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Comparison of diffusive and active sampling methods for the determination of nitrogen dioxide in urban air

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Summary

Three different methods are compared for the sampling and determination of nitrogen dioxide in urban air; the NO/NO_x-monitor and active and diffusive sampling using sodium iodide as absorbent. For weekly averages the results from the diffusive sampler were within 10 - 20 % of the results for the two other methods in the concentrations range 15 - 30 µg NO₂ m⁻³. The detection limit for the diffusive sampler was 1 µg NO₂ m⁻³ (7 days), the average precision was 5 % and the accuracy was estimated to 20 %. The active iodide method agreed very well with the NO/NO_x-monitor. Compared on 24 h basis for a period of 3 months, covering a concentration range of 5 - 45 µg NO₂ m⁻³, the deviation between the two methods was within 5 %, and the absorption capacity of the iodide reagent was excellent as the breakthrough was below 1 %.

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1. Introduction

The most common sampling systems for the collection and determination of nitrogen dioxide in air have been bubblers or solid sorbents based on trietanolamine alone or combined with reagents such as guaiacol and sulphite. A drawback of this approach has been that the absorption of nitrogen dioxide is not quantitative, and an absorption efficiency factor has to be established. Recently Ferm (Ferm, 1991, 1993) has developed a method for the collection of nitrogen dioxide using iodide reagents based on methods used in the former USSR (Pavlenko and Volberg, 1992). The reagent is reported to be very efficient with absorption close to 100% at flowrates below 0.5 L min^{-1} . The method has found use both in ambient air as well as in urban air. The iodide reagent has also been used in the development of a diffusive sampler for nitrogen dioxide (Ferm, 1991, Ferm et. al. 1994).

Diffusional samplers have found increased use in air monitoring during the last years due to its simplicity and ease of use. Various designs of diffusive samplers have been developed. The classical diffusional sampler is the Palmes tube, which consist of a 7.1 cm long and 0.95 cm diameter tube and an area to length ratio of 0.1 cm (Palmes et. al. 1976). Due to its low area to length ratio the uptake rate of the Palmes tube is rather low. Yanagisawa and Nishimura (1982) developed a badge type diffusional sampler with a large rectangular surface and a short diffusion path. Ferm have recently designed a diffusive sampler for gases with a larger area to length ratio of 3.1 cm (1.0 cm length and 2.0 cm diameter, Ferm (1991)). While the Palmes tube takes advantage of the large length to area ratio to minimize the influence from turbulence in the front of the tube, the Ferm sampler has a teflon filter or a steel net as a diffusion barrier to prevent non-laminar diffusion in the relatively short diffusion path of 1.0 cm. The Ferm diffusive sampler has proved to be useful both for urban air as well as in remote areas with sampling periods from 1 - 2 weeks and have also shown promise at sampling periods as short as 24 h in urban air (Ferm et. al. 1994).

This paper reports the results of a field comparison with three sampling and analysis systems for nitrogen dioxide in urban air; a NO/NO_x -monitor and the iodide method in active mode and in diffusive mode.

2. Experimental

The diffusive sampler developed by Ferm has a diameter of 20 mm and a diffusion path of 10 mm. A steel net (0.15 mm thick with a porosity of 0.13) was

used as a wind shield. The gas collection medium in the sampler is a paper filter impregnated with NaI in NaOH. After exposure, the filter is leached with water added a small amount of triethanolamine. The formed nitrite is determined colorimetrically using the Griess reaction with a Technicon Traacs autoanalyser. The standards are matched with the iodide concentration in the extracts from the exposed samples, as the sensitivity of the colorimetric reaction system depends on the iodide concentration.

In the active nitrogen dioxide method using the NaI/NaOH reagent a glass-sinter in a glassbulb is impregnated with the reagent. The air sampling rate is 0.5 l min^{-1} , corresponding to about 0.7 m^3 for a typical sampling period of 24 h (Ferm 1993). The formed nitrite is determined colorimetrically as above. Details of the impregnation and analysis procedures for the diffusive and active samplers are given by Ferm (Ferm, 1991, 1993).

The NO/NO_x -monitor is produced by Monitor lab., Denver, USA, and based on the chemiluminescence principle using a heated molybdenum converter for reducing NO_2 to NO . The monitor was used in standard conditions as recommended by the manufacturer, with an averaging period of 1 h.

All the three methods used above by Norwegian Institute for Air Research (NILU) for the measurements of nitrogen dioxide are accredited according to EN 45001 by Norwegian Accreditation, Oslo.

The three sampling systems were compared at NILUs station in Nordahl Bruns gate in Oslo for three months from the middle of June 1995. This station is situated in the downtown area of Oslo city.

3. Results and discussion

3.1 The diffusive sampling method

The theory for the uptake of gasses by diffusive samplers has been described in detail in previous works (see Palmes et. al. (1976), Yanisagava and Nishimura (1982), Gair et. al (1991)). The uptake rate for a diffusive sampler is obtained by integrating Ficks law of diffusion for the gas under consideration using the diffusion coefficient and the dimensions of the sampler. The general formula for the calculation of the air concentration for a gas using a diffusive sampler over a given sampling period, is:

$$C_o - C_i = \frac{X}{t \cdot D} \cdot \left[\frac{L}{A} \right] \quad (1)$$

where

C_o	gas concentration in air ($\mu\text{g m}^{-3}$)
C_i	gas concentration at the adsorbent surface in the sampler ($\mu\text{g m}^{-3}$)
X	amount of the gas collected (μg)

t	time of exposure (sec)
D	diffusion coefficient of selected gas (cm ² sec ⁻¹)
L	length of diffusion path of the sampler (cm)
A	area of the diffusion path of the sampler (cm ²)

For samplers having a very reactive adsorbent, the C-term is usually close to zero and can be neglected. To calculate the uptake rate of a diffusional sampler, it is necessary to take into consideration the restrictors in the diffusion path. This depends on the geometry factor of the sampler (the L/A-term of equation 1) and for the Ferm sampler, equation 1 can be expressed as:

$$C_o - C_i = \frac{X}{t \cdot D} \cdot \left[\frac{L_R}{A_R} + \frac{L_F}{A_F} + \frac{L_N}{A_N} + \frac{L_{LBL}}{A_{LBL}} \right] \quad (2)$$

The explanation of the terms and the corresponding values are given in Table 1 and the total geometry factor is estimated in Table 2. When the total geometry factor (L/A) has been estimated, the total uptake rate may be estimated by combining the constants in equation (1), namely L/DA. The uptake rate may be estimated from equation 1 by using the constants (DA/L) by conversion of equation 1.

$$C_o - C_i = \frac{X}{t \cdot \frac{D \cdot A}{L}} \quad (3)$$

Table 1: Description of the geometry factors for the Ferm sampler

Geometry factor	Explanation	Dimensions for the Ferm sampler
L _R	Distance between the diffusion barrier filter and the active gas collection filter	1.0 cm
A _R	Total area of the sampler	3.14 cm ²
A _F	Pore area of the teflon prefilter (porosity 0.85)	2.67 cm ²
L _F	Thickness of teflon prefilter (Millipore FALP)	0.0175 cm
L _N	Thickness of the steel net	0.016 cm
A _N	Pore area of the steel net (porosity 0.13)	0.408 cm ²
L _{LBL}	Laminar boundary layer	0.15 cm
A _{LBL}	Area of boundary layer	3.14 cm ²

Table 2: Geometry factor for the Ferm sampler, calculated with and without the contribution from the steel net.

Factor	Input values cm / cm ²	Geometry factor with steel net, cm ⁻¹	Geometry factor without steel net, cm ⁻¹
L _R /A _R	1.0 / 3.14	0.318	0.318
L _F /A _F	0.0175 / 2.67	0.00655	0.00655
L _N /A _N	0.016 / 0.408	0.039	
L _{LBL} /A _R	0.15 / 3.14	0.0477	0.0477
Total geometry factor		0.4120	0.3728

The uptake rate according to this is estimated in Table 3. Using the same units (m, and days, (24 h)) for D, A and L, the uptake rate for the time unit one day (24 h), is 0.0357 m³ day⁻¹ using the terms DA/L.

Table 3: Estimation of uptake rate for the Ferm sampler.

		Unit	Values with steel net	Values without steel net
Diffusion coefficient (25°C)	D	m ² /sec	1.54 * 10-5	1.54 * 10-5
Diffusion coefficient (25°C)	D	m ² /24h	1.33	1.33
Geometry factor	L/A	m ⁻¹	41.2	37.3
Uptake rate	DA/L	m ³ /24h	0.0322	0.0357

The boundary layer is estimated (Table 1) to be 0.15 cm in this sampler (Ferm, 1991). As can be seen, the major contributor to the total geometry factor is the diffusion path from behind the diffusion barrier to the adsorbent. The contribution to the total geometry factor from the boundary layer is about 10 %, the steel net about 10 % and the teflon filter about 2 %.

Figure 1 shows the results for the measurements of nitrogen dioxide with the three methods and Table 4 shows the results of linear regression analysis of the comparisons. For comparisons with the diffusive sampler, the results for the monitor and the active NO₂ method was averaged for 7 days periods. Generally, the agreement between the three methods is fairly good, but it can be seen that the results for the diffusive sampler is somewhat lower than those for the monitor and the active method. However, as can be seen from Figure 2 and Table 4, the deviation is usually not larger than about 10 %. With the exception of one value, the results for the diffusive sampler is within 20 % of that of the monitor. The correlation coefficient (r^2) (Table 4) is about 0.80, and the slopes are 0.89 for the comparison with iodide method and 1.00 for the monitor.

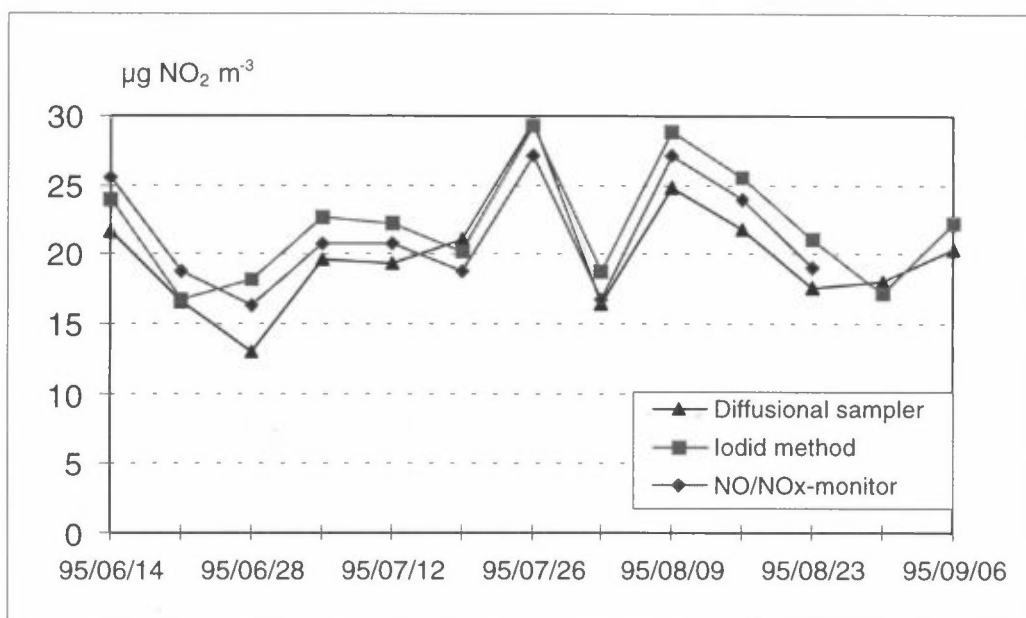


Figure 1: Measurements of NO₂ at Nordahl Bruns gate in Oslo in 1995 by three different methods.

Table 4: Results for linear regression analysis for the comparison of the three different methods shown in Figure 2 and and the two methods shown in Figure 4.

Averaging period	Y	X	N	Slope		Intercept		r ²
				a	s. dev.	b	s. dev.	
7days	Diffusive	Iodide	11	0.898	0.14	0.17	3.23	0.78
7 days	Diffusive	Monitor	11	1.00	0.17	-1.26	3.29	0.79
7days	Diffusive	Iodide	11	0.905	0.024			0.78
7 days	Diffusive	Monitor	11	0.944	0.028			0.79
24 h	Iodide	Monitor	90	0.990	0.022	1.26	0.49	0.96
24 h	Iodide	Monitor	90	1.04	0.008			0.96

The linear regression model $Y=aX + b$ and $Y = aX$ has been used for all the regression analysis. For the latter there is no values for the intercept term.

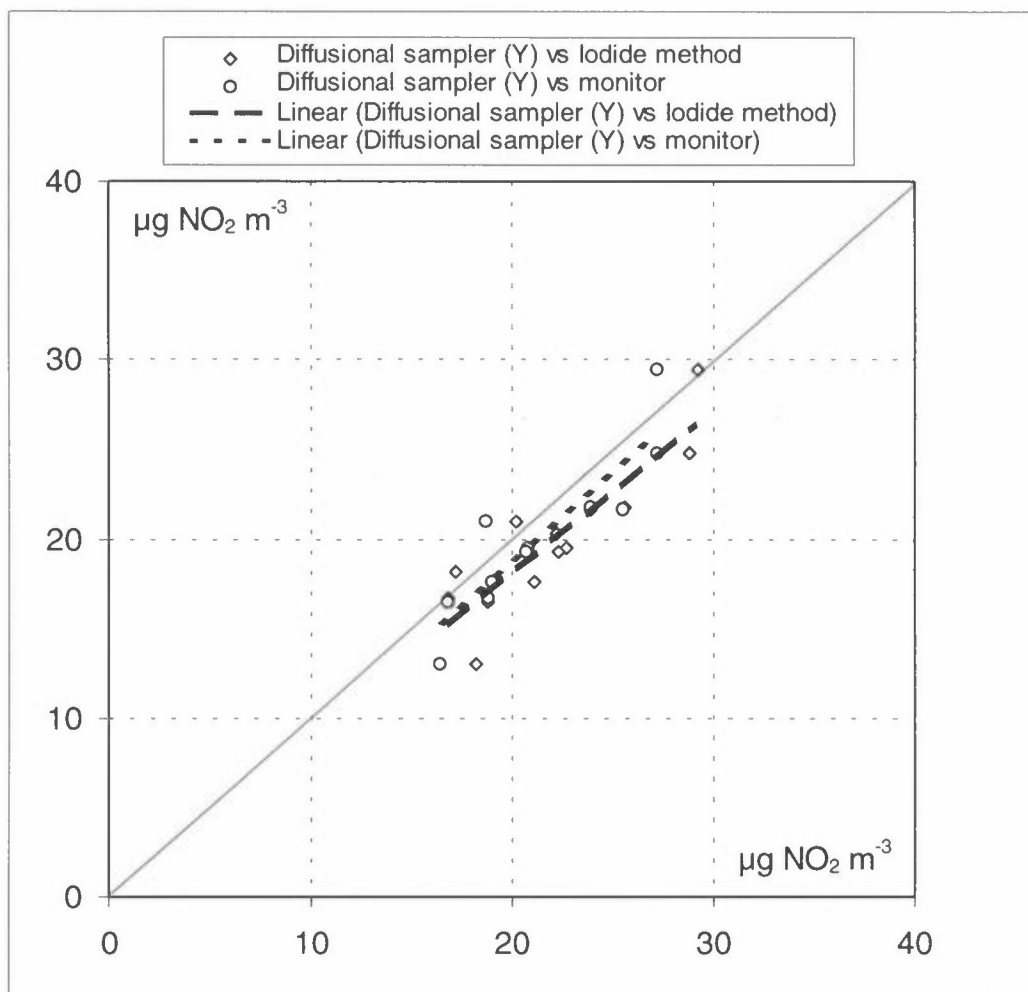


Figure 2: Comparison of the measurements of nitrogen dioxide by the three different methods. The results for the diffusional sampler is used as dependant variable (Y-value). The lines for the linear regression analysis are shown on the chart.

Ferm suggested that the steel net had no significant effect on the uptake rate for the diffusive sampler (Ferm, 1991). However, as can be seen from Table 2, the steel net contributes about 10 % to the total geometry factor, and will thus reduce the uptake rate by a corresponding percentage. If this was taken into account, the results for the diffusive sample would be 10 % higher. This would lead to that the linear regression slope for the diffusive vs. the iodide method would be 1.00 and 1.10 for the diffusive vs. the monitor method.

Another uncertainty in the uptake rate for the diffusive sampler is the estimate for the boundary layer in front of the samplers filter surface. The estimate used for this sampler have been established by Ferm (1991) who recommends a value of 0.15 cm for NO_2 . As shown in Table 2, a boundary layer of 0.15 cm gives a contribution of about 0.047 cm^{-1} of a total of 0.3728 cm^{-1} to the geometry factor i.e. an contribution of 13 %. A change of the boundary layer to 0.05 cm will change the geometry factor by 0.016 cm^{-1} (about 4 %).

Figure 3 shows the standard deviations of three parallel measurements for the diffusive sampler. The relative standard deviations of the measurements ranged between 0.2 - 2.4 $\mu\text{g NO}_2 \text{ m}^{-3}$ corresponding to 1 - 12 % relative standard deviations with an average of 5 % in the concentration range studied (15 - 30 $\mu\text{g NO}_2 \text{ m}^{-3}$). The difference between the results obtained by the diffusive sampler and the active sampling methods are about 5 - 10 %. Assuming that the results for the NO/NO_x -monitor are unbiased, the accuracy of the diffusive sampler for weekly exposure periods can be estimated to 20 % (by using the convention for estimating accuracy as bias plus 2 times the precision).

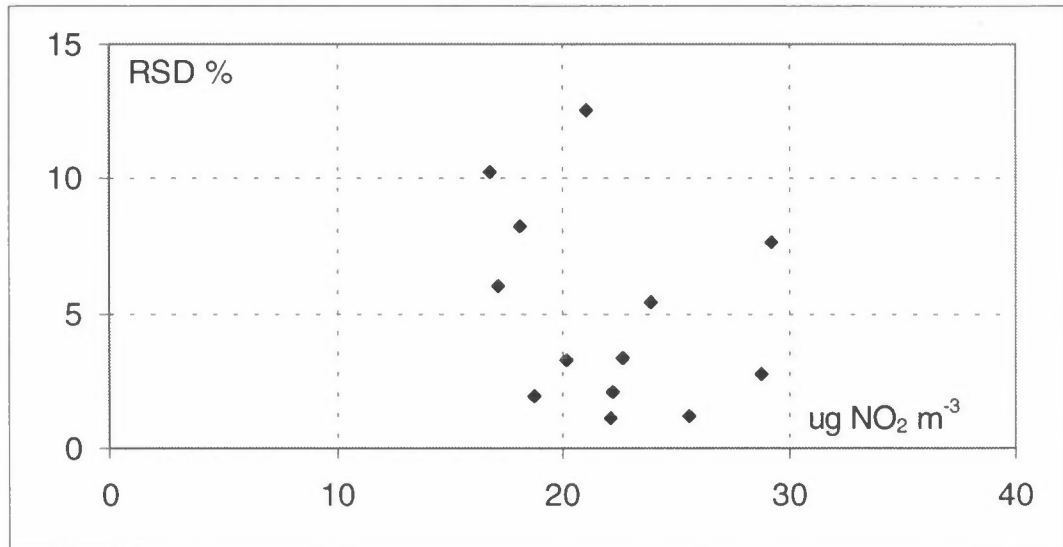


Figure 3: Relative standard deviations (RSD %) of measurements by the diffusive sampler compared to the concentrations levels measured (each point represents three parallel measurements).

It is worth noting that the uptake rate of this diffusional sampler may be calculated directly from the theoretic diffusion coefficient of nitrogen dioxide and the geometry factor of the sampler. The good agreement demonstrated above for the diffusional sampler compared to the active methods, proves that the adsorption of nitrogen dioxide at the active surface must be very rapid so that the C_i term in equation 1 is close to zero. Furthermore, the largest sources of error in the estimate of the uptake rate is the thickness of the laminar boundary layer and the contribution from the steel net.

Field blanks for the diffusive sampler were also collected during the sampling period of the comparison (the field blank samples were also stored for 7 days at the field station). The mean value of the field blank was 0.021 $\mu\text{g N}$ with a standard deviation of 0.024 $\mu\text{g N}$ (15 field blank samples). Using 3 times the standard deviation of the field blank as the detection limit, and a collection rate of 0.0357 $\text{m}^3 \text{ day}^{-1}$ (24 h), the detection limit for a sampling period of 7 days could be estimated to 0.29 $\mu\text{g N m}^{-3}$ or 1 $\mu\text{g NO}_2 \text{ m}^{-3}$ $((0.024 \cdot 3)/(0.0357 \cdot 7))$.

3.2 The active sampling method

Figure 4 shows the results for the measurements by the iodide method in active mode compared to those obtained by the NO/NO_x-monitor. As can be seen the agreement between the two methods is very good. The linear regression slope when the iodide method is independent variable (Y) is 0.99 and the intercept is 1.2. (Table 4, line 5 and 6). The two methods do not deviate more than 10 % in general.

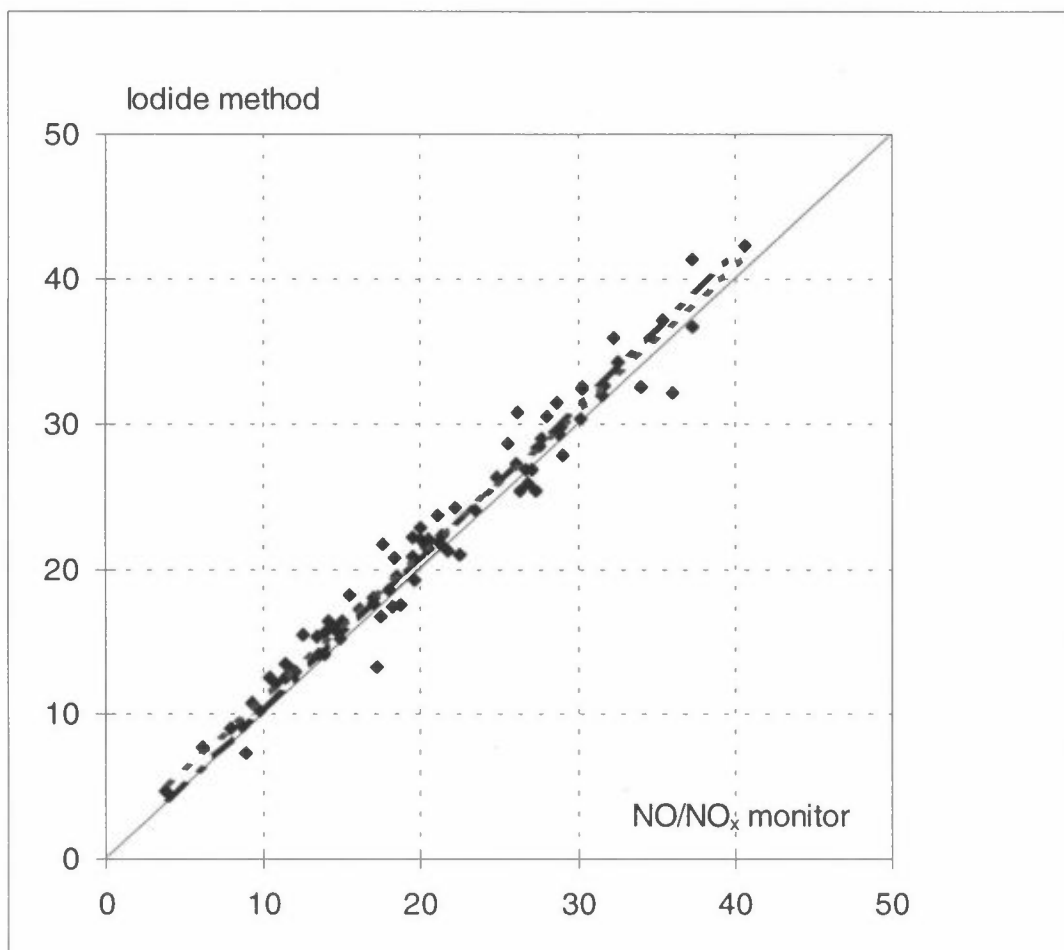


Figure 4: Scatter plots for the comparison of nitrogen dioxide determined by the NO/NO_x-monitor (hourly measurements averaged on 24 h) and the iodide method (24 h sampling periods). The linear regression lines are shown.

In this study it was also tested if there was any breakthrough of nitrogen dioxide for the iodide method in active mode, by using two sampling tubes in series for the whole 3 months sampling period. The results in Figure 5 shows that the breakthrough was very low, only 2 out of about 90 samples had a significant breakthrough above 0.5 µg NO₂ m⁻³. Generally the amounts collected on the second tube were below 0.1 µg NO₂ m⁻³ for the measurements in the range 5 - 40 µg NO₂ m⁻³. The iodide reagent thus has a collection efficiency better than 99% for collection of nitrogen dioxide at a flowrate of 0.5 l min⁻¹.

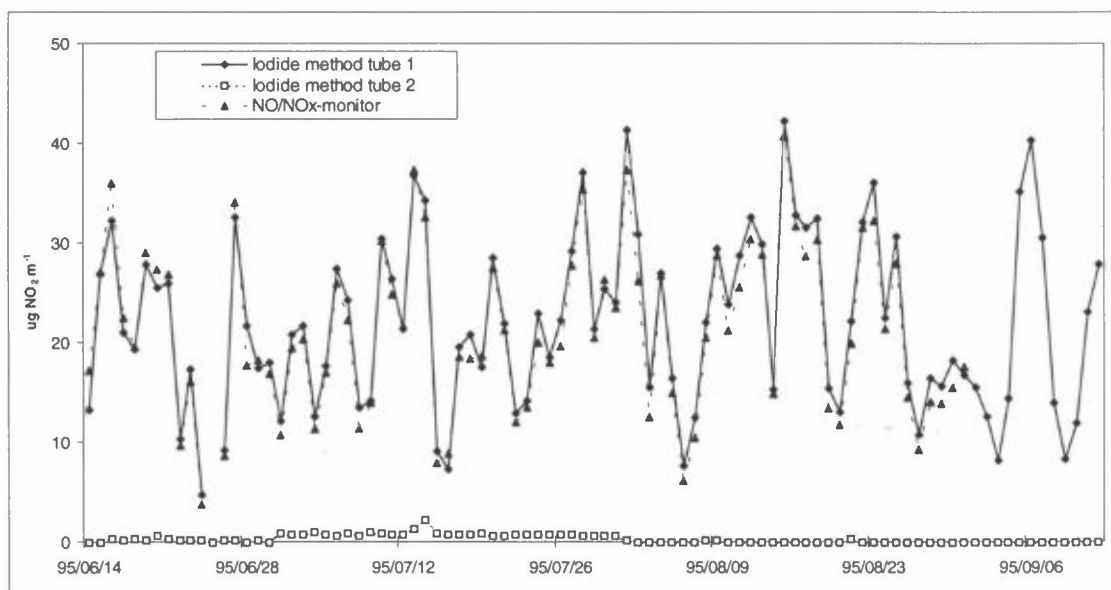


Figure 5: Time series for the determination of nitrogen dioxide by NO/NO_x-monitor(averaged on 24 h) and the iodide method in active mode (24 h sampling periods). The results for breakthrough for the iodide method is also shown.

4. Conclusions

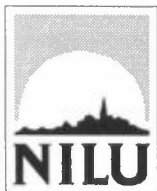
The diffusive sampler for NO₂ gives results which are comparable to the conventional active sampling methods. The strength of this diffusional sampler is that the uptake rate may be estimated directly from the diffusion coefficients of nitrogen dioxide and the geometry factor calculated from the dimensions of the sampler. The accuracy of the results for the diffusive sampler was estimated to 20 %. This is acceptable for monitoring of NO₂ in urban air. It might be possible to improve the accuracy by a renewed examination of the estimate for the thickness of the boundary layer and the contribution from the steel net. The agreement between the iodide method in active mode and the monitor is within 10 %, and there is practically no breakthrough for the iodide method at a sampling flow rate of 0.5 L min⁻¹.

4.1 Acknowledgements

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ABSTRACT The NO/NO _x -monitor and the iodide method are compared with a diffusional sampler for the sampling and determination of nitrogen dioxide in urban air. The results for the diffusional sampler were within 20% of the two other methods for weekly averages. The iodide method and the NO/NO _x -monitor showed good agreement; the deviation was within 5%.			
NORWEGIAN TITLE Sammenligning av passive og aktive prøvetakere for måling av nitrogendioksid i gateluft.			
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ABSTRACT (in Norwegian) NO/NO _x -monitor, iodidmetoden og en passiv prøvetaker ble sammenlignet for måling av NO ₂ i gateluft. Resultatene for den passive prøvetakeren var innenfor 20% av de to andre metodene. Resultatene for NO/NO _x -montoren og iodidmetoden var innenfor 5%.			

* Classification

A Unclassified (can be ordered from NILU)

B Restricted distribution

C Classified (not to be distributed)