the total absorption efficiency to below 100%.

At background stations in Norway, the SO₂ loading seldom exceeds 40% (with 15 µeqv KOH/cm²). At these levels, the impregnated filter method is considered better than the OECD (H₂O₂) method, which samples an air volume of 2-3 m³/24h. The OECD method often shows a positive bias at very low SO₂ concentrations. The impregnated filter method gives full absorption for low SO₂ loadings. Also the increased sampled air volume and small filter extract volume (about one fifth of the solution volume of the OECD method), results in a much better accuracy in the reported SO₂ concentrations.

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