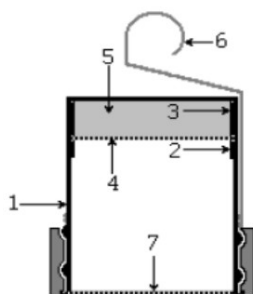


JRC Scientific and Technical Reports

Review of the application of diffusive samplers in the European Union for the monitoring of nitrogen dioxide in ambient air

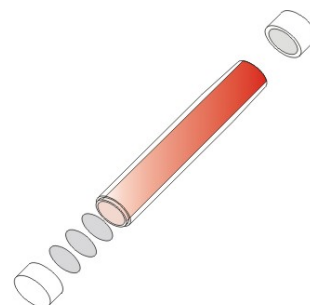
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Analyst



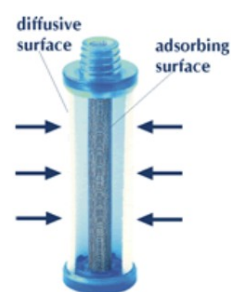
Ogawa



Palmes tube



Passam



Radiello

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Executive summary

A number of diffusive samplers that are used for long-term monitoring of nitrogen dioxide in the European Union were subjected to a review of their use and performance characteristics. The information collected was used:

- To draft conclusions about the feasibility of using the samplers for the long-term monitoring of nitrogen dioxide, with the particular aim of checking compliance with the European Union annual limit value of $40 \mu\text{g}\cdot\text{m}^{-3}$ (at 20°C and $101,2 \text{ kPa}$);
- To draft a proposal method for monitoring nitrogen dioxide using diffusive samplers that could be later used by the CEN Technical Committee 264 “Air Quality” Working Group 11 “Diffusive Samplers” to prepare a CEN standard devoted to the measurement of nitrogen dioxide in ambient air.

The main criteria for assessing sampler feasibility for both purposes were:

- Validation level of the samplers based either on application of EN 13528 part 2 or the Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods, including information about the uncertainty of results obtained using the samplers;
- Potential to meet European Air Quality Directive data quality objectives for indicative and/or fixed measurements;
- Extent or lack of information available to underpin the validity of results obtained using the different samplers;
- Number of different sources providing the above information;
- Differences in performance depending on site type (tube type): traffic, urban, rural;
- Possibility for users to analyse the samplers, e.g., based on procedures specified by manufacturers;
- Their current use throughout the European Union for measuring ambient air quality related to concentrations of nitrogen dioxide.

Of the samplers investigated, two tube-type samplers and a radial sampler were found to be used throughout the European Union for monitoring nitrogen dioxide in ambient air. Other samplers exist that are used mainly for other purposes. In addition, the tube-type samplers are used in monitoring networks for supplementary measurements to the fixed measurements at the level of an indicative method.

Based on the findings of the review, the samplers used in the European Union for ambient air quality monitoring purposes should be of the tube-type design with triethanolamine as sorbent. Sufficient information was available to underpin its potential for meeting European Union data quality objectives, at least for indicative measurements of nitrogen dioxide in ambient air. For other samplers, more supporting information would be needed to draw a similar conclusion.

In conclusion, it is recommended that the proposed method for monitoring nitrogen dioxide using diffusive samplers should be based on the tube-type sampler. If more information becomes available on the performance of the radial sampler, then this sampler could also be included in the standard.

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1 Introduction

Ambient air quality problems associated with levels of nitrogen dioxide (NO₂) are largely due to exceedances of annual limit values. Short-term limit values are only occasionally exceeded in the EU. Diffusive sampling would be an ideal technique for the assessment of compliance with long-term (i.e., annual) limit values for NO₂.

Recent developments indicate that earlier fundamental problems associated with diffusive sampling of NO₂ may have been overcome. Due to modifications in the design of the samplers, potential variations in sampler performance have been eliminated [1,2].

These developments should support the application of diffusive sampling for the assessment of NO₂ in ambient air. Already networks are in operation for routine measurements in many European countries (including Belgium, France, Germany, Switzerland and United Kingdom).

An additional stimulus for applying diffusive sampling is a provision in the ambient air quality directive 2008/50/EC [3] that the number of fixed monitoring sites may be reduced by up to 50 % in zones and agglomerations where supplementary methods for assessment such as modelling and indicative measurements are used. Prerequisites are that:

- The supplementary methods provide sufficient information for air quality assessment;
- The number of sampling points to be installed and the spatial resolution are sufficient to meet the relevant data-quality objectives.

Diffusive sampling methods should be capable of meeting these requirements.

However, the full validation of diffusive sampling methods e.g. according to EN 13528-2, and/or the demonstration of their equivalence with the reference method for NO₂ requires special facilities that are only available to well-equipped institutes/laboratories.

Other smaller institutes and monitoring networks wishing to apply diffusive sampling have to rely on external assistance from commercial/public laboratories. Although small-scale validation experiments and comparisons of diffusive samplers can be performed, it is not clear what the quality and comparability of the results produced by these laboratories could be.

In addition, suppliers of samplers may require that analysis of samplers provided is performed only by themselves. Although perhaps justifiable from a viewpoint of the experience required to correctly perform such analysis, this requirement imposes severe restrictions on the potential application of diffusive sampling.

The availability of a properly validated standard method for the measurement of NO₂ by diffusive sampling would permit the unrestricted use of diffusive samplers by all interested parties.

In August 2006, a New Work Item describing the standardization of a method for the measurement of NO₂ using diffusive sampling methods was submitted to CEN Technical Committee 264 "Air Quality". The proposed New Work Item was accepted.

In order to facilitate the drafting of a future CEN standard, the European Commission made available funding for a group of experts to draft a proposal method for monitoring NO₂ in ambient air with diffusive samplers. The group of experts carried out a literature review of existing information about NO₂ diffusive samplers, to be used as a basis for the subsequent development of the proposal method.

This report summarizes the findings of the literature review. Several different types of diffusive samplers in general use were identified. They may be classified as samplers based on sorption of NO₂ on triethanolamine (TEA), and "other" samplers.

In the chapter devoted to TEA-based samplers, four different samplers are described separately: two tube-type samplers, a badge-type sampler, and a radial-type sampler. In the chapter devoted to other samplers, one badge-type sampler is described.

Other samplers are known to exist, but are not described in this report due to a lack of information. A comprehensive list of samplers may be found in [4].

This report is not intended to specify the various applications of diffusive samplers. Relevant information may be found, e.g., in references [5] and [6].

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2 Samplers based on sorption by triethanolamine

2.1 Introduction

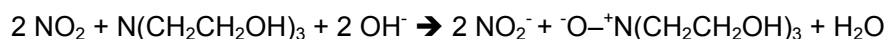
Since their introduction in 1976 for measuring personal exposure to nitrogen dioxide (NO₂) [1], diffusive samplers employing triethanolamine (TEA) as sorbent have been used. Diffusive samplers are an inexpensive method for measuring NO₂ in air over periods from one day to several weeks.

The characteristics of these samplers will be described in separate sections of this report. This section gives an overview of the general properties of TEA-based samplers.

2.2 The sorbent: triethanolamine

Triethanolamine (2,2',2''-nitrilotriethanol (C₂H₄O)₃N, TEA) is a hygroscopic pale yellow liquid with a melting point of 21,6 °C. It has been used as a sorbent for sampling NO₂ since the 1970s, initially in solution in a bubbler or impinger, or in the solid phase on molecular sieve [2]. Its capacity to remove NO₂ from the sampled air is high (90-100 %), as demonstrated using sequential sampling.

The proposed reaction pathway is the following [3].



The collected NO₂ is extracted as nitrite using water. The resulting extract may be analyzed by:

- Colorimetry after derivatization of the nitrite, using the Griess-Saltzman method [4];
- Ion chromatography with conductivity detection [5].

The stoichiometry of the above reaction is dictated to a large extent by the presence of water in the sampled air [3, 6]. The sudden decrease in sampling efficiency below -8 °C [7] suggests that a minimum of around 3 g H₂O m⁻³ is required for TEA to be effective as a sorbent in diffusive samplers.

2.3 Interferences

In addition to its reaction with NO₂, TEA also traps and reacts with other molecules to produce NO₂⁻ ions on extraction into aqueous solution. The two most important potential positive interferences, apart from the reaction of NO with O₃ during sampling, are from peroxyacetyl nitrate (PAN) and nitrous acid (HONO). Dosing of TEA absorbent with NO₃⁻ ions does not produce interference [8]. There is a negligible effect of exposure to O₃ alone in the short term; an atmosphere of 200 ppb of O₃ for 12 h converted less than 10 % of trapped (reacted) NO₂ to NO₃⁻ [9]; active co-sampling of 130 ppb O₃ and 10 ppb NO₂ using TEA on a filter at a relative humidity (RH) of 50 % produced no interference [10].

Interference from PAN is important in that PAN is quantitatively converted to NO₂⁻ on (naturally alkaline) TEA [11]. For tube-type samplers, interference from PAN was lower than 5 % (ppb:ppb) [12]. In practice, interference from PAN is likely to be very small under most exposure conditions, particularly in northern Europe [13]. However, it could be a significant interference in regions with high levels of photochemistry [14].

HONO gives 100 % interference, producing NO₂⁻ on reaction with TEA [10]. However, HONO concentrations in the EU air are likely to be small; even in cities they account for only a few percents of NO₂ concentrations [15].

Not unimportantly, both PAN and HONO would also be measured quantitatively as positive interference by a chemiluminescence NO_x analyzer using thermal conversion of NO₂ (also PAN and HONO) to NO, and would not lead to positive interferences when diffusive samplers are compared with continuous automatic samplers.

Ozone has been reported to interfere through reacting with nitrogen monoxide in the diffusion path of tube-type samplers [16]. However, this finding has not been confirmed by other studies [27].

Sulfur dioxide was found not to interfere with the measurement of NO₂ using tube-type samplers [17].

2.4 Effects of meteorological conditions

2.4.1 Temperature

One of the earliest tests of tube-type samplers showed a 15 % decrease in uptake rate between 27 °C and 15 °C, compared with a theoretical change of less than 2 %. This was attributed to a phase change from solid to liquid of TEA at 21 °C [18]. However, the role of the melting point of TEA was challenged by a later study [19], which showed that TEA solutions did not freeze, but formed a gel even at temperatures as low as -10 °C.

The effectiveness of TEA as a sorbent appears to be dependent on humidity. Some of the reported effects of temperature on uptake rate may be confounded by simultaneous changes in absolute humidity [20], leading to low effective uptake rates at low temperatures that are caused by a lack of water vapour rather than low temperatures *per se* [10, 21, 22]

One laboratory study (designed to evaluate tube-type samplers for use in Greenland) showed almost constant uptake rates from 20 °C down to -8 °C, then a linear decrease to around 30 % of the constant rate, at -28 °C [7]. Another laboratory study found no temperature dependence between 5 and 45 °C [20], while another study found an effect of extremes of temperature and relative humidity on uptake rates, and low uptake rates in the field in winter (by comparison with an automatic monitor) [24].

For short-path 'badge' type samplers the effectiveness of the absorbent may be limited by the rate of diffusion in the liquid phase [25], but this is unlikely to be an issue for the tube type, which has much slower uptake rates. Comparisons of a short path sampler with an active sampler suggest a dependence on temperature of around 1 % per °C [26]. Different designs of sampler have different temperature responses, which must be characterised before they can be used [27].

2.4.2 Relative humidity

The effect of humidity on uptake rate appears to be related to the use of TEA as a sorbent for NO₂, rather than any effect on the diffusion process. Most laboratory studies have used relative humidity (RH) as a measure of water vapour concentration, rather than absolute humidity, which may be more important. Early studies showed no effect of RH between 20 % and 60 % on a short path sampler at room temperature [28]. This was confirmed by subsequent studies with RH higher than 20 % at ambient temperatures [23, 29]. Studies with tube-type samplers between 5 % and 85 % RH at room temperatures (above 22 °C) showed a weak linear dependence of the uptake rate equivalent to an 18 % change in uptake rate between 20 % and 80 % RH [30].

Recent studies demonstrated a dependence on absolute humidity, expressed in terms of the uptake rate for a membrane-capped tube [27], equivalent to a 23 % change in uptake rate between 20 % and 80 % RH at 20 °C.

The effects of variations in absolute humidity on a short path sampler were also reported, with significant reductions in uptake at low RH at low temperature [20, 22].

Effects of humidity on tube-type sampler performance in the field were noted [31], with uptake changing by 17 % between 20 % and 80 % RH at 20 °C with wind velocity of 1 m.s⁻¹. If the uptake rate is dependent on absolute humidity, the above figures may not present a true picture of the dependence on temperature and relative humidity, because RH is a function of water vapour concentration (absolute humidity) and temperature.

However, in comparing results from diffusive samplers with those from automatic analyzers, it is important to note that automatic NO₂ analyzers also have a dependence on humidity, which may not

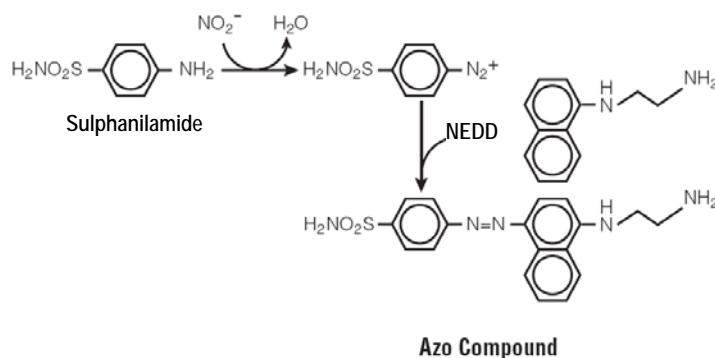
have been allowed for in comparing the response of diffusion tubes relative to automatic methods. The response of a chemiluminescence analyzer typically decreases by 0,5 % per g/m^3 of water vapour [32]. This is equivalent to a change of 5 % between 20 % and 80 % RH at 20 °C.

2.4.3 Air velocity

The effects of air velocity are highly dependent on the sampler design and will be discussed in the sampler-specific sections of the report.

2.5 Analysis of TEA-based samplers

The original method used by Palmes [1] for measurement of the trapped NO_2 relied on the colorimetric determination of NO_2^- using the diazotisation reaction with acidified sulphanilamide and N-(1-naphthyl)-ethylene diamine dihydrochloride (NEDD, sometimes also referred to as NEDA), with detection and quantification of the pink colour produced using photometric absorption spectroscopy at 537 - 542 nm. This colour reagent, or 'Saltzman reagent' has long been used for the quantification of NO_2^- in solution.



However, several authors used ion chromatography (IC) to quantify NO_2 uptake. The benefit of using IC was recognised over 20 years ago, in terms of a greatly improved limit of detection using tube-type samplers, compared with colorimetric analysis [5]. Using gradient elution IC, the limit of detection for tube-type samplers was measured as 4 ppb.hour, compared with 33 ppb.hour for a colorimetric method [12]. Other authors have shown a 14-fold decrease in the limit of detection [33].

2.6 Conclusions

Diffusive sampling of NO_2 using TEA-based samplers dates back 35 years. Meanwhile, a substantial number of studies have been devoted to investigating the behaviour of TEA-based diffusive samplers and their dependence on environmental conditions (presence of interferents, temperature, humidity).

Humidity is probably the most important environmental variable that affects the performance of diffusive samplers using TEA as absorbent. TEA does not perform quantitatively at low humidity. The data of Hansen et al. [7] suggest a loss of efficiency below -8 °C, equivalent to an air concentration of water vapour of about $3 \text{ g}/\text{m}^3$, or 35 % RH at 5 °C. At any given temperature, the effect of a change in relative humidity between 20 % and 80 % is to change uptake rates by about ± 15 % relative to the values at 50 % RH. In practice, the dependence on humidity has rarely been tested in the field, and the interaction between humidity and the reaction of TEA with NO_2 has not been investigated systematically.

The dependence of uptake rate on temperature is small and predictable, except in cold dry air. This deviation from theory is related to the use of TEA as the sorbent and appears to be caused by a lack of sufficient water vapour to ensure quantitative conversion of trapped NO_2 to NO_2^- ions. The availability of water is crucial to the way in which TEA reacts with NO_2 . As noted above, the sudden decrease in sampling efficiency below -8 °C suggests that a minimum of around $3 \text{ g H}_2\text{O}/\text{m}^3$ is required for TEA to be effective as the sorbent in diffusive samplers. This is unlikely to be a problem under most EU conditions, except for very cold, dry weather.

A number of compounds, particularly PAN and HONO are known to produce positive biases when co-sampled with NO₂. However, under typical EU conditions the biases are expected to be small.

Moreover, the current reference method for the measurement of NO₂ in ambient air which is based on thermal conversion of NO₂ to NO with detection of chemiluminescence, suffers from similar biases. Consequently, when comparing TEA diffusive samplers with this reference method, the effects of the interference cannot be quantified.

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3 The Palmes tube

3.1 Sampler design

The traditional NO_2 Palmes tube consists of an acrylic tube (of 71,16 +/- 0,20 mm long and 10,91 +/- 0,15 mm internal diameter) open at one end and two or three stainless steel mesh discs coated with a solution containing triethanolamine (TEA) at the closed end (see figure 3.1, a). A removable cap is used to close the open end of the tube after exposure. The NO_2 molecules diffuse through the air into the tube, following the concentration gradient and are trapped as nitrite ion on TEA. In a recent study, Gerboles et al. [1] proposed a modification of the traditional Palmes diffusion tube by fitting a Teflon membrane at the open end of the tube (see figure 3.1, b). This membrane was used to obtain a sampler free of wind speed effect. In the United Kingdom, a Teflon mesh is used instead of a membrane [2]. All ready-to-use Palmes tube components are commercially available.

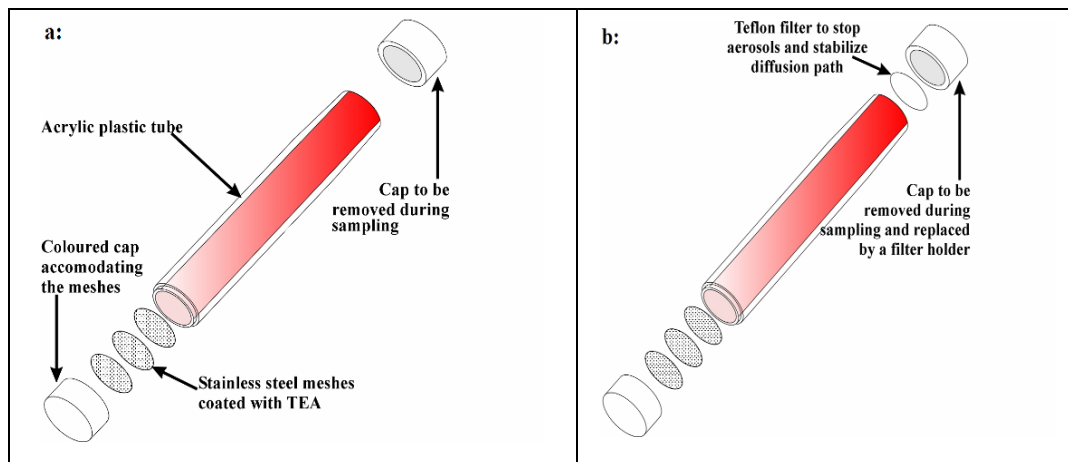


Figure 3.1.a: The traditional Palmes diffusion tube, b: The membrane-closed Palmes tube proposed by Gerboles et al. [1].

The coloured cap needs to be completely opaque and without cracks [2].

Samplers are mounted vertically, with the cap containing the coated discs uppermost. Positions allowing unrestricted movement of air around the sampler are selected. Diffusion tube samplers are fixed by spring clips to the supports (pylons or posts) using supports or spacers of different types. The samplers are, as far as practicable attached at 3-4 meter above the ground in order to avoid vandalism. To attenuate the effect of wind turbulence and improve the precision of measurements by Palmes tubes, it is recommended to use a protective device as for example, shown in Figure 3.2.



Figure 3.2: Cylindrical protective box

The decision to use a protective device should come first (before using a spacer). Criteria to use the protective box may be:

- To prevent exposure to direct sunlight;
- To prevent turbulence in the tube entrance (but at least $0,2 \text{ m}\cdot\text{s}^{-1}$ should be ensured);
- To avoid ingress of rain.

In the case of the membrane-closed Palmes tube proposed by Gerboles et al. [1], the protective box is not necessary since the membrane introduced at the open end of tube is intended for isolating the molecular diffusion path from air movements.

3.2 Sampler preparation

The Palmes tube described here needs to be assembled from individual parts. The tube, Teflon membrane and caps are cleaned in a glass container filled with ultra high purity water under magnetic stirring and changing the water every half an hour for 3 h. All components are then placed in an oven at 45°C until they are completely dry. The stainless-steel mesh discs are cleaned in an ultrasonic bath at 60°C for 5 h, with the water changed every half an hour. They are then placed in an oven and flushed with nitrogen at 125°C until they are completely dry. Three clean and dry discs are placed in the coloured cap with tweezers. Then, a tube is placed onto the coloured cap [1].

In practice, this procedure may be quite tedious. Less stringent procedures are described in [3] and [4].

In addition, the coating of the sampling substrate needs to be performed by the user itself. Different procedures for preparation are described [e.g. 5]. Methods of proven validity are:

- 50 % solution of TEA in acetone, grids dipped into solution and dried before assembly;
- 20 % solution of TEA in deionised water, 50 μl of solution pipetted onto grids already placed in end cap;

- 10 % solution of TEA in deionised water with 0,3 % of wetting agent (e.g. Brij-35), 40 µl of solution pipetted onto grids already placed in end cap.

3.3 Extraction and analysis

To determine the quantity of nitrite sampled by the Palmes tube, the Griess-Saltzman method is generally used. The Saltzman reagent consists of a solution of sulphanilamide (2 % w/v) and N-(naphthyl-1) ethylene diamine dihydrochloride (0,007 % w/v) in 5 % v/v ortho-phosphoric acid. A known volume of colorimetric reagent solution is introduced into the tube, and extraction is effected either by:

- Vortex shaking for a minimum of 15 s;
- Vibrating for a minimum of 10 min at 750 rpm.

Nitrite reacts in the phosphoric acid solution with sulphanilamide to give a diazonium salt that couples with naphthalene derivative to form an azo dye. It is recommended to allow the colour to develop at ambient temperature in the dark for a minimum time of 1 h. The absorbance of the azo dye is measured at 542 nm [4].

3.4 Expression of the NO₂ concentration

To calculate the airborne NO₂ concentration, the equation 3.1 is generally applied.

$$C_{NO_2} = \frac{(m_s - m_b)}{v \times t \times 10^{-6}} \quad (\text{eq. 3.1})$$

where

C_{NO_2} = NO₂ concentration in µg.m⁻³ at actual average temperature and pressure during the exposure;

m_s = mass of nitrite measured in the exposed sampler in µg;

m_b = mass of nitrite in the blank in µg;

v = uptake rate in cm³.min⁻¹;

t = sampling time in min.

Several authors also prefer to use equation 3.2 for the calculation of NO₂ concentration, with the uptake rate expressed in ng.ppb⁻¹.min⁻¹.

$$C_{NO_2} = 1,91 \frac{(m_s - m_b)}{v \times t} \quad (\text{eq. 3.2})$$

where

C_{NO_2} = NO₂ concentration in µg.m⁻³ at 20 °C and 101,3 kPa;

m_s = mass of nitrite measured in the exposed sampler in ng;

m_b = mass of nitrite in the blank in ng;

v = uptake rate in ng.ppb⁻¹.min⁻¹;

t = sampling time in min.

The coefficient 1,91 is used to convert ppb to µg.m⁻³ at 20 °C and 101,3 kPa.

3.5 Application range and conditions

The Palmes tube may be exposed for 1 to 5 weeks sampling periods according to results of field validation tests obtained from many sites across Europe [1, 2, 6-9]. Some users have exposed tubes for up to 8 weeks [10].

Results of validation studies described below suggest that the Palmes tube sampler, when properly prepared and exposed with sufficient protection from adverse influences, may be used over a temperature range from -5 °C to 40 °C, and a relative humidity range from 30% to 95%.

Detection limits for a one-week sampling period were found to be 1,4 [1] and 1,9 $\mu\text{g}\cdot\text{m}^{-3}$ [3], depending on the preparation procedure (see section 3.2). In a field experiment, the upper limit for NO_2 that was found in practice to lead to valid results for 5-week sampling was 150 $\mu\text{g}\cdot\text{m}^{-3}$ [2].

When stored in a clean refrigerator at 4°C before exposure, an unexposed tube may be stable for up to 1 year [11].

Stability tests of Palmes tubes after exposure were performed by Gerboles et al. [11] in a feasibility study of the preparation and certification of a reference material for NO_2 in diffusive samplers. The Palmes tubes were stored under two different conditions: at room temperature (22°C) in the dark and at 4°C in a refrigerator. It was demonstrated that the samples may be stable for at least one year under both conditions of storage. The results were in agreement with those obtained previously by Palmes et al. [12], where the samplers were found to be stable for at least 6 months.

3.6 Uptake rate

For the traditional Palmes diffusion tube without membrane, the theoretical uptake rate (72,8 $\text{cm}^3\cdot\text{h}^{-1}$) calculated using the diffusion coefficient of NO_2 in air and the dimensions of the sampler is currently the most common value. It has also been confirmed by test results in exposure chambers under standard conditions ($T=20^\circ\text{C}$, $\text{RH}=50\%$ and wind speeds between 0,1 and 0,3 $\text{m}\cdot\text{s}^{-1}$) [8].

The uptake rate is dependent on the air temperature and pressure during exposure. In appendix 2 of reference [2], a correction for the uptake rate is proposed (equation 3.3). Temperature correction raised to the power 1,5 instead of 1,81 have been proposed by other authors [4]. In most cases, the pressure correction may be neglected.

$$v_{T,P} = v_{ref} \left(\frac{273,2 + T}{273,2 + T_{ref}} \right)^{1,81} \frac{P_{ref}}{P} \quad (\text{eq. 3.3})$$

where

$v_{T,P}$ = uptake rate in $\text{cm}^3\cdot\text{min}^{-1}$ at temperature T and pressure P during sampling;

v_{ref} = uptake rate in $\text{cm}^3\cdot\text{min}^{-1}$ at the reference temperature and pressure;

T = actual temperature during sampling in °C;

T_{ref} = reference temperature in °C at which v_{ref} rate is given (for example if v_{ref} was calculated using a value of 0,154 $\text{cm}^2\cdot\text{s}^{-1}$ for the diffusion coefficient of NO_2 in air, the reference temperature is 21,1 °C);

P = actual pressure during sampling in kPa;

P_{ref} = reference pressure in kPa at which v_{ref} is given, in general 101,3 kPa.

To improve the accuracy of measurements by Palmes tubes, some authors established empirical equations to estimate the uptake rate as a function of influential environmental parameters. These equations were defined from the results of complete programs of tests in exposure chamber.

Plaisance et al. [8] proposed a first equation which allows the effects of temperature and humidity to be taken into account on the uptake rate of the open Palmes tube exposed in cylindrical box for 2-week sampling:

$$v = 72,8 \times (2,85 \times 10^{-3} \times [T] - 1,62 \times 10^{-4} \times [RH] + 4,96 \times 10^{-5} \times [T] \times [RH] + 0,9) \quad (\text{eq. 3.4})$$

where

v = uptake rate in $\text{cm}^3\cdot\text{h}^{-1}$;

T = temperature in °C.

Buzica et al. [9] provided another model-predicted uptake rate. It was deduced from tests in exposure chamber carried out by applying a fractional factorial plan of experiments with 5 factors at two levels

(wind speed, temperature, humidity, NO₂ concentration level and sampling time). The equation predicts the uptake rate of the Palmes tube without membrane exposed from 1 to 2 weeks:

$$v = 7,4 \times 10^{-4} + 2,72 \times 10^{-5} \times T + 1,43 \times 10^{-5} \times RH + 5,81 \times 10^{-4} \times w \quad (\text{eq. 3.5})$$

where

v = uptake rate in ng.ppb⁻¹.min⁻¹;
 T = temperature in °C;
 RH = relative humidity in %;
 w = wind speed in m.s⁻¹.

For the Palmes tube equipped with a Teflon membrane proposed by Gerboles et al. [1], the membrane introduced a resistance to molecular diffusion. Therefore the uptake rate of the sampler could not be determined using the first Fick's law, but was instead estimated by laboratory experiments in exposure chamber. Gerboles et al. carried out the same program of tests as described in [9] and derived a model-predicted uptake rate for the membrane-closed Palmes tube exposed from 3 to 14 days:

$$v = \frac{1}{2} (134 + 0,86RH - 0,00130 t + 1,28T + 3,18w) 10^{-5} \times \left(1 + \sqrt{1 - \frac{0,64 \cdot 10^{-5} m}{t ((134 + 0,86RH - 0,00130 t + 1,28T + 3,18w) 10^{-5})^2}} \right) \quad (\text{eq. 3.6})$$

where

v = uptake rate in ng.ppb⁻¹.min⁻¹;
 T = temperature in °C;
 RH = relative humidity in %;
 w = wind speed in m.s⁻¹;
 m = mass of nitrite in ng;
 t = exposure time in min.

3.7 Environmental effects

3.7.1 Air velocity

Some studies [8, 9, and 13] reported that the greatest effect on the uptake rate of a traditional open Palmes tube may be attributed to wind velocity. An increase in uptake rate was observed with increasing air velocities usually following a logarithmic trend [8, 13]. The effect starts from very low wind velocities (between 0,1 m.s⁻¹ and 0,2 m.s⁻¹).

The magnitude of the uptake increase was found to be about 60 % over the wind velocity range of 0 m.s⁻¹ to 7 m.s⁻¹ [13]. Other authors [8, 9] confirmed that the increase rate was high, about 40 % from 1 m.s⁻¹ to 2.8 m.s⁻¹. An effective and practical way for reducing the effect of air turbulence was demonstrated by the use of a cylindrical protective box (figure 3.2).

Buzica et al. [9] observed that for the open Palmes tube the effect of the wind speed was ±25 % of the average uptake rate, while the effects of the relative humidity and temperature were smaller, at ±10 % and ±7 %, respectively.

Gerboles et al. [1] proposed the addition of a porous membrane at the open end of the Palmes tube. It removes the high influence of wind speed and wind direction on uptake rate. With the addition of the membrane, the wind becomes a minor influencing factor.

3.7.2 Temperature and relative humidity

Temperature and humidity were found to have a smaller influence on the response of the sampler (see above) with the uptake rate increasing linearly by 0,3 %·°C⁻¹, in agreement with the theoretical dependence of the diffusion coefficient of NO₂ on temperature.

A maximum bias in the uptake rate of nearly +10 % was observed under particularly extreme conditions (temperature higher than 30 °C and relative humidity higher than 80 %) [8].

3.7.3 Interferences

Potential interferences from nitrous acid (HONO) and peroxyacetyl nitrate (PAN) which give rise to nitrite ion must be recognised. However, neither compound is likely to be present at sufficient concentrations or over sufficiently long periods to cause serious interferences in most situations. Gair et al. [14] found only a positive interference lower than 6 % which they considered non-significant.

Heal et al. [15] and Jenkins [16] showed that the chemical reaction between O₃ and NO within diffusion tubes may lead to an overestimation of the measured NO₂ concentration. The light transmission characteristics of the acrylic tube used for sampling showed some attenuation in the photochemically important region, possibly leading to changes in the photochemical equilibrium in the air actually inside the sampler.

This information, together with ozone data, was used to model the system for typical conditions of exposure of urban and rural areas. The model showed an increase in NO₂ of about 11 % in rural and 6 % in urban areas. The photochemical reaction is only of importance during daylight and even in the more sensitive rural areas the effect would be difficult to detect.

In field tests carried out by Atkins et al. [17] and Bush et al. [18], no differences were found in the performance of the diffusion tube at rural and urban locations. Likewise, the laboratory experiments in an exposure chamber [1] revealed no bias of O₃ on the NO₂ measurements by Palmes tubes.

3.8 Validation of sampler performance

3.8.1 Comparisons with reference methods

Palmes tubes were validated for outdoor use in several studies. The first extended outdoor evaluation was carried out by Atkins et al. [17] at two sites (rural and urban locations) using the Palmes tubes (10 % TEA/water solution with 0,3 % of the wetting agent Brij-35) and the theoretical uptake rate.

Precision was found to be satisfactory with coefficients of variation for batches of 10 Palmes tubes between 5 % and 8 % for NO₂ concentrations above 5 ppb, which appeared to be independent of NO₂ level and sampling duration (1 week or 4 weeks). Parallel measurements using chemiluminescence analysers and diffusion tubes revealed a good agreement between the two methods. Regression analysis on 42 paired measurements produced a line with a slope not significantly different to 1 and a correlation coefficient above 0,98, over a range of concentrations of 3 ppb to 60 ppb. There was no difference in the performance of the Palmes tube at the rural (NO₂ lower than 30 ppb) and urban (NO₂ higher than 30 ppb) locations.

Gladius et al. [6] confirmed the good agreement between NO₂ measurements carried out with Palmes tube and co-located chemiluminescence analysers at three sites in Denmark and Italy. However, samplers (33 % TEA/acetone solution) at sheltered locations slightly overestimated NO₂ (less than 10 % of overestimation) at concentration levels above 15 ppb. An opposite trend was found at concentrations lower than 15 ppb.

Heal et al. [15] observed overestimations of NO₂ measured by Palmes tubes (50 % TEA/acetone solution) against co-located chemiluminescence analyser at an urban site in Edinburgh (UK). The average ratios of Palmes tube to analyser NO₂ were 1,27 (n=22), 1,16 (n=34) and 1,11 (n=7) for exposures of 1, 2 and 4-weeks, respectively. Based on further modelling of the diffusion, the authors concluded that the overestimation of NO₂ by Palmes tubes could be explained by the generation of excess NO₂ due to the reaction of NO with O₃ inside the tube.

Bush et al. [18] co-located Palmes tubes (50 % TEA/acetone solution) with chemiluminescence analysers at 17 urban monitoring stations in the UK for a one year period. Highly significant correlations (above 0,95) were found between all Palmes tube exposure types (sampling time of 2

and 4 weeks with sheltered and unsheltered samplers) and co-located chemiluminescence analysers. The uncertainty calculated from the overall differences between Palmes tube measurements and the chemiluminescence measurements of NO₂ was estimated to be between ±24 % and 38 % for individual Palmes tube measurements, but reduced between ±10 % and 18 % for annual averages. Differences due to the exposure period and exposure procedure were found, but these were not large.

Tang et al. [10] compared measurement results obtained with Palmes tubes (both open and equipped with a membrane, using protective shelters consisting of a sheet of curved stainless steel painted black, open to the air on 3 sides) with those from chemiluminescence reference analyzers. Comparative measurements were performed at 5 sites: 3 urban sites and 2 rural sites.

Exposure periods were 1, 2, 4 and 8 weeks. In general, it was found that open tubes overestimated NO₂ concentrations at urban sites (average levels around 20 ppb) by almost 30 % to 35 % on average. At the rural site (average levels around 4 ppb) the results agreed much better (ratios between 0,98 and 1,03).

Results obtained with membrane tubes were 10 % lower on average than the reference values for the 4-week sampling period, but were in excellent agreement with those obtained over an 8-week exposure period. At the rural site, the membrane tubes yielded levels that were about 75 % of those of the reference analyzers.

During 2001-2002, CEN/TC264 WG11 (Diffusive sampling) performed a small-scale pilot study at two locations in which 6 replicate samplers of different types of diffusion samplers were exposed for two weeks, in parallel with measurements from a chemiluminescence analyser. These results have not been published and were provided by CEN for the purpose of the present report. Samplers were analysed by the suppliers. The results for two Palmes tube samplers are reported in table 3.1.

Table 3.1: Results of CEN pilot study for Palmes tube samplers

Willebroek	NO₂ (µg.m⁻³)	Ratio Palmes/reference
<i>Reference</i>	40,8	
Palmes 1	52,8	1,30
Palmes 2	57,1	1,40
Teddington	NO₂ (µg.m⁻³)	Ratio Palmes/reference
<i>Reference</i>	13,8	
Palmes 1	17,6	1,28
Palmes 2	18,7	1,36

Both Palmes tubes were found to overestimate NO₂ concentrations.

Buzica et al. [19] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler was exposed in replicate (6) for a period of 14 days, except in the laboratory trial “high” (see table 3.2).

Table 3.2: Laboratory conditions (intercomparison of Buzica et al.)

Parameter	High	Low
Exposure time (d)	7	14
Concentration (µg.m ⁻³)	80	40
Air velocity (m.s ⁻¹)	2,5	1,0
Temperature (°C)	25	5
Relative humidity (%)	75	30

Five laboratories participated with different implementations of the Palmes tube (with and without shelter; with membrane). The results obtained for the samplers are presented in table 3.3.

Table 3.3: Results field tests, (intercomparison of Buzica *et al.*)

Lab high	NO₂ (µg.m⁻³)	Ratio Palmes/reference
<i>Chemiluminescence</i>	76,8	
Palmes open 1	125,8	1,64
Palmes open 2	138,5	1,80
Palmes sheltered 1	96,5	1,26
Palmes sheltered 2	97,0	1,26
Palmes membrane	71,5	0,93
Lab low	NO₂ (µg.m⁻³)	Ratio Palmes/reference
<i>Chemiluminescence</i>	43,5	
Palmes open 1	46,0	1,06
Palmes open 2	37,2	0,86
Palmes sheltered 1	32,6	0,75
Palmes sheltered 2	35,8	0,82
Palmes membrane	40,4	0,93
Genevilliers	NO₂ (µg.m⁻³)	Ratio Palmes/reference
<i>Chemiluminescence</i>	41,6	
Palmes open 1	45,2	1,09
Palmes open 2	42,5	1,02
Palmes sheltered 1	47,2	1,14
Palmes sheltered 2	40,5	0,97
Palmes membrane	40,5	0,97
Fontainebleau	NO₂ (µg.m⁻³)	Ratio Palmes/reference
<i>Chemiluminescence</i>	14,1	
Palmes open 1	13,1	0,93
Palmes open 2	12,4	0,88
Palmes sheltered 1	11,6	0,82
Palmes sheltered 2	11,8	0,83
Palmes membrane	12,4	0,88

Apart from the results of the laboratory trial “high”, the results are comparable with those of the reference method (chemiluminescence, CLS).

The precision of the replicate measurements ranged from 3 % to 9 %, except for the laboratory trial “high”, where some values exceeded 10 %.

Plaisance *et al.* [8] produced a large series of comparison data (n = 52) between diffusion tubes (10 % TEA/water solution with 0,3 % of the wetting agent Brij-35) with and without protection device (cylindrical box) and the chemiluminescence analyser carried out at four French urban monitoring stations for ten months. No systematic differences in measurements were observed between the two techniques, using both the theoretical uptake rate and model-predicted uptake rate (see section 3.6).

A lower scattering of points around the regression line (the slope was not significantly different from 1) was found for Palmes tubes set in the protective device and with the model-predicted uptake rate, revealing a significant improvement in the precision of measurements.

The ISO 13752 standard (1998) was used to evaluate the expanded uncertainty of the Palmes tubes under field conditions. Using the model-predicted uptake rate and the protective device, the expanded uncertainty is reduced to < 25%, implying that this diffusion sampler fulfils the uncertainty requirement for indicative measurements of EU Directive 2008/50/EC.

Buzica et al. [9] investigated the performance of Palmes tube (10 % TEA/water solution with 0,3 % of the wetting agent Brij-35) at one background location in comparison with the chemiluminescence analyser. The use of the theoretical uptake rate gave a high coefficient of correlation ($r^2 = 0,97$) between the measurements of two methods, but resulted in a substantial underestimation (slope 0,75) of the NO₂ concentration measured by the Palmes tube. By applying the model-predicted uptake rate established in this study (see section 3.6), this bias was corrected. For individual measurements, the Palmes tube was shown to comply with the 25% uncertainty requirement.

Gerboles et al. [1] carried out the field tests of the membrane-closed Palmes tube (10 % TEA/water solution with 0,3 % of the wetting agent Brij-35) at the EMEP station in Ispra (I). Forty pairs of data (passive samplers vs chemiluminescence) were collected over a range of concentrations from 8 to 45 $\mu\text{g}\cdot\text{m}^{-3}$. Data were analysed to evaluate the equivalence of this sampler to the reference method for NO₂ (chemiluminescence method) in accordance to the Guide to the Demonstration of Equivalence of ambient air monitoring methods [20]. The relative between sampler uncertainty was found to be 3,7%, a value that satisfies the requirement for NO₂ ($\leq 5\%$) defined in the Guide.

The regression line obtained by applying the method of ISO 6143 (2001) for the reference results of the chemiluminescence analyzer versus those of the membrane-closed Palmes tube revealed no systematic bias in measurements (a slope of $1,05 \pm 0,045$ and an intercept of $-0,24 \pm 0,93$).

To determine the NO₂ concentrations measured by the membrane-closed Palmes tube, the model-predicted uptake rate was used (see section 3.6). From the results of these field tests and in accordance with the Guide of Demonstration of Equivalence, the expanded uncertainty was calculated to be 17% for an individual sampler measurement when the NO₂ concentrations were higher than 20 $\mu\text{g}\cdot\text{m}^{-3}$. For the estimation of annual average concentrations, the relative expanded uncertainty was found to be 12% at the limit value of 40 $\mu\text{g}\cdot\text{m}^{-3}$, satisfying the data quality objective for indicative measurements (25%). According to these experiments, the membrane-closed Palmes tube for NO₂ could become equivalent to the reference method even for fixed measurements [21].

Through AEA Technology (United Kingdom), annual average data for a large number of monitoring sites for both Palmes tube samplers and reference monitors [22] were provided. In summary, two methods were used for the preparation of the sampler substrates:

- 50 % solution of TEA in acetone, grids dipped into solution and dried before assembly;
- 20 % solution of TEA in deionised water, 50 μl of solution pipetted onto grids already placed in end cap.

The two datasets derived from different preparation methods were evaluated according to the methodology of the Guide for the Demonstration of Equivalence [20]. By applying an orthogonal regression forced through the origin (0,0), the results given in the figures 3 and 4 were obtained. One may notice that using an orthogonal regression forced through the origin, the intercept is still be slightly different from (0,0).

<i>REGRESSION OUTPUT</i>	
slope, b	1,023
uncertainty of b	0,014
intercept, a	0,6
uncertainty of a	0,59
number of data pairs	83
<i>EQUIVALENCE TEST RESULTS</i>	
random term	5,2 $\mu\text{g.m}^{-3}$
bias at LV	1,5 $\mu\text{g.m}^{-3}$
combined uncertainty	5,4 $\mu\text{g.m}^{-3}$
relative uncertainty	13,6%
reference uncertainty	1,0 $\mu\text{g.m}^{-3}$
limit value	40 $\mu\text{g.m}^{-3}$

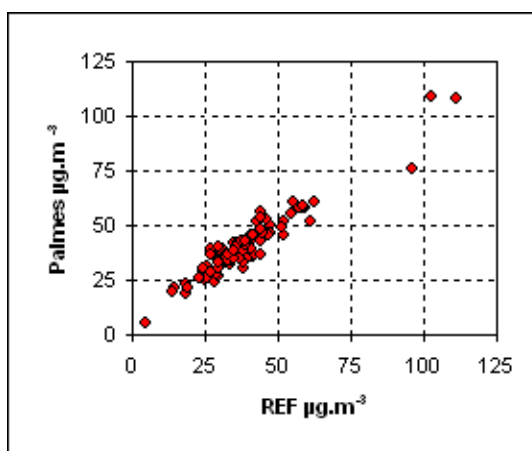


Figure 3.3: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Palmes substrate 20 % TEA in water vs chemiluminescence analyser

<i>REGRESSION OUTPUT</i>	
slope, b	0,906
uncertainty of b	0,014
intercept, a	-0,3
uncertainty of a	0,71
number of data pairs	116
<i>EQUIVALENCE TEST RESULTS</i>	
random term	7,6 $\mu\text{g.m}^{-3}$
bias at LV	-4,1 $\mu\text{g.m}^{-3}$
combined uncertainty	8,6 $\mu\text{g.m}^{-3}$
relative uncertainty	21,6%
reference uncertainty	1,0 $\mu\text{g.m}^{-3}$
limit value	40 $\mu\text{g.m}^{-3}$

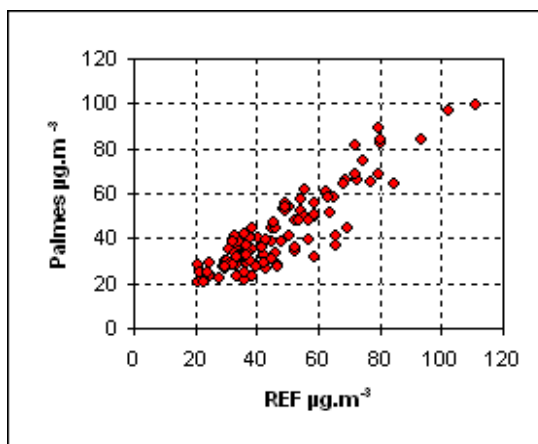


Figure 3.4: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Palmes substrate 50 % TEA in acetone vs chemiluminescence analyser

The results suggest that preparation of the sampling substrate using 20 % TEA in water leads to a better comparability with reference data.

Currently, a comparison is ongoing in the United Kingdom in which Palmes tube samplers and Radiello samplers are exposed at a traffic site in London. Results of this comparison were not available at the time of the drafting of this report.

3.9 Measurement uncertainty

3.9.1 GUM approach

A French Guide [24] is fully devoted to the assessment of measurement uncertainty from the application of the Palmes tube for measurement of NO_2 . In a fully worked example based on practical data, the relative expanded uncertainty at NO_2 concentration of $37 \mu\text{g.m}^{-3}$ was calculated to be 32 % for a single measurement of 2 weeks duration.

The main contribution to this uncertainty (around two thirds of total uncertainty) was from the uptake rate. The uncertainty of the uptake rate was assessed from tests performed by JRC using Palmes

tubes with a cylindrical protective box in an exposure chamber, under two extreme environmental conditions, yielding low and high values of uptake rate [19] which represented worst case scenarios. Hence, the 32 % represents a worst-case estimate. Practical values are expected to be lower.

3.9.2 Direct approach

From the comparisons described above, estimates of the uncertainty associated with NO₂ measurements performed with Palmes tubes were made.

Based on a series of 52 comparison data using an ISO 13752 approach, Plaisance et al. [8] estimated the expanded uncertainty to be < 25 % for a sampler in protective box, using a model-predicted uptake rate.

This finding was confirmed by Gerboles et al. [1], and by Buzica et al. [21], again when using a modelled uptake rate. For the membrane tube, the relative expanded uncertainty of individual measurement results at the level of the annual limit value (40 µg.m⁻³) was estimated to be 17 %.

When aggregating individual results to form an annual average, the relative expanded uncertainty reduced to 12 %. To reach this level of uncertainty, knowledge of average temperature, pressure and relative humidity and wind speed during exposure is a prerequisite.

3.10 Application in EU monitoring networks

Palmes tube samplers are extensively used e.g. in Denmark, France, the Netherlands, Spain and the United Kingdom for supplementary measurements to fixed measurements at the level of an indicative method. Other applications include identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

3.11 Conclusions

The Palmes tube-type diffusive sampler is suitable for long-term monitoring of NO₂ in ambient air. Exposure periods of 1 to 8 weeks are feasible. The lower detection limit for a 1-week sampling period varied with the meticulousness of the sampler preparation procedure, and generally was between 1,4 µg.m⁻³ and 2 µg.m⁻³. The upper limit for a 5-week exposure period was at least 150 µg.m⁻³.

Information about the precision of the sampler showed that it is usually better than 5 % when using a barrier or shelter to reduce effects of wind-induced turbulence. Without these, the precision was generally higher.

Comparisons of sampler results with those obtained from reference monitors (chemiluminescence) gave varying results; however, the results are generally consistent within the uncertainties of the methods. At urban sites, where unprotected open tubes were used, a tendency was observed towards overestimation of NO₂ concentrations.

When using membrane-capped tubes in combination with model equations describing the uptake rate as a function of temperature, humidity, wind speed etc. the comparability improved.

When the uncertainty associated with the measurement results was evaluated according to the Guide to the Expression of Uncertainty in Measurement, the relative expanded uncertainty of individual results was estimated to be 32 % for worst-case conditions (when using a single value for the uptake rate independent of environmental conditions). When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO₂, better results were obtained (generally < 25 %).

These findings suggest that the Palmes tube is at least suitable for performing long-term measurements of NO₂ for indicative purposes, and possibly even for fixed measurements.

When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 15 % due to the reduction of random effects on uncertainty.

3.12 References

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4 The Passam sampler

4.1 Sampler design

The Passam sampler, which is based on the Palmes tube design, is shown in figure 4.1 and consists of an opaque polypropylene tube. The tube is slightly conical. The dimensions of the tube have been measured by Ecole de Mines de Douai [1, p. 46] (see figure 4.1).

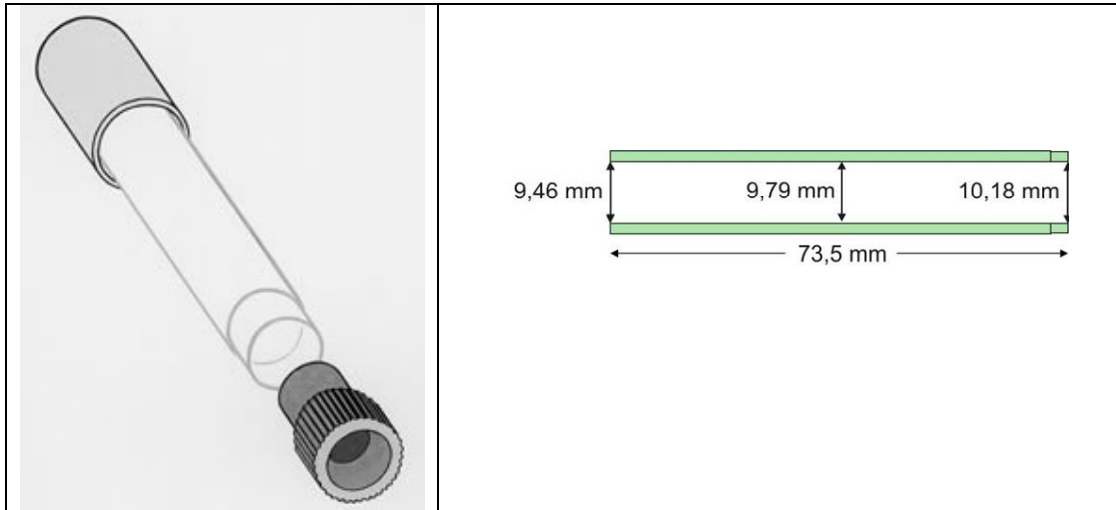


Figure 4.1: Passam tube design

At the narrow end, 3 stainless steel screens are mounted, which are coated by dipping into a solution of TEA - acetone 1:7. Shelf life of the sampling substrate of up to 2 years has been found [2]. Passam tubes are exposed in specific shelters [3]. These shelters are designed to protect the samplers from environmental factors such as rain, excessive radiation and wind. The shelters are an integral component of the measurement method (see figure 4.2).



Figure 4.2: Passam protective shelter

In order to reduce the effect of wind-induced turbulence the sampler may be equipped with a membrane or a glass frit [4].

4.2 Extraction and analysis

The manufacturer describes the determination of the collected NO₂ by colorimetry, after reaction with sulphanic acid and N-1-naphthylethylenediamine [3].

4.3 Application range and conditions

Information on application ranges and conditions given in table 4.1 was provided by the manufacturer [3].

Table 4.1: Application ranges and conditions

Parameter		Application ranges/Conditions
Sampling time		1 – 4 weeks
Working range		1 – 200 µg.m ⁻³
Detection limit		0,8 µg.m ⁻³ for 1-week exposure 0,4 µg.m ⁻³ for 2-week exposure
External influences	Wind speed	Influence of wind speed < 10 % up to 4,5 m.s ⁻¹ when using protective shelter
	Turbulence at kerb sites	Use of membrane recommended because of potential increase of uptake rate
	Temperature	No effect between 5 and 40 °C
	Humidity	No effect between 20 and 80 % RH
Storage	Before use	12 months
	After exposure	4 months
Cross sensitivity		Nitric oxide and sulfur dioxide do not interfere
		Presence of PAN will lead to high results

Field studies showed that exposure periods of up to 6 weeks are feasible without introducing differences [4].

4.4 Uptake rate

The uptake rate of the Passam tube was determined in a series of laboratory experiments [5] designed as prescribed in EN 13528 part 2. In addition, the results of a series of comparisons performed by Buzica *et al.* [6] were used to validate these earlier results.

The manufacturer reported a nominal uptake rate of 0,85 cm³.min⁻¹ ± 11 % for a reference temperature of 9 °C and a reference pressure of 950 mbar.

When applying Fick's first law of diffusion, an uptake rate of 0,947 cm³.min⁻¹ was calculated at a temperature of 21 °C and pressure of 101,3 kPa [1, p. 47].

For practical purposes, users may correct the uptake rate to actual conditions of temperature and pressure by applying equation 3.3. In most cases, the pressure correction may be neglected. Other authors proposed e.g. 4.1 with a temperature correction raised to the power of 1.5 instead of 1.81 ([1], page 74):

$$v_{T,P} = v_{ref} \left(\frac{273,2 + T}{273,2 + T_{ref}} \right)^{1,5} \frac{P_{ref}}{P} \quad (\text{eq. 4.1})$$

where

- $v_{T,P}$ = uptake rate in cm³.min⁻¹ with temperature T and Pressure P during sampling;
- v_{ref} = uptake rate in cm³.min⁻¹ at reference temperature and pressure;
- T = actual temperature during sampling in °C;
- T_{ref} = reference temperature in °C at which v_{ref} rate is given;
- P = actual pressure during sampling in kPa

P_{ref} = reference pressure in kPa at which v_{ref} is given.

When applying a glass frit [4] to reduce effects of wind-induced turbulence, the uptake rate reduces to $0,827 \text{ cm}^3 \cdot \text{min}^{-1}$.

4.5 Environmental effects

4.5.1 Air velocity

The migration of NO_2 molecules to the absorption layer at the lower end of the diffusive sampler is determined by the length of the diffusion path. Eddies created by wind turbulence can shorten the diffusion path, thereby increasing the uptake rate and producing higher results. This phenomenon can be eliminated in one of two ways:

- by using protective shelters;
- by equipping the sampler inlet with a membrane.

Protective shelters

Protective shelters reduce the wind velocity at the sampler openings (the sampler and the shelter are an integral system): $0,5 \text{ m} \cdot \text{s}^{-1}$ outside corresponds to about $0,1 \text{ m} \cdot \text{s}^{-1}$ inside the shelter [3, 6] (see figure 4.3).

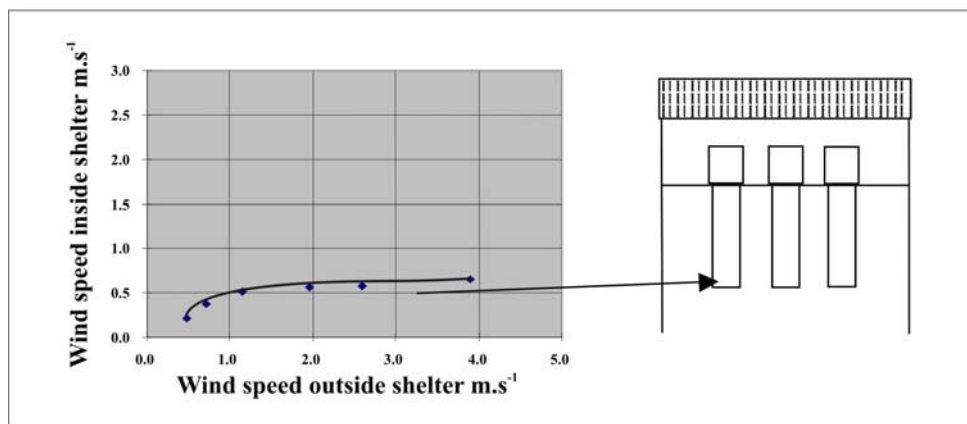


Figure 4.3: Effect of protective shelter on wind velocity inside the shelter

Effect of diffusion barrier like membranes or glass frit

The effect of using a polyethylene membrane on the relative uptake rate is illustrated in the figure 4.4.

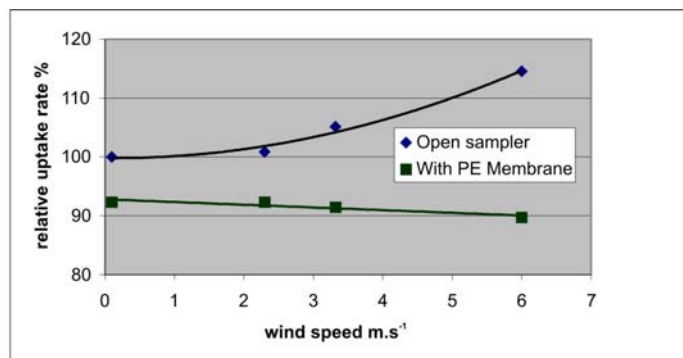


Figure 4.4: Relative uptake rate with and without membrane.

However, membranes affect the uptake rate of a diffusive sampler. The tested membranes (Fluoropore $1 \mu\text{m}$, Glass fibre EPM 2000 and Polyethylene $15\text{-}45 \mu\text{m}$) produced a decrease around

10% ± 4%. The results of the tests with different membranes are reported in table 4.2. The tests were conducted in a glass chamber with concentrations of 50 and 100 µg.m⁻³ and wind speeds of 0,01 and 0,5 m.s⁻¹. By using membranes, an additional resistance to the diffusion of NO₂ towards the absorbent is introduced (see section 3.7.1). This resistance tends to change with sampling conditions and creates another source of uncertainty. However, this uncertainty was found to be lower than the effect of wind velocities above 2 – 3 m.s⁻¹ for open tubes without protective shelters.

Table 4.2: Uptake rate for membrane closed Passam samplers relative to open tube

Membrane type	50 µg.m ⁻³ 0,5 m.s ⁻¹	100 µg.m ⁻³ 0,01 m.s ⁻¹	100 µg.m ⁻³ 0,5 m.s ⁻¹
Fluoropore 1 µm	90 %	95 %	94 %
Glass fibre EPM 2000	91 %	93 %	94 %
Polyethylene 14-45 µm	87 %	90 %	89 %

4.5.2 Relative humidity

No influence of relative humidity between 20 and 80% was observed [8]. No data are available for extreme conditions such as dry desert areas and wet tropic areas.

Under European climatic conditions, no humidity effects were reported [9].

4.5.3 Temperature

To investigate the influence of temperature, two glass chambers were set up in series. Six laboratory tests were performed. One chamber was always set at a controlled temperature of 20°C, while the second one was set at different temperatures between -15 and 50 °C (see figure 4.5). For each test, paired uptake rates (one at 20 °C and one at the temperature under test) were determined by exposure and analysis of several samplers in the chambers. For each paired uptake rate, a relative difference with reference to the uptake rate at 20 °C was calculated. Figure 4.5 shows that in the range of 5 to 40 °C, the uptake remained nearly constant and that it does not need any correction [8] according to temperature during exposure.

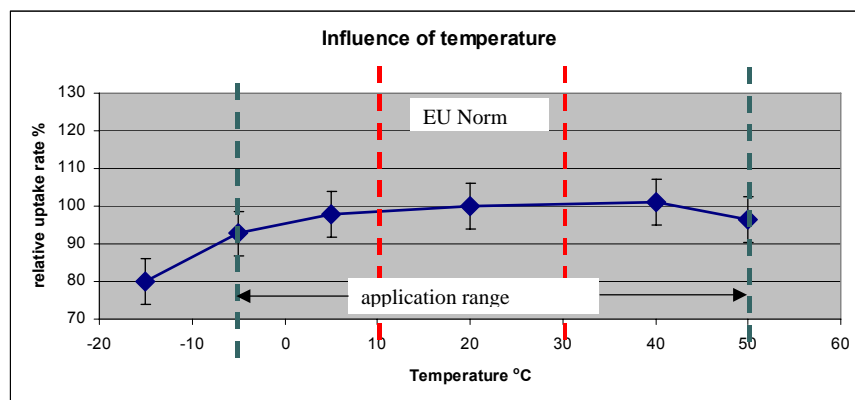


Figure 4.5: Effect of temperature on uptake rate, error bars represent the standard deviation of the relative uptake rates

In a year-long study conducted in Switzerland at 3 monitoring sites, where meteorological data were collected, comparisons between measurements by Passam samplers and chemiluminescence analysers were carried out [8]. A correlation analysis was performed between the meteorological factors and the ratios of NO₂ concentrations measured by the analysers to the diffusive sampler values. In total, 78 2-week pairs of measurements were available. All samplers were equipped with protective shelters. No influence of wind velocity and radiation was observed (see table 4.3). There was a slight correlation with temperature and humidity, although the median test was negative in all cases.

Table 4.3: Correlation coefficients of meteorological parameters with the ratios of NO₂ measurements carried out with chemiluminescence analyses out of diffusive samplers

	Temperature	Humidity	Wind speed	Radiation
Unit	°C	% rel.	m/sec	Watt/m ³
Correlation r	0.136**	0.113**	0.021	-0.019
Range _{min}	-0.7	42	0.7	15
Range _{max}	23	85	2.6	273
Median	11.2	67	1.4	112
Median test	n.s.	n.s.	n.s.	n.s.

** = 99% significance level.

In a Swiss alpine Valley 1800 m above sea level, a measurement comparison between a chemiluminescence monitor and the Passam samplers was performed. The mean temperature in the coldest season was -4,1 °C. No differences in results of the two methods were observed for temperatures above - 5 °C [3].

4.5.4 Pressure

A pressure effect of 0,5 % decrease in uptake rate with an increase in ambient air pressure of 10 mbars has been observed [8].

4.5.5 Interferences

Burri has studied the interferences of NO, SO₂ and ozone. No effects could be shown when single substances were applied [10].

4.6 Validation of sampler performance

4.6.1 Comparisons with reference methods

Basic validation studies 1986 – 1988

To validate the diffusive sampling system, comparisons with continuous monitors were performed [10]. The comparisons were made at 5 different monitoring sites over one year. 184 weekly monitoring pairs were collected. The concentration values of the monitors were standardized to 9 °C and 950 mbar. The results are compiled in figure 4.6.

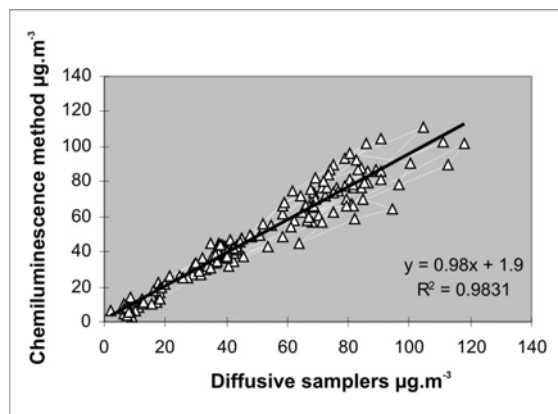


Figure 4.6. Relationship between results of Passam and chemiluminescence monitors

Reports from cantons of Switzerland

Comparisons of yearly means

In figure 4.7, the results of comparisons of annual NO_2 averages are shown. Each point is characterized by 50 to 70 diffusive sampler measurements over one year and a complete data set of chemiluminescence analyser results. The exposure period was two weeks. Under these conditions, varying meteorological factors such as humidity, wind, temperature etc. were automatically considered.

The 95 % confidence interval was calculated to be $\pm 4 \mu\text{g.m}^{-3}$ at the level of the Swiss long-term limit value of $30 \mu\text{g.m}^{-3}$. This figure is valid for the investigations conducted from 1987 to 1994. Figure 4.7 shows that the uptake rate of the sampler remained constant from 1987 to 1994 and from 1995 to 2000. The ratio of NO_2 measured by samplers vs monitors was 0,98 from 1987 to 1994. The same ratio (1,01), was not significantly different from 1995 to 2000. The difference in R^2 values may be explained by the larger range of NO_2 concentrations measured between 1987 and 1994.

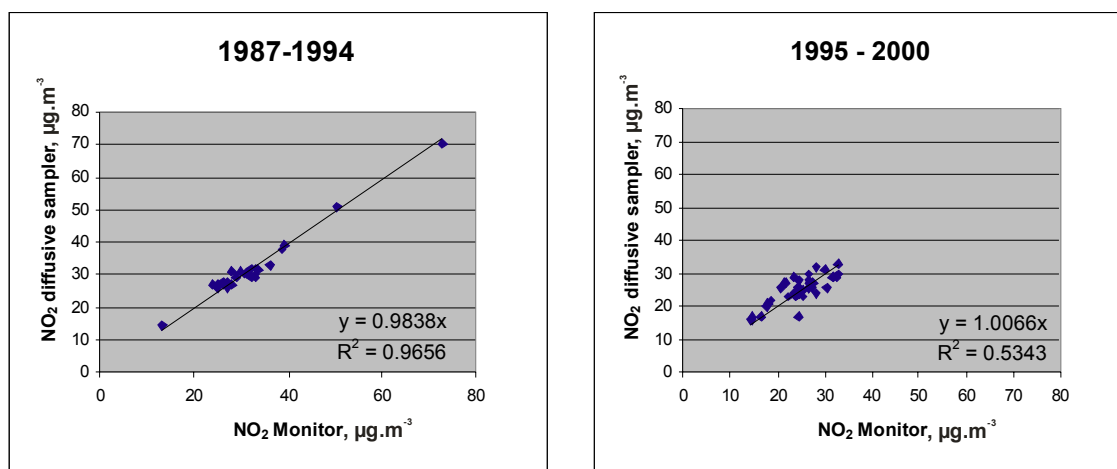


Figure 4.7. Relationship between results of Passam and chemiluminescence monitors

Comparisons of single pairs

Table 4 gives a regression analysis for individual NO_2 concentrations measured using Passam samplers and chemiluminescence analysers. The data were communicated by the Environmental Agencies of the cantons of Grison, Basel and Bern (CH). For each sampling site, the slope/intercept of the regression line, the percentage of variation expressed by the regression line (R^2) and the number of samples are given. Samplers were exposed for 2 weeks.

Table 4.4: Comparisons of individual NO₂ measurements by Passam samplers and chemiluminescence analyser at field sites. Results of environmental agencies in Grison, Basel and Bern (CH)

Canton	Type of site	Year	Slope	Intercept	R ²	n
Bern	city background	2005	1,15	-3,4	0,939	26
		2006	0,96	-0,91	0,975	26
		2007	0,94	-0,03	0,928	26
	agglomeration, highway	2005	1,49	-25	0,780	26
		2006	1,12	-9,1	0,889	26
		2007	1,22	-12,7	0,889	26
Basel	city	2001/02	1,15		0,954	124
Grison	industrial	2001-2003	0,94	-6,8	0,700	166
	traffic		0,94	-3,1	0,840	54
	rural		0,9	-1,1	0,890	113
	mountain city,suburb		1,09	-0,9	0,850	128
	mountain city, traffic		1,08	-7,3	0,860	41
	traffic		1,12	-11,4	0,570	25
	mountain		1,16	-11,1	0,750	24
	highway		0,97	-1,2	0,740	231
	mountain village		1,26	-5,8	0,930	15
highway	0,26	16,4	0,130	58		
Neuchatel	city	2005	1,13	0	0,927	27

Near highways and in cities, site-specific discrepancies were sometimes observed (see figure 4.8). In general, an overestimation of the concentration of NO₂ in the vicinity of highly trafficked streets was observed [11]. The deviations are most likely due to traffic-induced vertical air turbulence.

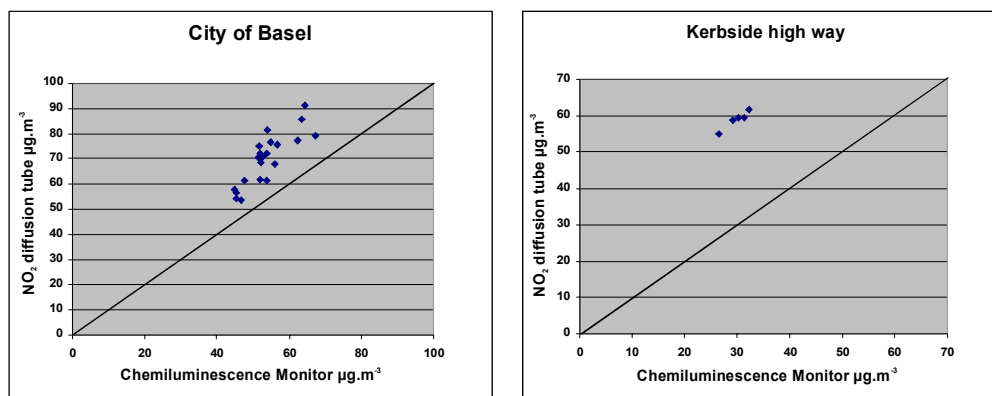


Figure 4.8. Examples of relationships between results of Passam and chemiluminescence monitors for specific city and highway conditions

Reports from outside Switzerland

In 2001-2002, CEN/TC264 WG11 performed a small-scale pilot study at two locations in the UK. At each location, 6 replicate samplers of different NO₂ passive samplers were exposed for two weeks, in parallel with measurements from a reference chemiluminescence analyser. Samplers were provided and analysed by the suppliers. The unpublished results for the exposed Passam samplers are reported in table 4.5.

Table 4.5: Results of CEN pilot study for Passam samplers

Willebroek	NO ₂ (µg.m ⁻³)	Ratio Passam/reference
Reference	40,8	
Passam	55,0	1,35
Teddington	NO ₂ (µg.m ⁻³)	Ratio Passam/reference
Reference	13,8	
Passam	20,2	1,46

Passam samplers were found to overestimate NO₂ concentrations.

Experiments in France at various sites also concluded that the Passam tubes overestimated NO₂ concentrations, when using the uptake rate of 0,85 cm³.min⁻¹ (see figure 4.9). In order to obtain correct values, a uptake rate of 0,947 (21 °C, 101,3 kPa) should be used, reducing the results of the Passam tubes by about 11 %. [1, p. 47].

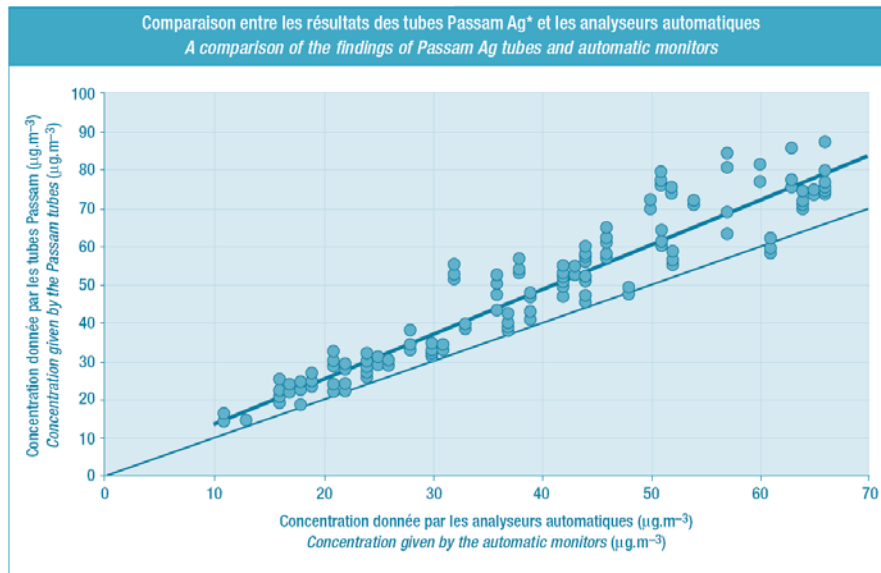


Figure 4.9: Relationship between results of Passam and chemiluminescence monitors

ASPA (the French air quality Alsace network) reported slopes of linear regressions between results of chemiluminescence monitors and Passam tubes from 0,95 to 1,15 (see table 4.6). The NO₂ concentrations were corrected to 20 °C and 1013 mbar according to equation 4.1. The slope/intercept of the regression line, the percentage of variation expressed by the regression line (R²) and the number of samples are given. Samplers were exposed for 2 weeks.

Table 4.6: Comparisons of individual NO₂ measurements by Passam samplers and chemiluminescence analyser at field site. Results of ASPA in France

ASPA	Type of site	Year	Slope	Intercept	R ²	n
1	agglomeration	2005	1,15	-3,42	0,939	25
2	rural	2005	0,964	-0,91	0,975	25
3	agglomeration	2005	0,953	-0,03	0,928	25
4	city centre	2005	1,006	1,29	0,963	25
5	city centre	2005	1,023	2,36	0,989	25

Buzica et al. [6] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler type was exposed in batches of 6 samplers for a period of 14 days, except in the laboratory trial “high” (see table 4.7).

Table 4.7: Laboratory conditions (intercomparison of Buzica et al.)

Parameter	High	Low
Exposure time (d)	7	14
Concentration ($\mu\text{g.m}^{-3}$)	80	40
Air velocity (m.s^{-1})	2,5	1,0
Temperature ($^{\circ}\text{C}$)	25	5
Relative humidity (%)	75	30

The results obtained for the Passam sampler (implemented by an external laboratory following the Passam protocol), are presented in table 4.8.

Table 4.8: Results of Passam sampler analysed by an external laboratory (intercomparison of Buzica et al.)

Location	CLS ($\mu\text{g.m}^{-3}$)	Passam ($\mu\text{g.m}^{-3}$)	Ratio
Laboratory, high	76,8	97 \pm 5	1,27
Laboratory, low	43,5	39,5 \pm 0,7	0,91
Genevilliers	41,6	53,1 \pm 0,3	1,28
Fontainebleau	14,1	15,7 \pm 0,4	1,11

CLS: chemiluminescence method

The Passam tubes were found to overestimate NO_2 concentrations, confirming the findings reported in [1] (see table 4.8). This was attributed to the use of an uptake rate for reference conditions differing considerably from the exposure conditions.

In 2004-2005, Pfeffer et al. [4] performed an extensive study into the use of Passam tubes. Tubes were exposed for periods from 2 to 6 weeks at 10 different sites in North-Rhine Westphalia in Germany (LANUV network). In this investigation, a diffusion barrier consisting of a porous glass membrane was fitted at the open end of all samplers. The uptake rate of the tubes, derived from the comparison with reference method according to EN 14211 was $0,8270 \pm 0,0085 \text{ cm}^3.\text{min}^{-1}$. When comparing concentrations measured with the reference method and the modified Passam sampler by linear regression, the site-specific slope derived for each monitoring site generally did not differ significantly from the slope calculated from the complete data set at the 95% confidence level. The site-specific slopes varied between 0,93 and 1,11. The between-sampler uncertainty obtained from replicate sampling was $1,2 \mu\text{g.m}^{-3}$. The tubes were subsequently used in the LANUV monitoring network. They were further investigated for consistency with the reference method. No deviations were observed when comparing 789 data pairs of results [12].

In France, Passam samplers were extensively compared to the chemiluminescence reference method [13]. During the years 2005, 2007 and 2008 samplers were exposed side-by-side with the reference method at 6 locations (5 in 2005) with exposure periods of 4 weeks, resulting in a total of 181 valid data pairs. From the results reported, it was observed that the data capture of the Passam samplers (100%) was higher than that of the reference method (95,5%). Further, when subjecting the data to the evaluation of equivalence [14], the results presented in figure 4.10 were found. The evaluation revealed excellent agreement between the results of both methods. The resulting uncertainty, 13 % for a 95 % confidence level, fulfils the 15 % uncertainty requirement for fixed measurements of NO_2 . The ratio of the overall means of diffusive sampling results and reference results was 0,98.

REGRESSION OUTPUT		
slope b	0,975	
uncertainty of b	0,010	significant
intercept a	0,1	
uncertainty of a	0,19	
number of data pairs	181	
EQUIVALENCE TEST RESULTS		
random term	2,4	$\mu\text{g.m}^{-3}$
bias at LV	-0,9	$\mu\text{g.m}^{-3}$
combined uncertainty	2,6	$\mu\text{g.m}^{-3}$
relative uncertainty	6,4%	pass
reference uncertainty	1,0	$\mu\text{g.m}^{-3}$
limit value	40	$\mu\text{g.m}^{-3}$

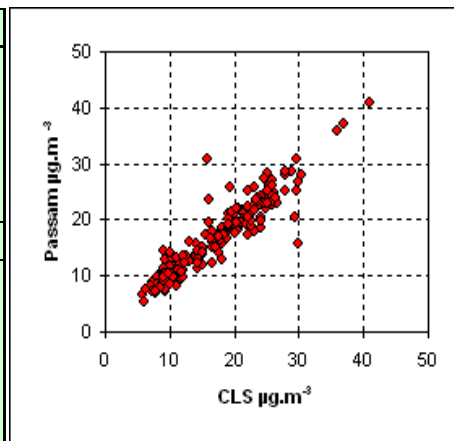


Figure 4.10: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Passam sampler vs chemiluminescence analyser

4.7 Measurement uncertainty

4.7.1 GUM approach

Passam applied the (indirect) GUM approach for the evaluation of the uncertainty associated with the measurement of NO_2 using the Passam tube [15]. The uncertainty assessment was based on the following measurement equation:

$$C_{\text{NO}_2} = \frac{(m_d - m_b) \cdot 10^6}{v \cdot t} \quad (\text{eq 4.2})$$

where

- C_{NO_2} = ambient concentration in $\mu\text{g.m}^{-3}$;
- m_d = mass of desorbed analyte in μg ;
- m_b = blank of analyte in μg ;
- v = diffusive uptake rate in $\text{cm}^3.\text{min}^{-1}$;
- t = exposure time in min.

The input quantities and their uncertainties are defined as follows:

- u_{md} : Uncertainty of the mass of measured nitrite. The standard uncertainty is characterised by the standard deviation of the calibration function;
- u_{mb} : Blank values: the variation of blank value has to be added to u_{md} in absolute terms;
- u_v : Uncertainty of uptake rate. The variation of this term is given by the standard deviation of repeated verification experiments in standard atmospheres;
- u_t : Exposure time. This term is in general negligible at exposure times of more than one week.

An additional term is introduced, which covers the uncertainties associated with between-sampler precision, micro-environmental factors, variations in the geometry of samplers etc.

- u_p : Variation of multiple samples at the same site. The size of this term is estimated by the median of triplicate samplers in the field.
- u_{ext} : External influences such as temperature, wind speed, humidity. This term has to be taken into account, if the samplers are used in extreme conditions. This term has to be estimated.

The combined uncertainty u_c is calculated using equation 4.3.

$$u_c^2 = u_v^2 + u_{md}^2 + u_{mb}^2 + u_p^2 + u_t^2 + u_{ext}^2 \quad (\text{eq. 4.3})$$

The expanded uncertainty is calculated by using a coverage factor of 2. Detailed figures for u_v , u_p and u_{mb} are given in [16]. The coefficient of variation of replicates is reported in [17] to be 1,7 %. The uncertainty figures are re-evaluated every year [16].

The expanded uncertainty calculated in the above manner varies between 20 % and 25 % (see figure 4.11). The data quality objective of EU Directive 2008/50/EC for indicative measurements is generally fulfilled.

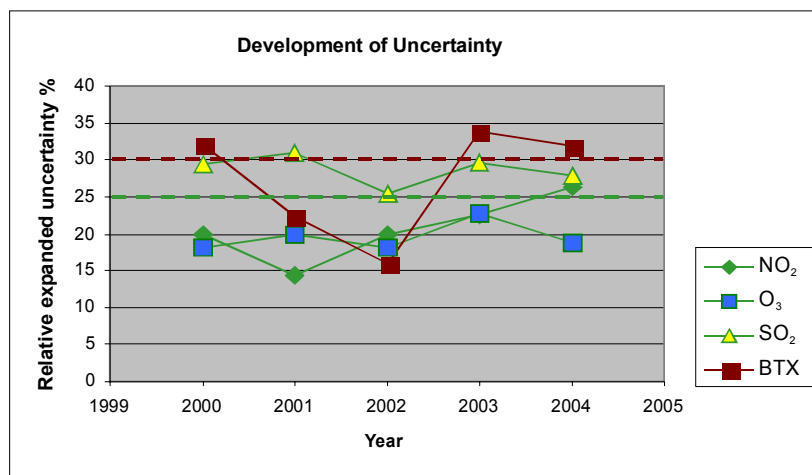


Figure 4.11: Relative expanded uncertainty of Passam results from 2000 to 2004 as monitored by the manufacturer

4.7.2 Direct approach

A comprehensive uncertainty evaluation using a direct approach was performed by Pfeffer et al. [4]. At 10 monitoring sites, parallel measurements were performed with Passam samplers and the EU reference method (EN 14211) for more than one year. A modified Passam tube equipped with a porous glass membrane was used.

From the comparisons with reference values obtained from the chemiluminescence monitors, a relative expanded uncertainty for single results between 21 % and 25 % at $40 \mu\text{g}\cdot\text{m}^{-3}$ was calculated for exposure periods of 2 to 6 weeks. Calculation according to the guide to demonstration of equivalence for 4-weeks exposure resulted in an expanded uncertainty of 22 %. In this calculation, the uncertainty of the reference method results was set to zero. Consequently, the uncertainty represents the worst case [18].

It is unlikely that these results were biased, since the estimation of the uptake rate was based on NO₂ values measured using the reference method (EN 14211). The estimation of the uptake rate was performed using measurements at 10 different monitoring sites and over 14 months (as the slope of the mass uptake versus sampled dose, see figure 4.12). With all these different sampling conditions, the influencing parameters (either chemical or meteorological) encompassed a large range of possible values. It is therefore likely that most of the sources contributing to the uncertainty of the reference method and of the diffusive sampling method were randomised. For this reason, it seemed to be justified to divide the uncertainty of single values by the square root of 12 when calculating annual averages from 12 monthly values. Consequently, the uncertainty of annual averages based on monthly measurements should be less than 10 %. This means that the EU data quality objective of 15 % is safely met for annual means.

In 2004/2005, the uptake rate was evaluated by parallel measurements with chemiluminescence analysers. It was found to be $0.827 \text{ cm}^3\cdot\text{min}^{-1}$ (see figure 4.12). At this time, the monitors in the

monitoring network were logically not type approved according to the new CEN standard EN 14211 published in 2005.

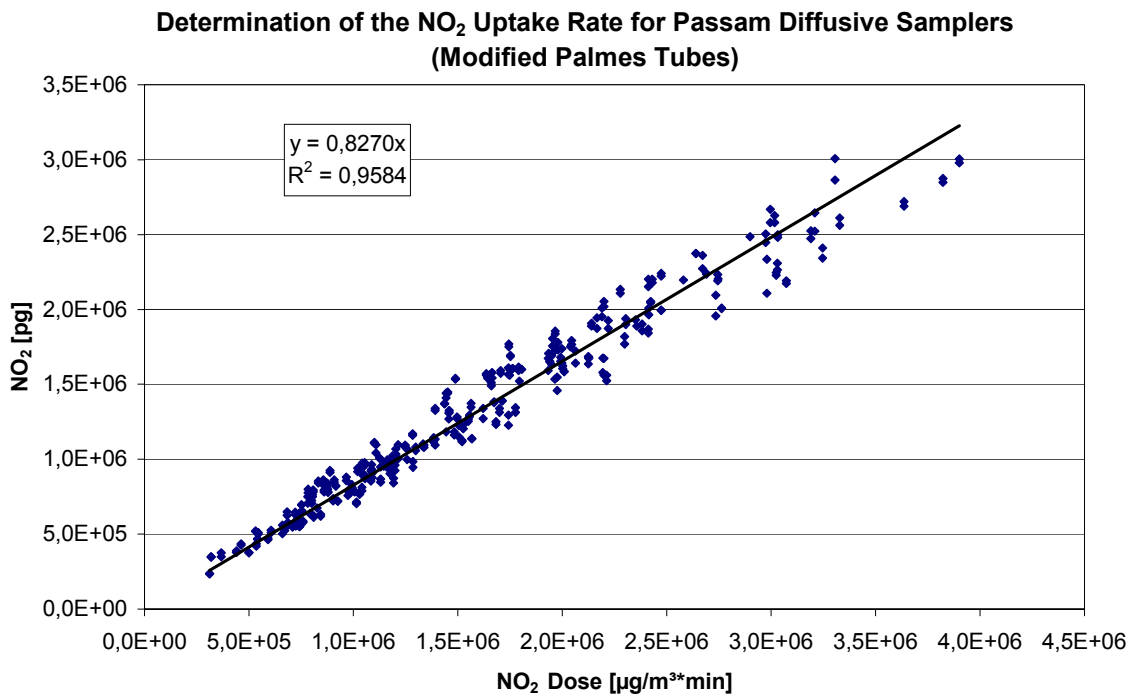


Figure 4.12: Relationship between mass of NO₂ obtained by analysis and NO₂ dose sampled

The uptake rate found in the validation experiments was continuously checked by ongoing parallel measurements with the chemiluminescence method from 2006 to 2008 at six to eight stations. Results for 2006 showed an excellent congruence of the annual averages measured by the chemiluminescence method and with the diffusive samplers [12, 18].

In 2007 and 2008, slight and increasing differences were found at various stations showing higher values of the continuous measurements compared with the diffusive samplers [12].

Comprehensive investigations were performed to find technical reasons for this phenomenon. It was shown that all handling details of the diffusive sampler technique remained unchanged over the years. But in the network of continuous analysers, old instruments were replaced stepwise by new monitors that were type approved according to EN 14211 in order to meet the requirements of Annex VI D of the new European directive 2008/50/EC. The new generation of instruments therefore appears to give higher results for NO₂ in some situations, especially in high ambient humidity conditions. Similar effects were found during inter-laboratory comparisons in the German networks [19].

When sufficient data of parallel measurements are available, it may be necessary to adjust the uptake rate of the diffusive samplers accordingly.

ASPA performed parallel measurements with Passam samplers and the EU reference method (EN 14211) at 5 monitoring sites (rural to city sites) for 1 year using two-week exposure periods [1] (see figure 4.13). The raw data of diffusive samplers, delivered by Passam, were corrected for temperature and pressure according to equation 4.1. Applying the direct approach described in EN-ISO 20988, an expanded uncertainty of 14,4 % at 40 µg.m⁻³ was obtained. This figure is similar to the results obtained when evaluating uncertainty for the 3-year data set of monthly measurement results provided by Lig'air [13].

This shows that the uncertainty tends to meet the data quality objective of EU Directive 2008/50/EC for fixed measurements.

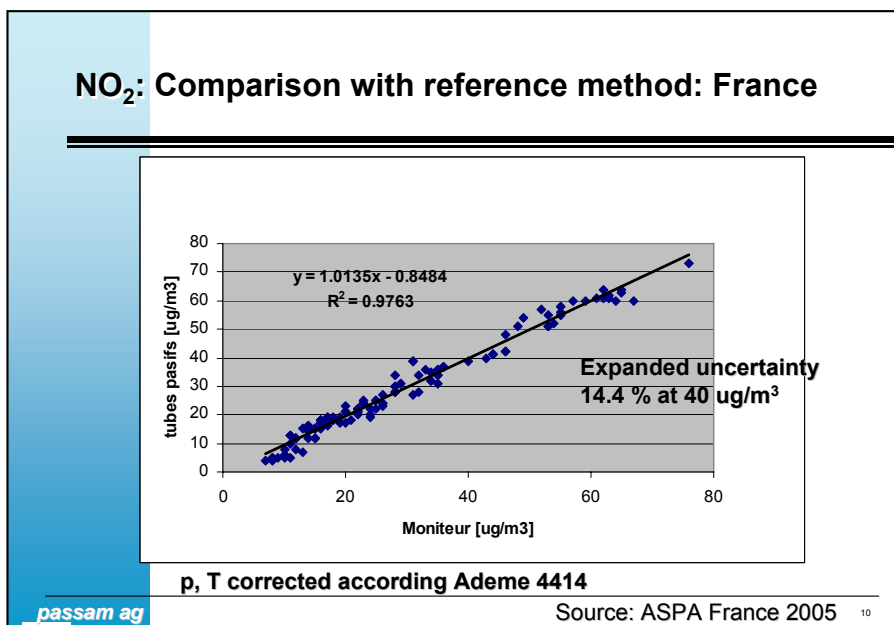


Figure 4.13: Relationship between results of Passam tubes and chemiluminescence monitors, Field site in France (ASPA)

4.8 Application in EU monitoring networks

Passam tube samplers are used e.g. in Cyprus, France, Germany, Italy, Lithuania and Romania for supplementary measurements to the fixed measurements at the level of an indicative method. Other applications include identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

4.9 Conclusions

The Passam tube-type diffusive sampler is suitable for long-term monitoring of NO₂ in ambient air. Exposure periods of 1 to 6 weeks are feasible. The lower detection limit for a 2-week sampling period is reported to be 0,4 µg.m⁻³.

Information about the precision of the sampler indicates that this is usually better than 5 %.

The comparability of sampler results with those obtained from continuous reference monitors (chemiluminescence) vary somewhat, with ratios of average results generally ranging from 0,9 to 1,3. This variability may be reduced, when :

- Uptake rates are converted to actual conditions of temperature and pressure;
- Membranes are introduced into the sampler inlet, particularly for traffic-related sites.

When the uncertainty associated with the measurement results is evaluated according to the Guide to the Expression of Uncertainty in Measurement, relative expanded uncertainties of individual results were between 20 and 25 %. When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO₂, similar and even better results were obtained.

These findings suggest that the Passam tube is at least suitable for performing long-term measurements of NO₂ for indicative purposes and possibly even for fixed measurements.

When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 15 % due to the reduction of random effects on uncertainty.

4.10 References

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5 The Ogawa badge

5.1 Sampler design

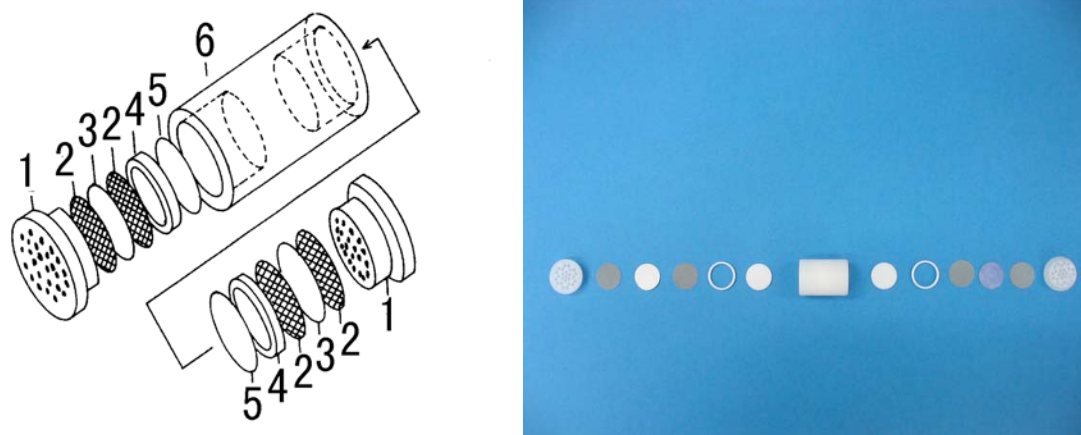


Figure 5.1: Ogawa sampler design

1. Diffuser end cap
2. Stainless steel mesh
3. Sampling filter (14,5 mm ϕ)
4. Teflon ring
5. Teflon disk
6. Body (15 mm ID; 19 mm OD; 6 mm length)

The Ogawa sampler [1] (see figure 5.1) is a badge-type sampler that can be equipped with a sampling filter on either side of the sampler body. Sampling filters consist of cellulose fibre. Both filters can be coated with triethanolamine (TEA) for the sampling of NO_2 in ambient air. Coated filters may be supplied by the manufacturer. However, literature reveals that filters may also be coated by users themselves [2].

The presence of a second filter permits the simultaneous collection of NO_2 and nitrogen oxides equal to the concentration of nitrogen monoxide (NO) plus NO_2 . In this case, the second filter is coated with TEA and 2-phenyl-4,4,5,5-tetramethyl imidazoline-3-oxide-1-oxyl (PTIO), which is a specially prepared reagent for oxidising NO to NO_2 . This filter then collects both species as NO_2 . The concentration of NO can be obtained as a difference in NO_2 concentrations found on the two differently coated filters.

5.2 Extraction and analysis

The manufacturer recommends the determination of the collected NO_2 by colorimetry after reaction with sulphanilamide and N-1-naphthylethylenediamine. However, literature reveals the use of ion chromatography for the measurement of nitrite on the filter [3,4]. In that case, co-sampled sulfur dioxide can also be simultaneously measured.

5.3 Application range and conditions

The manufacturer recommends exposure periods from 24 to 168 hours, but indicates that for low concentrations it is possible to sample for up to 30 days. In practice, samplers have been exposed for up to 4 weeks [4].

Although not explicitly stated in [1], the information provided suggests that the samplers may be used over a temperature range from $-10\text{ }^\circ\text{C}$ to $40\text{ }^\circ\text{C}$, and a relative humidity range from 50 % to 80 %.

The sampler should always be exposed with a shelter as provided by the manufacturer.

Detection limits given by the manufacturer are 2,3 ppb for 24-hour sampling, and 0,32 ppb for 1-week sampling. The upper limit for 1-week sampling is reported to be 3600 ppb.

The manufacturer specifies the following conditions for storage of coated filters, samplers and sampled filters upon refrigeration:

- Coated filters sealed in original glass vial with aluminium pouch : 90 days
- Sampler loaded with coated filter(s) placed in bag in sealed brown vial : 60 days
- Exposed sampler placed in bag in sealed brown vial : 14 days*
- Filter extract in sealed amber glass vial : 90 days.

* Filters should be analyzed as soon as possible after exposure.

5.4 Uptake rate and environmental effects

The Ogawa Protocol [1] provides information about the uptake rate of the sampler in the form of a coefficient α , which is a function of temperature and relative humidity. After analysis of an Ogawa sampler, NO_2 is calculated using equation 5.1

$$C_{\text{NO}_2} = \alpha \cdot \frac{m}{t} \quad (\text{eq. 5.1})$$

where

- C_{NO_2} = concentration of NO_2 in ppb;
- α = dose according to the uptake mass in $\text{ppb} \cdot \text{min} \cdot \text{ng}^{-1}$, (converse of an uptake rate);
- m = mass of nitrite determined by analysis on a single filter in ng;
- t = exposure time in min.

α may be calculated for a given temperature and relative humidity using the semi-empirical equation 5.2.

$$\alpha = \frac{10^4}{0,677 \cdot P \cdot RH + 2,009 \cdot T + 89,8} \quad (\text{eq 5.2})$$

where

- RH = ambient air relative humidity in %;
- T = ambient temperature in °C.

P is calculated using equation 5.3.

$$P = \left[\frac{2P_n}{P_T + P_n} \right]^{\frac{2}{3}} \quad (\text{eq. 5.3})$$

where

- P_n = saturated water vapour pressure at 20 °C in mm of Mercury (Hg) = 17,53
- P_T = saturated water vapour pressure at temperature T in mmHg.

The variation of α as a function of temperature and relative humidity is presented in table 5.1 and figure 5.2.

Table 5.1: Variation of α in ppb.min.ng-1 as a function of temperature and relative humidity

RH (%) / T (°C)	0	5	10	15	20	25	30	35	40
20	92,4	85,3	79,3	74,2	69,7	65,7	62,2	59,0	56,0
30	85,2	79,4	74,5	70,3	66,5	63,2	60,2	57,4	54,8
40	79,0	74,3	70,3	66,8	63,7	60,9	58,3	55,8	53,5
50	73,6	69,8	66,5	63,6	61,0	58,7	56,5	54,4	52,4
60	68,9	65,8	63,1	60,7	58,6	56,7	54,8	53,0	51,3
70	64,8	62,2	60,0	58,1	56,4	54,8	53,2	51,7	50,2
80	61,2	59,0	57,2	55,7	54,3	53,0	51,8	50,5	49,2
90	57,9	56,1	54,7	53,5	52,4	51,4	50,4	49,3	48,2

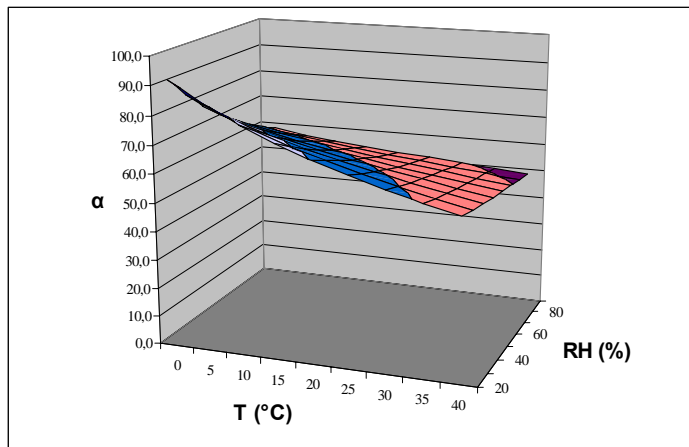


Figure 5.2: Variation of α in ppb.min.ng-1 according to Temperature (T) and relative humidity (RH)

In order to calculate a uptake rate in more common units of $\text{cm}^3 \cdot \text{min}^{-1}$, equation 5.4 can be used for the conversion.

$$V = \frac{10^3}{\alpha} \cdot \frac{V_{m,air}}{46,0055} \quad (\text{eq. 5.4})$$

where

$V_{m,air}$ = molar volume of the sampled air.

5.5 Validation of sampler performance

5.5.1 Comparisons with reference methods

The Ogawa protocol describes a comparison between the results of the sampler and a reference method performed within the frame of the original validation of the sampler (Yokohama City Research Institute of Environmental Science, Yokohama, Japan, Report No. 128, March 1997; see [1]). The results are presented in figure 5.3. The y-axis represents results obtained with the sampler, the x-axis results of the reference method. Unfortunately, the sampling period is unknown.

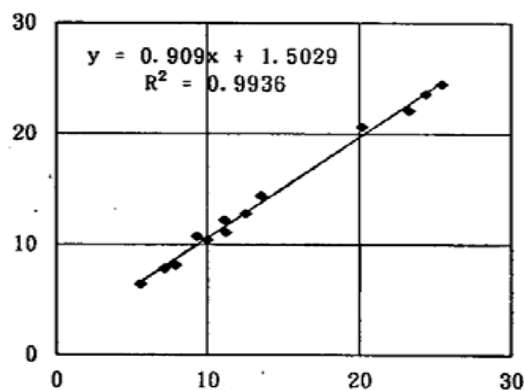


Figure 5.3: Comparison between results of the Ogawa sampler with the chemiluminescence method. X and y axis represent the results of the diffusive sampling method and reference method, respectively

In a further Japanese report supplied by Ogawa USA (no reference available), a comparison was reported between the Ogawa sampler and chemiluminescence monitoring at Funakoshi environmental station. Samplers were exposed during two 5-week periods in July/August 1999 and January/February 2000. Sampling periods of 1, 2, 3, 4 and 5 weeks were used, samplers being exposed in triplicate. The sampler results obtained were internally consistent over the 5-week period. Ratios of results of samplers and chemiluminescence monitors ranged between 0,95 and 1,16, with better comparability observed in the winter period. No information was provided of sampler precision.

Bytnerowicz et al. [5], in a study devoted to the measurement of several air pollutants in Sequoia National Park, measured NO_2 over the period of May to October 1999 both by the chemiluminescence method and by using the Ogawa sampler. The samplers were exposed in duplicate for consecutive two-week periods. The mean values found by the Ogawa sampler and the chemiluminescence method were 2,6 and 2,0 ppb, respectively. The precision of mean value determined by the Ogawa sampler was 5,6 %.

Buzica et al. [6] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler type was exposed in batches of 6 samplers for a period of 14 days, except in the laboratory trial "high" (see table 5.2).

Table 5.2: Laboratory conditions (intercomparison of Buzica et al.)

Parameter	High	Low
Exposure time (d)	7	14
Concentration ($\mu\text{g.m}^{-3}$)	80	40
Air velocity (m.s^{-1})	2,5	1,0
Temperature ($^{\circ}\text{C}$)	25	5
Relative humidity (%)	75	30

The results obtained for the Ogawa sampler operated by Lab L – following the Ogawa protocol – are presented in table 5.3.

Table 5.3: Results of Ogawa sampler operated by Lab L (intercomparison of Buzica et al.)

Location	CLS ($\mu\text{g.m}^{-3}$)	Ogawa ($\mu\text{g.m}^{-3}$)	Ratio
Laboratory, high	76,8	132 \pm 19	1,72
Laboratory, low	43,5	46,4 \pm 2,6	1,07
Genevilliers	41,6	41,4 \pm 0,9	1,00
Fontainebleau	14,1	14,8 \pm 3,1	1,05

CLS: chemiluminescence method

Apart from the results of the laboratory trial “high”, the results were comparable with those of the reference method (chemiluminescence, CLS). An explanation for the aberrant results at high air velocity may be that Lab L did not use a protective cover in the laboratory trials. The laboratory “high” trial yielded large variations in results for all participants, with mean results ranging from 54 to 188 $\mu\text{g}\cdot\text{m}^{-3}$. The precision of the results was also variable, ranging from 2 % to 20 %.

Singer et al. [7] validated the samplers e.g. by parallel measurements with a chemiluminescence analyser. Samplers were exposed for 1 week. They reported a good correlation, with samplers producing slightly lower results (8 % on average). They reported the precision for the sampler to be better than 5 %. The detection limit for a 1-week sampling period was reported to be 0,2 ppb (analysis performed by colorimetry).

Swaans and Goelen [8] reported the results of field tests in Belgium in which a number of diffusive samplers were compared by parallel measurements with a reference monitor. The exposure period was 14 days; each sampler was exposed in triplicate. The results are presented in table 5.4.

Table 5.4: Results field tests in Belgium

Location	CLS ($\mu\text{g}\cdot\text{m}^{-3}$)	Ogawa ($\mu\text{g}\cdot\text{m}^{-3}$)	Ratio
Borgerhout	44,7	47,3 ± 5,2	1,06
Gent	21,0	22,4 ± 2,1	1,07
Borgerhout	51,4	50,6 ± 0,2	0,98
Gent	27,3	25,6 ± 2,7	0,94

Again, results obtained with the Ogawa sampler were comparable to those obtained with the chemiluminescence method. However, the precision of the triplicate results was rather high for 3 trials (≈ 10 %).

Additional work performed by these authors involved a comparison of analyses by ion chromatography and colorimetry. The colorimetric method was found to give a lower detection limit (factor 3). Otherwise, the results obtained were similar.

Sather et al. [9] compared results of 24- and 96-hour diffusive samplers with those from a chemiluminescence analyser. Correlations were good, improving with prolonged sampling duration. Duplicate samplers yielded mean absolute differences of 1,6 to 1,9 ppb for average levels of 22 ppb to 23 ppb.

Sather et al. [4] performed parallel measurements of Ogawa samplers with the US-EPA Federal Reference Method (FRM: the chemiluminescence method) for one year at 6 locations in El Paso, Texas. The extensive dataset resulting from these comparisons was kindly made available by Dr. Sather of US-EPA. Unfortunately, the results received were rounded which may affect comparability at low levels.

The samplers were exposed for different periods: 2, 3 and 4 weeks. All samplers were exposed in duplicate. The mean average difference found between sampler pairs is 0,3 ppb. All results of the trials are presented in tables 5.5 to 5.7.

Table 5.5: Measurement by the US Federal Reference Method (FRM) and Ogawa sampler at two monitoring sites. Exposure period: 2 weeks; results in ppb. Bold figures represent averages.

UTEP			Skyline		
<i>FRM</i>	<i>Ogawa</i>	<i>Ratio</i>	<i>FRM</i>	<i>Ogawa</i>	<i>Ratio</i>
25	29	1,16	17	17	1,00
22	23	1,05	12	13	1,08
23	25	1,09	13	12	0,92
23	25	1,09	15	13	0,87
18	19	1,06	9	10	1,11
19	19	1,00	11	11	1,00
14	16	1,14	7	7	1,00
17	18	1,06	8	8	1,00
16	16	1,00	8	7	0,88
15	14	0,93	7	7	1,00
14	14	1,00	6	5	0,83
14	12	0,86	6	6	1,00
12	12	1,00	6	6	1,00
14	13	0,93	7	6	0,86
12	12	1,00	6	5	0,83
15	14	0,93	7	6	0,86
14	14	1,00	8	6	0,75
13	14	1,08	7	6	0,86
20	21	1,05	10	9	0,90
13	15	1,15	7	6	0,86
16	17	1,06	8	9	1,13
17	20	1,18	8	12	1,50
18	20	1,11	8	11	1,38
19	21	1,11	10	12	1,20
23	26	1,13	13	16	1,23
23	25	1,09	14	17	1,21
17,3	18,2	1,06	9,2	9,3	1,02

Table 5.6: Measurement by the US Federal Reference Method (FRM) and Ogawa sampler at two monitoring sites. Exposure period: 3 weeks; results in ppb. Bold figures represent averages.

Ascarate			Santa Teresa		
<i>FRM</i>	<i>Ogawa</i>	<i>Ratio</i>	<i>FRM</i>	<i>Ogawa</i>	<i>Ratio</i>
21	26	1,24		7	
22	23	1,05	6	6	1,00
22	22	1,00	5	4	0,80
18	19	1,06	5	4	0,80
16	18	1,13	3	3	1,00
19	16	0,84	2	1	0,50
16	13	0,81	1	0	
18	13	0,72	1	0	
13	12	0,92	3	2	0,67
10	9	0,90	3	2	0,67
13	12	0,92	4	3	0,75
15	14	0,93	3	3	1,00
18	17	0,94	5	5	1,00
18	17	0,94	4	3	0,75
19	20	1,05	6	6	1,00
20	20	1,00	6	6	1,00
26	26	1,00	7	7	1,00
17,9	17,5	0,98	4,0	3,6	0,91

Table 5.7: Measurement by the US Federal Reference Method (FRM) and Ogawa sampler at two monitoring sites. Exposure period: 4 weeks; results in ppb. Bold figures represent averages.

Socorro			Desert View		
FRM	Ogawa	Ratio	FRM	Ogawa	Ratio
17	20	1,18	14	14	1,00
17	18	1,06	12	11	0,92
14	14	1,00	11	10	0,91
13	12	0,92	7	5	0,71
12	9	0,75	8	6	0,75
12	8	0,67		3	
7	7	1,00		4	
9	8	0,89		6	
10	9	0,90		6	
12	11	0,92	11	9	0,82
14	14	1,00	9	8	0,89
15	15	1,00	12	13	1,08
19	19	1,00	15	15	1,00
13,2	12,6	0,94	11,0	8,5	0,90

By studying the ratios of the mean results obtained by the FRM and the Ogawa sampler, their comparability was evaluated. It was observed that results were comparable for a 2-week exposure period, with the samplers slightly overestimating the reference concentrations. Sampler results for 3- and 4-week periods were generally lower than those of the FRM.

Using this extensive dataset, an attempt to evaluate the equivalence of the sampler with the reference method according to the Guide to the Demonstration of Equivalence [10] was made. The results are presented in figure 5.4.

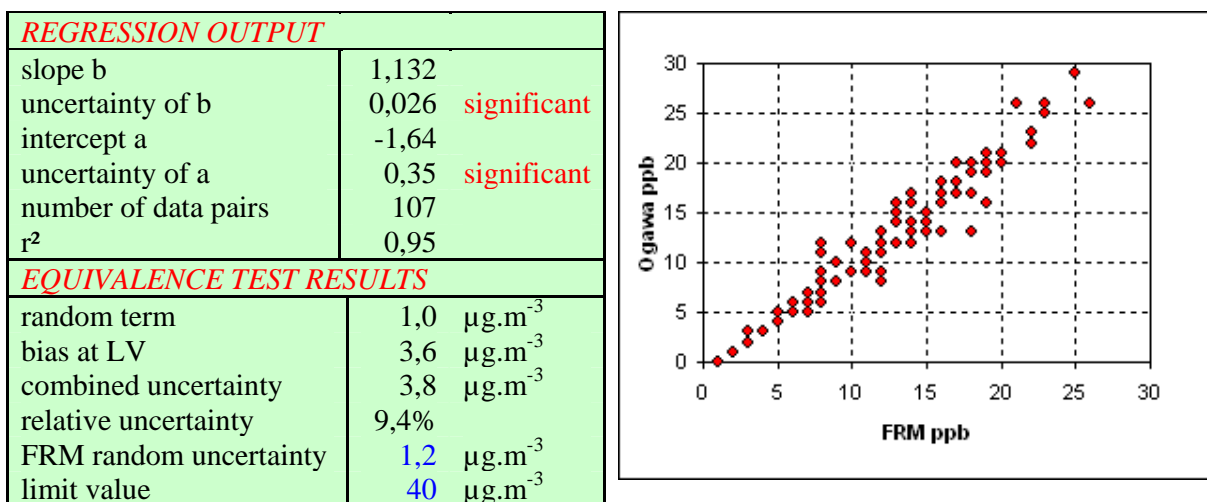


Figure 5.4: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Ogawa sampler vs chemiluminescence analyser (FRM)

The evaluation indicated that, without a recalibration of the uptake rate, keeping the slope and intercept results obtained, this sampler did not meet the data quality objective (DQO) of the EU directive for fixed measurements, as its expanded uncertainty exceeds 15 %, but satisfied the DQO for indicative measurements.

Mosqueron et al. [11] performed a comparison between the sampler and reference method within the frame of quality assurance of an indoor and ambient air exposure study.

The ratio between the means of 49 paired results was 0,97 for an exposure period of 48 hours. When exposing the sampler at both ends, a good correlation was observed between the two results.

Sarnat et al. [12] determined a series of performance characteristics for the sampler when sampling for a period of 24 hours. They found detection limits of 6,4 and 10,8 ppb depending on the sampling season. By measuring with a collocated reference method they determined the precision and accuracy of the sampler to be 17 % and 106 %, respectively.

Van Roosbroeck et al. [13] performed a comparison between the sampler and reference method within the frame of quality assurance of the application of the sampler.

They reported a mean relative difference of 3 %, and a correlation coefficient of 0,96 for an exposure period of 48 hours. The precision of duplicate sampler measurements was reported to be < 5 %.

5.5.2 Miscellaneous information about performance characteristics

A number of publications reported additional information about practical detection limits and precision of the sampler.

Gilbert et al. [3] used samplers to study levels of NO₂ near highways. Employing ion chromatography for analysis, they reported a detection limit for 1-week sampling of 0,7 ppb. The precision of results for duplicate samplers ranged from 6 to 20 %.

Yang et al. [14] used samplers to measure concentrations of NO₂ in indoor air and the penetration of NO₂ from outside to indoor air. Samples were taken over 24-hour periods. Each week duplicate measurements were performed, resulting in an average precision of 8,3 %.

Mukerjee et al. [15] performed a field comparison between samplers and reference monitors. The samplers were exposed for 3, 4 and 7 days for 3 consecutive weeks, with 7-day sampling paralleling 3+4-day sampling. Due to monitor malfunctioning, no definitive conclusions about correlations between results were presented. The study provided information about repeatability and detection limits. Unfortunately, the authors did not report the internal consistency of the 3+4- and 7-day results. The sampler precision was found to be better than 5 %. The detection limit found was lower than 1,3 ppb.

5.6 Measurement uncertainty

No information was found in the literature of (systematic) assessments of measurement uncertainties associated with the use of the Ogawa sampler, e.g., performed according to the Guide to the Expression of Uncertainty in Measurement. When using results from [4] and [6] to make a direct estimation of uncertainties, results found are between 3 % and 23 % expanded relative uncertainty indicating the suitability of the sampler for indicative long-term monitoring of NO₂. However, further systematically obtained information is needed to substantiate such a claim.

5.7 Application in EU monitoring networks

The Ogawa sampler has been used in Spain. To date, there is no reference found of the sampler being used for ambient air monitoring purposes in the EU. Applications are in the field of indoor air monitoring.

5.8 Conclusions

The Ogawa badge-type diffusive sampler is suitable for long-term monitoring of NO₂ in ambient air. Exposure periods of 2 to 4 weeks are feasible. Lower detection limits reported vary somewhat, but are certainly below 1 µg.m⁻³ for a 2-week exposure period.

Information provided about the precision of replicate samples again is variable. Results range from 2 to 20 %. However, frequently precisions better than 5 % are reported.

It is not always clear, though, whether the results of duplicated measurements are based on application of two separate samplers or on analysis of the two filters on either side of the sampler.

When exposed for 14 days or more in the field, the comparability of sampler results to those obtained with continuous reference monitors (chemiluminescence) were good, with ratios of average results ranging from 0,90 to 1,07. The availability of sampler results upon long-term exposure is better than 90 %. Absence of data in comparisons is due to malfunctioning of reference monitors rather than malfunctioning of the sampler.

When using the methodology of the EU Guide to the Demonstration of Equivalence to the results of the US-EPA El Paso study, the sampler is found to pass the uncertainty requirement for indicative measurements. The random uncertainty found for the relation between sampler results and reference method indicate that by correcting the uptake rate the sampler may pass the criterion for fixed measurements. However, the study has been performed in conditions that are atypical of the EU.

No information has been found about any uncertainty assessment of the results obtained with the sampler, e.g., according to the Guide to the Expression of Uncertainty in Measurement.

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6 The Radiello radial sampler

6.1 Sampler design

The Radiello sampler is a radial-type diffusive sampler that was developed by Fondazione Salvatore Maugeri in Italy [1]. Its cylindrical outer surface acts as diffusive membrane: the gaseous molecules move axially parallel towards an adsorbent bed which is cylindrical too and coaxial to the diffusive surface [2] (see figure 6.1).

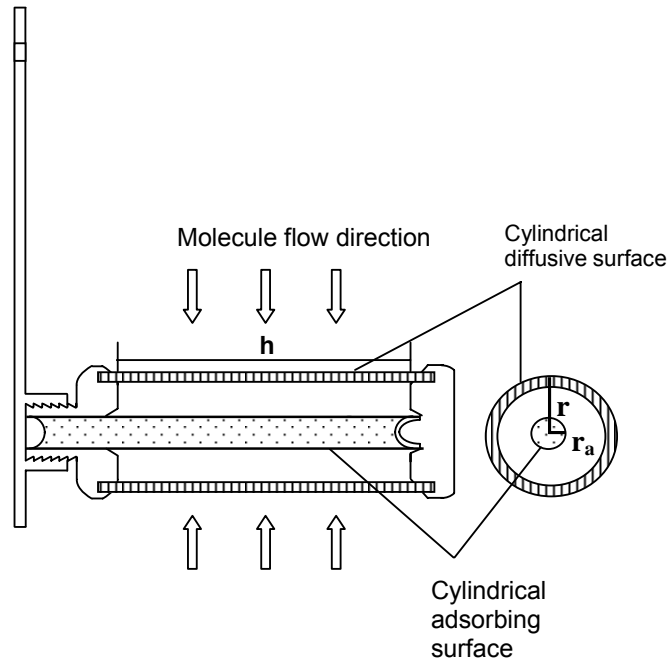


Figure 6.1: Radiello sampler design

According to manufacturer's general instructions, exposure for a long time in a wet atmosphere generally does not affect the sampling performances of the Radiello sampler. Nevertheless the sorption of large quantities of water by the cartridges can sometimes affect the sampler performance. Therefore a shelter is important to protect Radiello samplers from rain.

For outdoor exposures, a mountable polypropylene shelter is available (see figure 6.2). It was designed to be mounted easily and without any tool in the field. The shelters are open on three sides. Pylons and posts are recommended as carriers [3]. Once assembled, it ensures the best compromise between protection against rain and wind. It can house up to four samplers and is able to fit a wide range of pole diameters.



Figure 6.2: Radiello shelter

The diffusive body can be fitted on a supporting plate either in a vertical or horizontal position as shown in figure 6.3.



Figure 6.3: Supporting plate for the Radiello sampler

The adsorbing cartridges are impregnated with a mixture of TEA/water, which also contains traces of ethanol. Further details on the coating and preparation protocol were requested from the manufacturer, but were not provided due to reasons of confidentiality.

The manufacturer recommends and describes the determination of the collected NO₂ by colorimetry after reaction with sulphanilamide and N-1-naphthylethylenediamine [4].

6.2 Application range and conditions

According to the manufacturer [4], the uptake rate of NO₂ is constant in the range from 2000 µg.m⁻³.min to 10⁷ µg.m⁻³.min (1 ppb to 500 ppb NO₂ for 7-day exposure or 0,5 ppb to 250 ppb for 14-day exposure). The limit of quantification after 7 days exposure is 1 ppb.

The range of meteorological conditions where the use of the Radiello sampler is applicable is given in table 6.1. Exposures up to 15 days are feasible for NO₂, but if relative humidity is higher than 70 % for the entire sampling duration, the manufacturer recommends a sampling time shorter than or equal to 7 days. Due to the fact that TEA is very hygroscopic, even if water does not actually interfere with sampling or analysis, the excess water adsorbed by the cartridge could cause some loss of adsorbing medium by percolation.

Table 6.1: Application range of NO₂ Radiello sampler [4]

Parameter	Range where no effect on uptake rate is observed
Temperature	-10 °C to 40 °C
Relative humidity	15 % to 90 % (maximum RH value 70 % for 14-day exposure); avoid moisture condensation upon the membrane
Wind speed	0,1 m.s ⁻¹ to 10 m.s ⁻¹ The outdoor shelter is required for ambient air measurements
Sampling duration	Up to 15 days If RH>70 %: preferably not longer than 7 days

According to the manufacturer [4], the cartridges are stable for at least 12 months before and 4 months after exposure, if stored in the dark at 4 °C. Expiry date is printed on the plastic bag. At least two cartridges belonging to the same lot should be kept as blanks.

6.3 Extraction and analysis

Information on procedures for extraction of sampler cartridges and analysis of sample extracts are available from the manufacturer [4]. The analytical procedures comprise both colorimetry using the Griess-Saltzman method for NO₂ and ion chromatography for SO₂. An alternative ion chromatographic procedure is available from Swaans et al. [5]. The extraction procedure appears to be a critical factor. During a laboratory and field comparison of NO₂ diffusive samplers by the Joint Research Centre [6], extraction of nitrite from the Radiello cartridge using a vortex shaker for 1 minute at 2500 rpm was found not to be sufficient and needed 1 or 2 repetitions before complete extraction. Another method based on ultrasonic extraction for 25 minutes of the cartridge placed in a glass container with 10 ml of Millipore water gave complete recovery of nitrite.

After tubes were vigorously shaken for two minutes, the contact period between absorption liquid and cartridge was also extended to 1,5 hours by Swaans et al. [5] to ensure complete extraction of nitrite.

6.4 Expression of the NO₂ concentration

To calculate the airborne NO₂ concentration, equation 6.1 is generally applied:

$$C_{\text{NO}_2} = 1,91 \frac{(m_s - m_b)}{u \times t} \quad (\text{eq 6.1})$$

where

- C_{NO_2} = NO₂ concentration in µg m⁻³ at 20 °C and 101,3 kPa;
- m_s = mass of nitrite measured in the exposed sampler in ng;
- m_b = mass of nitrite measured in a blank sampler in ng;
- u = uptake rate in ng.ppb⁻¹.min⁻¹;
- t = sampling time in min.

The coefficient 1,91 is used to convert the NO₂ concentration from ppb in µg m⁻³ at 20 °C and 101,3 kPa.

6.5 Uptake rate

The uptake rate was determined by the manufacturer as 31,5 cm³.min⁻¹ at 25 °C (corresponding to 0,141 ng.ppb⁻¹.min⁻¹). The laboratory validation data used for the current model of Radiello NO₂ sampler were supplied by the manufacturer. They are presented in table 6.2. They included the results of two sets of exposure tests at two temperature levels (25 °C and 2 °C) each including three sets of six samples exposed for variable sampling time (approx. 3, 5, 7 days). For one temperature level (9,5 °C), an average value was given while for the other two levels all the individual values were reported.

Table 6.2: Validation data of the Radiello sampler supplied by the manufacturer

First test: temperature 25 °C									
Exposure 1									
<i>Camp</i>	μg	<i>T</i> (°C)	<i>NO₂</i> (ppb)	<i>Exposure time</i> (min)	<i>NO₂</i> (ppb*min)	ν (ng/ppb*min)	ν <i>mean</i>	<i>St. dev.</i>	<i>% rsd</i>
1°-1	12,90	25,1	22,5	3684	82852	0,156			
1°-2	9,67	25,1	22,5	3684	82852	0,117			
1°-3	11,76	25,1	22,5	3684	82852	0,142			
1°-4	10,24	25,1	22,5	3684	82852	0,124			
1°-5	11,38	25,1	22,5	3684	82852	0,137			
1°-6	7,84	25,1	22,5	3684	82852		0,135	0,015	11,4
Exposure 2									
<i>camp</i>	μg	<i>T</i> (°C)	<i>NO₂</i> (ppb)	<i>Exposure time</i> (min)	<i>NO₂</i> (ppb*min)	ν (ng/ppb*min)	ν <i>mean</i>	<i>St. dev.</i>	<i>% rsd</i>
2°-1	20,54	25,1	23,2	6777	157125	0,131			
2°-2	23,89	25,1	23,2	6777	157125	0,152			
2°-3	22,50	25,1	23,2	6777	157125	0,143			
2°-4	18,52	25,1	23,2	6777	157125	0,118			
2°-5	22,69	25,1	23,2	6777	157125	0,144			
2°-6	21,62	25,1	23,2	6777	157125	0,138	0,138	0,012	8,7
Exposure 3									
3°-1	30,21	25,0	22,9	9650	220877	0,137			
3°-2	35,78	25,0	22,9	9650	220877	0,162			
3°-3	30,53	25,0	22,9	9650	220877	0,138			
3°-4	32,11	25,0	22,9	9650	220877	0,145			
3°-5	37,48	25,0	22,9	9650	220877	0,170			
3°-6	33,50	25,0	22,9	9650	220877	0,152	0,151	0,013	8,7
						<i>ν overall mean</i>	0,141		
Second test: temperature 2 °C									
Exposure 1									
<i>camp</i>	μg	<i>T</i> (°C)	<i>NO₂</i> (ppb)	<i>Exposure time</i> (min)	<i>NO₂</i> (ppb*min)	ν (ng/ppb*min)	ν <i>mean</i>	<i>St. dev.</i>	<i>% rsd</i>
1°-1	8,91	2,2	27,0	3962	107008	0,083			
1°-2	7,21	2,2	27,0	3962	107008	0,067			
1°-3	6,83	2,2	27,0	3962	107008	0,064			
1°-4	7,52	2,2	27,0	3962	107008	0,070			
1°-5	9,04	2,2	27,0	3962	107008	0,084			
1°-6	4,99	2,2	27,0	3962	107008		0,074	0,009	12,8
Exposure 2									
2°-1	12,77	2,1	27,0	6900	186166	0,069			
2°-2	15,99	2,1	27,0	6900	186166	0,086			
2°-3	14,41	2,1	27,0	6900	186166	0,077			
2°-4	17,00	2,1	27,0	6900	186166	0,091			
2°-5	14,54	2,1	27,0	6900	186166	0,078			
2°-6	17,19	2,1	27,0	6900	186166	0,092	0,082	0,009	11,2

Table 6.2: Validation data of the Radiello sampler supplied by the manufacturer (continued)

Exposure 3									
<i>camp</i>	μg	<i>T</i> (°C)	<i>NO</i> ₂ (ppb)	<i>Exposure time</i> (min)	<i>NO</i> ₂ (ppb*min)	ν (ng/ppb*min)	ν <i>mean</i>	<i>St. dev.</i>	<i>% rsd</i>
3°-1	17,95	2,1	26,9	9688	260828	0,069			
3°-2	21,93	2,1	26,9	9688	260828	0,084			
3°-3	20,29	2,1	26,9	9688	260828	0,078			
3°-4	24,08	2,1	26,9	9688	260828	0,092			
3°-5	23,20	2,1	26,9	9688	260828	0,089			
3°-6	26,80	2,1	26,9	9688	260828		0,082	0,009	11,3
						ν <i>overall mean</i>	0,080		
Third test: temperature 9,5 °C									
<i>T</i> (°C)	<i>NO</i> ₂ (ppb)	<i>Exposure time</i> (min)		<i>NO</i> ₂ (ppb*min)	ν (ng/ppb*min)		ν <i>mean</i>		
9,5	22	10080		221760			0,100		

6.6 Environmental effects

6.6.1 Air velocity

The uptake rate was reported to be invariant with wind speed between 0,1 m.s⁻¹ and 10 m.s⁻¹ [4].

6.6.2 Relative humidity and temperature

The uptake rate was reported to be invariant with humidity in the range 15 % to 90 % [4].

However, a significant effect of temperature and relative humidity on uptake rate was observed by Swaans et al. [5]. The temperature effect from 10 °C to 30 °C corresponds to the temperature effect given by the supplier of the samplers (see section 6.7.1). High relative humidity (70 % to 80 %) caused a strong non-reproducible decrease of uptake rate for NO₂ at 24 hour experiments, but this effect was not observed at longer exposures except for the tests at -5 °C. At temperature below zero, in combination with high relative humidity, the sampler showed anomalous behaviour for NO₂. The possible effect of concentration level and exposure time for NO₂ needs further research.

The NO₂ uptake rate at 25 °C and 101,3 kPa should be corrected so as to reflect the actual sampling conditions. According to the manufacturer's instruction manual [4], the temperature effect for NO₂ on the uptake rate is taken into account using equation 6.2.

$$\nu_T = \nu_{25} \left(\frac{273+T}{273+T_{ref}} \right)^{7,0} \quad (\text{eq. 6.2})$$

where

ν_T = uptake rate at the temperature T ranging from -10 to 40 °C in ng.pp^b⁻¹.min⁻¹;

ν_{25} = reference uptake rate at 25 °C; 0.141 ng.pp^b⁻¹.min⁻¹;

T = temperature ranging from from -10 to 40°C;

T_{ref} = reference temperature of 25 °C.

The exponential coefficient of 7,0 is derived from the results of the laboratory validation study performed by the manufacturer (see section 6.5).

6.6.3 Pressure

The effect of atmospheric pressure (P) on the uptake rate of the Radiello sampler (ν) is usually insignificant. Even though ν linearly depends on P, the extent of variation of atmospheric pressure

rarely exceeds 3 kPa about the average value of 101,3 kPa at sea level. An error of $\pm 3\%$ on uptake rate and usually within $\pm 1,5\%$ results if no correction for pressure is applied.

6.7 Validation of sampler performance

6.7.1 Laboratory tests

During the course of year 2002, the NO₂ Radiello sampler was changed by the manufacturer. Since then the cartridges have been made from microporous polyethylene instead of polyester fibre. Afterwards the sampler's manual was also modified a number of times.

Consequently, the results from studies performed using the old type of Radiello cannot be considered in this review. This concerns e.g. results from validation studies performed by the Joint Research Centre Institute for Environment and Sustainability [11], and results from the Resolution project¹. The validation data presented here relate to the latest version of the Radiello NO₂ diffusive sampler.

In 2005, a validation study of Radiello combined NO₂-SO₂ diffusive sampler [5] was performed by the Flemish Institute for Technological Research (VITO, Belgium). This was the result of lack of agreement between NO₂ samplers and chemiluminescence analyzers from the VMM automatic network, particularly in case of frost, after changes to the sampler by the supplier. The sampler was first validated under controlled laboratory conditions and subsequently compared with NO₂-(SO₂) results of 3 other type of samplers in a field comparison at two locations: Ghent-Mariakerke and Borgerhout in Flanders.

Laboratory exposures at different temperatures (-5, 10 and 30 °C) and relative humidities (0, 50 and 80 % RH) in combination with varying concentration levels and exposure times were carried out, with a focus on extreme conditions (see table 6.4). Typical environmental levels at the monitoring locations of the VMM network for acidic deposition during former campaigns were 10, 20 and 40 µg.m⁻³ NO₂. Under laboratory conditions, exposures were carried out at higher concentrations levels during shorter times within the linear range of 3000–5.10⁶ ppb.min according to manufacturer's instructions [4]. By choosing this approach, a better accuracy of the generated higher gas concentrations was achieved. This made it possible to draw better conclusions about the effects on the uptake rate.

Table 6.4: Laboratory validation set up

NO ₂ (ppb)	Temperature (°C)	Relative humidity (%)	Exposure time
73	-5	80	24 h
18	-5	80	4 days
73	10	0	24 h
73	10	50	24 h
146	10	50	24 h
293	10	50	24 h
73	10	80	24 h
146	10	80	24 h
293	10	80	24 h
11	10	80	14 days (336 h)
73	30	0	24 h
73	30	50	24 h
73	30	80	24 h
18	30	0	4 days
18	30	80	4 days

¹ RESOLUTION Development of a high spatial resolution atmospheric monitoring model to verify the actual emissions reduction of ozone precursors foreseen by Auto-Oil program), LIFE99ENV/IT/081, http://ec.europa.eu/environment/life/project/Projects/index.cfm?fuseaction=home.createPage&s_ref=LIFE96%2520ENV%252FIT%252F000070&area=2&yr=1996&n_proj_id=1114

The average uptake rate for NO₂ for 24 hour exposures at 10 °C and 50 % RH and tested concentration levels (73, 146 and 293 ppb NO₂) was 0,076 ± 0.011 ng ppb⁻¹ min⁻¹. Uptake rates during all experiments were lower than the uptake rate given in the instruction manual of the sampler. As already mentioned in section 6.6.2, a significant effect of temperature and relative humidity on the sampler uptake rate was observed. The temperature effect from 10 to 30 °C corresponds to the temperature effect given by the supplier of the samplers. Exposures to high relative humidity (70 to 80 %) for 24 hours caused a strong non-reproducible decrease of uptake rate for NO₂ (see figure 6.3). However, this effect was not observed for longer exposures, except for the tests at -5 °C. At temperatures below zero in combination with high relative humidity, the sampler showed anomalous behaviour for NO₂.

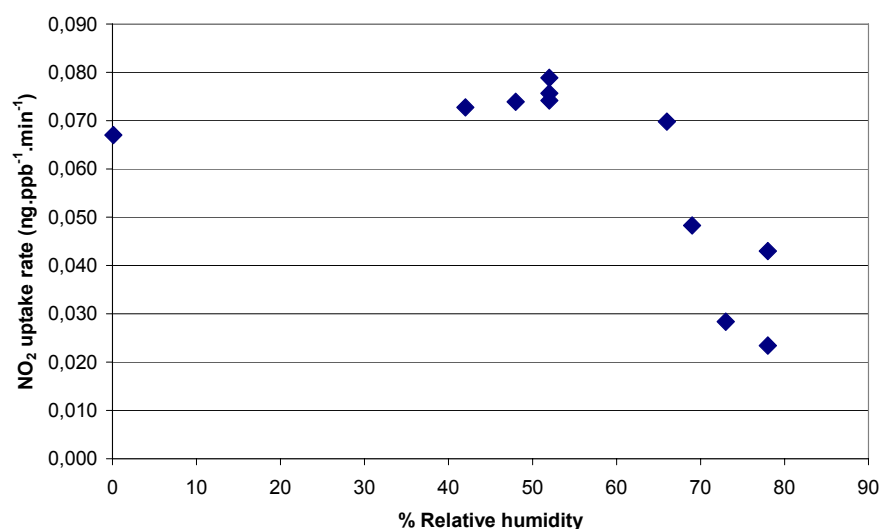


Figure 6.3: NO₂ uptake rate of Radiello sampler at 10 °C versus % relative humidity (24 h exposure)

6.7.2 Comparisons with reference methods

Buzica et al. [6] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler type was exposed in batches of 6 samplers for a period of 14 days, except in the laboratory trial “high” (see table 6.5).

Table 6.5: Laboratory conditions (intercomparison of Buzica et al.)

Parameters	High	High
Exposure time (d)	7	14
Concentration (µg.m ⁻³)	80	40
Air velocity (m.s ⁻¹)	2,5	1,0
Temperature (°C)	25	5
Relative humidity (%)	75	30

The results obtained for the Radiello sampler operated by Lab H, following the manufacturer protocol, are presented in table 6.6.

Table 6.6: Results of Radiello sampler operated by Lab H (intercomparison of Buzica et al.)

Location	CLS (µg.m ⁻³)	Radiello (µg.m ⁻³)	Ratio
Laboratory, high	76,8	54,1 ± 1,5	0,70
Laboratory, low	43,5	30,0 ± 1,0	0,69
Genevilliers	41,6	44,7 ± 1,3	1,075
Fontainebleau	14,1	12,0 ± 0,9	0,85

During the laboratory tests, the samplers were not protected by a shelter, but a holder was used. For the NO₂ laboratory exposures, the uptake rate was calculated using the model equation given in the previous operating manual (2002). By applying the equation of the operational manual version 01/2003 to the laboratory tests (the one given in equation 6.2), the corrected concentrations were in closer agreement with the reference values than with those calculated with the previous model of the uptake rate.

Swaans and Goelen [5] reported the results of field tests in Belgium in which a number of diffusive samplers have been compared by parallel measurements with a reference monitor. The exposure period was 14 days; each sampler was exposed in triplicate. The results are presented in table 6.7. The Radiello samplers were desorbed using a vortex shaking method (a method based on ultrasonic desorption has also been used).

Table 6.7: Results of field tests in Belgium

Location	CLS ($\mu\text{g}\cdot\text{m}^{-3}$)	Radiello ($\mu\text{g}\cdot\text{m}^{-3}$)	Ratio
Borgerhout	55	52,8 ± 8,8	0,96
Gent	37	33,2 ± 7,3	0,92
Borgerhout	44,7	47,4 ± 5,1	1,06
Gent	21,0	16,0 ± 2,1	0,76
Borgerhout	51,4	35,1 ± 3,0	0,68
Gent	27,3	18,2 ± 3,5	0,67

The agreement between measurements performed with Radiello samplers and chemiluminescence analyzer was acceptable, but in some cases the relative standard deviation of the replicates exceeded 30 %. The ratios Radiello samplers/NO₂ analyzer for the different site campaigns ranged from 0,67 to 1,06. In general, the performance of the Radiello sampler was better in the field than during laboratory validation (see table 6.6), although for certain periods samplers gave lower NO₂ concentrations than the continuous analyzer. Conditions were more extreme during the laboratory validation than during the field tests.

Results of comparative measurements between NO₂ Radiello diffusive samplers and chemiluminescence analyzers from 3 French air quality monitoring networks are given in table 6.8.

The results from French studies (personal communication to the authors) confirmed that the Radiello sampler tends to underestimate the concentrations of NO₂ measured by the chemiluminescence analyzers.

Ratios found ranged from 0,57 to 0,99 with one exception (1,42) for concentrations ranging from 22 to 49 $\mu\text{g}\cdot\text{m}^{-3}$. For a 7-day exposure period the effect appears to be larger than for 14-day exposure.

Other available validation data regarding the NO₂ Radiello sampler exist, but do not apply to the current sampler [7 - 9]. Also the data from the CEN/TC 264 WG11 pilot study date from 2000-2001 and do not apply to the current sampler since the sampler was changed in 2002.

Currently, a comparison is ongoing in the United Kingdom in which Palmes tube samplers and Radiello samplers are exposed at a traffic site in London. Results of this comparison were not available at the time of the drafting of the report.

Table 6.8: Results of French studies

Laboratory	Sampling site	Nb of samplers	Sampling time (days)	Start	End	NO2 tube (ppb)	NO2 tube ($\mu\text{g.m}^{-3}$)	NO2 chemiluminescence ($\mu\text{g.m}^{-3}$)	Ratio Tube / Chemiluminescence	Temperature	Mass of nitrite (μg)
ATMOSF/AIR Bourgogne		1	7	23/10/07	30/10/07	12,8	20,9	36,9	0,57	8,4	0,171
ATMOSF/AIR Bourgogne		1	7	30/10/07	6/11/07	13,5	21,7	36,6	0,59	6,6	0,168
ATMOSF/AIR Bourgogne		1	7	13/11/07	20/11/07	16,8	25,5	41,2	0,62	1,3	0,158
ATMOSF/AIR Bourgogne		1	7	20/11/07	27/11/07	19,8	31,7	49,0	0,65	6,5	0,168
ATMOSF/AIR Bourgogne		1	7	27/11/07	4/12/07	15,6	24,6	38,1	0,64	4,6	0,164

Laboratory	Site	Nb of samplers	Exposure	Start	End	NO2 $\mu\text{g}/\text{m}^3$ - tube 1	NO2 $\mu\text{g}/\text{m}^3$ - tube 2	NO2 chemiluminescence ($\mu\text{g.m}^{-3}$)	Ratio Tube / Chemiluminescence
LIM/AIR	Urban	2	14	10/10/06	24/10/06	37,4	26,1	22,4	1,42

	Site	Nb of samplers	Exposure	Start	End	NO2 $\mu\text{g}/\text{m}^3$ tube 1	NO2 $\mu\text{g}/\text{m}^3$ tube 2	NO2 $\mu\text{g}/\text{m}^3$ - tube 3	NO2 chemiluminescence in $\mu\text{g}/\text{m}^3$	Ratio Tubes mean / Chemiluminescence	Ratio Tube 1 / Chemiluminescence	Ratio Tube 2 / Chemiluminescence	Ratio Tube 3 / Chemiluminescence
	ARLES												
AIRFOBEP	Urban	2	14	2/23/2007	3/9/2007	20,3	25,4		27,4	0,84	0,74	0,93	
AIRFOBEP	Urban	1	14	3/9/2007	3/26/2007	21,3			27,8	0,77	0,77		
AIRFOBEP	Urban	2	14	3/26/2007	4/11/2007	25,9	26,3		31	0,84	0,84	0,85	
AIRFOBEP	Urban	1	14	10/24/2007	11/7/2007		28,3		33	0,86		0,86	
	SALON												
AIRFOBEP	Urban	2	14	2/23/2007	3/9/2007	21,5	18,2		21,7	0,91	0,99	0,84	
AIRFOBEP	Urban	2	14	3/9/2007	3/26/2007	26,4	25,2		28,8	0,9	0,92	0,88	
AIRFOBEP	Urban	2	14	3/26/2007	4/11/2007	31,8	30,4		31,4	0,99	1,01	0,97	
AIRFOBEP	Urban	2	14	10/24/2007	11/7/2007	17,7	15,5		26,4	0,63	0,67	0,59	
	MARIGNANE												
AIRFOBEP	Urban	3	14	2/23/2007	3/9/2007	38	43,4	37,9	42,3	0,94	0,9	1,03	0,9
AIRFOBEP	Urban	3	14	3/9/2007	3/26/2007	27,2	25,7	26,7	32,9	0,81	0,83	0,78	0,81
AIRFOBEP	Urban	2	14	3/26/2007	4/11/2007	38,6	38,4		44,3	0,87	0,87	0,87	
AIRFOBEP	Urban	2	14	10/24/2007	11/7/2007	38,3		39	46,9	0,82	0,82		0,83

6.8 Measurement uncertainty

6.8.1 GUM approach

The manufacturer in its instruction manual reports an uncertainty of 11,9 % for NO₂ measurements for a probability of 95 % that the true value is within the resulting interval. The method of calculation was requested from the manufacture but was not available.

VITO estimated the NO₂ expanded uncertainty as being 30 % at a 95 % confidence level for the Radiello sampler used to simultaneously determine NO₂ and SO₂ [5]. This uncertainty was estimated using the results of 24-hours laboratory experiments performed in an exposure chamber at 10 °C and 50 % of relative humidity. The estimation was carried out according to the GUM method based on equation 6.3. The contributions of all parameters affecting the uncertainty of measurements are given in table 6.9.

$$C = 1,91 \frac{(m_d - m_b) \cdot 10^6}{v \cdot t} \quad (\text{eq. 6.3})$$

where

- C = ambient concentration in µg.m⁻³;
- m_d = mass of desorbed analyte in µg;
- m_b = blank of analyte in µg;
- v = diffusive uptake rate in ng ppb⁻¹.min⁻¹;
- t = exposure time in min.

Table 6.9: Uncertainty of NO₂ measurements by Radiello calculated using VITO laboratory experiments

Uncertainty source	x	u(x)	u(x)/x
nitrite in desorption liquid mg/l	1,3	0,02	0,02
volume of desorption liquid (ml)	6,00	0,08	0,01
absolute amount of nitrite on sampler (µg)	7,62	0,2	0,02
nitrite in desorption liquid from blank sampler (mg/l)	0,09	0,009	0,1
volume of desorption liquid (ml)	6,00	0,08	0,01
absolute amount of nitrite on blank sampler (µg)	0,54	0,05	0,1
nitrite mass after blank-correction (µg)	7,08	0,2	0,03
temperature (T) during measuring period (K)	277,2	1	0.0036
uptake rate (ng ppb ⁻¹ .min ⁻¹) at T	0,064	0,010	0,151
sampling duration (min)	20108	10	0,0005
NO₂ Concentration in ambient air (ppb)	5,46	0,8	0,15

The relative standard uncertainty of the measured NO₂ concentration is 15 %, the expanded uncertainty at a 95 % confidence level (k=2) is then 30 %. This measurement uncertainty is not valid in case of sampling time of 24 hours combined with high relative humidity since a strong decrease of uptake rate may occur under these exposure conditions.

The major source of uncertainty is found to be the uptake rate.

6.8.2 Direct approach

When combining data reported in tables 6.6, 6.7 and 6.8 for all field comparisons of Radiello samplers exposed for 14 days with the chemiluminescence reference method, a total of 26 sets of comparison data were available. These were used to make an estimate of the uncertainty of NO₂ concentrations

measured with the Radiello sampler by applying the approach described in the Guide to the Demonstration of Equivalence [10]. The result of this estimation is given in figure 6.4.

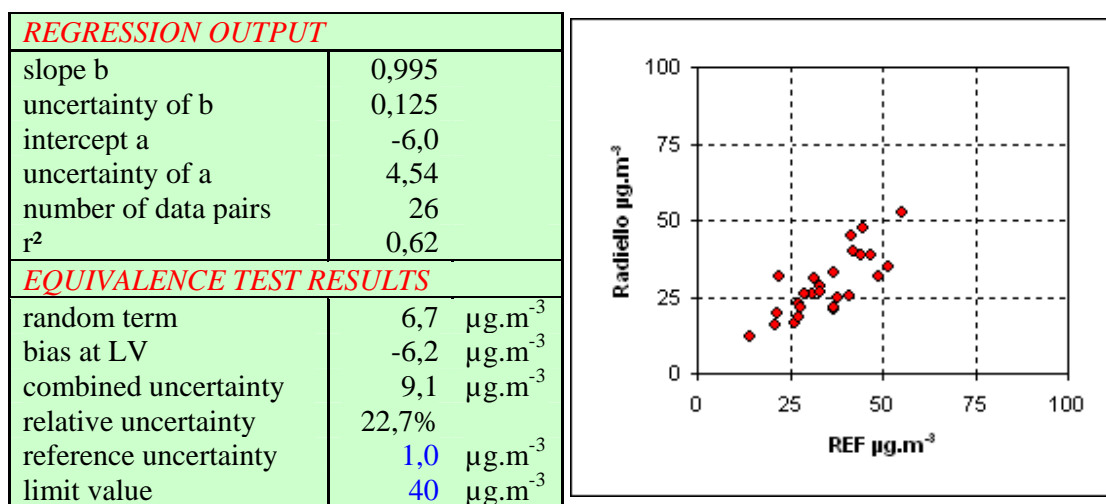


Figure 6.4: Uncertainty for annual averages according to the Guide to the Demonstration of Equivalence, Radiello sampler vs chemiluminescence analyser (REF)

The relative standard uncertainty calculated in this way was 22,7 %, leading to an expanded uncertainty (95 % confidence) of 45 %. The uncertainty is affected significantly by a systematic underestimation of concentrations by about 6 $\mu\text{g}\cdot\text{m}^{-3}$.

6.9 Application in EU monitoring networks

Radiello samplers are used e.g. in Belgium, France, Italy, Slovakia and Spain for surveys aimed at, e.g. identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

6.10 Conclusions

The Radiello radial-type diffusive sampler may be used for long-term monitoring of NO_2 in ambient air. Exposure periods of 1 day to 2 weeks are feasible. The lower detection limit for a 2-week sampling period was reported to be 0,9 $\mu\text{g}\cdot\text{m}^{-3}$. Results of a laboratory study in which the sampling period was restricted to one day showed an underestimation of NO_2 concentrations by a factor of 2 when applying the uptake rate specified by the manufacturer. The reason for this may be a transient period of sorption at the beginning of the sampling period.

Information about the precision of the sampler from field campaigns revealed that the precision relative standard deviation varied around 10 %.

The comparability of sampler results with those obtained with continuous reference monitors (chemiluminescence) varied, with ratios of average results ranging from 0,6 to 1,4. In general, Radiello showed a trend to underestimate concentrations measured by reference monitors. However, the number of field data available was too limited to be conclusive.

When the uncertainty associated with the measurement results for a one-day exposure was evaluated according to the Guide to the Expression of Uncertainty in Measurement, a relative expanded uncertainty of individual results of 31 % was found. When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO_2 , similar results were obtained.

These findings suggest that the Radiello sampler did not satisfy the uncertainty data quality objective for indicative measurements of NO_2 , for which an uncertainty ≤ 25 % is required.

When aggregating results to form annual average values, the relative expanded uncertainty was further reduced to levels below 25 % due to the reduction of random effects on uncertainty.

The information collected about the uncertainty of individual measurement results did not correspond with information supplied by the manufacturer stating an expanded measurement uncertainty of 12 %. However, information about the assessment approach used by the manufacturer was (currently) unavailable.

The possible effect of concentration level, high humidity and exposure time for NO₂ needs further research.

6.11 References

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7 Other samplers : the Analyst

7.1 Sampler design

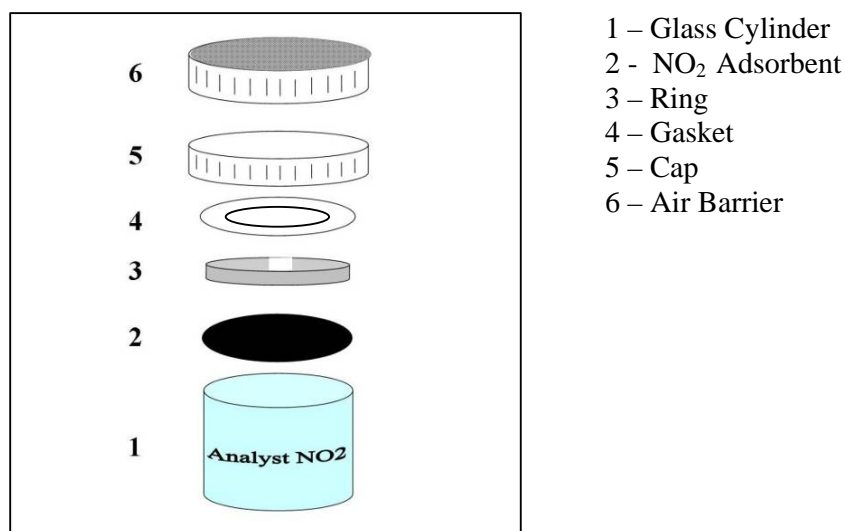


Figure 7.1: Analyst sampler design

The body of the sampler (see figure 7.1, part 1) is a cylindrical glass vial (inner =2,04 cm, length=2,54 cm) with a threaded cap at one end (parts 4 and 5). NO₂ is collected on a disc of impregnated carbon paper filter (part 2) placed at the bottom of the vial and held in position by a stainless steel ring (part 3). To avoid turbulent diffusion inside the vessel, the open end is protected during sampling using a fine stainless steel and plastic screen (part 6). Before and after sampling, the screen is replaced with a polyethylene cap (part 5), which houses a silicone gasket (part 4).

Application range and conditions

The following information was compiled for the application range and conditions of the sampler [1].

Detection limit: 1 ppb (corresponding to 3 standard deviations of 12 blanks for a one-week exposure).

Exposure time: From 1 week to 2 months. Shorter exposure times for high concentrations

Shelter: The experience gained in many monitoring study showed that a rain and wind shield (see figure 7.2 a) was sufficient for an effective protection of the Analyst sampler. When a strong influence of wind is expected it is recommended to use the shelter shown in figure b.

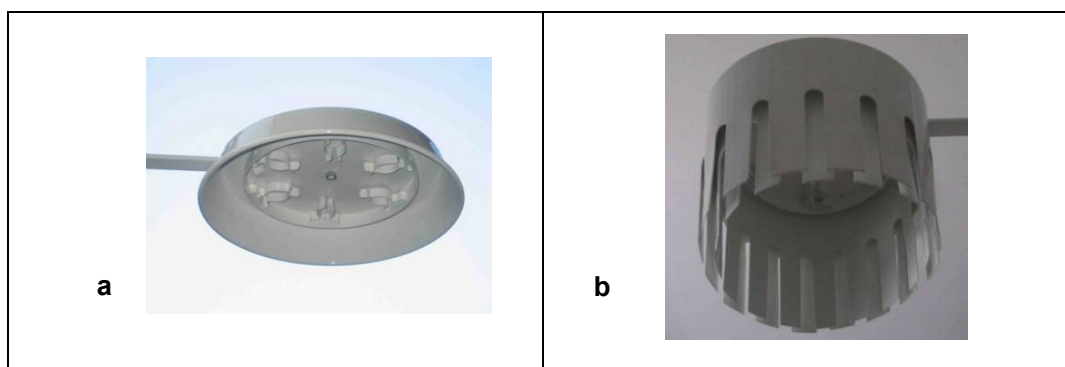


Figure 7.2: Shelters for the Analyst sampler

7.2 Sampler storage

Before use: 6 months.

After exposure: 2 months in a cold and dry place.

The stability of the nitrite collected decreases if the samplers are withdrawn from the field, when they have been recently exposed to very high relative humidity (e.g. rain). If the samplers cannot be analysed immediately (within two or three days after exposure), the manufacturer advises to collect the samplers when the weather is fine and stable for one or two days before ending the sampling. If this is not possible, the samplers must be dried over silica gel or allowed to equilibrate indoors before closing them and storing them in a fresh and dry place.

7.3 Extraction and analysis

Nitrogen dioxide, adsorbed as nitrite, can be determined by ion chromatography. A method using the standard Griess-Saltzman reaction for nitrite followed by colorimetric analysis can also be used.

After exposure, the filters are extracted with eluent (2,7 mM Na₂CO₃ and 0,3 mM NaHCO₃). The extraction of nitrite is carried out in the same sampler by adding 5 ml of the extraction solution (eluent). The nitrite ion concentration is determined using ion chromatography (Dionex equipped with a column IONPAC AS12A). The concentration of nitrite is calculated from calibration graphs with sodium nitrite standards.

Stock standard solutions of 1000 µg.ml⁻¹ may be purchased as certified solutions from different manufacturers, or can be prepared by dissolving 0,7499 g of oven-dried sodium nitrite in 0,5 l of de-ionised water. The working standard solutions for the preparation of the calibration curve are made as follows:

- 10 ml of the stock solution are added to a 200 ml flask that is filled to the mark with the Dionex eluent;
- Subsequent dilutions are carried out using a 10 ml pipette and the appropriate volumetric flasks;
- A set of standards in the range 0 to 3,0 of µg.ml⁻¹ nitrite anion are prepared to calibrate the ion chromatograph.

For low-level applications, more diluted standards may be necessary.

7.4 Calculation of ambient air concentration

Equation 7.1 is used to calculate the NO₂ concentration in air (expressed in µg.m⁻³) in which v is 11.7 cm³.min⁻¹ at 20 °C (see 7.5).

$$C_{\text{NO}_2} = \frac{(m_s - m_b)}{v \times t \times 10^{-6}} \quad (\text{eq 7.1})$$

where

C_{NO_2} = NO₂ concentration in µg m⁻³ at 20 °C;

m_s = mass of nitrite measured in the exposed sampler in µg;

m_b = mass of nitrite measured in a blank sampler in µg;

v = uptake rate in cm³.min⁻¹ at 20 °C;

t = sampling time in min.

This formula assumes that the average temperature during sampling is 20 °C. If the temperature T is significantly different, a correction to C_{NO_2} can be applied multiplying by coefficient calculated using equation 7.2.

$$v_{T,P} = v_{ref} \left(\frac{273,2 + T}{273,2 + T_{ref}} \right)^{1,8} \quad (\text{eq. 7.2})$$

where

- u_T = uptake rate in $\text{cm}^3 \cdot \text{min}^{-1}$ at temperature T during sampling;
- u_{ref} = uptake rate in $\text{cm}^3 \cdot \text{min}^{-1}$ at the reference temperature of 20 °C, $11.7 \text{ cm}^3 \cdot \text{min}^{-1}$;
- T = actual temperature during sampling in °C;
- T_{ref} = reference temperature in °C at which u_{ref} rate is given (20 °C).

7.5 Uptake rate and environmental effects

The NO_2 uptake rate may be calculated directly from the theoretical diffusion coefficient of NO_2 and the geometry of the sampler. The rate at which NO_2 is transferred through the vial depends on the average concentration in the ambient air according to Fick's law which is integrated along the diffusion path length to give equation 7.3.

$$m = \frac{(C - C_0)DA t}{L} \quad (\text{eq. 7.3})$$

where

- m = mass uptake in μg ;
- C = concentration of NO_2 in $\mu\text{g} \cdot \text{m}^{-3}$;
- C_0 = concentration of NO_2 at the surface of the sorbent in $\mu\text{g} \cdot \text{m}^{-3}$ (close to zero);
- D = diffusion coefficient of NO_2 in air in $\text{m}^2 \cdot \text{min}^{-1}$;
- A = cross-sectional area of the diffusion path in m^2 ($3,27 \cdot 10^{-4} \text{ m}^2$);
- t = exposure time in min;
- L = length of the diffusion path in cm (0,0254 cm).

By substitution and using the diffusion coefficient at 25 °C, the NO_2 uptake rate was calculated using equation 7.3 and found to be $12,3 \pm 0,5 \text{ cm}^3 \cdot \text{min}^{-1}$.

The uptake rate was also determined by comparing measurements of the chemiluminescence reference method and of the Analyst samplers for concentrations between 100 and $1300 \mu\text{g} \cdot \text{m}^{-3}$ at 20 °C and 50 % of relative humidity. When calculating the slope of the regression line of the two methods of measurements, the uptake rate of the Analyst sampler was $11,7 \pm 0,6 \text{ cm}^3 \cdot \text{min}^{-1}$ [1].

The fairly good agreement between the estimation of the uptake rate using the theory of diffusion and by indirect measurements demonstrates both that NO_2 absorption on the carbon coated surface is very rapid and that the C_0 term in equation 7.3 must be close to zero.

A series of laboratory tests were undertaken to demonstrate the effect of fluctuating concentrations of NO_2 on the sampler response. In these experiments, dilution of NO_2 from a permeation tube was varied over the exposure time by using a pump. NO_2 changed between 50 (i.e. when the pump was on) and $500 \mu\text{g} \cdot \text{m}^{-3}$ (i.e. when the pump was off) every hour. This concentration change was repeated overnight. The results of these experiments showed that the uptake rate of variable NO_2 concentrations was within 5 % of those obtained at constant concentration [1].

To study the influence of relative humidity on the collection efficiency of the sampler, the amount of nitrite collected per unit time and concentration was determined over a range of 20 % to 80 % relative humidity at $500 \mu\text{g} \cdot \text{m}^{-3}$ of NO_2 for 10 h at 25 °C. The uptake rates were unaffected by relative humidity and averaged around $11,9 \pm 0,8 \text{ cm}^3 \cdot \text{min}^{-1}$.

The interference of ozone was studied by exposing samplers previously loaded with NO_2 to an ozone mixture in an exposure chamber (3 samplers were exposed to $400 \mu\text{g} \cdot \text{m}^{-3}$ O_3 for 5 h). Ozone was measured using UV absorption analyzer. Ozone had no measurable interference effect.

7.6 Validation of sampler performance

In 2001-2002 CEN/TC264 WG11 “Diffusive samplers” performed a small-scale pilot study at two locations in which 6 samplers were exposed for two weeks, accompanied by parallel measurements with a reference monitor. The results for the exposed Analyst samplers are reported in table 7.1.

Table 7.1: Results of CEN pilot study for the Analyst sampler

Willebroek	NO₂ (µg.m⁻³)	Ratio Analyst/reference
<i>Reference</i>	40,8	
Analyst	112	2,74
Teddington	NO₂ (µg.m⁻³)	Ratio Analyst/reference
<i>Reference</i>	13,8	
Analyst	18,0	1,30

Analyst samplers were found to overestimate NO₂ concentrations. The overestimation for the experiment at Willebroek could be explained by the fact that the sampler was exposed without a shelter in very windy conditions in an open field, contrary to manufacturer recommendations.

A validation study carried out at an urban background site (Villa Ada, Rome, Italy), side-by-side with a chemiluminescence analyser, showed that the Analyst sampler for NO₂ is characterised by an expanded uncertainty lower than 21 %, well within the limit required by EU Directive 2008/50/EC for indicative measurements [1].

This field validation consisted of two elements:

- A study into the integrated response of samplers over different sampling periods;
- A comparison with a reference analyzer according to ISO 13752.

The study entailed the comparison of 35 pairs of results from the chemiluminescence analyser and the Analyst sampler over a full range of average wind-speed conditions ranging from 1,4 m.s⁻¹ to 2,0 m.s⁻¹ over fortnight sampling periods. Average daily wind velocity values ranged from 0,7 m.s⁻¹ to 4,2 m.s⁻¹.

Buzica et al. [2] organized a series of 4 comparisons in which different samplers operated by different laboratories were exposed both under laboratory and field conditions. Each sampler type was exposed in batches of 6 samplers for a period of 14 days except in the laboratory trial “high” (see table 7.2).

Table 7.2: Laboratory conditions (intercomparison of Buzica et al.)

Parameter	High	Low
Exposure time (d)	7	14
Concentration (µg.m ⁻³)	80	40
Air velocity (m.s ⁻¹)	2,5	1,0
Temperature (°C)	25	5
Relative humidity (%)	75	30

The results obtained for the Analyst sampler operated by Lab B are presented in table 7.3.

Table 7.3: Results of the Analyst sampler operated by Lab B (intercomparison of Buzica et al.)

Location	CLS (µg.m⁻³)	Analyst (µg.m⁻³)	Ratio
Laboratory, high	76,8	111 ± 5	1,44
Laboratory, low	43,5	43,3 ± 1,0	1,00
Genevilliers	41,6	55,9 ± 1,4	1,34
Fontainebleau	14,1	15,0 ± 0,5	1,06

These results show a somewhat “mixed” performance, although the laboratory “high” trial yielded large variations in results for all participants, with mean results ranging from 54 to 188 $\mu\text{g}\cdot\text{m}^{-3}$. The precision of the results was good, usually within 10 %.

7.7 Measurement uncertainty

The accuracy of the samplers in comparison to the chemiluminescence technique, expressed as percent relative error was found to be better than $\pm 20\%$ at 20 ppb of NO_2 . The relative standard deviation on 12 samplers is 7 % [1].

No further information is available, e.g. assessments based on application of the Guide to the Expression of Uncertainty in Measurement.

7.8 Application in EU monitoring networks

Applications appear to be mostly in indoor air monitoring, e.g., for studies into protection of cultural heritage. No references to applications in ambient air monitoring have been found.

7.9 Conclusions

The Analyst badge-type diffusive sampler may be used for long-term monitoring of NO_2 in ambient air. Exposure periods of 1 to 2 weeks are feasible. The lower detection limit for a one-week exposure period was reported to be 1,9 $\mu\text{g}\cdot\text{m}^{-3}$.

The precision of replicate samples was generally within 10 %. However, the number of studies reported is limited.

The comparability of sampler results with those obtained with continuous reference monitors (chemiluminescence) was acceptable, with ratios ranging from 1,0 to 1,4. However, it must be emphasized that the number of studies on which this conclusion was based is limited.

No information was available on the availability of sampler results upon long-term exposure. However, from the laboratory experiments it could be concluded that an exposure period of at least 4 months is feasible for sites characterized by concentrations up to 200 $\mu\text{g}\cdot\text{m}^{-3}$.

When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO_2 , the accuracy was reported to be $\pm 20\%$.

No information was found about any uncertainty assessment of the results obtained with the sampler, e.g., according to the Guide to the Expression of Uncertainty in Measurement.

7.10 References

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8 Summary of findings, conclusions and recommendations

8.1 Summary of findings

A number of diffusive samplers that are used for long-term monitoring of nitrogen dioxide (NO₂) were subjected to a review of their use and performance characteristics. The samplers were selected on the basis of their general availability in the European Union:

- The Palmes tube sampler;
- The Passam tube sampler;
- The Ogawa badge sampler;
- The Radiello radial sampler;
- The Analyst badge sampler.

The IVL sampler, although a sampler in frequent use throughout the European Union, was not included in the review, since most information about this sampler is considered a proprietary secret by the manufacturer.

The information collected was used to:

- Draft conclusions about the feasibility of using the samplers for the long-term monitoring of NO₂, with the particular aim of assessing compliance with the European Union annual limit value of 40 µg.m⁻³ (at 20 °C and 101,2 kPa);
- Draft a proposal method for monitoring NO₂ using diffusive samplers, for future use by CEN Technical Committee 264 “Air Quality” Working Group 11 “Diffusive Samplers” as a CEN standard devoted to the measurement of NO₂ in ambient air.

Main criteria for the assessment of sampler feasibility for both purposes were:

- The validation level of the samplers, based either on application of EN 13528 part 2 or the Guide to the Demonstration of Equivalence of Ambient Air Monitoring Methods, including information about the uncertainty of results obtained using the samplers;
- From this: the potential to meet European Air Quality Directive data quality objectives for indicative and/or fixed measurements;
- The extent or lack of information available to underpin the validity of results obtained using the different samplers;
- The number of different sources providing the above information;
- Differences in performance depending on site type (tube type): traffic, urban, rural;
- The possibility for users to analyse the samplers, e.g., based on procedures specified by manufacturers;
- Their current use throughout the European Union for measuring ambient air quality related to concentrations of NO₂.

The conclusions for each individual sampler are reported below.

8.1.1 The Palmes tube sampler

Palmes tube samplers are extensively used e.g. in Denmark, France, the Netherlands, Spain and the United Kingdom for supplementary measurements to the fixed measurements at the level of an indicative method. Other applications include identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

A number of methods exist for the preparation of the TEA-based sampling substrate. Only 3 of these have been proven to give reliable results in practice.

Palmer tube samplers are generally analysed by colorimetry applying the Griess-Saltzman methodology.

The Palmer tube-type diffusive sampler is suitable for long-term monitoring of NO₂ in ambient air. Exposure periods of 1 to 8 weeks are feasible. The most commonly used exposure period is 2 or 4 weeks. The lower detection limit for a 2-week sampling period will vary with the meticulousness of the sampler preparation procedure, and will generally be between 0,7 and 1 µg.m⁻³. The upper limit for a 2-week exposure period is at least 375 µg.m⁻³.

Unused and exposed samplers may be stored for several months under specific conditions (dark; air tight; reduced temperatures).

A large body of literature evidence from various sources was available about the application of Palmer tube samplers for the monitoring of NO₂ in ambient air. A considerable number of studies reported the performance in side-by-side comparisons with reference monitors (chemiluminescence).

Generally, these comparisons gave varying results; however, the results are generally consistent within the uncertainties of the methods. At urban sites, where unprotected open tubes were used, a tendency was observed towards overestimation of NO₂ concentrations.

When using membrane-capped tubes in combination with model equations describing the uptake rate as a function of temperature, humidity, wind speed etc., the comparability improved.

When the uncertainty associated with the measurement results was evaluated according to the Guide to the Expression of Uncertainty in Measurement, the relative expanded uncertainty of individual results was estimated to be 32 % for worst-case conditions (when using a single value for the uptake rate independent of environmental conditions).

Assessments of measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO₂, generally gave relative expanded uncertainties below 25 %. These findings suggest that the Palmer tube is at least suitable for performing long-term measurements of NO₂ for indicative purposes, and possibly even for fixed measurements.

When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 15 % due to the reduction of random effects on uncertainty.

8.1.2 The Passam tube sampler

Passam tube samplers are used e.g. in Cyprus, France, Germany, Italy, Lithuania and Romania for supplementary measurements to the fixed measurements at the level of an indicative method. Other applications include identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

The preparation of the TEA-based sampling substrate is performed by the manufacturer.

Passam tube samplers are generally analysed by colorimetry applying the Griess-Saltzman methodology.

The Passam diffusive sampler is suitable for long-term monitoring of NO₂ in ambient air. Exposure periods of 1 to 6 weeks are feasible. The lower detection limit for a 2-week sampling period is reported to be 0,4 µg.m⁻³. The most commonly used exposure period is 2 or 4 weeks.

Unused and exposed samplers may be stored for several months under specific conditions (dark; air tight; reduced temperatures).

A large body of literature evidence from various sources was available about the application of Passam tube samplers for the monitoring of NO₂ in ambient air. A considerable number of studies reported the performance in side-by-side comparisons with reference monitors (chemiluminescence).

The comparability of sampler results with those obtained with reference monitors varied somewhat, with ratios of average results generally ranging from 0,9 to 1,3. This variability may be reduced, when:

- Sampling rates are converted to actual conditions of temperature and pressure;
- Membranes are introduced into the sampler inlet particularly for traffic-related sites.

When the uncertainty associated with the measurement results was evaluated according to the Guide to the Expression of Uncertainty in Measurement, relative expanded uncertainties of individual results from 20 to 25 % resulted. When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO₂, similar and even better results were obtained. When combining results from a number of studies in France, a relative expanded uncertainty of 13 % was calculated, qualifying the sampler for the fixed measurement regime of EU Directive 2008/50/EC.

These findings suggest that the Passam tube is at least suitable for performing long-term measurements of NO₂ for indicative purposes and possibly even for fixed measurements. When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 15 % due to the reduction of random effects on uncertainty.

8.1.3 The Ogawa badge sampler

The Ogawa sampler has been used in Spain. To date, there is no reference found of the sampler being used for ambient air monitoring purposes in the EU. Applications are mainly in the field of indoor air and exposure monitoring. The preparation of the TEA-based sampling substrate is performed by the manufacturer.

Ogawa samplers are generally analysed by colorimetry applying the Griess-Saltzman methodology.

The Ogawa badge-type diffusive sampler is suitable for long-term monitoring of NO₂ in ambient air. Exposure periods of 2 to 4 weeks are feasible. Lower detection limits reported vary somewhat, but are below 1 µg.m⁻³ for a 2-week exposure period.

Unused and exposed samplers may be stored for several months under specific conditions (dark; air tight; reduced temperatures).

A number of studies from various sources were available about the application of Ogawa samplers for the monitoring of NO₂ in ambient air mainly in the United States of America. A limited number of studies reported the performance in side-by-side comparisons with reference monitors (chemiluminescence).

When exposed for 14 days or more in the field, the comparability of sampler results to those obtained with continuous reference monitors (chemiluminescence), was good, with ratios of average results ranging from 0,90 to 1,07. The availability of sampler results upon long-term exposure was better than 90 %. Absence of data in comparisons was due to malfunctioning of reference monitors rather than malfunctioning of the sampler.

No information is available about any uncertainty assessment of the results obtained with the sampler, e.g., according to the Guide to the Expression of Uncertainty in Measurement.

When using the methodology of the EU Guide to the Demonstration of Equivalence to the results of the US-EPA El Paso study, the sampler was found to pass the uncertainty requirement for indicative measurements. The random uncertainty found for the relation between sampler results and reference

method indicated that by correcting the uptake rate the sampler may pass the criterion for fixed measurements. However, the study was performed under conditions that are atypical of the EU.

8.1.4 The Radiello radial sampler

The Radiello sampler is used in the EU e.g. in Belgium, France, Italy, Slovakia and Spain for surveys aimed at, e.g. identification of hot spots, mapping, zoning, trend analysis, source apportionment, impact on vegetation, assessment of exposure of population, verification of dispersion models etc.

The preparation of the TEA-based sampling substrate is performed by the manufacturer.

Radiello radial samplers are generally analysed by colorimetry applying the Griess-Saltzman methodology.

The Radiello radial-type diffusive sampler may be used for long-term monitoring of NO₂ in ambient air. Exposure periods of 1 day to 2 weeks are feasible. The lower detection limit for a 2-week sampling period was reported to be 0,9 µg.m⁻³. Results of a laboratory study in which the sampling period was restricted to one day showed an underestimation of NO₂ concentrations of a factor of 2 when applying the uptake rate specified by the manufacturer. The reason for this may be a transient period of sorption at the beginning of the sampling period.

The comparability of sampler results with those obtained with continuous reference monitors (chemiluminescence) varied, with ratios of average results ranging from 0,6 to 1,4. In general, Radiello showed a trend to underestimate concentrations measured by reference monitors. However, the number of field data available was too limited to be conclusive.

When the uncertainty associated with the measurement results for a one-day exposure was evaluated according to the Guide to the Expression of Uncertainty in Measurement, a relative expanded uncertainty of individual results of 31 % was found. When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO₂, similar results were obtained.

These findings suggest that the Radiello does not satisfy the uncertainty data quality objective for indicative measurements of NO₂, for which the uncertainty shall not exceed 25.

When aggregating results to form annual average values, the relative expanded uncertainty may be further reduced to levels below 25 % due to the reduction of random effects on uncertainty.

The information collected about the uncertainty of individual measurement results does not correspond with information supplied by the manufacturer stating an expanded measurement uncertainty of 12 %. However, information about the assessment approach used by the manufacturer is (currently) unavailable.

The possible effect of concentration level, high humidity and exposure time for NO₂ needs further research.

8.1.5 The Analyst badge sampler

Applications of the Analyst sampler appear to be mostly in indoor air monitoring, e.g., for studies into protection of cultural heritage. No references to applications in ambient air monitoring were found apart from the ones of the manufacturer.

To date, the preparation of the sampling substrate is performed by the manufacturer.

Analyst samplers are generally analysed by ion chromatographic determination of the nitrite formed after sorption on the sampling substrate.

The Analyst diffusive sampler is suitable for long-term monitoring of NO₂ in ambient air. Exposure periods of 1 to 2 weeks are feasible. The lower detection limit for a one-week exposure period is 1,9 µg.m⁻³.

The comparison of sampler results with those obtained with continuous reference monitors (chemiluminescence) showed ratios ranging from 1,0 to 1,4. On one occasion a ratio of 2,7 has been found in an early study. However, the number of studies was very limited.

No information was available on the availability of sampler results upon long-term exposure, e.g. for a period of one year.

When assessing measurement uncertainty by direct approaches, e.g., from parallel measurements with the reference method for measurement of NO₂, a single study reported the accuracy to be ± 20 %.

No further information was found about any uncertainty assessment of the results obtained with the sampler, e.g., according to the Guide to the Expression of Uncertainty in Measurement.

8.2 Conclusions and recommendations

Based on the findings summarised above, the following conclusions were drawn.

- The Palmes tube, Passam tube and Radiello radial sampler are in general use in the European Union for monitoring NO₂ in ambient air. Of these, the two tube-type samplers are used in ongoing air quality monitoring for supplementary measurements to the fixed measurements at the level of an indicative method.
- The Ogawa badge and Analyst badge are not in general use in the European Union for ambient air monitoring of NO₂.
- The extent to which results of validation studies are available differs considerably between samplers. For the tube-type samplers, a substantial number of sources were identified. For the Ogawa badge and Radiello radial sampler information was more restricted. For the Analyst badge information was even scarcer.
- The available information suggests that, in general, the tube-type samplers may at least meet the EU uncertainty data quality objectives for indicative measurements. Application of membranes or shelters generally improves their performance. In some cases uncertainties were found that would qualify the samplers for fixed measurements.
- For the Ogawa badge sampler, the current limited information available suggests a potential to meet the EU uncertainty requirement for indicative measurements. However, the conditions of the study on under which this finding is based were not really representative for average European Union conditions. More information would be needed to draw firmer conclusions about the validity of the results produced by the sampler for monitoring NO₂ in ambient air.
- For the Radiello radial sampler, the current limited information available suggests that the sampler is not able to meet the EU uncertainty requirement for indicative measurements. The sampler generally appears to systematically underestimate NO₂ concentrations. More information would be needed to draw firmer conclusions about the validity of the results produced by the sampler for monitoring NO₂ in ambient air. It is recommended to further investigate the possible effects of concentration level, high humidity and exposure time for NO₂.
- For the Analyst badge insufficient information is currently available to draw a quantitative conclusion about its potential to meet EU data quality objectives for the monitoring of NO₂ in ambient air. The limited information available gives mixed findings. More information would be

needed to draw firmer conclusions about the validity of the results produced by the sampler for monitoring nitrogen dioxide in ambient air.

On the basis of the above conclusions it is recommended that experts draft, a proposal method, based on the tube-type sampler, for monitoring nitrogen dioxide using diffusive samplers to be later used by CEN/TC 264 Working Group 11 "Diffusive Samplers" to prepare a new standard. Should further information become available in time on the performance of the Radiello radial sampler, which provides supporting evidence of its validity and its potential to meet EU data quality objectives, this sampler may still be considered and be included in the standard.

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Abstract

A number of diffusive samplers that are used for longer-term monitoring of nitrogen dioxide in the European Union were subjected to a review of their use and performance characteristics. The information collected was used to evaluate the capacity of diffusive samplers for monitoring the European Union annual limit value of 40 $\mu\text{g}\cdot\text{m}^{-3}$.

A bibliographic review was carried out to determine the availability of validation data for these samplers, their capacity to meet the data quality objectives for indicative and/or fixed measurements of the European Directive, the possibility for users to analyse the samplers and their current use throughout the European Union for measuring ambient air quality.

Two tubes-type samplers and a radial sampler were found to be used throughout the European Union. Based on the findings of the review, only for tube-type samplers based on the application of triethanolamine as the sorbent, sufficient information was available to underpin the potential of these samplers for meeting the European Union data quality objectives for nitrogen dioxide monitoring.

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