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# REBUILT PHILIPS SO<sub>2</sub> MONITOR ON MOBILE PLATFORM

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## REBUILT PHILIPS SO, MONITOR ON MOBILE PLATFORM

#### **1** INTRODUCTION

It has been demonstrated (Grochowski 1984; 1985) that a rebuilt Philips  $SO_2$ monitor model PW 9700 can measure  $SO_2$  in very small concentrations, down to 1 µg  $SO_2$  per m<sup>3</sup> of air. Two rebuilt monitors proved to be very stable and reliable in the laboratory, although selectivity problems at small  $SO_2$  concentrations still need further investigation. Since the monitors perform continuously and in near-real time, they can be of great help in field studies of  $SO_2$  emissions from various sources. This report describes a series of experiments performed with such a  $SO_2$  monitor installed in a van.

#### 2 RESULTS

Although the rebuilt monitor must still be considered as a prototype, it has endured the mechanical strain of being handled in the field without problems during the testing period. With the instrument van parked and the engine running over periods of 10-30 minutes, the sensitivity of the monitor was the same as in stationary operation ( $\approx 1 \ \mu g \ SO_2/m^3$ ), and the signal-to-noise ratio was unchanged. Vibrations and shock occurring while driving increase the noise level by a factor of 2-3.

After some modifications made during the field experiments the instrument response lags 20s with respect to the sample gas input. The instrument has two outputs with time constants of 7s and 100s respectively (when the input is quickly changed from clean air to air with a stable  $SO_2$  concentration, the time constant is measured from the time the instrument output starts responding and until the output reaches 67% of the final reponse). Sensitivity and usable response time when "plume-hunting" is dependent upon background noise. A passing diesel truck may give a signal of typically 20s duration and a peak height of approximately 80 µg  $SO_2/m^3$ . To filter out such unwanted signals it is necessary to use the slow output when measuring in areas with heavy traffic. The minimum detectable plume size is estimated to be of the order of 20 µg  $SO_2/m^3$  peak height for a 10 minute traverse (time taken to drive from one edge of the plume to the other) at a moderate traffic load. In heavy traffic the minimum detectable plume size is estimated to be 80  $\mu$ g SO<sub>2</sub>/m<sup>3</sup> for a 15 minute traverse. Both these hypothetical plume sizes can be difficult to separate from local variations in traffic load.

In areas with little or no traffic, a plume having a peak concentration of  $10 \ \mu g \ SO_2/m^3$  for a 20s traverse can be detected on the fast output. It is essential, of course, to keep the instrument van's own exhaust clear of the air intake. The conditions should also be stable enough for traverses to be run several times with repeatable results.

The instrument has been calibrated with an AID Portable Calibration System model 340A and a liquid SO<sub>2</sub>-filled permeation tube. The permeation rate of the tube was known within  $\pm$ 1% of the given value. Errors in the reading of the calibrator flowmeters may, however, be considerably larger (in the range of  $\pm$ 5%). Calibrations were performed with SO<sub>2</sub> concentrations from 82 to 534 µg SO<sub>2</sub>/m<sup>3</sup>. The instrument will give usable readings from 1 to 3000 µg SO<sub>2</sub>/m<sup>3</sup>. Linearity errors and possible hysteresis effects outside the calibrated area are unknown. Interference from e.g. NO<sub>2</sub> and O<sub>3</sub> may give signals equivalent to as much as  $\pm$ 3 µg SO<sub>2</sub>/m<sup>3</sup> (Grochowski, 1985).

Experiments with the material TEFLON PFA (perfluoro alcoxy, used for tubing and fittings) have so far been very successful. The material does not release gases that interfere with SO<sub>2</sub> measurements in the rebuilt Philips monitor. SO<sub>2</sub> adsorption/desorption is similar to that experienced with TEFLON PTFE. PFA is a true thermoplastic material with mechanical properties far superior to those of ordinary teflon. Mechanical stability is essential to ensure leak-proof connections during vibrations and shock. Chemically FPA is said to be "nearly as inert as teflon". This has so far proved to be sufficient.

#### **3 DESCRIPTION OF THE VARIOUS EXPERIMENTS**

#### A: INSTALLATION, ZERO, CALIBRATION

The rebuilt monitor A (Grochowski, 1984, with continuous regeneration of the electrolyte) was installed in the van on 8 February, 1985. The van was parked in the NILU storehouse and the instrument powered from the mains supply.

In the period from 8 February to 12 February, zero point and calibration was checked. The zero point was stable 12 hours after the installation. (After subsequent reinstallations, the zero point usually stabilised within 2 hours). The calibration was not satisfactory, because the calibration equipment available at the time (based on a Philips diffusion bottle) was not temperature-stabilised.

#### B: ZERO POINT DURING DRIVING

The first test drive was done on 12 February. A gasoline powered 220VAC generator unit was mounted on a small trailer. The sample air was filtered through a glass cylinder containing activated charcoal. Large initial disturbances were caused by a loose signal connection to the strip-chart recorder. After this fault was corrected, during normal driving (which causes vibrations, shock, temperature changes and possibly electromagnetic disturbances) the zero drift was  $\leq \pm 1 \ \mu g \ SO_2/m^3$ .

#### C: MEASUREMENTS AT RÆLINGSÅSEN, 13 FEBRUARY, 1985

Quite large and quickly varying signals were registered. The Philips chopper amplifiers cannot handle negative signals. This means that the electrical zero must be adjusted at some positive voltage, and the zero point will shift on the chart paper when the recorder range is changed. The long response time of the instrument ( $\approx$  20s dead time, and time constant 60 s for this version) made it impossible to determine which peaks were only due to local traffic interference.

## D: INFLUENCE OF THE EXHAUST FROM THE INSTRUMENT VAN

14 February was a cold day, with a temperature inversion and very weak easterly winds over Lillestrøm. At the Stalsberg Churchyard next to øvre Rælingsveg, the wind was moving up a small valley from Lillestrøm, without being influenced by nearby traffic. With the van turned into the wind, a very stable reading of 10 µg SO<sub>2</sub>/m<sup>3</sup> was obtained. With the van facing in the opposite direction, the signal was very unstable with peaks up to 45 µg SO<sub>2</sub>/m<sup>3</sup> apparently caused by exhaust drifting towards the sample intake. These experiments were repeated with identical results.

A similarly undisturbed site at the upwind side of Lillestrøm was located on the east side of Mosesvingen, where a very stable signal of 3  $\mu$ g SO<sub>2</sub>/m<sup>3</sup> was registered. The strip-chart recording from these experiments is shown in Figure 1. The recorded SO<sub>2</sub> concentrations are based upon calibrations with the Philips diffusion bottle (Model PW 9740/20). A calibration performed at NILUS K-lab, 1984-06-27, first gave a mass loss of 13.5  $\mu$ g SO<sub>2</sub>/hour from this source. Subsequent analysis performed at K-lab indicate, however, that this diffusion rate may be low by a factor of 1.4.

#### E: SHORT RESPONSE TIME

The output of the original Philips monitor has a time constant of approximately 40 s. Grochowski has changed this value to 60 s. On 1985-02-15 the time constant of the electrical system was changed to approximately 7 s. The noise level increased from sub-readable to 1  $\mu$ g SO<sub>2</sub>/m<sup>3</sup> peak-to-peak. During a test drive to Garderåsen, noise increased to 2  $\mu$ g SO<sub>2</sub>/m<sup>3</sup> peak-to-peak. Local traffic influence now gave quick and large signals (up to 56  $\mu$ g SO<sub>2</sub>/m<sup>3</sup>). The deadtime of the instrument was determined to be approximately 20 s. This is slightly more than the calculated time needed for sample air to pass the intake system and enter the electrolytic cell.

#### F: MEASUREMENTS FROM A MOVING VAN

The gasoline-fueled generator was replaced by an electronic inverter, generating 220VAC from the van's 12VDC supply. The SO<sub>2</sub> monitor with a magnetic voltage stabilizer and the inverter draws about 30A at 12V.

To detect a plume of SO<sub>2</sub>, the quickly varying signals due to local traffic emissions have to be filtered out. Since a fast instrument response is needed to detect a narrow plume, a simple solution to this problem does not exist. Under unfavourable conditions, with strong local traffic influences, it is impossible to distinguish a narrow plume from the background.

A second-order active filter with a time constant of 100 s was built into the A monitor. A two-channel strip-chart recorder was used to register both the fast and the slow channel reponses (time constants 7 s and 100 s, respectively) at the same sensitivity level. On 1985-02-12 the instrument was taken on a test drive in downtown Oslo. The strip-chart recording is shown in Fig. 2. The fast channel registered peak signals, due to single cars passing; diesel trucks give the largest signals. The slow channel did not react much to these rapid changes in SO<sub>2</sub> concentration. In cases where the same route was followed twice, the slow signal appeared to be reproduced, whereas the fast signal changed at random.

#### G: CALIBRATION

Earlier calibrations of the modified monitor have been based on a Philips diffusion bottle (Grochowski, 1984; 1985). There is, however, still a confusion about the diffusion rate from this bottle.

From 1985-03-13 to 1985-03-15 the monitor was calibrated with an AID Portable Calibration System model 340A and a liquid  $SO_2$ -filled permeation tube having a permeation rate of 826 µg  $SO_2$ /minute. The results obtained are shown in Table 1.

The results show that  $SO_2$  concentrations from approximately 20 µg/m<sup>3</sup> to 600 µg/m<sup>3</sup> give a signal of 0.95 ±0.05 mV per µg/m<sup>3</sup>. The data base is too small, however, to distinguish linearity errors from random experimental errors.

$SO_2$ concentration $\mu g/m$	Voltage mV	Sensitivity mV per µg/m <sup>3</sup>	
82	78.4	0.96	
126	122	0.97	
126	114	0.90	
246	240	0.98	
534	480	0.90	

Table 1: Results of modified Philips SO<sub>2</sub> monitor calibration with AID permeation tube calibrator.

#### H: TEST OF TEFLON PFA

During the calibration experiments sampling line tubing made from TEFLON PFA (Per fluoro alcoxy) was also tested. This is a true thermoplastic material with mechanical properties far superior to those of ordinary teflon. Chemically it is said to be "nearly as inert as teflon".

A piece of 1/4" PFA tubing, 3 m long, was used to supply 80 µg SO<sub>2</sub>/m<sup>3</sup> from the calibrator to the monitor. No differences in signal could be detected when the PFA tubing was used in the system. When an activated charcoal filter was placed before the PFA tubing, only a slight "tailing" could be observed. This means that no SO<sub>2</sub> had been adsorbed on the tubing walls. It still is necessary to test the PFA tubing with very low SO<sub>2</sub> concentrations, and to check, whether surface properties will change during long-term exposures. The PFA tubing had been conditioned with a clean airstream for two weeks before the experiments.

Similar experiments with an unused 1/4" PTFE tube 7 m long resulted in severe "tailing" (adsorption/desorption of SO<sub>2</sub> on the tubing walls). New tubing must be conditioned for several days with a clean airflow before a stable zero signal is obtained.

#### 4 REFERENCES

Grochowski, Z.(1984) Measurement of sulphur dioxide in the ppb range. (Norwegian Institute for Air Research, Lillestrøm (NILU TR 12/84).

Grochowski, Z.(1985) Description of a coulometric instrument for background measurements of sulphur dioxide. Norwegian Institute for Air Research, Lillestrøm (NILU TR 1/85).



SO\_ measurements downstream and upstream of Lillestrøm on Fig. 1: 1985-02-4 (a cold day with temp. inversion and slight wind from east). The measurements were performed in a parked van with the engine running.



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3 STIKKORD (à maks. 20 a SO <sub>2</sub> -monitor	anslag) ppb-område	mobile måling	ger			
REFERAT Philips SO <sub>2</sub> -monitor er tidligere modifisert for målinger i ppb-området. Nye modifikasjoner muliggjør bruk i bil under fart. Vibrasjoner gir økt støy, deteksjonsgrensen stiger fra 1 μg/m <sup>3</sup> til 3 μg/m <sup>3</sup> . Deteksjon av plumer vurderes. Eksempler på mobile målinger vises.						
TITLE						
ABSTRACT Philips S0 monitors have previously been modified for measurements in the ppb-range. New modifications allow mobile ope- ration. Vibrations increase the noise signal, and the detection limit increases from 1 $\mu$ g/m to 3 $\mu$ g/m <sup>3</sup> . Detection of plumes is considered, and examples of mobile measurements are presented.						

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