

# IVL REPORT

L91-172

## A sensitive diffusional sampler

Göteborg 1991-03-13

Swedish Environmental Research Institute

Martin Fern

B-1020  
Göteborg  
1991

**IVL**  
**INSTITUTET FÖR VATTEN- OCH LUFTVÅRDSFORSKNING**  
SWEDISH ENVIRONMENTAL RESEARCH INSTITUTE

<b>Organisation/Organization</b> INSTITUTET FÖR VATTEN- OCH LUFTVÅRDSFORSKNING	<b>RAPPORTSAMMANFATTNING</b> <b>Report Summary</b>
<b>Adress/Address</b> Box 47086 402 58 GÖTEBORG	
<b>Telefonnr/Telephone</b>	<b>Projekttitel och ev SERIX projektnr</b>
<b>Rapportförfattare (efternamn, tilltalsnamn)</b> Author (surname, christian name) Ferm, Martin	<b>Anslagsgivare för projektet/Project sponsor</b>  IVL
<b>Rapportens titel och undertitel/Title and subtitle of the report</b>  A sensitive diffusional sampler.	
<b>Sammanfattning/Summary</b>  A short, wide and thereby sensitive diffusional sampler for use in ambient air has been developed. In order to avoid turbulent diffusion inside the sampler, the inlet is covered by a thin porous membrane filter. Gases are also transported by molecular diffusion in the laminar boundary layer in front of the membrane. The thickness of this layer is not negligible in comparison with the length of the sampler. It can be measured using an extra sampler with an impregnated filter that directly faces the ambient air. The sampler has been tested for three gases. For a sampling time of one month, the measuring ranges are approximately $0.05-70 \mu\text{g NO}_2/\text{m}^3$ (0.02-40 ppb), $0.3-200 \mu\text{g SO}_2/\text{m}^3$ (0.1-80 ppb) and $0.2-20 \mu\text{g NH}_3/\text{m}^3$ (0.2-30 ppb).	
<b>Förslag till nyckelord samt ev anknytning till geografiskt område, näringsgren eller vattendrag/Keywords</b>  Nitrogen dioxide, sulphur dioxide, ammonia, analysis, atmosphere	
<b>Bibliografiska uppgifter/Bibliographic data</b>  IVL - publ.            B-1020	
<b>Beställningsadress för rapporten/Ordering address</b>  IVL, Biblioteket Box 21060, S-100 31 Stockholm, Sweden	

## A sensitive diffusional sampler

Martin Fern

Swedish Environmental Research Institute  
P.O. Box 47086, S-402 58 Gothenburg, Sweden

13/3 -91

### Abstract

A short, wide and thereby sensitive diffusional sampler for use in ambient air has been developed. In order to avoid turbulent diffusion inside the sampler, the inlet is covered by a thin porous membrane filter. Gases are also transported by molecular diffusion in the laminar boundary layer in front of the membrane. The thickness of this layer is not negligible in comparison with the length of the sampler. It can be measured using an extra sampler with an impregnated filter that directly faces the ambient air. The sampler has been tested for three gases. For a sampling time of one month, the measuring ranges are approximately  $0.05\text{-}70\ \mu\text{g NO}_2/\text{m}^3$  (0.02-40 ppb),  $0.3\text{-}200\ \mu\text{g SO}_2/\text{m}^3$  (0.1-80 ppb) and  $0.2\text{-}20\ \mu\text{g NH}_3/\text{m}^3$  (0.2-30 ppb).

### Introduction

There is sometimes a need for determination of air pollutants at places where electricity is not available, as e.g. at remote places far from local sources. Sometimes small, light and silent samplers are needed, for instance for personal use and when the spatial concentration distribution near ground level is measured in a city. All these requirements are met in a diffusive sampler. It can be applied for all gases that can be trapped on a filter, if no losses to the walls or the inlet occur. The first sampler was developed for determination of  $\text{H}_2\text{O}$  and  $\text{SO}_2$  (Palmer and Gunnison 1973). Liquid or granular sorbents were used to trap the gases. The sampler became more practical when an impregnated filter was used to measure the  $\text{NO}_2$  concentration in indoor air (Palmer et al. 1976). It could only be used at low wind speed and not during longer sampling periods. These problems were later overcome by replacing the impregnation and using a stainless steel net in the open end as a wind screen (Fern 1986). A lot of samplers have been constructed since Palmer diffusive tube was developed (Rose and Perkins 1982 and Moore 1987) This paper describes a sampler aimed for determination of low concentration in ambient air. It has so far been used for  $\text{NO}_2$ ,  $\text{SO}_2$  and  $\text{NH}_3$ . Other advantages with diffusional sampling is that field



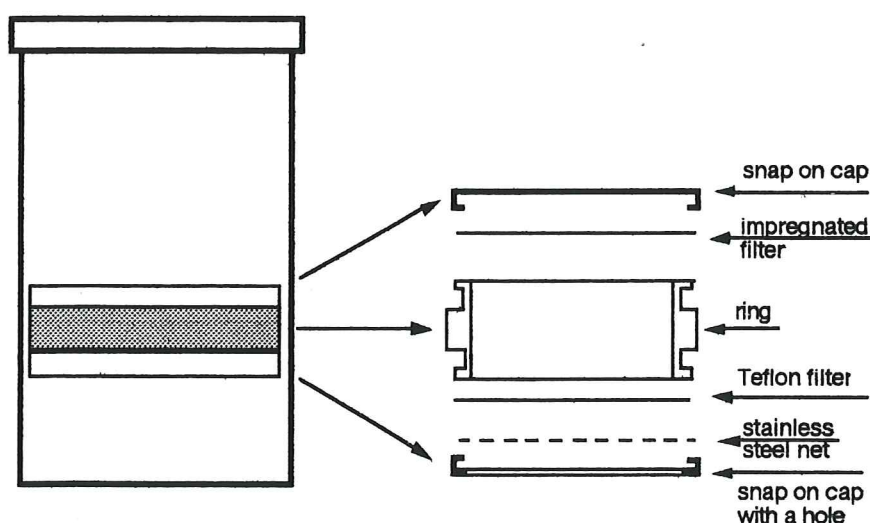
calibration is not necessary, the concentration is integrated all the time without interruption and they can be produced at a low cost.

### Principle

The gas which concentration should be determined is trapped on a solid sorbent or a filter impregnated with a water soluble substance. The sorbed amount must be proportional to the ambient concentration of the gas. In volumetric techniques this is accomplished by passing air at a constant flow through the sorbent. In diffusional sampling the gas is passively transported to the sorbent by molecular (thermal or laminar) diffusion. The diffusion rate is made constant by placing the impregnated filter inside a tube.

### Description of the sampler

The sampler consists of a polypropylene ring which is turned from a 25 mm O.D. standard tube. An impregnated filter (Whatman 40,  $\varnothing$  25 mm) is placed on top of the sampler. The filter is attached by putting on a snap-on cap. The cap is made of low density polyethylene and is commercially available as a snap-on cap for vials. A teflon filter (Fluoropore<sup>®</sup> FALP  $\varnothing$  25 mm) is placed under the lower opening. The filter can be protected from mechanical destruction by a stainless steel net. The net is punched out from a large net having a thread diameter of 0.080 mm and a mesh size of 0.125 mm. The teflon filter and the steel net are attached by another snap-on cap. A 20 mm centred hole is punched out in this cap. During storage and transport the sampler is kept in a 36 ml polypropylene vial with a similar but wider snap-on cap.



*Fig 1. Storage container with diffusional sampler.*

### Choice of sorbents

The filter must act as a perfect or almost perfect sink, otherwise the equations for calculating the results will not be valid. Chemisorption on the filter is therefore preferable.

Huygen (1962) collected  $\text{SO}_2$  on alkali impregnated filters and determined the amount of  $\text{SO}_3^{2-}$  trapped. At high relative humidities several impregnation solutions could be used. At low humidities the potassium salts are better than sodium, because they are more hygroscopic. The use of glycerin further improves the collection efficiency at low humidities and stabilizes trapped  $\text{SO}_2$  as  $\text{SO}_3^{2-}$ . The formed  $\text{SO}_3^{2-}$  is, however, oxidized to  $\text{SO}_4^{2-}$  within a couple of days. Huygen recommended a solution of 20% KOH and 10% glycerin for trapping  $\text{SO}_2$ . This solution has also been used by Johnsson and Atkins (1975). They used  $\text{K}_2\text{CO}_3$  instead of KOH, which is closer to the final composition of KOH exposed to air, and leached the filters in a dilute  $\text{H}_2\text{O}_2$  solution and determined the amount of  $\text{SO}_4^{2-}$ . A good correlation between this filter technique and  $\text{H}_2\text{O}_2$  bubbler method was observed. Lewin and Zachau-Christiansen (1977) found that KOH alone could be used at r.h. above 30%. KOH has also been used to trap formic- and acetic acid (Rosenberg et al. 1988).  $\text{NH}_3$  reacts with acids even if they are in a solid form. Phosphoric, phosphorous, boric, oxalic and citric acid have previously been used. Oxalic acid is rather volatile, but advantageous to use when a glass surface is coated because its deliquescent point is very high. This is not an important property when hydrophilic filters are used. An acid with a lower volatility like citric acid can therefore be used (Bos 1980). Citric acid dissolved in acetone is convenient to use because the acetone solution is very stable and the solvent evaporates quickly during the impregnation (Leuning et al 1985).

### Impregnation and analysis

For impregnation cellulose filters (Whatman 40) are used because they are hydrophilic, and easy to impregnate. Before the impregnation they are leached in de-ionized water for about one hour and dried. The impregnation is made in the following way. Filters are placed in snap on caps and attached to the rings. They are placed in a desiccator and 50  $\mu\text{l}$  sorbent solution is added to each filter. The desiccator is then evacuated. The filters are dried in about five minutes and the membrane filters (and steel nets) are attached by the hollow cap. The samplers are then immediately placed in their storage containers.



After exposure the impregnated filters are removed and placed in a vial containing 4 ml solution. The vial is closed by the cap that previously was used in the sampler. The label on the transport vial is moved to the leaching vial and the sampler is shaken for about 15 min before analysis. The polypropylene ring and the wind shield are washed in an ultrasonic bath before being reused.

### NO<sub>2</sub>

The impregnation solution consists of 10 g KI, 1 g NaAsO<sub>2</sub>, 5 g ethylene glycol in 84 g methanol. The NO<sub>2</sub><sup>-</sup> concentration of the leachate is determined spectrophotometrically after mixing with a diazotating reagent (1:1). I<sup>-</sup> may interfere with the NO<sub>2</sub><sup>-</sup> analysis. This has been noted when Flow Injection Analysis (FIA) is used. The result depends on the concentration of I<sup>-</sup>, especially at low I<sup>-</sup> levels. This artifact can be solved by leaching the filters in a high concentration of I<sup>-</sup> (4 ml 1 % KI solution).

The diazotating reagent is prepared by adding 8 ml phosphoric acid to about 0.5 l water. 8 g sulphanilamide and 0.2 g NEDA (N-(1-Naphtyl) ethylenediamine dihydrochloride) are dissolved and the total volume is adjusted to 1 l with water. 15 min after mixing one part of leachate with one part of reagent the colour is read at 540 nm. NO<sub>2</sub><sup>-</sup> standards containing the same I<sup>-</sup> concentration as the samples must be used. If FIA is used a negative peak may be observed if water is used as eluent. This dip can be avoided by using the 1% KI solution instead of water. The blank of an impregnated filter is about 1 nmol.

### SO<sub>2</sub>

The impregnation solution consists of 4 % K<sub>2</sub>CO<sub>3</sub> in water. The filter are leached in 4 ml dilute H<sub>2</sub>O<sub>2</sub> solution (0.03%) to ensure complete oxidation of SO<sub>3</sub><sup>2-</sup>. The analysis is made by ion chromatography (IC). IC is known as a technique free of interferences. A mixture of carbonate and bicarbonate is normally used as eluent in suppressed chromatography. The concentration of carbonate in the leachate is, however, not negligible in comparison to the concentration in the eluent. Slightly shorter retention times and 5-10% different peak heights may therefore occur. The standard solutions should therefore contain ≈2.5 mM Na<sub>2</sub>CO<sub>3</sub>. The blank of an impregnated filter is around 4 nmol, which is close to the value for an unimpregnated filter.

NH<sub>3</sub>

The impregnation solution consists of 2% citric acid in acetone. The analysis is made by flow injection analysis. The sample is injected in a water stream. It is then mixed with a stream of sodium hydroxide. This stream passes a teflon membrane. On the other side of the teflon membrane a water stream is flowing. Its OH<sup>-</sup> concentration is registered by measuring the colour of an added pH indicator. The blank of an impregnated filter is around 15 nmol, which is slightly higher than the value for an unimpregnated filter.

Sampling

A convenient way to protect the samplers from precipitation is to mount them under a Frisbee (plastic plate). The Frisbee is nailed horizontally to a wooden pole with the rounded edge facing downwards. The samplers are attached using small (13 by 25 mm) double-sided self-adhesive foam pads. This way of mounting the samplers has been found suitable near the arctic circle as well as in tropical regions.

Calculation of the concentration

The concentration is obtained from Fick's first law  $\varnothing = -D \cdot dC/dL$ . Where  $\varnothing$  is the flux of the gas (the amount that is net transported per unit time and area),  $D$  is the diffusion coefficient of the sampled gas in air and  $dC/dL$  is the concentration gradient which is negative in the direction of the flow. The flux is calculated from  $X/(A \cdot t)$  where  $X$  is the amount trapped on the filter.  $A$  is the cross section area and  $t$  the exposure time. The concentration difference over a section of the sampler is then calculated from:

$$\Delta C = - \frac{X \cdot \Delta L}{t \cdot D \cdot A} \quad (1)$$

Figure 2 shows the different concentration gradients during sampling.

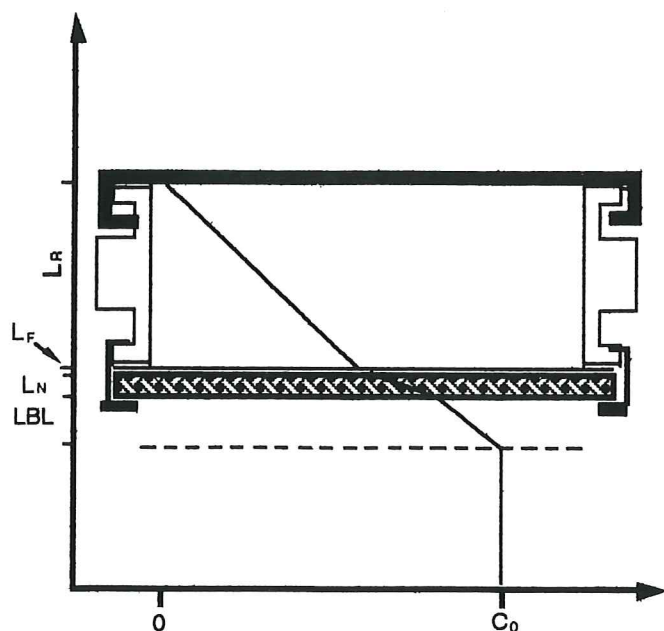


Fig 2. The concentration gradient outside and inside the sampler

There is a thin stagnant air layer outside the sampler in which gases are transported by laminar diffusion, instead of turbulent. The thickness of this laminar boundary layer is here denoted  $L_{LBL}$ . It depends on the wind speed and the turbulence of the ambient air and is about 1 to 2 mm. The thickness of the steel net and the filter are denoted  $L_N$  and  $L_F$  respectively.  $L_R$  is the length of the ring. The cross section areas are denoted with  $A$  and have the same indexes. During sampling the fluxes of the gas through all sections are equal, i.e. nothing is adsorbed on the walls, which, as earlier mentioned, is a prerequisite. The ambient concentration  $C_0$  can be calculated by adding all concentration differences over all sections i.e.:

$$C_0 = \frac{X}{t \cdot D} \left( \frac{L_R}{A_R} + \frac{L_F}{A_F} + \frac{L_N}{A_N} + \frac{L_{LBL}}{A_R} \right) \quad X = \frac{C_0 \cdot t \cdot D}{\left( \frac{L}{A} + \frac{L_F}{A_F} \right)} \quad (2)$$

$A_F$  is the total area of all the pores in the filter. The Fluoropore filter has 85 % porosity and a thickness of 175  $\mu\text{m}$ . The thickness of the steel net is 0.16 mm and it's porosity about 13 %. The thickness of the laminar boundary layer can be set to 1.5 mm, but it can actually be measured during the sampling period. An extra sampler with an impregnated filter directly exposed to the air is then used. This filter is, however, easily contaminated by, for instants, particle deposition, so it is better to place it behind the teflon filter (and the steel net if it is used) measure the three last terms in eq. 2. If the sorbed amount on this filter is denoted  $Y$  the ambient concentration is:



$$C_0 = \frac{Y}{t \cdot D} \left( \frac{L_F}{A_F} + \frac{L_N}{A_N} + \frac{L_{LBL}}{A_R} \right) \quad (3)$$

$C_0$  is obtained by solving the equation system 2 and 3 i.e.

$$C_0 = \frac{X \cdot L_R}{t \cdot D \cdot A_R} \cdot \frac{Y}{(Y-X)} \quad (4)$$

The thickness of the laminar boundary layer is then calculated from eq. 3. The diffusion coefficients ( $\text{cm}^2\text{s}^{-1}$ ) can be measured experimentally or estimated from the following semiempirical expression (Gilliland 1934).

$$D = \frac{0.0043 \cdot T^{3/2} \sqrt{\frac{1}{M_A} + \frac{1}{M_B}}}{(V_A^{1/3} + V_B^{1/3})^2 \cdot P} \quad (5)$$

in which  $T$  is the absolute temperature (K),  $M_A$  is the molecular weight of the gas (g) and  $M_B$  the average molecular weight of air (29 g).  $V_A$  is the mole volume of the gas in liquid form at the normal boiling point (ml) and  $V_B$  is the corresponding value for air (29.9 ml).  $P$  is the total pressure (atm). Sometimes the mixing ratio is used instead of the concentration, i.e. the concentration of the trace gas divided by the concentration (density) of the air. The density of the air is according to the equation of the state of an ideal gas =  $M_B \cdot P / (R \cdot T)$ . The temperature and pressure dependence of the calculated mixing ratio will thus be  $T \cdot P / (T^{3/2} \cdot P) = 1/\sqrt{T}$ . i.e. independent of the pressure and a temperature dependence of about 2 % per °C.  $D$  for  $\text{NO}_2$  has been estimated to  $1.54 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$  (21°C) (Palmer et al. 1976) and for  $\text{NH}_3$   $2.54 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$  (25°C) (Coulson and Richardson 1954). The diffusion coefficient for  $\text{SO}_2$  is  $1.32 \cdot 10^{-5} \text{ m}^2 \text{ s}^{-1}$  (20°C) but it has a temperature dependence of  $T^{1.75}$  (Fish and Durham 1971).

### Experimental

Triethanolamine was first used as a sorbent for sampling  $\text{NO}_2$  in urban air. It was, however, found that it could not be used for long-time sampling (several weeks). Successive samples gave a higher average concentration than samples covering the whole period. The reason for this was never understood. Other sorbents like NaOH and guaiacol (Buttini et al. 1987) and  $\text{KI} + \text{NaAsO}_2 +$  ethylene glycol were tried instead (Possanzini et al. 1984). The

latter one was chosen because the samples had a very good storage stability, before as well as after sampling, and the results were always additive (successive sampling agrees with long time sampling). This sorbent is very efficient but not a perfect sink. It can therefore not be used when rapid sorption is needed as eg. in denuders or to measure the thickness of the laminar boundary layer. In the first experiments long and narrow diffusional samplers were used. They were protected from wind effects using a stainless steel net instead of a membrane filter. A 50 mm long sampler with a diameter of 12 mm but without a wind shield gave higher  $\text{NO}_2$  concentrations in outdoor air, than one protected by a steel net. The over-estimation varied from one sampling period to another and was about 50 %. There was no difference when they were compared indoors.

This long and narrow diffusional sampler (with a steel net) has been used during one month, parallel with volumetric methods (24-hour sampling), in 49 Swedish towns.  $\text{NO}_2$  was sampled on sintered glass filters impregnated with the same sorbent as the diffusional samplers.  $\text{SO}_2$  was trapped in a bubble flask containing 0.03%  $\text{H}_2\text{O}_2$ . The results are shown in Fig 3-4.

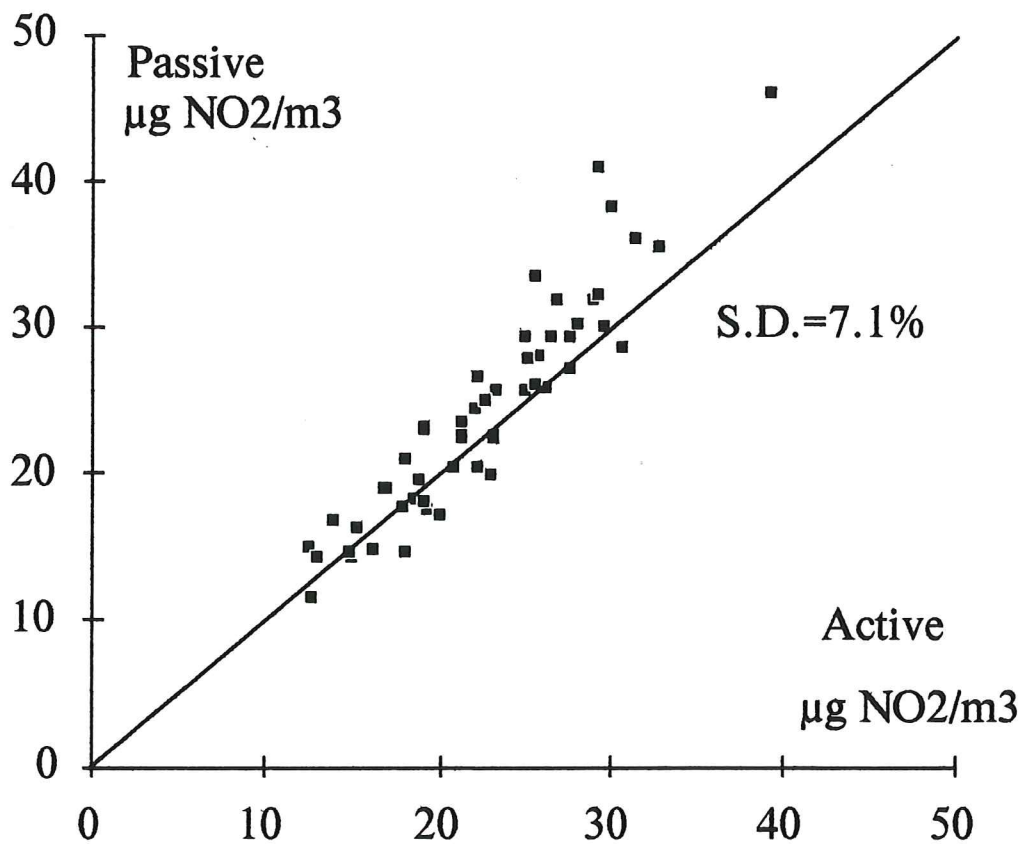


Fig 3 Comparison between active and diffusional sampling at 49 Swedish towns.

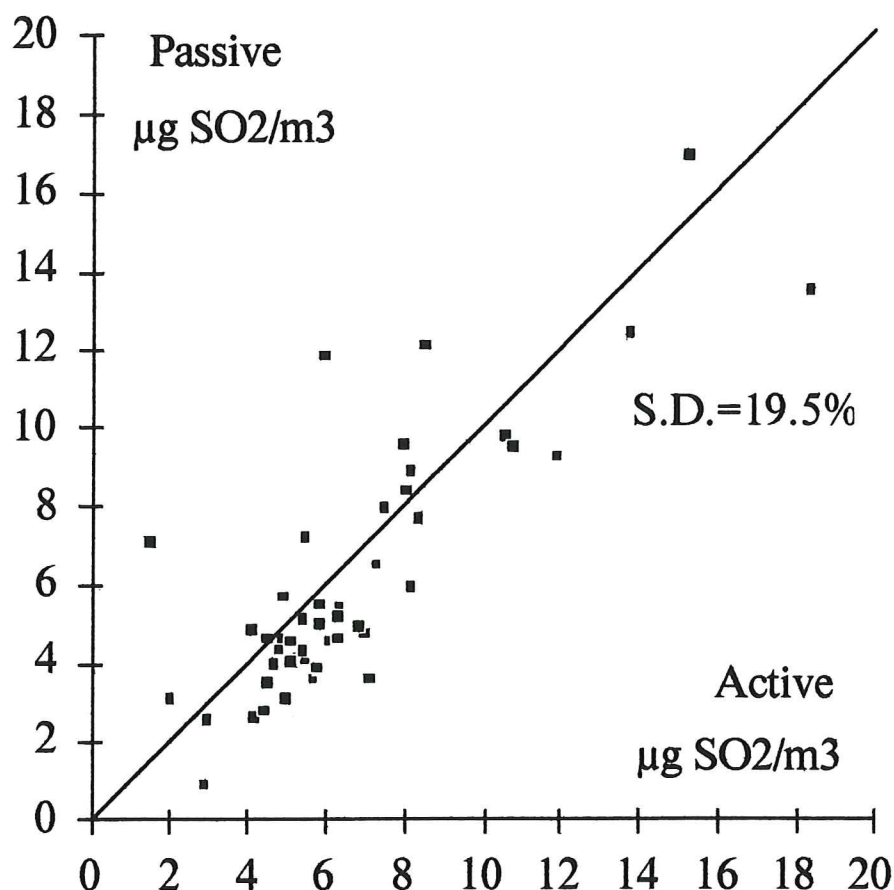


Fig 4 Comparison between active and diffusional sampling at 49 Swedish towns.

The detection limits for the volumetric methods are about  $0.2 \mu\text{g NO}_2/\text{m}^3$  and  $0.6 \mu\text{g SO}_2/\text{m}^3$ . The relative standard deviations for duplicate samples (diffusional) were 5.0 % and 10.0 % respectively.

Comparisons between the longer diffusional, the more sensitive one described in this paper and the volumetric techniques, have been made at some Swedish background stations. The figures are listed in Table 1.  $\text{SO}_2$  measurements were made during a European intercomparison within the framework of EMEP which was held at Vavihill. As can be seen from the table, long and narrow samplers were used together with two different lengths of the more sensitive one and the bubbler. In all tests two to four samplers were used parallelly and the relative standard deviations are given behind the concentrations. The thickness of the laminar boundary layer is also given when measured. The sensitive sampler with two different impregnations for  $\text{SO}_2$ , with and without stainless steel nets to protect the membrane filters, were tested at Rörvik. As can be seen the steel nets do not affect the results. The steel nets may be necessary to use in the forest near bird nests or when used as a personal sampler. In all tests described here the blanks were much



higher than the figures given in the text because the filters were dried using a hot air stream instead of a desiccator. The sensitive sampler was also used for  $\text{NO}_2$  during this test. In another test at Rörvik a new sorbent (8 % NaI, 0.4 %  $\text{Na}_2\text{CO}_3$ , in water) was used parallelly. It seems to give similar results as the original receipt.

Very few measurements have been made on  $\text{NH}_3$ , but two are given in Table 1. The test in the lab shows that the laminar boundary layer can be substantial in indoor air. In this test directly exposed impregnated filters, similar but with teflon filters in front of it and similar with both teflon filters and steel nets in front of it, gave comparable results for the laminar boundary layer (5.6, 5.9 and 5.8 mm respectively). A comparison with cylindrical denuders for  $\text{NH}_3$  gave reasonable agreement but the measurements were not completely synchronous.

Table 1 Parallel tests performed with diffusional samplers. All concentrations are given in  $\mu\text{g}/\text{m}^3$  and the laminar boundary layer in mm.

Vavihill Jan- Feb '90

L	$\emptyset$	[SO <sub>2</sub> ]	
mm	mm	$\mu\text{g}/\text{m}^3$	
50	12	$13.0 \pm 1.1$	
10	20	$12.1 \pm 0.4$	$L_{\text{LBL}} = 0.9$
20	20	$13.3 \pm 0.2$	$L_{\text{LBL}} = 1.0$
active		11.7	

Rörvik Sept-Oct '90

L	$\emptyset$	[SO <sub>2</sub> ]		
10	20	$3.7 \pm 1.0$	$L_{\text{LBL}} = 1.5$	$\text{K}_2\text{CO}_3$ , steel net
10	20	$3.8 \pm 0.6$	$L_{\text{LBL}} = 1.6$	$\text{K}_2\text{CO}_3$
10	20	$3.7 \pm 1.0$	$L_{\text{LBL}} = 1.8$	$\text{Na}_2\text{CO}_3$ , steel net
10	20	$3.5 \pm 0.4$	$L_{\text{LBL}} = 1.2$	$\text{Na}_2\text{CO}_3$
active		3.7		

L	$\emptyset$	[NO <sub>2</sub> ]
10	20	$5.3 \pm 0.7$

active 5.5

Rörvik Nov-Jan '90-'91

L	$\emptyset$	[NO <sub>2</sub> ]	
10	20	$8.9 \pm 0.5$	
10	20	$10.0 \pm 0.3$	NaI
active		9.6	

Blentarp Jul-Aug '89

L	$\emptyset$	[NH <sub>3</sub> ]	
50	12	$5.4 \pm 0.5$	
10	20	$4.6 \pm 0.5$	$L_{\text{LBL}} = 2.1$

Our laboratory Sept-Oct '90

L	$\emptyset$	[NH <sub>3</sub> ]	
10	20	$5.0 \pm 0.0$	$L_{\text{LBL}} = 5.8$ Steel net

## References

- Bos R. (1980) Automatic measurement of atmospheric ammonia. *J. Air Pollution Control Assoc.* **30**, 1222-1224
- Buttini P. Di Palo V. and Possanzini M. (1987) Coupling of denuder and ion chromatographic techniques for NO<sub>2</sub> trace level determination in air. *Sci Total Environ* **61**, 59-72
- Coulson J. M. and Richardson J. F. (1954) *Chemical Engineering*, Vol. 1, p. 239 Pergamon Press, Oxford.
- Ferm M. (1986) Further developments of a diffusional sampler for NO<sub>2</sub>. (in Swedish) IVL-L86/180 (1986-06-30) 11pp Swedish Environmental Research Institute P.O.Box 47086 S-402 58 Gothenburg, Sweden
- Fish B. R. and Durham J. L. (1971) Diffusion coefficient of SO<sub>2</sub> in air. *Environ. Lett.* **2**, 13-21
- Gilliland E.R. (1934) Diffusion coefficient in gaseous systems. *Ind Engng Chem.* **26**, 681-685
- Huygen C. (1962) The sampling of sulfur dioxide in air with impregnated filter paper *Analytica Chimica Acta* **28**, 349-360
- Johnson and Atkins D.H.F. (1975). An airborne system for the sampling and analysis of sulphur dioxide and atmospheric aerosols. *Atmospheric Environment* **9**, 825-829
- Leuning R. Frey J.R. Denmead O.T. and Simpson J.R. (1985) A sampler for measuring atmospheric ammonia flux. *Atmospheric Environment* **19**, 1117-1124
- Lewin E. and Zachau-Christiansen B. (1977) Efficiency of 0.5N KOH impregnated filters for SO<sub>2</sub>-collection. *Atmospheric Environment* **11**, 861-862
- Moore G. (1987) Diffusive sampling - A review of the theoretical aspects and state-of-the-art. Proc. Diffusive sampling, an alternative approach to workplace air monitoring. Symposium held in Luxemburg 22-26 Sept 1986 (Ed. Berlin A., Brown R.H. and Saunders K.J.) Royal Society of Chemistry, 1-13
- Palmes E.D. and Gunnison A.F. (1973) Personal monitoring device for gaseous contaminants. *Am. Ind. Hyg. Assoc. J.* **34**, 78-81
- Palmes E.D., Gunnison A.F., DiMattio J. and Tomczyk C. (1976) Personal sampler for nitrogen dioxide. *Am. Ind. Hyg. Assoc. J.* **37**, 570-577

Possanzini M., Febo A. and Cecchini F. (1984) Development of a KI annular denuder for NO<sub>2</sub> collection. *Analyt. Lett.* 17, 887-896

Rose V.E. and Perkins J.L. (1982) Passive dosimetry - state of the art review. *Am. Ind. Hyg. Assoc. J.* 43, 605-621

Rosenberg C., Winiwarter W., Gregori M., Pech, G., Casensky V. and Puxbaum H. (1988) Determination of inorganic and organic volatile acids, NH<sub>3</sub>, particulate SO<sub>4</sub><sup>2-</sup>, NO<sub>3</sub><sup>-</sup> and Cl<sup>-</sup> in ambient air with an annular diffusion denuder system. *Frezenius Anal. Chem.* 331, 1-7