



THE USE OF PALMES DIFFUSION TUBES FOR MEASURING NO₂ IN HOMES

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Abstract

The results of exposure chamber and field validation tests of NO₂ diffusion tubes are reported. In an exposure chamber about 50 test runs at various relative humidities were performed. The field validation consisted of comparisons between tubes and a chemiluminescence monitor in 9 homes during several days in kitchen, living room, bedroom and outdoors. The results indicate a dependency on relative humidity, while the often quoted accuracy of 10% for the diffusion tubes might be too optimistic for the use of the tubes in homes.

Keywords

Indoor, NO₂, diffusion tubes, passive sampler.

Introduction

Palmer diffusion tubes (Palmer et al., 1976) are used widely as convenient samplers for NO₂ measurements indoors. These passive samplers are acrylic tubes with stainless steel wire mesh, coated with the NO₂ absorbent triethanolamine, inserted at the closed end of the tube. Atmospheric NO₂ is transferred from the open end of the tube to the absorbent at the closed end by molecular diffusion, which follows Fick's first law :

$$Q = - D.C.\frac{A}{Z}.t$$

where Q = quantity of transferred NO₂ (moles)

D = diffusion coefficient of NO₂ in air (cm²/sec)

C = NO₂ concentration at the open end of the tube (moles/cm³)

A = cross-sectional area of the tube (cm²)

Z = the length of the tube (cm)

t = time of exposure of the tube (sec)

The absorbed NO₂ is analysed spectrophotometrically at 540 nm about 20 minutes after adding 2.1 ml Saltzman reagent to the tube. NO₂ concentrations are calculated with the aid of the theoretical diffusion coefficient of NO₂ in air of 0.154 cm²/sec.

Ideally the uptake rate of a diffusive sampler is a constant for a specific pollutant, since it depends only on the geometry of the sampler under standardised conditions. In practice, however, the uptake rate may vary with changes in pollutant concentration, exposure time, atmospheric temperature, humidity, turbulence, etc. Thus the uptake rate has to be determined under a variety of conditions, both in laboratory and field trials.

In the case of NO₂ diffusion tubes only limited test programs have been performed. The diffusion tubes were tested by the U.S. National

Bureau of Standard (Cadoff et al., 1979), and by Warren Spring Laboratory in the U.K. (Apling et al., 1979). A lower detection limit of the tubes of about $600 \mu\text{g}/\text{m}^3$ over a 1 hour sampling period (or $4 \mu\text{g}/\text{m}^3$ over one week) was established. Accuracy was demonstrated to be better than $\pm 10\%$; precision was better than $4 \mu\text{g}/\text{m}^3$ for a one week sampling period.

Only one field validation study with NO_2 reference measurements has been published to date to our knowledge. In this study, diffusion tubes were exposed over a period of 24 - 144 hours in the kitchen of three homes. A Bendix NO_x chemiluminescence monitor was used as reference method. The differences in NO_2 concentrations obtained with the two methods were within the accuracy range of the monitor (8 - 9%) (Apling et al., 1979).

Recently Hoen et al. (1984), reported a good agreement between average results of diffusion tubes and a continuous monitor. This was, however, not a direct comparison, as the average NO_2 concentration of the tubes was calculated from a regression model for the periods of heater use.

NO_2 diffusion tubes were also used in several indoor NO_2 pollution studies in the Netherlands (Boleij et al., 1982; Remijn et al., 1984; Noy et al., 1984).

The tubes were tested in the laboratory and, later, we made use of an opportunity to compare the tubes with the results of a chemiluminescence monitor in a field study in 9 homes during 10 periods of several days. As the field study was not set up for comparing the tubes and the monitor some shortcomings had to be accepted. The results of both tests are discussed.

Materials and methods

The laboratory tests were carried out in a 240 l exposure chamber, in which the test tubes were exposed to NO₂ concentrations of about 300 µg/m³ during periods of 20 to 75 hours at room temperature. The tubes were 8 cm long and had an inner diameter of 1 cm. The NO₂ concentrations were generated by a dynamic dilution system; pressurized air was passed through columns of activated charcoal and molecular sieve (5A Mesh) and mixed with NO₂ from a NO₂ permeation device. The NO₂ concentration in the exposure chamber was monitored continuously with a Bendix chemiluminescence monitor during the test runs.

The monitor was calibrated, after zero adjustment with zero air from the dilution system, against 270 µg/m³ NO from a certified cylinder of Spectraseal NO calibration gas and against the known NO₂ concentration in the mixing chamber of the dynamic dilution device. Periodically, the monitor was cross-referenced against other monitors and calibration systems at the laboratory. Following Stevenson et al. (1979) an overall maximum accuracy error was estimated at 10%.

At first, laboratory tests were performed at a relative humidity of less than 5%. The influence of humidity was expected to be of minor importance. 10 successful tests were conducted, with a minimum of 10 exposed tubes in each test.

Later also 41 successful humidity controlled test runs were carried out in the range of 5 - 85% relative humidity.

In the field tests duplicate diffusion tubes were placed near the monitor sampling points in living room, bedroom and outdoors. In the kitchen duplicate tubes were placed near the most central of three different sampling points, from which a mixed air sample was drawn to the monitor. Again a Bendix chemiluminescence monitor was used

including a field calibration procedure with the aid of a cylinder with zero air, a Spectraseal certified cylinder with NO calibration gas of $295 \mu\text{g}/\text{m}^3$, and a Tracor portable permeation device with a NO_2 permeation tube. Periodically the monitor was checked against a permanent NO_2 dynamic dilution system and compared with other monitors at the laboratory. Again an overall maximum accuracy error was estimated at 10%.

With the aid of a valve each location was monitored during one minute out of each 6 minutes period, with the exception of outdoors, which was only measured one minute every hour. As outdoor concentrations are more stable than indoor concentrations, this was considered to be acceptable against the background of achieving more frequent indoor sampling.

Ten sampling periods of 3 to 12 days in 9 different homes were available for comparison between the tubes and the monitor.

Results

Exposure chamber

From the results of the initial laboratory tests, experimental diffusion coefficients were calculated. They are presented in table 1. The coefficient of variation of D over the 10 tubes in each run ranged from 4 to 11% with an average of 7.5 %. The coefficient of variation of the average D from the different runs was 6%.

The experimental D with an average value of $0.115 \text{ cm}^2/\text{sec}$ was consistently lower than the value of $0.154 \text{ cm}^2/\text{sec}$ used by Palmes.

The value of $0.115 \text{ cm}^2/\text{sec}$ was used on the basis of these results in our early work (Boleij et al., 1982, a,b; Lebret et al., 1983; Noy et al., 1984; Fischer et al., 1984, a,b, 1985; Hoek et al., 1984, a,b,c; Brunekreef et al., 1984; Remijn et al., 1984; Brunekreef et al., 1985; Noy et al., 1985).

For the humidity controlled experiments the coefficient of variation over the tubes in each run varied between 3 and 6%. The pooled results of the different tests are shown in figure 1.

A dependency on relative humidity is suggested by the data.

The regression line fitted through these data is :

$$D = 0.120 + 0.00038 \text{ R.H. } (R^2 = 0.65; F = 73.4; df = 1,39; p \leq 0.001).$$

Field tests

In the field tests the coefficients of variation of the series of duplicate samples were about the same as in the laboratory tests.

The results of the simultaneously measured tube and monitor concentrations are given in table 2. Tube concentrations were calculated with the theoretical diffusion coefficient of $0.154 \text{ cm}^2/\text{sec}$.

In 4 homes the kitchen and living room were in the same room, which resulted in similar NO_2 levels in kitchen and living room for those homes.

The overall correlation coefficient for all measurements was 0.93, while the correlation coefficients for the various locations varied between 0.83 and 0.95. The correlation was even better if home no. 7 was considered as an outlier and not taken into account. The overall coefficient of variation between all tube and monitor measurements was 14% and without home no. 7 10%.

In all kitchens, the results of the tubes were higher than those of the monitor. The ratio was on average 1.33. For living room and bedroom the ratios averaged on 0.88 and 0.85 respectively. Outdoors the average ratio was 1.03. In considering the results we must bear in mind that the kitchen results might be biased by the mixed sampling of the monitor and the outdoor results by the relatively low sampling frequency.

Discussion

The precision of the diffusion tubes in our tests was comparable with findings reported by Apling et al. (1979) and Cadoff et al. (1979). In dry air, the experimentally derived D of $0.115 \text{ cm}^2/\text{sec}$ was systematically lower than the value of $0.154 \text{ cm}^2/\text{sec}$ used by Palmes et al., (1976). Such differences in diffusion coefficients derived in different ways are not uncommon (Reid and Sherwood, 1966). Several factors can be responsible for the observed differences.

Firstly, a temperature effect on the performance of the tubes is reported by Girman et al. (1983). Probably due to a liquid-solid phase transition of the triethanolamine absorbent at 21°C they observed that at 15°C the collection efficiency of the tubes was 15% less than at 27°C . During our exposure tests, the temperature in the exposure chamber was always 22°C or higher.

Secondly, starvation may occur at the open end of the tube at very low air velocities. Under these conditions, an external boundary layer in which NO_2 transport is controlled by diffusion, will lengthen the diffusion path. With formulas as derived by Tompkins and Goldsmith (1977) and Brown et al. (1981) a starvation error of about minus 12% was calculated for the experimental conditions during our test runs, with air velocities between $0.05 - 0.1 \text{ cm}/\text{sec}$. This starvation error is not large enough to explain completely the observed differences in experimental and theoretical D .

Thirdly, humidity effect might be responsible for the differences. The results of the humidity tests suggest that a humidity effect on the performance of the tubes does exist.

The important question, however, is how the distribution of differences in air velocity, humidity and temperature in homes will affect the performance of the diffusion tubes for indoor measurements. Changes in

temperature from 15 - 25°C and R.H. from 30 - 80% between different rooms and in a single room over a measurement period of several days are realistic conditions in Dutch homes. Furthermore, little is known about air velocities near the objects and surfaces to which the tubes are normally attached.

The field validation tests resulted in varying ratios between monitor and tube concentrations for the different sampling locations.

An explanation for the observed differences may be an unrecognized systematic bias in the continuous monitoring equipment and sampling arrangements :

- The monitor might have underestimated the NO₂ concentration because of quenching by water vapor (Matthews et al., 1977). High humidity of kitchen air during the use of gas appliances and NO₂ production is likely.
- Inhomogenous mixing of the air in the kitchens might also have affected the ratio, as the tubes sampled the air only at one point, whereas the monitor measured a mixed sample from three different sampling points.

Another explanation for the differences between tubes and monitor is the existence of a temperature, humidity and/or starvation effect on the tubes. A different distribution of these parameters over the four sampling locations would explain the differences in tube/monitor ratios between the locations. It can not, however, completely explain the high ratio in the kitchen.

Whatever the reason, or combination of reasons, for the observed differences is, the often quoted accuracy figure (< 10%) from the studies of Apling et al. (1979) and Cadoff et al (1979) seems too

optimistic for the use of the tubes in homes, although some reservations have to be made because of the not ideal set up of the field comparison. Further research is needed, especially on the influence of humidity on the performance of diffusion tubes. For the time being the theoretical diffusion coefficient of $0.154 \text{ cm}^2/\text{sec}$ seems the best choice for calculating the results of diffusion tube measurements in field studies.

Acknowledgement

Part of this study was supported by the Ministry of Housing, Physical Planning and Environment.

TABLE 1. Laboratory experiments; experimental diffusion coefficients (D) and coefficient of variation (CV) from 10 exposure experiments at a relative humidity of less than 5% (9 - 10 tubes each run).

Run	Concentration (ppb)	Exposure time (h)	D (cm ² /sec)	CV %
1	167	45	0.105	9.5
2	160	53	0.104	8.5
3	165	21.5	0.116	11.4
4	164	74	0.106	6.7
5	165	73	0.105	7.5
6	162	29	0.124	6.3
7	163	70	0.115	7.3
8	158	48	0.121	6.8
9	157	66.5	0.123	7.5
10	162	26	0.119	7.6

FIGURE 1. Experimental diffusion coefficients calculated from the results of 41 humidity controlled laboratory experiments at various relative humidities.

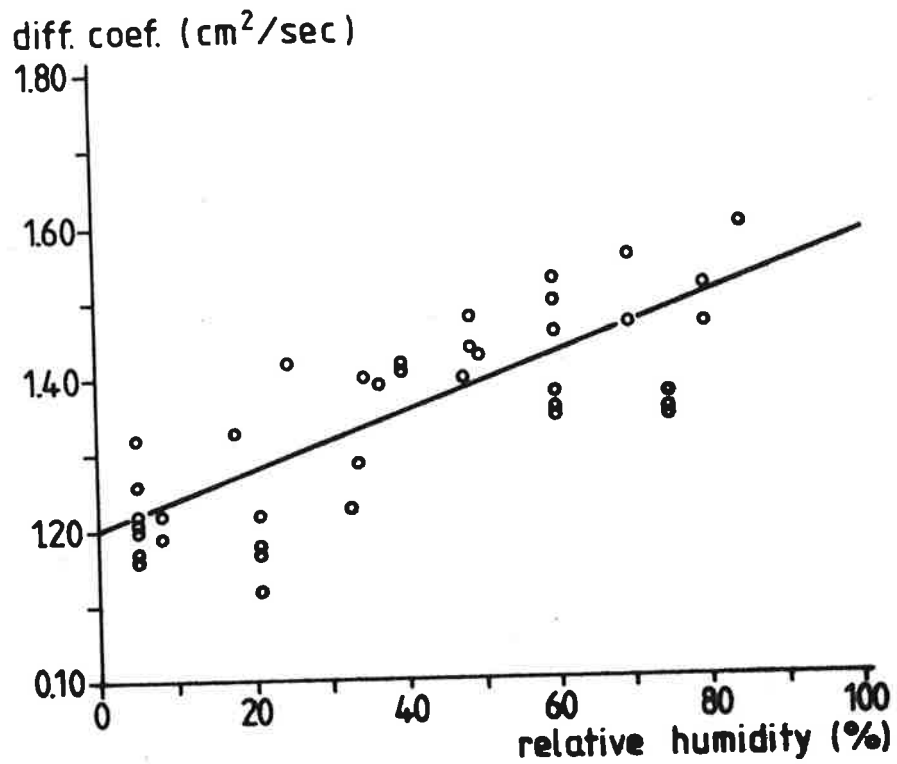


TABLE 2. NO₂ concentrations (in µg/m³) at four sampling locations during 10² periods in 9 homes, measured simultaneously with duplicate diffusion tubes and a chemiluminescence monitor.

Home nr. and sampling period		kitchen	living room	bedroom	outdoors
home 1 4 days	monitor	188	74	54	42
	tubes	229	56	46	43
	ratio	1.22	0.76	0.85	1.02
home 2 7 days	monitor	146	81	53	58
	tubes	185	73	46	68
	ratio	1.27	0.90	0.87	1.17
home 3 7 days	monitor	54	43	30	37
	tubes	64	43	25	37
	ratio	1.18	1.00	0.83	1.00
home 4* 12 days	monitor	36	32	22	26
	tubes	42	37	25	38
	ratio	1.17	1.16	1.14	1.46
home 5 8 days	monitor	52	39	15	50
	tubes	61	40	15	41
	ratio	1.17	1.03	1.00	0.82
home 6* 7 days	monitor	93	92	40	76
	tubes	105	90	34	68
	ratio	1.12	0.98	0.85	0.89
home 7 3 days	monitor	63	35	34	40
	tubes	116	16	29	40
	ratio	1.83	0.46	0.85	1.00
home 7 5 days	monitor	89	39	40	36
	tubes	174	17	25	28
	ratio	1.96	0.44	0.63	0.78
home 8* 4 days	monitor	40	33	22	25
	tubes	45	30	22	27
	ratio	1.13	0.91	1.00	1.08
home 9* 8 days	monitor	156	116	91	52
	tubes	207	132	44	54
	ratio	1.33	1.14	0.48	1.04

* homes, in which kitchen and living room were in the same room.

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