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NO_2 Sequential Air Sampler

NILU SS2000

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Contents

Summary

A comparison is made of the new filter sampler NILU SS2000 versus monitor with chemiluminescence detector (NO_x-NO monitor) and the older filter sampler NILU-FK, respectively. The performance of NILU SS2000 is shown to be in good agreement to NO_x-NO monitor. It is found that the difference between average concentration obtained by NILU SS2000 and the NO_x-NO monitor is within the uncertainty of the latter technique. In addition, linear regression of the NO_2 concentrations obtained by NILU SS2000 and NO_x-NO monitor is found to give an R^2 value of 0.95.

It is also found that the performance of NILU SS2000 is in good agreement with the old sequential sampler NILU-FK. The linear regression has an R^2 value of 0.96 and it is only a 6 % difference in the average results between NILU-FK and NILU SS2000.

NO_2 Sequential Air Sampler NILU SS2000

1 Introduction

The NILU SS2000 is a user-friendly automatic filter sampler for gasses developed by NILU Products. The sampler may be used for gases, which can be absorbed on impregnated filters, or other kinds of substrate e.g. the iodide absorption method for NO_2 developed by Ferm and Sjödin (1993).

In the study presented in this report, NILU SS2000 was compared with the older sequential NO_2 sampler (NILU-FK) and a monitor with chemiluminescence detector. The chemical principle for NILU-FK and NILU SS2000 is similar and both samplers have the possibility to measure 8 samples in an automatic sequence. The main difference between these two manual methods will to a large extent be due to differences in the flow volume. By use of NILU-FK a constant flow over the entire sampling period is assumed. NILU SS2000 offers improved flow control. A programmable logic controller (PLC) controls the NILU SS 2000. The flow is set with a restrictor and measured with a mass flow meter. The sample volumes are recorded in standard litres accumulated over the sampling period. In this way SS2000 will record the actual flow through each sample. The user can set the desired start time for 8 samples in a sequence. The sampling will normally start at the same time every day at 24 hours interval.

2 Chemical principle for NILU SS 2000 and NILU-FK

Ambient air with a flow rate of ca 0.5 l min^{-1} is drawn through an air intake and glass filter impregnated with sodium iodide (NaI) and sodium hydroxide (NaOH). The nitrogen dioxide (NO_2) is absorbed on the filter and reduced quantitatively to nitrite (NO_2^-) by the iodide. In addition, carbon dioxide (CO_2) is absorbed and converted to carbonate (CO_3^{2-}) by the NaOH. The NO_2^- formed on the filter is extracted with deionised water containing Triethanolamin (TEA). TEA is used to oxidise I_2 that may have been formed during sampling. After extraction the concentration of NO_2^- may be determined photometrically by the Griess method.

Measurement range
With a sampling time of 24 hours, a total sample volume of 0.72 m^3 and an extraction volume of 4 ml it may thus be possible to detect between 0,1 and 10 µg of NO_2 m^{-3} in ambient air. Exposed samples are stable for several weeks, which allows transfer to a remote laboratory for analysis.

2.1 Sampling efficiency

The sampling efficiency is greater than 98 % with a flow rate of 0,5 l min^{-1} at 15 % RH. The efficiency is better than 98 % at 60 % RH even up to 4 l min^{-1}.

2.2 Interferences

Interference studies showed negligible formation of nitrate on the NaI/$NaCO_3$ substrate. Nitric oxide formation was also never observed behind the filter and no oxidation of nitrite by ozone were found. The absorption of PAN (peroxyacetyl nitrate) and the subsequent formation of nitrite on the alkaline NaI filter have been demonstrated with about 20% absorption (Ferm and Sjödin, 1993). This causes a positive interference, which can be severe if the PAN-concentration is higher than the concentration of NO_2. This may happen in very remote areas, but normally the PAN-concentrations are lower than the NO_2 concentrations. Thus, the PAN interference does not seem to be a serious problem.

3 Chemical principle for the chemiluminescence detector

In this work an ML9841A Nitrogen Oxides Analyzer from Monitor Labs, USA was used. The instrument will in this report be referred to as "NO_x-NO monitor". The technique is based on the following reaction mechanisms:

$$\mathbf{NO + O_3 \longrightarrow NO_2^* + O_2}$$
$$\mathbf{NO_2^* \longrightarrow NO_2 + h\nu \qquad h\nu = 500\text{-}3000\ nm}$$

When NO reacts with O_3, excited nitrogen dioxide (NO_2^*) is formed. NO_2^* will immediately decay to NO_2 in ground state while emitting broad band radiation in the spectral region from about 500 nm to3000 nm with a peak at 1100 nm. Since one NO molecule is required to produce one NO_2^* molecule, the intensity of the emitted radiation is directly proportional to the NO concentration in the sample.

The chemiluminescent reaction only occurs between NO and O_3 and concentrations of NO_2 are measured indirectly. Analysis of NO_2 is performed by chemically reducing NO_2 to NO in a converter. In practice the air sample is passed through the converter. Any NO which is normally present in the air sample will pass the converter unchanged and the total NO_x concentration will be measured. Part of the air sample will be reacted with O_3 without having passed the converter. This NO concentration will be subtracted from the former concentration of NO_x to yield the final NO_2 concentration.

3.1 NO_x-NO monitor specifications

Lower detectable limit:	0.5 ppb or 0.2% of concentration reading, whichever is greater.
Resolution:	0.001 ppm
Precision:	0.5 ppb or 1% of reading, whichever is greater.
Sample flow rate:	640 ml min^{-1}.

4 Description of the NILU SS2000 sampler

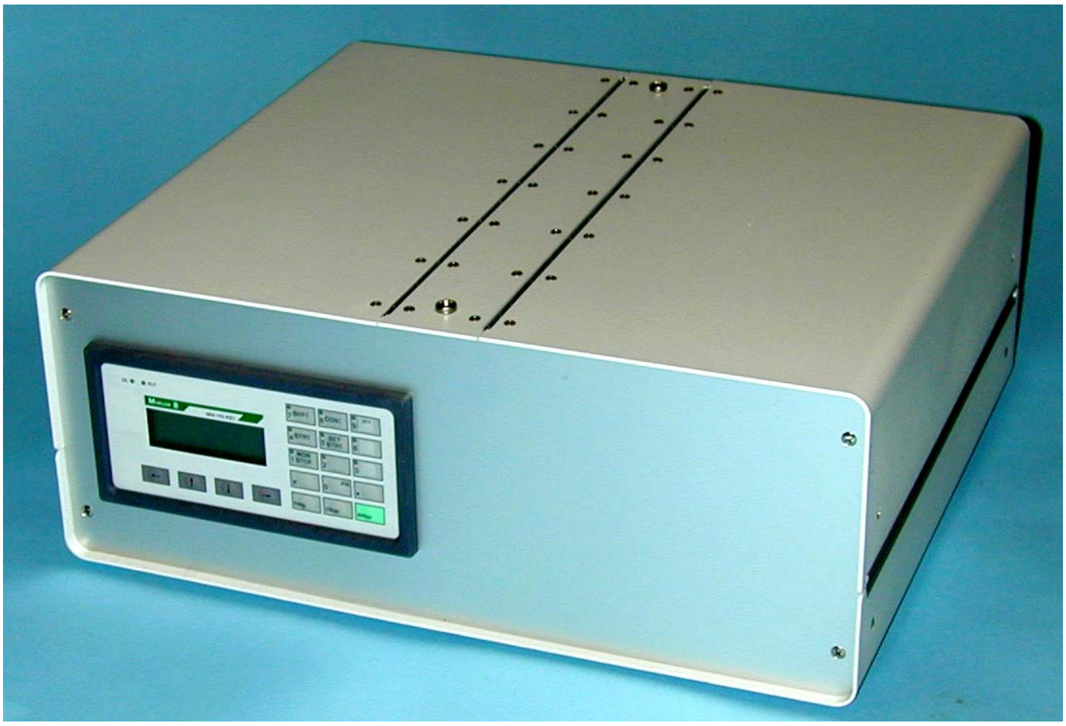

Figure 1: NILU SS2000 sampler.

4.1 Instrument layout

The instrument consists of two sections. One section contains the sample air manifold while the other contains the electronics, the display and the pump. The lid is in two halves. Users should usually only access the sample side.

4.2 Sintered glass filter

A 4 mm thick sintered glass filter 25 mm i.d. with a porosity of 40–60 μm enclosed in a glass bulb as shown in Figure 2 is used as a substrate for the impregnation. The filter holder is leak proof and the samples can be stored at room temperature before as well as after sampling. The glass bulbs should be connected to the sampling line using short pieces of silicon tubing. Note that the sinter should be nearest to the tube leading to the solenoid valve. During transport the silicon tubing must be closed by pieces of glass, plastic rods or appropriate caps made of PP, PE or PTFE teflon.

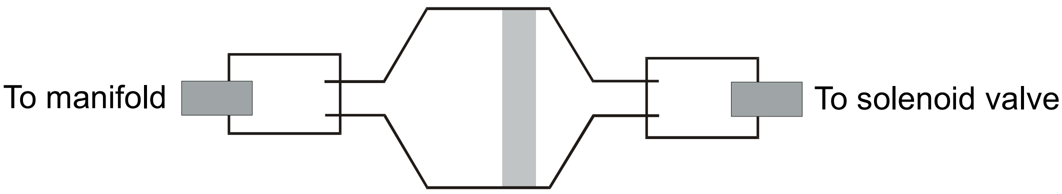

Figure 2: Sintered glass filter in a glass bulb.

4.3 Air inlet

An inverted funnel made of PTFE teflon, polypropylene, borosilicate or polyethylene should be used in order to prevent entrance of precipitation at the sampling point.

4.4 Tubing

The sampling tube connection between the air inlet and the absorption system should be as short as possible, and made of PTFE teflon, polypropylene, borosilicate glass or polyethylene.

4.5 Flow control

The present flow control is passive. A glass capillary tube sets the flow. The mass flow sensor records and stores the accumulated volume for each sample. The flow meter is calibrated at 25 °C and 1013,25 mbar. The flow meter should be checked with a reference flow meter like BIOS.

4.6 Pump

A linear motor, free piston, pump pulls in the sample air. This pump has a free flow capacity of approximately 6 l min^{-1} of air. An electronic pump control is under development and will be introduced later. The pump will then even work when the sampler is running from the back-up battery

The pump is fixed to the sampler floor on spacers. Disconnect at the pump relay and loosen the four screws to replace the pump.

4.7 Filterholder with pre-filter

A filter installed in a NILU-filterholder should be used in front of the absorption system in order to remove particulate matter. The filter must be inert to NO_2. A teflon membrane filter with a pore size 1–2 µm or a Whatman 40 cellulose filter or equivalent may be used. The filterholder and the connections to the sampling line must be airtight. The pre-filter can be used for one week.

5 Performance test of NILU SS2000 against other samplers

The parallel measurements using NILU SS2000, NILU-FK and NO_x-NO monitor were undertaken outside the Norwegian Institute for Air Research at Kjeller, Norway during the time period 18 June to 23 July 2000. A similar comparison of six NILU-FK samplers was performed at Kjeller in August 1996 (Schaug et al., 1998). In this report, data from the comparison of NILU-FK 4 and 5 are used as a reference data set. Whenever the manual methods are compared with monitor data, the latter method is used as the reference method, as specified as the reference measurement method to be used by the EU directives. The results of the performance test are regarded as acceptable if:

1. The linear regression has correlated with a R^2 value at least 0.9, and
2. The difference between the average concentration obtained by NILU SS2000 and the reference method is less than 10%.

5.1 Results and discussion

The results are shown in Figure 3 to Figure 5 along with an overview of the statistical results presented in Table 1 to Table 4.

5.1.1 NILU SS2000 versus NILU-FK

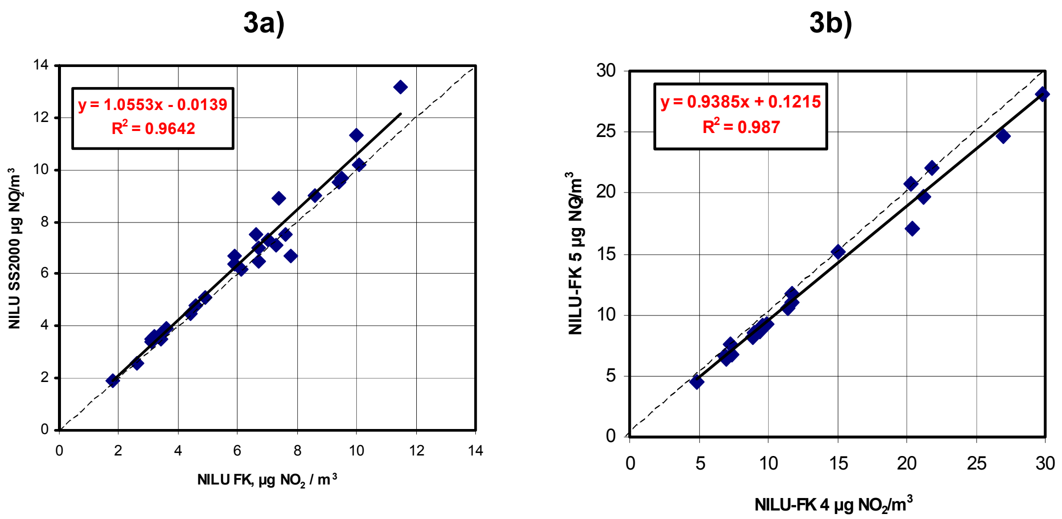

Figure 3: Correlation between: a) NILU SS2000 and NILU-FK, b) NILU-FK 4.

As can be seen from Figure 3a, there is good agreement between NILU SS2000 and NILU FK. The linear regression has an R^2 value of 0.96. It is only a 6% difference in the average results between NILU-FK and NILU SS2000 (see Table 1).

Table 1: Comparison of NILU SS2000 versus NILU-FK.

	NILU-FK NO_2 µg/m^3		NILU SS2000 NO_2 µg/m^3	Difference %
Average	6.33		6.74	6.5
Median	6.60		6.70	1.5
No. of sample pairs		25		
Average difference		-0.41		
Median difference		-0.30		
M.MAD		0.30		
CoV(%)		4.5		

Taking into account that the measured air volume for NILU-FK has an uncertainty of 7%, the results are acceptable. In addition, there is some uncertainty whether the air volume for NILU-FK should be corrected since the SS2000 air volume is given with standard pressure and temperature.

For comparison, the difference in the average results between two NILU-FK (Figure 3b and Table 2) is found to be 5% and the linear regression has an R^2 of 0.98. This indicates even further the agreement in performance between NILU-FK and NILU SS2000.

Table 2: Comparison of NILU-FK4 versus NILU-FK5.

	NILU-FK no. 4 NO_2 µg/m^3		NILU-FK no. 5 NO_2 µg/m^3	Difference %
Average	13.22		12.53	-5.22
Median	9.85		9.23	-6.29
No. of sample pairs		21		
Average difference		0.69		
Median difference		0.58		
M.MAD		0.36		
CoV(%)		3.61		

To avoid extreme values in the data sets compared to influence on the results, the median value, M.MAD (modified median absolute deviation) and CoV (coefficience of variance) are compared. M.MAD is a non-parametric measure of the spread difference between corresponding daily results from two samplers and become similar to the standard deviation when the differences show a normal distribution (Sirois and Vet, 1994). M.MAD is calculated as follows:

$$M.MAD = \frac{1}{0.6745} median(|e_i - median(e_i)|)$$

where e_i is the difference between the two data sets in the measured point i

$$CoV = \frac{M.MAD}{median(\overline{C})} *100\%$$

where $\overline{C}$ is the average between the two corresponding results.

As can be seen from Table 1, the difference between the median value for NILU FK and NILU SS2000 is 1.5%. The M.MAD obtained from comparison of NILU-FK and NILU SS2000 is somewhat lower than M.MAD obtained from comparison of two NILU-FK. This may be due to the difference in the NO_2 concentration level when the two different comparisons were arranged. Even so, both comparisons show a CoV below 10%.

5.1.2 NILU SS2000 versus NO_x-NO monitor

The results of the comparison of NILU SS2000 versus NO_x-NO monitor are shown in Figure 4a and Table 3. Linear regression shows an R^2 of 0.95 which is within the criteria listed.

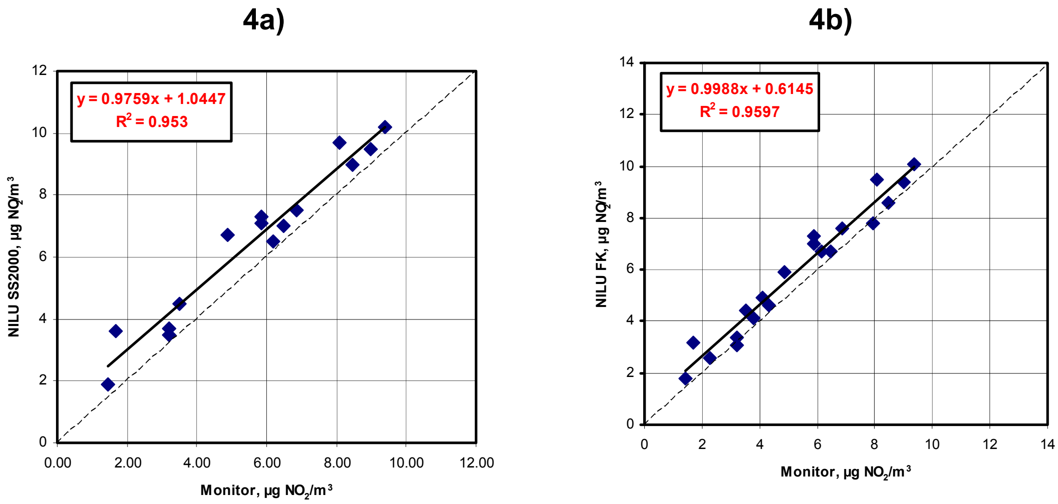

Figure 4: Correlation between: a)NILU SS2000 and monitor, and b) NILU FK and NOx-NO monitor

The difference in average concentration is 13.6%, which do not meet the listed criteria. The reason might be that data set consist of only 15 points and thus is very sensitive to extreme values. In addition, a larger uncertainty was expected in the NO_x-NO monitor results at this concentration level. However, the calculated M.MAD value is comparable to M.MAD obtained from the comparison of NILU-FK versus NO_x-NO monitor (see Table 4) and the CoV are below 10% for both NILU SS2000 and NILU-FK versus NO_x-NO monitor. Figure 4a and Figure 4b also indicate a systematic difference when results from both SS2000 and NILU-FK are compared with the NO_x-NO monitor results. However, these differences are within the uncertainty in the NO_x-NO monitor readings (0.5 ppb) inclusive the uncertainty of zero-point determination.

Figure 5 illustrates the good agreement between NILU-SS2000, NILU-FK and NO_x-NO monitor.

Table 3:Comparison of NILU SS2000 versus NO_x-NO monitor.

	NILU SS2000 NO_2 µg/m^3	NO_x-NO monitor NO_2 µg/m^3	Difference %
Average	6.15	5.41	13.6
Median	6.67	5.87	13.6
No. of sample pairs	15		
Average difference	0.85		
Median difference	0.59		
M.MAD	0.41		
CoV(%)	7.02		

Table 4: Comparison of NILU-FK versus NO_x-NO monitor.

	NILU-FK NO_2 µg/m^3	NO_x-NO monitor NO_2 µg/m^3	Difference %
Average	5.79	5.37	7.8
Median	5.90	5.87	3.5
No. of sample pairs	21		
Average difference	0.42		
Median difference	0.41		
M.MAD	0.49		
CoV(%)	8.43		

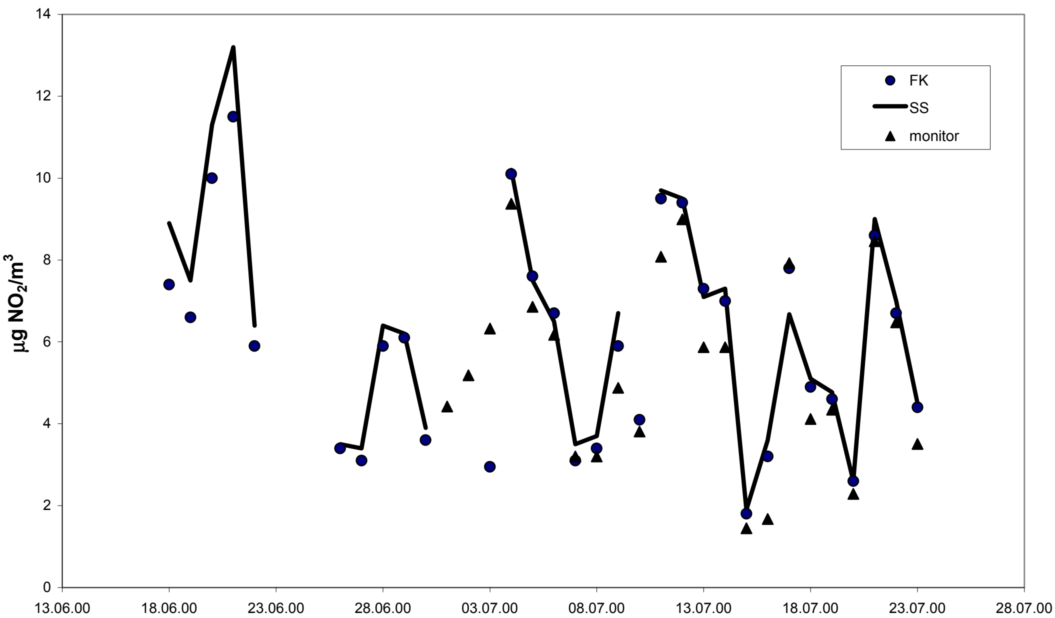

Figure 5: Comparison of NO_2 measurements using NILU-FK, SS2000 and monitor

6 Conclusions

It is shown that the performance of NILU SS2000 meets the data objective of an R^2 value of at least 0.9 in a linear regression of the NO_2 concentrations against the NO_x-NO monitor measurements. The difference between the average concentration obtained by NILU SS2000 and the NO_x-NO monitor is within the uncertainty of the latter technique. In addition, the calculated CoV is below 10%. The overall conclusion is that the performance of NILU SS2000 is in good agreement to NO_x-NO monitor.

It is also shown that the performance of NILU SS2000 is in good agreement with the old sequential sampler NILU-FK. The difference in average concentrations is below 10% and the linear regression correlates with an R^2 value above 0.9.

7 References

Ferm, M. and Sjödin, Å. (1993) Proposal of an impregnated filter technique for monitoring of NO_2 at EMEP stations. In: *EMEP Workshop on Measurements of Nitrogen-Containing Compounds. Les Diablerets, Switzerland, July 1992*. Ed. by R. Ballaman, R. Gehrig, I.M. Kvalvågnes and J. Schaug. Lillestrøm, Norwegian Institute for Air Research (EMEP/CCC-Report 1/93). pp. 173-181.

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Sirois, A. and Vet, R. J. (1994) The comparability of precipitation chemistry measurements in the Canadian air and precipitation monitoring network (CAPMoN) and three other north American networks. In: *EMEP Workshop on the Accuracy of Measurements. Passau, 1993.* Ed. by T. Berg and J. Schaug. Kjeller, Norwegian Institute for Air Research (EMEP/CCC-Report 2/94). pp. 88-114.

For more information on NILU SS2000: http://www.nilu.no/products/

Appendix A

Instrument layout, display and operator panel commands

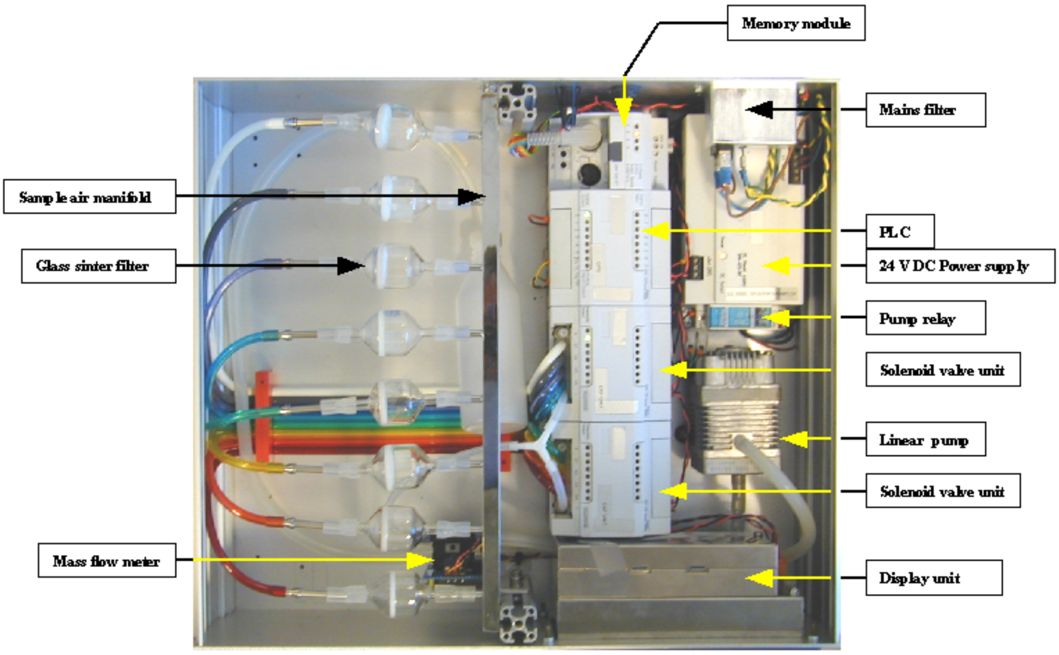

Figure A. 1: Instrument layout (lid removed).

The sampler layout, as shown above, is designed so that one half contains the electronics, pump, valve unit and display, while the other half is for the intake manifold, filter holders, silencer and flow meter.

Please note where the four fuses are placed. There is one fuse each for the display and battery and two for the mains power receptacle.

The pneumatic side of the sampler is the only side needed to be accessed by the user under normal use. There are two panel screws on each side of the lid. Remove the two screws to get access to the sampling chamber.

Remove the four countersunk screws in the front panel and carefully pull out the front panel to get at the flow meter, display or display fuse.

The PLC (control unit), valve units, pump relay and power supply are all fixed to a DIN standard rail on the floor of the instrument. Locate the small "loop" on the side of each unit, insert a small flat-headed screwdriver in the "loop" and press the "loop" outwards to disengage the lock holding the unit in place. Please do remember to disconnect the internal flat cable between the valve units and/or the PLC before disassembly.

The operator panel with display has its own real time clock with battery back up. The PLC will use this clock rather than its own to keep track of time. This is to enable the operator to adjust the system time without the need of a programming tool. The display has 4 lines of 20 characters to display the system status.

The display will show the active sample number, present flow, time and accumulated sampling time for the active sample when the sampler is operating. This is the main display. The operator can check the accumulated volumes for each exposed filter by means of the <RIGHT> arrow. The “LEFT” arrow will bring you back to the main display. The display will also revert back to main window after 15 seconds without interference from the operator. “UP” and “DOWN” arrows let you display text, which may lie outside your field of view.

Figure A.2: Operator panel layout.

SET correct DATE and TIME:
Push <enter> and hold until the display below appears. Select “TIM” with the arrow keys. Push <enter> again.

The cursor will appear on the day field. Adjust the day with <UP> or <DOWN> arrow. Hit <enter> cursor will move to month field. The field is adjusted like the previous field. Hit <enter> again. You advance to next field by pushing <enter>. Hit <enter> again if the field should remain as it is. Finally you hit “clear” to exit the date adjust mode. The new date will be effective after exit.

SET STRT, set start time:
which will recur every 24 hours by pushing <SET STRT> i.e. the #5 key pad on the panel. Push <ins> i.e. #0 key pad. Enter hours for instance 07 with the key pads. Hit <enter>. Push <SET STRT> again and then <ins>. Move to the minutes with the <RIGHT> arrow. Enter the minutes for instance 15 with the key pads. Then hit <enter>. The display should now read **Start time: 07:15**. The display will automatically revert to the main display.

NON STOP:
This button will toggle between continuous sampling and single sequence sampling. Single sequence will stop after the eighth filter is sampled. In continuous mode the sampler will retain pertinent data for the active filter when you temporarily stop the sampling to change filters. You simply push the <CONT> button to resume sampling on the active filter when the filters are changed. Selected mode will show up as continuous with the green LED lit and single sequence when the LED is off.

STRT:
Starts the sampling. This button toggles between start and stop. So when you want to stop sampling for some reason like changing filters, you actually hit <STRT>. Please observe that the sample filter is incrementing with one every second time you hit <STRT>. Start/stop status is indicated with <STRT> LED lit when the sampler is running.

CONT:
Is used to resume sampling without advancing to next filter.

prn:
is used to print out all data from the display. An optional printer will be introduced in a later version of the instrument. You can, however, transmit the data to a computer by means of a terminal emulating program and an interface cable to the display unit.

Appendix B

Sampling procedure

The standard operating procedure (SOP)

The following SOP is based on: daily sampling (24h average) and change of seven samples once a week.

1. Check that the filter being exposed and the present flow are correct. Please note the sample number and exposure time and check that this coincides with your settings.
2. Read and note all sample volumes in the field log. The volumes appear one sample after the other when you press the <RIGHT> arrow. Please observe that shortly after volume display the display will revert to the present active sample and you will have to press the <RIGHT> arrow the appropriate number of times to recall the sample you were reading. Active sample will only read flow and not volume.
3. Write down volume and exposure time in the field log
4. Hit <STRT> button to temporarily stop the sampling.
5. Check that the <STRT> and <NON STOP> light emitting diodes (LEDs) go off.
6. Remove the 7 exposed glass bulbes and seal them with red protection plugs. Leave the glass bulb that is active.
7. Disconnect the filterholder (prefilter) from its fitting and replace it with a new one.
8. Mark 7 new glass bulbs with site name and date before you connect them to their correct position on the manifold.
9. Close off inlet by pinching the silicone tube between manifold and intake filter.
10. Hit <CONT>. The LEDs lights up and the pump starts.
11. Wait till the displayed flow drops to zero and hit <STRT> again to stop.
12. Hit <SHFT> button and check that all 8 sample flows go down to zero. The sampler will automatically shift through all 8 filters. You will probably reach zero flow just as it changes to next sample.
13. If not, trouble-shoot for leakages and test again.
14. Remove the pinch.
15. Hit <SHFT> again and check that all 8 sample flows reach normal value i.e. 0,5 litres per minute. The sampler will automatically shift through all 8 filters.
16. If not, trouble-shoot for blockage.
17. Mark in the field log that leaking has been tested.
18. Hit <CONT> to continue sampling on the filter that was active. Reconfirm that you are in NON-STOP mode if that is your intention. Selection is made with the <NON STOP> key.

You can get back to the main display by pushing the <LEFT> arrow.

17. The "Remarks" column in the field log is used for information of importance to the local operator, e.g. power failure. If possible, the period of "no current" shall be given.
18. The field log should be sent together with the exposed glass sinters to the lab.

Trouble shooting:

Table A.1: List of different problems and possible solutions.

Problem	Possible solution
No response when switched on.	Check that main power is present. Check main fuses.
No response from display. Pump starts.	Check display fuse.
No flow	Check that pump is running. If not check relay and connections between relay, PLC and power supply.
No flow with pump running.	Check tube connection between pump unit and flow meter.
Excessive flow, (more than normal).	Check tube connection between flow meter and valve unit.
Fail to pass leak test.	Check all tube connections between inlet tube and filter as well as all connections up to and including flow meter. It is important to check that the two small plugs in pos. 3.0 of each valve unit are in place and not leaking.

Appendix C

Circuit diagram for NILU SS2000

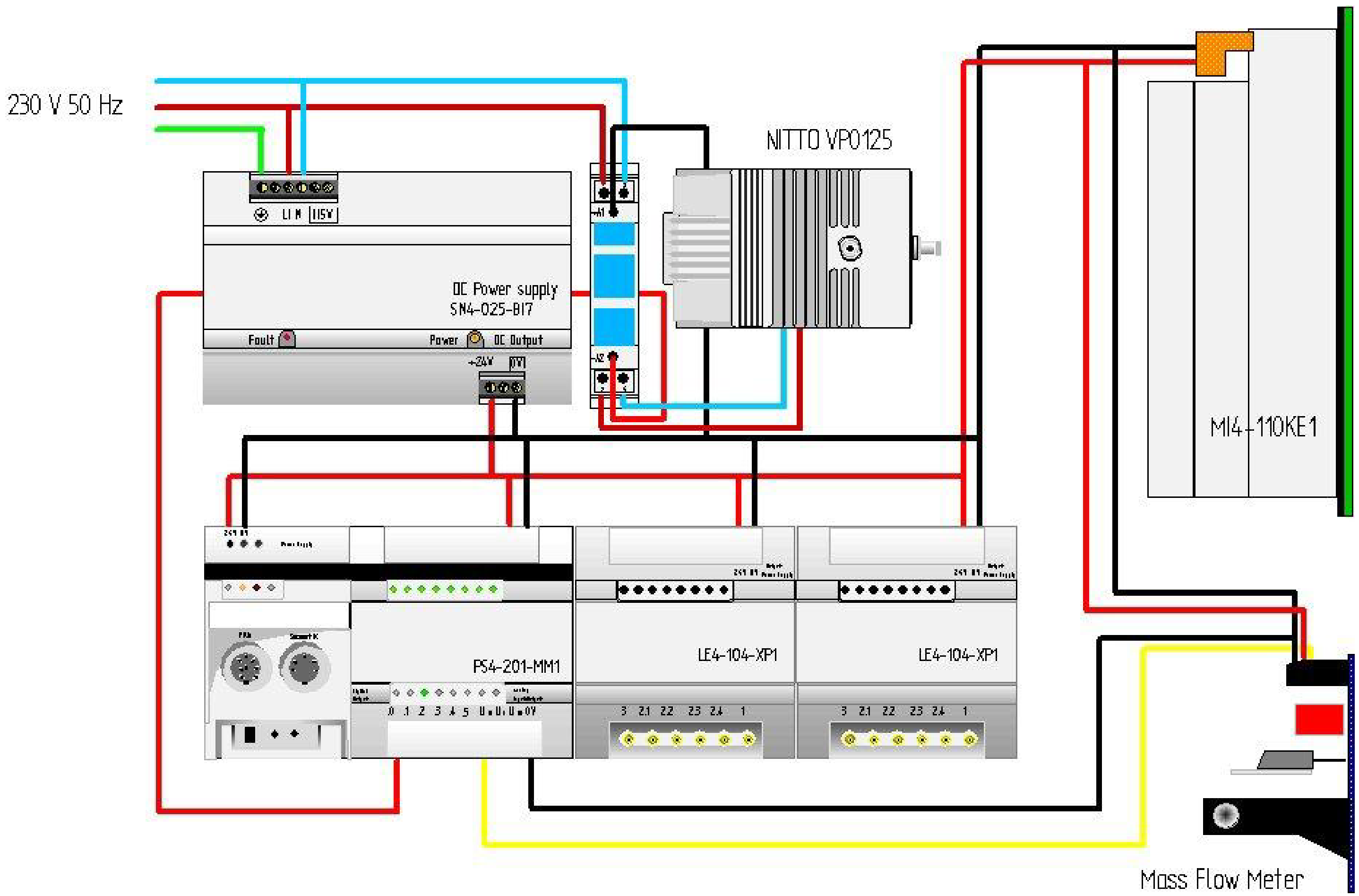

Figure C.1: Wiring diagram for NILU SS2000.

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ABSTRACT

A comparison is made of the new filter sampler NILU SS 2000 versus NO_x-NO monitor and NILU-FK, respectively.

NORWEGIAN TITLE

NO_2 sekvensiell luftprøvetaker NILU SS2000

KEYWORDS

Filter sampler	NO_2 sampler	

ABSTRACT (in Norwegian)

Resultater fra sammenlikningen av NILU SS2000 med henholdsvis NO_x-NO monitor og NILU-FK.

** Classification*	*A*	*Unclassified (can be ordered from NILU)*
	B	*Restricted distribution*
	C	*Classified (not to be distributed)*