A sensitive diffusional sampler

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### Sammanfattning/Summary

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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 0.05-70 µg NO₂/m³ (0.02-40 ppb), 0.3-200 µg SO₂/m³ (0.1-80 ppb) and 0.2-20 µg NH₃/m³ (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 H₂O and SO₂ (Palmes 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 NO₂ concentration in indoor air (Palmes 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 (Ferm 1986). A lot of samplers have been constructed since Palmes 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 NO₂, SO₂ and NH₃. 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, Ø 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® FALP Ø 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.

![Diagram of the sampler](image.png)

*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 SO₂ on alkali impregnated filters and determined the amount of SO₃²⁻ 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 SO₂ as SO₃²⁻. The formed SO₃²⁻ is, however, oxidized to SO₄²⁻ within a couple of days. Huygen recommended a solution of 20% KOH and 10% glycerin for trapping SO₂. This solution has also been used by Johnsson and Atkins (1975). They used K₂CO₃ instead of KOH, which is closer to the final composition of KOH exposed to air, and leached the filters in a dilute H₂O₂ solution and determined the amount of SO₄²⁻. A good correlation between this filter technique and H₂O₂ bubbler method was observed. Lewin and Zachau-Christianesen (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). NH₃ 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 µl 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.

$\text{NO}_2^-$

The impregnation solution consists of 10 g KI, 1 g NaAsO$_2$, 5 g ethylene glycol in 84 g methanol. The NO$_2^-$ concentration of the leachate is determined spectrophotometrically after mixing with a diazotating reagent (1:1). I$^-$ may interfere with the NO$_2^-$ analysis. This have been noted when Flow Injection Analysis (FIA) is used. The result depends on the concentration of I$^-$, especially at low I$^-$ levels. This artifact can be solved by leaching the filters in a high concentration of I$^-$ (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$_2^-$ standards containing the same I$^-$ 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.

$\text{SO}_2^-$

The impregnation solution consists of 4% K$_2$CO$_3$ in water. The filter are leached in 4 ml dilute H$_2$O$_2$ solution (0.03%) to ensure complete oxidation of SO$_3^{2-}$. 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$_2$CO$_3$. The blank of an impregnated filter is around 4 nmol, which is close to the value for an unimpregnated filter.
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⁻ 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 \( \Phi = -D \cdot \frac{dC}{dL} \). Where \( \Phi \) 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 \( \frac{dC}{dL} \) is the concentration gradient which is negative in the direction of the flow. The flux is calculated from \( \frac{X}{A \cdot t} \) 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:

\[
\Delta C = \frac{X \cdot \Delta L}{t \cdot D \cdot A}
\]  

(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.:

$$
C_0 = \frac{X}{tD} \left( \frac{L_R}{A_R} + \frac{L_E}{A_F} + \frac{L_N}{A_N} + \frac{L_{LBL}}{A_R} \right)
$$

$$
X = \frac{C_0 \cdot tD}{(L_R + L_E)}
$$

(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 $\mu$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:
\[ C_0 = \frac{Y}{t \cdot D} \left( \frac{L_F}{A_F} + \frac{L_N}{A_N} + \frac{L_{BL}}{A_R} \right) \]  \hspace{1cm} (3)

\[ C_0 = \frac{X \cdot L_R}{t \cdot D \cdot A_R} \cdot \frac{Y}{(Y-X)} \]  \hspace{1cm} (4)

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

\[ D = \frac{0.0043 \cdot T^{3/2}}{\left( \frac{1}{M_A} + \frac{1}{M_B} \right)} \cdot \left( \frac{V_A^{1/3} + V_B^{1/3}}{2} \right)^2 \cdot P \]  \hspace{1cm} (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 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 = \( \frac{M_B \cdot P}{(R \cdot T)} \). The temperature and pressure dependence of the calculated mixing ratio will thus be \( T \cdot P \cdot \left( \frac{3}{2} \cdot P \right) = \frac{1}{\sqrt{T}} \), i.e. independent of the pressure and a temperature dependence of about 2 \( \% \) per °C. D for NO\(_2\) has been estimated to 1.54 \( \cdot 10^{-5} \) m\(^2\) s\(^{-1}\) (21°C) (Palmes et al. 1976) and for NH\(_3\) 2.54 \( \cdot 10^{-5} \) m\(^2\) s\(^{-1}\) (25°C) (Coulson and Richardson 1954). The diffusion coefficient for SO\(_2\) is 1.32 \( \cdot 10^{-5} \) m\(^2\) 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 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 KI + 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 NO₂ 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. NO₂ was sampled on sintered glass filters impregnated with the same sorbent as the diffusional samplers. SO₂ was trapped in a bubble flask containing 0.03% H₂O₂. The results are shown in Fig 3-4.

![Graph showing comparison between active and diffusional sampling at 49 Swedish towns.](image-url)

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 μg NO₂/m³ and 0.6 μg SO₂/m³. 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. SO₂ measurements were made during a European intercomparison within the framework of EMEP which was held at Vavilhill. 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 SO₂, with and without stainless steel nets to protect the membrane filters, were tested at Rövik. 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 NO₂ during this test. In another test at Rörvik a new sorbent (8 % NaI, 0.4 % Na₂CO₃, in water) was used parallelly. It seems to give similar results as the original receipt.

Very few measurements have been made on NH₃, 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 NH₃ gave reasonable agreement but the measurements were not completely synchronous.

Table 1 Parallel tests performed with diffusional samplers. All concentrations are given in µg/m³ and the laminar boundary layer in mm.

<table>
<thead>
<tr>
<th>Location</th>
<th>L</th>
<th>Ø</th>
<th>[SO₂]</th>
<th>mm</th>
<th>mm</th>
<th>µg/m³</th>
<th>LLBL=</th>
<th>Notes</th>
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<tr>
<td>Vavilhill Jan-Feb '90</td>
<td>50</td>
<td>12</td>
<td>13.0 ± 1.1</td>
<td>10</td>
<td>20</td>
<td>12.1 ± 0.4</td>
<td>0.9</td>
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<tr>
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<td>20</td>
<td>20</td>
<td>13.3 ± 0.2</td>
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<td>11.7</td>
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<tr>
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<td>10</td>
<td>20</td>
<td>3.7 ± 1.0</td>
<td>LLBL= 1.5</td>
<td>K₂CO₃, steel net</td>
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<tr>
<td>Rörvik Nov-Jan '90-'91</td>
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<td>3.8 ± 0.6</td>
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<td>LLBL= 1.8</td>
<td>Na₂CO₃, steel net</td>
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<tr>
<td>L</td>
<td>Ø</td>
<td>[NO₂]</td>
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<td>5.3 ± 0.7</td>
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<tr>
<td>active</td>
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<tr>
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<td>8.9 ± 0.5</td>
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<td>5.4 ± 0.5</td>
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References


