Determination of Nitrogen Dioxide with KI-impregnated sintered Glass Filters

NERI Technical Report No. 74
1993

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Ministry of the Environment
National Environmental Research Institute
May 1993

Data sheet

Title:	Determination of Nitrogen Dioxide with KI-impregnated sintered Glass Filters
Authors:	Gudrun Hilbert
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Serial title and no.:	NERI Technical Report No. 74
Publisher:	Ministry of the Environment. National Environmental Research Institute ©
Year of publication:	May 1993
Typist:	P. Johnsen
Laboratory assistance:	L. Grundahl, T. Frederiksen, B. Vaabengaard and L. Christensen
Please quote:	Hilbert, G. (1993): Determination of Nitrogen Dioxide with KI-impregnated sintered Glass Filters. National Environmental Research Institute. 23 pp. - NERI Technical Report No. 74. Reproduction permitted only when quoting is evident.
Terms:	Nitrogen Dioxide, NO_2, Volumetric filter technique, KI method, field intercomparisons
ISBN:	87-7772-102-0
ISSN:	0905-815X
Printed by:	Grønager's Bogtryk & Offset
Number of pages:	23
Circulation:	100
Price:	DKK 40 (incl. 25% VAT, excl. freight)
For sale at:	National Environmental Research Institute Department of Emissions and Air Pollution P.O. Box 358, Frederiksborgvej 399, DK-4000 Roskilde Denmark Tel: +45 46 30 12 00 Fax: +45 46 30 12 14

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A method for determination of nitrogen dioxide (NO_2) is described. NO_2 is sampled on sintered glass filters impregnated with a solution containing KI and $NaAsO_2$ which reduces NO_2 to NO_2^-. The concentration of NO_2^- is determined after extraction with water by spectrometric determination.

The experimental procedure is described together with a documentation of the method.

Sampling efficiency

A high sampling efficiency with low deviation (98% ± 1%) is found for 24-hour measurements, while the KI method should not be used for longer sampling periods because of a lower and more varying sampling efficiency.

Detection limit

The detection limit is found to 0.2 μg NO_2-N/m^3 for 24-hour sampling, which is far below most NO_2 concentrations in Danish background areas.

Reproducibility

Parallel measurements have shown a reproducibility of 20%, but it is expected to be possible, to improve the reproducibility by a modification of the flow control and volume determination.

Interferences

HNO_2 interferes 100% with NO_2, but the HNO_2 concentrations are expected to be much lower than the NO_2 concentrations. Furthermore about 20% PAN might be sampled as NO_2^-, and during PAN episodes the importance of this interference can not be excluded. There is also a risk for a negative O_3 interference, when the O_3 concentrations are high.

A good correlation is found between the KI method and the Tecan monitor, which is known to have few interferences. Therefore interferences for the KI method seems to be of minor importance during a 1-month intercomparison (winter) with different concentration profiles and meteorological conditions.

KI/TGS-ANSA

When comparing the KI method with the TGS-ANSA method (used from 1985 to 1989 in the Danish monitoring programme in background areas) large variations in the results are found, but the correlation is not significant different from 1:1. As the KI method has been documented by an EMEP intercomparison and a comparison with the Tecan monitor, the large variations between the TGS-ANSA and the KI method are probably caused by problems with the TGS-ANSA method, e.g. variability of the absorption efficiency.

1 Introduction

Different methods for determination of atmospheric nitrogen dioxide (NO_2) has been used *(Ferm, 1992)*. For monitoring in background areas a low detection limit and few interferences is of special importance. Furthermore the method should be easy to run with a long distance between the laboratory and the measuring stations.

KI method

The KI method for determination of NO_2 is described by *Ferm (1992)*. NO_2 is sampled on sintered glass filters impregnated with a solution containing KI and $NaAsO_2$ which reduces NO_2 to NO_2^-. The concentration of NO_2^- is determined after extraction with water by spectrometric determination. In this report the KI method as run by NERI is described.

NO_2 method for background monitoring

The KI method has been used from June 1989 for 24-hour measurements of NO_2 in the Danish monitoring programme on background stations *(Hovmand & Grundahl, 1991; Hovmand et al., 1992)*.

From October 1985 to June 1989 an impinger method (TGS-ANSA) was used. Before change of NO_2 method parallel measurements with the two methods were run.

Now a modification of the KI method is planned without the toxic $NaAsO_2$ in the impregnation solution and with NaI instead of KI. This new method is not described in this report.

2 Description of the KI method

2.1 Experimental procedure

Sintered glass filters

Sintered glass filters (Ø=25mm, porosity 60 µm) enclosed in a glass bulb is used for sampling of NO_2. In *Figure 1* a glass filter is shown mounted with silicone tubing and quick connectors for fitting the sampling equipment.

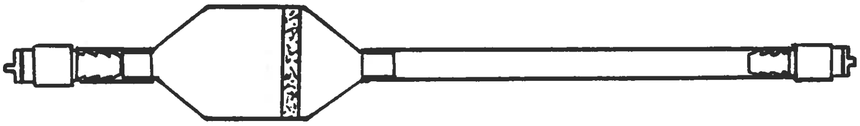

Figure 1. Sintered glass filter mounted with silicone tubing and quick connectors.

Impregnation

The filters are impregnated with 500 µl of a methanol solution containing KI (11.34% w/w), $NaAsO_2$ (1.14% w/w) and ethyleneglycol (5.79% w/w). The methanol is evaporated by blowing an NO_2 free air stream through the filter.

Sampling

The impregnated filters are exposed for normally 12 or 24 hours with a flow rate of about 0.6 l/min.

Sampling equipment

The NO_2 sampler designed and built at NERI is shown in *Figure 2*.

The flow is determined by a critical orifice, which is chosen to give a flow rate of about 0.6 l/min. The gasmeter shows the total volume in m^3 for all channels, while the counters for each channel are read in "step" which are proportional to the volume. The volume for each channel is calculated as the counting multiplied with a gas factor expressed in m^3/step.

The time for channel change is determined by the timer; the sampler has 8 channels, therefore the samples have to be changed once a week in case of 24 hour measurements.

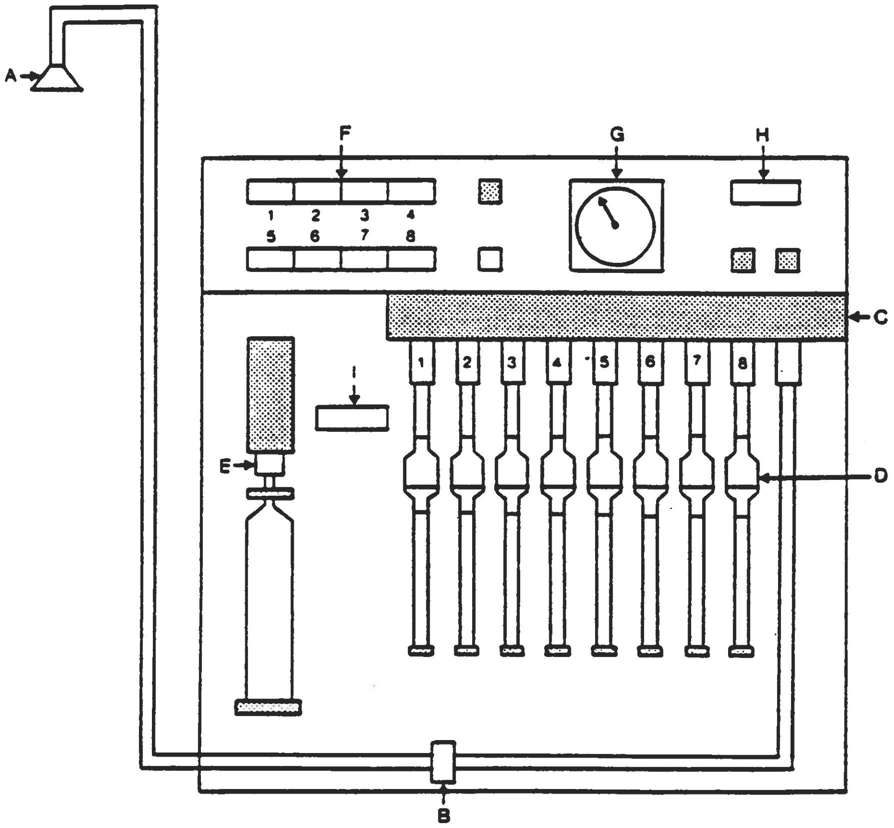

Figure 2. NO_2 sampler with KI-impregnated glass filters.

A	Air inlet
B	Particle filter (not analyzed)
C	Manifold
D	Sintered glass filters
E	Critical orifice, about 0.6 l/min.
F	Volume counters ("step") for each channel
G	Timer for channel change
H	Hour counter
I	Gasmeter (m^3)

Extraction

After exposure the filters are extracted with water. 4 ml of purified water is added and the filters are shaken for half an hour before they are emptied.

Analysis

NO_2^- in the extract is analyzed by the "segmented flow analysis" principle. NO_2^- reacts with sulfanilamide and acid to a diazonium ion, which are making a red diazo compound with N-(1-naphthyl, ethylene diamin). The spectrophotometric detection is made at 520 nm.

To minimize the matrix effect from the samples, KI is added to the standards in a concentration similar to the concentration in the samples.

2.2 Chemical reactions during sampling

Reactions

During sampling NO_2 is reduced to NO_2^- in the water/ethylene glycol film on the filters. To prevent a loss of NO_2^- as HNO_2 the film has to be alkaline:

$$NaAsO_2 + 2\,H_2O \rightleftarrows H_3AsO_3 + Na^+ + OH^- \qquad (1)$$

NO_2 is reduced to NO_2^- by I^-:

$$2\,NO_2 + 3\,I^- \rightarrow I_3^- + 2\,NO_2^- \qquad (2)$$

I_3^- is reduced back to I^- by $H_2AsO_3^-$, which is the strongest reducing agent:

$$I_3^- + H_2AsO_3^- + 3\,OH^- \rightleftarrows HAsO_4^{2-} + 3\,I^- + 2\,H_2O \qquad (3)$$

This means, that the overall reaction, where I^- acts as a catalyst, can be written:

$$2\,NO_2 + H_2AsO_3^- + 3\,OH^- \xrightarrow{I^-} 2\,NO_2^- + HAsO_4^{2-} + 2\,H_2O \qquad (4)$$

The reactions are described in more details by *Ferm (1992).*

2.3 Documentation of the KI method

Sampling efficiency

From sampling with two filters in series at Ll.Valby (close to arable land, 35 km west of Copenhagen) June-July 1992 the sampling efficiency was found to be 98% ± 1% (n=16) for 24-hour measurements and 89% ± 8% (n=4) for 72-hour measurements. The worse sampling efficiency for the 72-hour measurements seems not to be caused by capacity problems, because the sampling efficiency did not depend on the amount and NO_2 sampled. The difference in sampling efficiency for 24-hour and 72-hour samplings indicates that the KI method should not be used for sampling periods longer than 24 hours.

The effect of humidity of the air on the sampling efficiency has been investigated by *Sjödin & Ferm (1988).* There was no break through of NO_2 neither at a dew point at -40°C nor at a dew point at -4°C (flow rate 0.2 l/min).

Stability

The filters can be stored at room temperature before as well as after sampling. Before extraction the samples can be stored for at least half a year without changes occurring in its NO_2^- content *(Ferm, 1992).*

The stability of impregnated unexposed filters has been tested in connection with measurements in the Greenland Arctic *(Grundahl, 1992).* 6 filters, which had been at the Greenland measuring station for about 5 months without getting exposed, was tested in Denmark against new prepared filters. There was no systematical difference in concentration obtained with new prepared and 5 month old filters.

After extraction the NO_2^- concentration in the solution is found stable for at least 4 weeks. The NO_2^- analysis was repeated with a time difference of up to 4 weeks, and the difference between the two results seemed not to depend on the time difference.

Reproducibility

The reproducibility is calculated as:

$$S = \sqrt{\frac{\sum di^2}{2n}}$$

where di is the difference between parallel samplings, and n is the number of parallel samplings.

From 55 parallel samplings at Ll.Valby January 1992 the reproducibility was found to 20%, where the mean concentration was 5.7 µg NO_2-N/m^3.

The deviation between the two parallel samplings was getting higher during the measuring campaign due to problems with the volume counters at the sampling equipment. (For the first quarter of the measurements the reproducibility was 10% and for the first half it was 14%). It is expected to be possible to improve the reproducibility by a modification of the flow control and volume determination.

Detection limit

The detection limit is calculated as three times the standard deviation for the field blank values. The blank values for two measuring stations during 1992 were 0.14 µg/filter ± 0.06 (n=91); a normal 24-hour sampling volume is 0.86 m^3 (flow rate 0.6 l/min).

The detection limit is then calculated to 0.2 µg NO_2-N/m^3 for 24-hour sampling, which is far below most NO_2 concentrations in Danish background areas *(Hovmand et al., 1992).*

2.4 Interferences

Side reactions increasing or decreasing the NO_2^- concentrations are described by *Ferm (1992)* and *Sjödin & Ferm (1988).*

NO

Possible NO interference has been studied by comparing NO_2 measured with respectively the KI method and the chemiluminescence method at different NO:NO_2 ratios *(Sjödin & Ferm, 1988).* The highest NO:NO_2 ratio was 4:1 (24 hour mean) and there was found no systematical difference between the KI and the chemiluminescence method. From this results it is concluded that there is no interference from NO at a NO:NO_2 ratio below 4:1. In background areas the NO:NO_2 ratio normally is far below 4.

SO_2

Interference from SO_2 has been examined by adding SO_2 to a NO_2 containing air mixture in the laboratory. 150 µg SO_2/m^3 showed no interference on the NO_2 determination for a 24 hour sampling time *(Sjödin & Ferm, 1988)*. The magnitude of the NO_2 concentrations tested is not shown.

O_3

O_3 (and other oxidants) is expected to yield a potential negative interference due to oxidation of NO_2^- on the filters to NO_3^-. But a hypothesis until now is that O_3 will get reduced by iodide, which is present on the filters in large amounts. Determination of NO_3^- on the filters has not been carried out because of analytical problems: iodide disturbs the analysis on a ion chromatograph, and furthermore NO_3^- is not stable in a solution containing KI *(Sjödin & Ferm, 1988)*.

Interference from O_3 has been tested using laboratory mixtures of NO_2 and O_3 in air and comparing the KI against the chemiluminescence method. For NO_2 concentrations at 25-50 µg NO_2/m^3 and O_3 concentrations at 80-200 µg/m^3 there was found equal results from the two measuring methods (KI: flow 0.2 l/min, 24 hour), indicating no interference from O_3 in urban areas. In background areas the NO_2 concentrations will often be lower and the O_3 higher, why there is a risk for an O_3 interference *(Sjödin & Ferm, 1988)*.

PAN

Some PAN might be sampled on the KI filters as NO_2^-, then interfering with the NO_2 determination. Interference from PAN has been investigated in the laboratory by adding synthesized PAN in hexane solution to humidified clean air *(Sjödin & Ferm, 1988)*. Using the KI method on this air showed 15-20% interference from PAN. During PAN episodes with e.g. 2 ppb PAN, the PAN interference will then cause an overestimation of NO_2 with 0.8 µg NO_2/m^3. PAN interference has been investigated in the field by measuring PAN in parallel with NO_2. For the NO_2 determination there were used two filters in series because possible interference would show up on both filters. NO_2^- measured on the back filters were below the detection limit (0.3 µg NO_2/m^3) even during PAN episodes, indicating no important PAN interference. The authors have no explanation for the different PAN interference found in laboratory and field test, but say that synthetic air and outdoor air might behave different to the KI filters *(Sjödin & Ferm, 1988)*.

HNO_2

HNO_2 is sampled on the alkaline filters as NO_2^-, which means that HNO_2 interferes 100% with NO_2, but the HNO_2 concentrations is expected to be much lower than the NO_2 concentrations *(Andersen & Hilbert, 1993; Hovmand et al., 1992)*.

3 Intercomparisons

3.1 EMEP NO_2 field intercomparison

An EMEP (European Monitoring and Evaluation Programme) field intercomparison of measuring methods for NO_2 was held at Taunus Observatory, Frankfurt am Main, Germany, April-May 1991 *(Fähnrich et al., 1993)*. In *Figure 3* the results are shown for the KI method run by respectively Denmark, Sweden and Norway together with the mean of all measurements from Taunus.

It is seen, that the NO_2 concentrations from the KI method run by the three different laboratories are very close and that the correlation with the mean of all measurements are good.

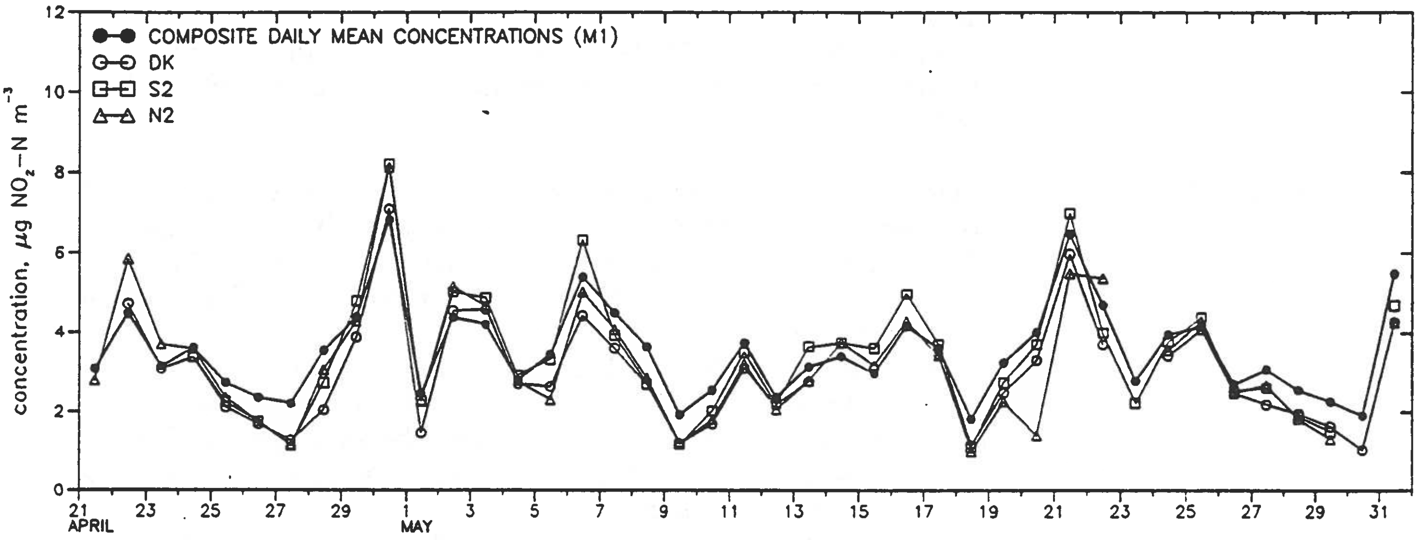

Figure 3. (Reproduced after *Fähnrich et al., 1993*). Results from the EMEP field intercomparison of measuring methods for NO_2.

Composite daily mean concentrations: mean of all NO_2-measurements.

DK:	NO_2 measured with the KI method by NERI, Denmark
S2:	NO_2 measured with the KI method by IVL, Sweden
N2:	NO_2 measured with the KI method by NILU, Norway

3.2 Tecan monitor and passive sampling

During a 1-month period in January-February 1992 a field intercomparison of different methods for measuring NO_2 were run at Ll. Valby in connection with a TOR (Tropospheric Ozone Research) campaign *(Nielsen et al., 1993)*.

The methods were:

1) KI-impregnated filters
2) Passive samplers
3) Tecan monitor

The methods and the intercomparison is described in more details by *Hilbert et al. (1992)*.

Tecan

The Tecan NO_x monitor is a 1-channel chemiluminescence monitor with photolytic conversion of NO_2 to NO.

The Tecan monitor has very few interferences in determination of NO_2, because a very small part of the nitrogen containing compounds other than NO_2 is converted to NO by the photolytic conversion.

A low pressure (10-12 mBar) in the reaction chamber reduces the interference from water vapor to an insignificant level *(Hilbert et al., 1992)*.

Passive sampling

The passive samplers are commercially produced sampler developed for measurement of personal exposure to NO_2 in ambient air *(Yanagisawa & Nishimura, 1982)*. They have been used with good experiences to study the NO_2 exposure of children in Copenhagen *(Stadslægen, 1992)*.

The passive sampler consists of an open box with a filter impregnated with triethanolamine (TEA) covered by 5 layers of hydrophobic filters (see *Figure* 4). After exposure the impregnated filter is extracted with water and analyzed by spectrometry. The sampling period was 24- or 48-hour.

To protect the passive sampler from rain and strong winds it was mounted in a funnel turned upside down *(Hilbert et al., 1992)*.

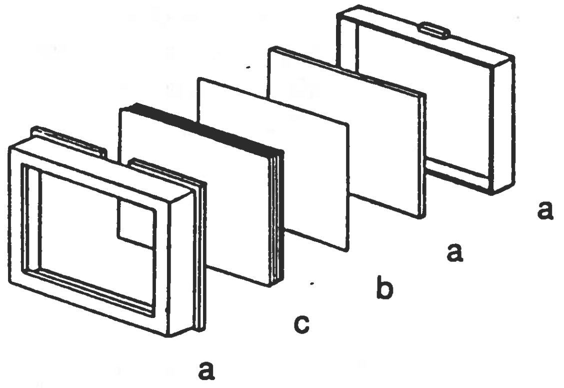

Figure 4. Passive sampler.

a	Badge case made of polypropylene, opening to air on one side with a size of 38 x 26 mm.
b	Absorbent sheet of cellulose fibre filter with thriethanolamine (TEA) to absorb NO_2.
c	Diffusion controlling mat consisting of a pile of hydrophobic fibre filter made of a fluorine containing polymer.

KI method/Tecan

The comparison between the KI method and the Tecan monitor shows a good correlation close to 1:1 (see *Figure 5*). As the Tecan method is known to have very few interferences, interferences for the KI method seems to be of minor importance during the 1-month intercomparison (winter) with different concentration profiles and meteorological conditions.

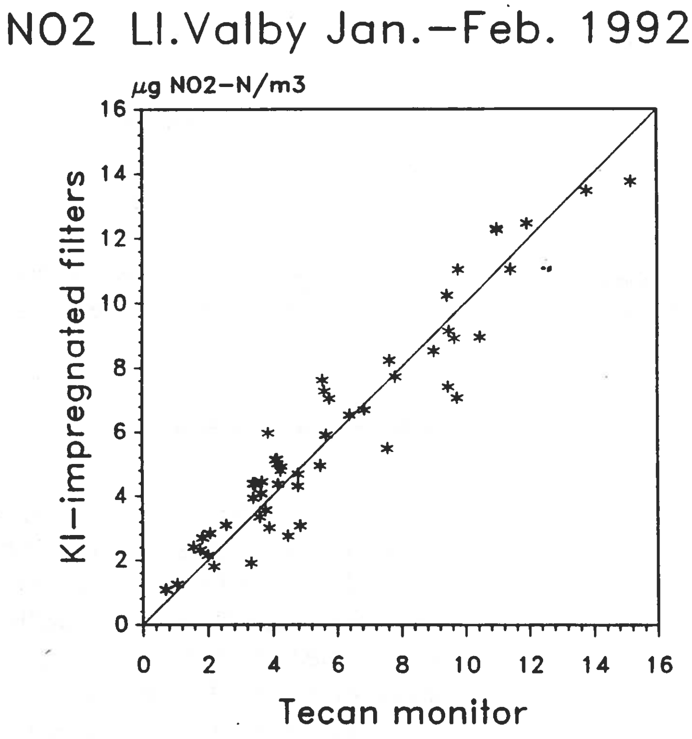

Figure 5. KI-impregnated filters compared to Tecan monitor (12-hour mean).

Passive/KI/Tecan

NO_2 measurements with the passive sampler correlates well with the two other methods (see *Figure 6*), but seems to be slightly lower. The reason for this might be, that the collection efficiency used for calculation of the air concentration for the passive sampler was too high.

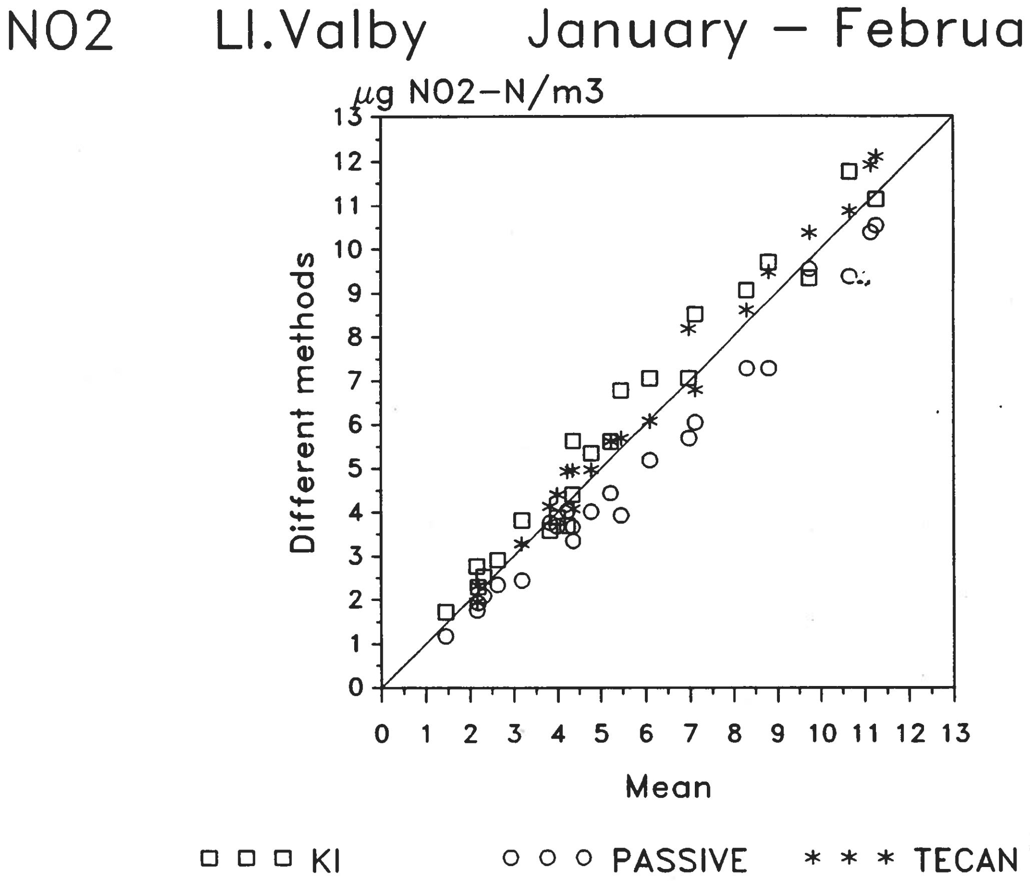

Figure 6. NO_2 concentrations in µg NO_2-N/m^3 from KI-impregnated filters, passive samplers and Tecan monitor compared to the mean of the three methods (24- or 48-hour mean).

3.3 TGS-ANSA

TGS-ANSA

In the TGS-ANSA method air was drawn through an impinger (modified polyethylene bottle, see *Figure 7*) containing a TGS absorption solution of Triethanolamine, Guaiacol and Sodium metabisulfite. The concentration of nitrite produced during sampling was determined colorimetrically by reacting the nitrite ion with sulfanilamide and ANSA (8-anilino-naphthalenesulfonic acid ammonium salt) and measuring the absorbance at 550 nm. The results were corrected with an absorption efficiency of 80% (*Hanssen & Ladegård; 1982*).

NO_2 method

The TGS-ANSA method was used in the Danish monitoring programme from October 1986 to June 1989 for determination of NO_2; in June 1989 the method for determination of NO_2 was changed to the KI method after parallel sampling.

The reasons for changing of NO_2 method were difficulties with the TGS-ANSA method: transportation of toxic liquids, evaporation of water from the bottles and a poor sampling effiency of 80%, which was expected to vary. Furthermore large variations between impinger methods (TGS-ANSA and Salzman) were found in a Nordic intercomparison *(Areskoug & Oyola, 1988))*

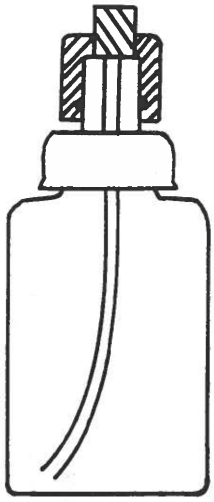

Figure 7. Modified 100 ml PE-bottle used as impinger for the TGS-ANSA NO_2 measuring method.

TGS-ANSA/KI

In autumn 1988 and spring 1989 the TGS-ANSA method was compared with the new KI method; in *Figure 8* the results are shown marked with time period. An orthogonal regression of the data showed no significant difference from a 1:1 correlation (95% level). During time period A (October 21 to November 7 1988) the KI method measured more than the TGS method, while the two methods showed similar concentrations during time period B (November 8 to December 21 1988); during time period C (March 21 to May 24 1989) a large variation in the results are found. Looking for an explanation for the varying correlation between the two methods, the air sampling and the analysis etc. in the laboratory has been checked; nothing indicating an error was found. The relation between NO_2 measured with the two methods has been compared with the relative humidity and the temperature; no correlation was found.

As the KI method has now been documented by the EMEP intercomparison and the comparison with the Tecan monitor (see the former sections), the large variations in the relation between the TGS-ANSA and the KI method are probably caused by problems with the TGS-ANSA method, e.g. variability of in the absorption efficiency.

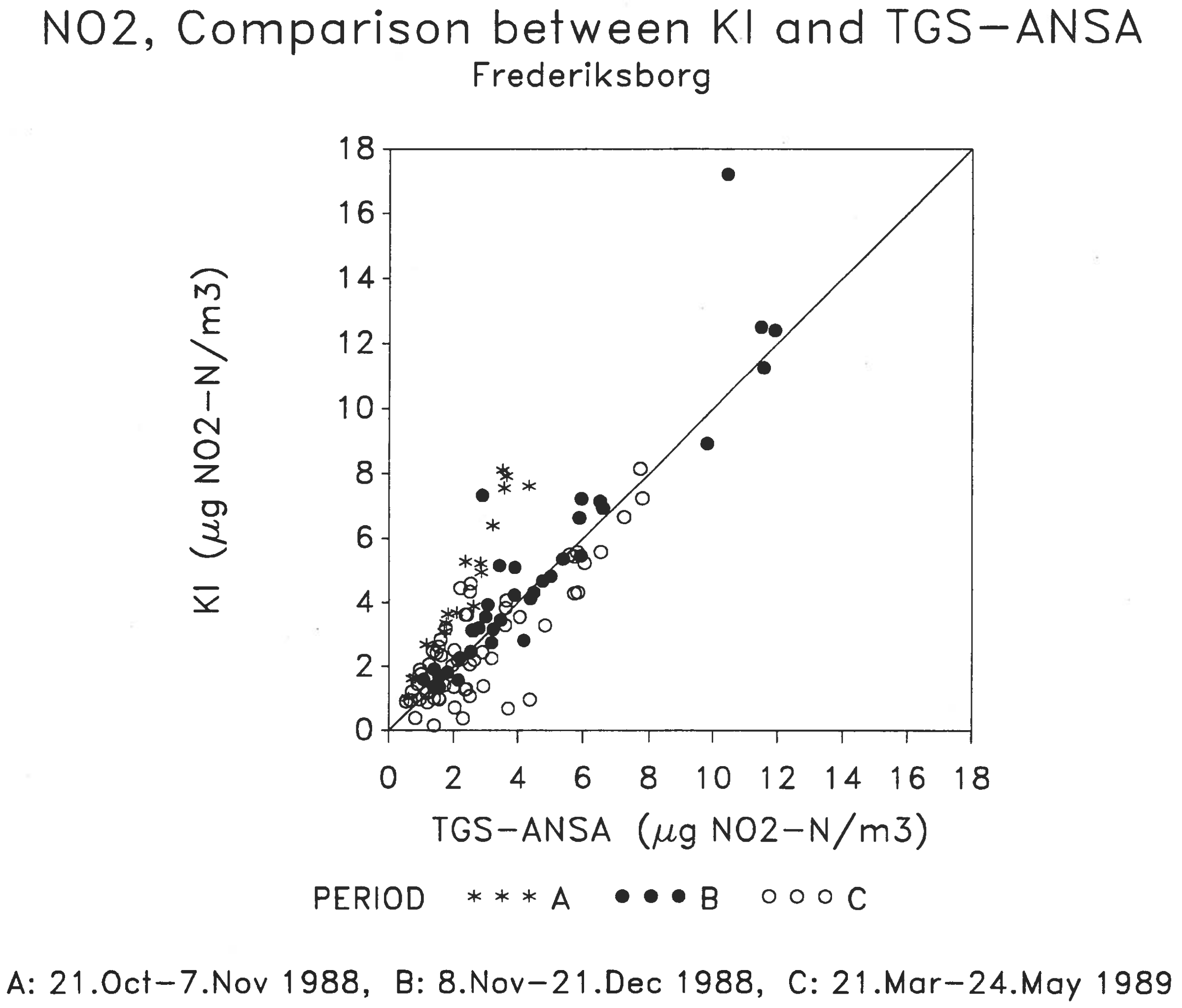

Figure 8. NO_2 comparison between the KI and TGS-ANSA method. The observations is marked with time period.

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