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A SIMPLE METHOD FOR DETERMINATION OF GASEOUS NITROUS
ACID IN THE ATMOSPHERE

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Fyll bara i en sida. Bifoga om möjligt ett ex av rapporten!

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A simple method for determination of gaseous nitrous acid in the atmosphere.

Sammanfattning av rapport (fakta med huvudvikt på resultatet)

A denuder technique for sampling and analysing nitrous acid at sub ppb level is described. After sampling the denuder is leached in water and the NO₂-concentration is determined spectrophotometrically. The detection limit for 24 hours sampling is better than 0.02 ppb. PAN might be an important interference in background air during summer-time conditions. The method was tested on synthetic gas mixtures of NO, NO₂ and HNO₂. It has appeared that HNO₂ can be formed by heterogeneous reactions at surfaces. Measurements in the city of Gothenburg indicate that the major pathway for HNO₂-formation in urban air is the reaction between NO, NO₂ and water vapor.

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Summary

A denuder technique for sampling and analysing nitrous acid at sub ppb level is described. After sampling the denuder is leached in water and the NO_2^- concentration is determined spectrophotometrically. The detection limit for 24 hours sampling is better than 0.02 ppb. PAN might be an important interference in background air during summertime conditions. The method was tested on synthetic gas mixtures of NO, NO_2 and HNO_2 . It has appeared that HNO_2 can be formed by heterogeneous reactions at surfaces. Measurements in the city of Gothenburg indicate that the major pathway for HNO_2 -formation in urban air is the reaction between NO, NO_2 and water vapor.

A SIMPLE METHOD FOR DETERMINATION OF GASEOUS NITROUS ACID IN THE ATMOSPHERE

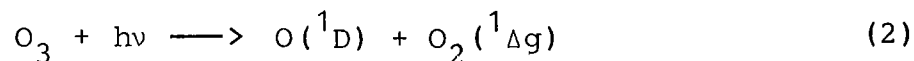
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1. Introduction

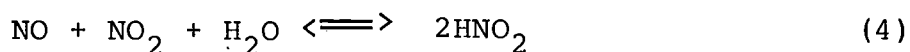
Gaseous nitrous acid is considered to play an important role in atmospheric chemistry, mainly due to its ability to produce OH-radicals through direct photolysis:



Generally, at least in background air, ozone is considered to be the predominant source of OH-radicals through the reactions:



However, in urban areas where ozone concentrations normally are very low due to the high concentrations of NO_x , HNO_2 might be an important source of OH-radicals, since it can be formed homogeneously or heterogeneously through reaction between NO, NO_2 and water:



Hence, in urban air significant amounts of HNO_2 may be formed and stabilized during the nighttime, which may lead to an increased production of OH-radicals at sunrise due to the daylight photolysis according to reaction (1) (Perner and Platt 1979).

Some interests have also been focused on HNO_2 concerning its role in the formation of possible harmful nitrosamines in the atmosphere (Fahmy and Fahmy 1976).

In spite of the increasing interest in the role of HNO_2 in atmospheric chemistry during the last years, only a limited number of measurements in ambient air have been reported so far.

Two principally different methods have been used. HNO_2 has been measured directly in the atmosphere by differential optical absorption spectroscopy in the ultraviolet region. The detection limit depends on weather conditions, and is usually between 0.02 and 0.05 ppb. Measurements have been made at several sites in Western Europe as well as in the United States (Perner and Platt 1979; Platt and Perner 1980; Kessler et al. 1981; Platt et al. 1980).

HNO_2 has also been measured by absorption in either pure distilled water (Cox et al. 1976) or dilute alkali (Nash 1974). The detection limit for these methods are 0.1 ppb slightly less at 24 hours sampling. The wet chemical method has disadvantages in being sensitive for interferences from such compounds as NO_2 and peroxyacetyl nitrate (Cox et al. 1976). This might explain the unexpected high values of atmospheric HNO_2 obtained by Nash (1974).

In this report, a simple method for measuring daily mean values of HNO_2 concentrations with high accuracy and a low detection limit is described. HNO_2 is selectively separated from NO_2 by sorption in a denuder with sodium-carbonate as the active sorbent.

The detection limit is better than 0.02 ppb HNO_2 with a sampling rate of 2 l min^{-1} and 24 hours sampling. This method is suitable for measurements of HNO_2 in background air as well as in urban air.

2. Instrumentation and methods

2.1 Sampling

The inside wall of a hollow sodium glass tube with an inside diameter of 0.4 cm and an outside diameter of 0.6 cm and a length of 75 cm (fig. 1), is coated with a thin layer of solid sodium carbonate (Na_2CO_3) in the following manner.

Using a pipette ball, a 1% (by weight) solution of sodium hydroxide (NaOH) in methanol is sucked up through the tube to a height of 60 cm, thus leaving 15 cm of the denuder uncoated at one end. The solution is drawn off and the wall is dried with air, which has passed over NaCO_3 , with a flow of approximately 6 l min^{-1} . The liquid methanol evaporates quickly and a smooth coating of NaOH is obtained, which is converted to Na_2CO_3 within a minute by the CO_2 -content in the airstream. Both ends of the denuder are then sealed with Parafilm until being used for sampling.

During sampling the denuder should be mounted vertically with the unimpregnated part, the air inlet, downwards.

At sampling sites with a wet climate the denuder should be heated to a temperature somewhat higher ($5-10^{\circ}$ C) than the ambient air temperature, otherwise the Na_2CO_3 -layer can be dissolved by water droplets, e.g. from fog. The dissolution and possible subsequent recrystallization might influence the sampling efficiency. Figure 2 shows how the equipment can be arranged during outdoor sampling to prevent such effects.

The inlet of the denuder is protected against rain by means of a polyethylene funnel. For the heating a 3 meter long metal band with high electric resistance is wound around the glass tube. The heating wire is kept in place by two clips and protected on the outside by another glass tube. A very low voltage is necessary for the heating if the outer glass tube is isolated with frigolite.

The sampling rate preferred is about 2 liters per minute. A laminar flow is then achieved in the 60 cm-impregnated part of the denuder and the collection efficiency for HNO_2 after the 60 cm passage is better than 95%. The air flow is maintained by a small membrane pump with a critical orifice. The total volume of air sucked through the denuder during a 24-h sampling is measured by a volume gasmeter. After sampling the denuder is sealed again at both ends with Parafilm in order to prevent contamination during transport and storage.

2.2 Analysis

The denuder ends are released from the Parafilm and a pipette ball is attached to the uncoated end of the denuder. The other end is dipped into a 25 ml-Pyrex cup

containing 5 ml of distilled water. The water is sucked up through the tube of about 70 cm height. The leaching solution is allowed to flow back into the cup, and the procedure is repeated. 5 ml of Griess-Saltzman reagent (140 ml of glacial acetic acid, 5 g of sulfanilic acid and 20 ml of 0.1% N-(1-naphtyl)ethylenediaminedihydrochloride diluted to 1 liter with distilled water) is then added to the leaching solution. After mixing and colour development for 15 minutes, the colour is read at 550 nm against the leaching solution of an unexposed denuder, prepared in the same manner as described above. The concentration of NO_2^- is calculated from a standard curve. The absorbance of the leaching solution of an unexposed denuder is very uniform and low compared to the absorbance of unexposed reagent or distilled water, normally corresponding to less than 1 nmole when the absorbance of unexposed reagent is set at zero. The detection limit is better than $2 \cdot 10^{-9}$ moles NO_2^- in 10 ml solution, which corresponds to the lowest detectable amount from a 24-h sample (sampling rate 2 liter per minute) of 0.6 nmole/m^3 (0.02 ppb) HNO_2 .

3. Theoretical and practical examination of the method

3.1 General

One of the great advantages of the denuder technique is its ability to separate the gaseous phase from the particle phase of a chemical constituent without disturbing the ambient equilibrium conditions as an artifact of sampling. This was utilized in the determination of atmospheric ammonia and ammonium (Ferm 1979). In the same paper the theoretical principles of the denuder technique are described. In the special case of HNO_2 , which is expected

to occur almost exclusively in the gas phase, the aims in designing the sampling procedure is to get a defined sorption efficiency and to investigate possible interference from other oxidized nitrogen compounds such as NO_2 and PAN.

3.2 Choice of sorbent

NaHCO_3 has previously been used as a sorbent for trapping hydrogen fluoride (Pack et al. 1959). HF and HNO_2 are both weak acids of similar strength. NaHCO_3 is, however, not soluble in any solvent which is volatile enough to make a smooth coating. NaOH is soluble in methanol which is suitable for this purpose. When a thin layer of the NaOH solution is dried in air it will be converted to Na_2CO_3 by reaction with CO_2 .

3.3 Sorption efficiency

In a series of laboratory runs the sorption efficiency of Na_2CO_3 coated denuders for gaseous nitrous acid was investigated. HNO_2 in the gas phase was produced in the following manner.

A dilute ($1.5 \cdot 10^{-3}$ M) solution of sodium nitrite in water was slowly ($0.6-1.2 \text{ ml hr}^{-1}$) added by means of a infusion syringe to a 2 M sulphuric acid solution under intense mixing. A dry, clean airstream (5 l min^{-1}) was passed through the vessel, where the reactants were mixed and the gaseous HNO_2 formed. Normally, two equivalent sampling systems, each consisting of three Na_2CO_3 denuders, a gas volume meter, a membrane pump and a critical orifice in series were connected in parallel to the airstream from the outlet of the reaction vessel (fig. 3).

Sampling time was generally about 1 hour. After exposure the NO_2^- amounts in the denuders were analyzed according to the previous description.

A summary of the results are given in table 1. The equilibrium constant for the homogeneous reaction 4 shows that practically all produced HNO_2 should be decomposed to NO and NO_2 when equilibrium is reached. According to the rate constant for 4 the reaction is too slow to change the HNO_2 concentration during the short sampling time in the denuders. When most HNO_2 is removed in the first two denuders it seems, however, that the reaction goes in the opposite direction. This indicates that small amounts of HNO_2 are formed during the transport through the denuders from NO and/or NO_2 present in the gas stream.

If the sorption efficiency is considered to be the same for the first two denuders, it can be calculated from

$$E = \frac{a-b}{a} \quad (\text{A})$$

where a is the concentration of NO_2^- in the first denuder and b in the second. The relationship between the sorption efficiency for a hollow tube which acts as a perfect sink for a certain gas and the air flow rate is given by Davies (1966):

$$E = 1 - 0.819 \exp(-14.6272\Delta) - 0.0976 \exp(-89.22\Delta) - 0.01896 \exp(-212\Delta) \quad (\text{B})$$

$$\Delta = \frac{\pi DL}{4F}$$

where

E = the fraction that is sorbed by the tube

D = the diffusion coefficient for the gas

L = length of tube

F = airflow

Values of the efficiencies calculated from eq. A with the corresponding diffusion coefficients for sampling at some different flow rates are presented in table 1.

The diffusion coefficient seems very constant when the efficiency is less than 98%. When the efficiency is higher than 98% the figure becomes affected by the NO_2^- production. A small change in the efficiency when it is near 100% causes a drastic change in the diffusion coefficient. The diffusion coefficient depends on the size and molecular weight of the gas. It is likely that the constant for HNO_2 is very close to the coefficient for NO_2 . The diffusion coefficient for NO_2 has been estimated to $1.54 \cdot 10^{-5} \text{ m}^2/\text{s}$ at 21.1°C by Palmes *et al.* (1976). The values obtained here are very close to this value. Na_2CO_3 can therefore be considered as a perfect sink for HNO_2 . If the efficiency is calculated from the D_{NO_2} , given by Palmes *et al.*, it comes very close to the efficiency measured and calculated from eq. A.

Table 1. Determination of sorption efficiency and diffusion coefficient for HNO_2 .

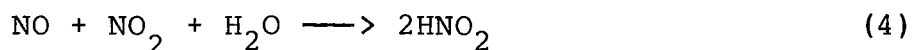
Flow rate l/min	HNO_2 in the denuders, respectively			E %	D m^2/s	E % (for $D = 1.54 \cdot 10^{-5}$)
	1st	2nd	3rd			
0.66	869	13.4	17.6	98.5	$0.64 \cdot 10^{-5}$	100
1.52	2359	42.9	13.7	98.2	1.40	98.7
2.05	1084	40.7	7.3	96.2	1.52	96.3
2.56	876	61.1	12.6	93.0	1.52	93.1
3.42	941	120	23.4	87.2	1.53	87.2

3.4 Interferences and formation of HNO₂ during sampling

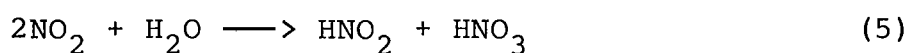
3.4.1 NO and NO₂

When HNO₂ is removed by the denuder during sampling the equilibrium concentration of HNO₂ with other gases will be displaced. More HNO₂ will be produced during the sampling. If those gases able to produce HNO₂ are present in higher concentrations than HNO₂ they will affect the measurement and too high values will be obtained.

In a series of laboratory experiments denuders were exposed to different gas mixtures of NO, NO₂ and H₂O. A typical result of such a test is presented in table 2. In order to see the production of HNO₂ during sampling an experiment with HNO₂ alone is presented as for comparison. If equations A and B are applied to the different parts of the denuders it can be seen that HNO₂ is produced all the time when NO and NO₂ are present. In these experiment a higher deposition often occurred after the gas had passed an uncoated surface. This can be due to a heterogeneous reaction between NO, NO₂ and water vapour as observed by Kessler et al. (1981):



Another possible pathway for HNO₂ formation is the reaction between NO₂ only and water vapour:



In order to investigate the relative importance of this reaction forming HNO_2 in the denuder during sampling, a series of laboratory runs were performed, where denuders were exposed to gas mixtures containing NO_2 and H_2O . When ozone was added in excess (several hundred ppb) to these mixtures, ensuring that no NO was present, there was a very small or negligible formation of HNO_2 in the denuder, compared to the amounts formed when ozone was not present.

This indicates that NO_2 alone or present together with excess ozone is not an interference of major importance, and that reaction (5) is markedly slower than reaction (4). In urban air reaction (4) taking part on the denuder wall might be an interference of importance, but as seen below, it is possible to adjust for this effect in the calculation of the ambient HNO_2 concentration.

3.4.2 PAN

The denuders capability of sorbing peroxyacetylnitrate $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ (PAN) was investigated. A solution of PAN in hexane was added continuously to an airstream by means of an infusion pump. PAN has 100% response on a chemiluminescent NO_x instrument as NO_2 , i.e. it is quantitatively reduced to NO by the catalytic converter. The PAN concentration in the air entering and leaving the denuder was monitored. At a PAN concentration of 10 ppb about half of the amount entering the tube was sorbed in a dry airstream and about a quarter was sorbed in humidified air. The denuder was then leached and analyzed for NO_2^- . PAN was found as NO_2^- in the leaching solution. Penket et al. (1977) found that PAN hydrolysis in an alkali solution give one NO_2^- ion for each PAN molecule.

The prerequisites of the formation of HNO_2 in urban air are more favorable during the winter season because the NO and NO_2 concentration are higher and the light intensity is lower. PAN on the other hand is formed photochemically and the highest ambient concentrations are found during summertime conditions. The PAN concentration has a minimum in the winter. The described method for determination of HNO_2 therefore seems to be more applicable for winter monitoring. For summer conditions adjustments for PAN concentrations are necessary.

Table 2. Sorption of NO_2^- as a function of distance for three denuders in series exposed to different gas mixtures. The flow rate is 2.05 l/min.

Distance from inlet cm	Gasmixture NO (100 ppb) + NO_2 (100 ppb) + H_2O			Gasmixture $\text{HNO}_2 + \text{H}_2\text{O}$ nmole NO_2^-/m^3			NO_2 (50 ppb) + H_2O + O_3 (in excess)		
	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
0-15	-	-	-	-	-	-	-	-	-
15-30	108.7	17.4	15.1	721	26.8	3.3	3.0	0.8	0.0
30-45	56.7	7.1	8.8	220	6.5	1.6	2.2	0.0	0.0
45-60	31.8	4.0	7.8	97.6	4.9	1.6	1.6	0.0	0.0
60-75	19.9	4.0	7.1	45.5	4.9	3.3	2.2	0.8	0.0

4. Comparison between measured HNO_2 concentration and equilibria values

The concentration of HNO_2 was measured on the roof of a 20 meter high building in the center of Gothenburg. Two or three denuders were connected in series and mounted outdoors. Sampling was done by sucking air at a flow of 2.1 l/min directly into the denuders without any inlet probe. The sampling time was 12 hours, either daytime 06-18 or nighttime 18-06. The nitrate concentrations in the denuders are presented in table 3. The high NO_2^- deposition in the 2nd and 3rd denuders indicates that also another process occurs in the denuders than the sorption of HNO_2 . It might be of the same kind as we observed in the lab experiments with high NO and NO_2 concentrations and low HNO_2 concentration. Then a production of HNO_2 occurred when the gas came in contact with an uncoated glass surface. It implies that a production of HNO_2 can also occur in the first denuder.

From equation B it can be calculated that the sorption efficiency for HNO_2 at a sampling rate of 2.1 l/min would be 96%. Thus 4% of the ambient HNO_2 concentration collected in the first denuder should be collected in the second.

If we assume that the NO_2^- deposition due to the formation of HNO_2 during sampling is the same in the first two denuders, we get

$$(b-p) = (a-p) \cdot 0.04 \quad (C)$$

where p is the HNO_2 concentration produced. Thus (a-p) is the concentration of the original ambient HNO_2 that is sorbed in the first denuder. The sorption efficiency should be 96%. Then we get for the HNO_2 concentration

$$\text{HNO}_2 = \frac{(a-p)}{0.96} = 1.085 \cdot a - 1.04 \cdot b \quad (D)$$

This formula is used for the calculation of the ambient HNO_2 concentration in table 3.

The equilibrium constant for the homogeneous reaction (4) is according to Chan (1976):

$$\ln K_p (\text{atm}^{-1}) = -15.56 \pm 0.62 + (4.73 \pm 0.19) \cdot 10^3/T \quad (\text{E})$$

Gas concentrations are often expressed in moles/m³.

From the equation of state of an ideal gas we get for this reaction

$$K_c = K_p \cdot R \cdot T \quad (\text{F})$$

By combining the equations and inserting a value for R we get

$$[\text{HNO}_2] = ([\text{NO}] [\text{NO}_2] [\text{H}_2\text{O}] \cdot 1.43 \cdot 10^{-11} \cdot T \cdot \exp(4730/T))^{0.5} \quad (\text{G})$$

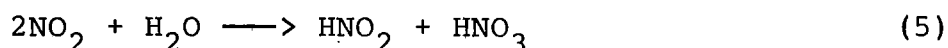
where all gas concentrations are expressed in moles/m³.

Concentrations of NO and NO₂, relative humidity and temperature were measured continuously at this station. HNO₂ can be produced from NO and NO₂ according to reaction 4.

Calculation of the 12 hours mean equilibrium concentration of HNO₂ was done for 1 hour mean values of [NO] [NO₂] and [H₂O]. This mean value is about 5-30% lower than if the concentration is calculated from the 12 hours mean values that are presented in table 4. The calculated equilibrium values for reaction 4 are plotted against the measured HNO₂ concentrations in figure 5. For night hours observed HNO₂ concentrations agree well with the

expected calculated equilibrium concentrations, while measurements during daylight periods are lower in comparison with the calculated equilibrium values. This can be explained by the decomposition of HNO_2 when exposed to light according to reaction 1.

HNO_2 can also be produced according to reaction 5.



The denuder described here can also be used for the measurements of gaseous HNO_3 (Ferm 1982). However, the HNO_3 concentrations were not measured at this site. Instead measurements of HNO_3 were made at a clean air station, 60 km south of Gothenburg as 24 hours mean values starting from 6 am. Earlier comparisons of gaseous HNO_3 on these two sites have shown that the concentrations are very similar (Grennfelt 1980).

The equilibrium constant for reaction 5 is given by England and Corcoran (1974) to $3.67 \cdot 10^{-27} \exp(4550/T) \text{ cm}^3 \text{ molecule}^{-1}$. The HNO_2 concentration in equilibrium with NO_2 and HNO_3 is thus

$$[\text{HNO}_2] = 2.21 \cdot 10^{-9} \exp(4550/T) [\text{NO}_2]^2 [\text{H}_2\text{O}] [\text{HNO}_3]^{-1} \quad (\text{H})$$

if all concentrations are expressed in moles/ m^3 .

Since the HNO_3 measurements are not synchronous with the other parameters only rough estimations of the HNO_2 levels can be done. Table 4 shows the calculated values.

The equilibrium values for reaction 5 are plotted against measured values in figure 4. This reaction seems to be far from equilibrium.

Table 3. Measurements of the HNO_2 concentration in urban air by sampling through two or three denuders in series.

1982 DATE	TIME	NO_2^- IN DENUDERS, RESPECTIVELY			$[\text{HNO}_2]$
		1st	2nd	3rd	
nmole/m ³					
9-10/3	18-6	83.9	19.9	15.0	70.3
17-18/3	18-6	25.8	2.6	1.2	25.3
18-19/3	18-6	30.8	6.3	3.4	26.9
20-21/3	18-6	12.9	2.9	-	11.0
21/3	6-18	10.1	1.7	-	9.2
21-22/3	18-6	14.9	3.6	-	12.4
22-23/3	18-6	95.2	14.7	5.2	88.0
23/3	6-18	48.1	21.0	7.1	30.3
24/3	6-18	27.2	3.2	1.5	26.2
26/3	6-18	12.6	5.5	-	8.0
27/3	6-18	20.4	2.4	-	19.6
28/3	6-18	15.1	3.6	-	12.6

*) d = daytime 06-18 GMT, d = nighttime 18-06 GMT

Table 4. Calculation of the equilibrium concentration of HNO_2 with NO , NO_2 , H_2O and HNO_3 according to reaction 2 and 3.

Date 1982	$[\text{NO}]$ nmole/m ³	$[\text{NO}_2]$ nmole/m ³	rel. Humidity %	t °C	$[\text{HNO}_2]$ according to reaction 4	$[\text{HNO}_3]^*$ nmole/m ³	$[\text{HNO}_2]$ according to reaction 5
9-10/3	1741	4941	58.6	3.1	386	49.6	3018
17-18/3	179	1232	56.2	6.8	56.4	20.2	453
18-19/3	339	1319	61.5	5.7	77.3	46.5	245
20-21/3	18	619	64.1	4.0	7.1	53.5	48
21/3	310	681	60.0	5.6	62.8	38.7	90.3
21-22/3	95.4	776	62.3	4.8	30.5		
22-23/3	633	2143	58.3	5.0	163	40.2	706
23/3	2485	1860	58.3	6.6	305	34.2	632
24/3	1421	1975	58.1	6.9	242	10.4	2339
26/3	1005	2186	56.9	9.1	210	25.1	1180
27/3	422	1764	60.0	7.1	119	21.3	942
28/3	634	1308	48.1	9.1	118	19.3	464

*) the HNO_3 concentration is a 24 hours mean value (6-6 GMT) at a remote station near Gothenburg.

5. Conclusions

The described sodium carbonate denuder provides a simple and cheap method for measuring nitrous acid in air with a high accuracy and a low detection limit. The accuracy and the detection limit is affected by the presence of gases such as NO, NO₂ and PAN, but in the case of NO and NO₂ it is possible to make adjustments for this interference. The method is recommended for measurements during wintertime conditions. During summertime conditions the simultaneous PAN-concentration, especially in background measurements, has to be observed.

The results presented in table 3 and 4 show that the measured ambient HNO₂-concentration is of the same order of magnitude as the equilibrium concentration calculated from equilibrium data of reaction 4 and measured mean values of NO, NO₂ and H₂O. In urban air this concentration implies that reaction 4 approaches equilibrium relatively quickly, and that earlier reported kinetic data for the homogeneous reaction 4 are not applicable for outdoor conditions. It is almost clear that reaction 4 occurring either homogeneously or heterogeneously is the most important for the HNO₂ formation in urban air. However, reaction 5 might be of importance in background air and during long-range transport when NO-concentrations are low.

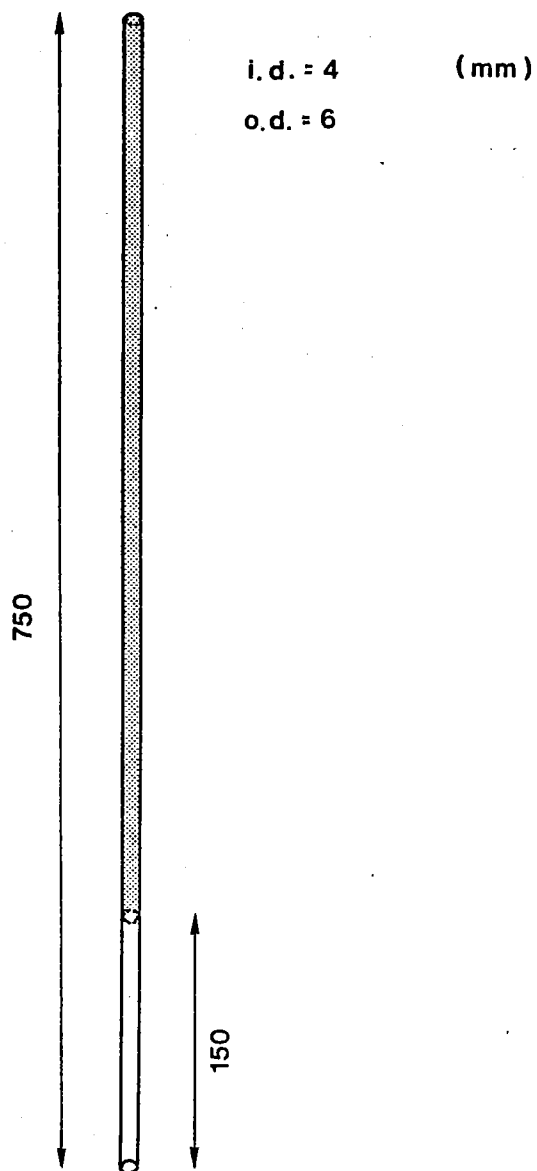


Figure 1. Sodium carbonate denuder

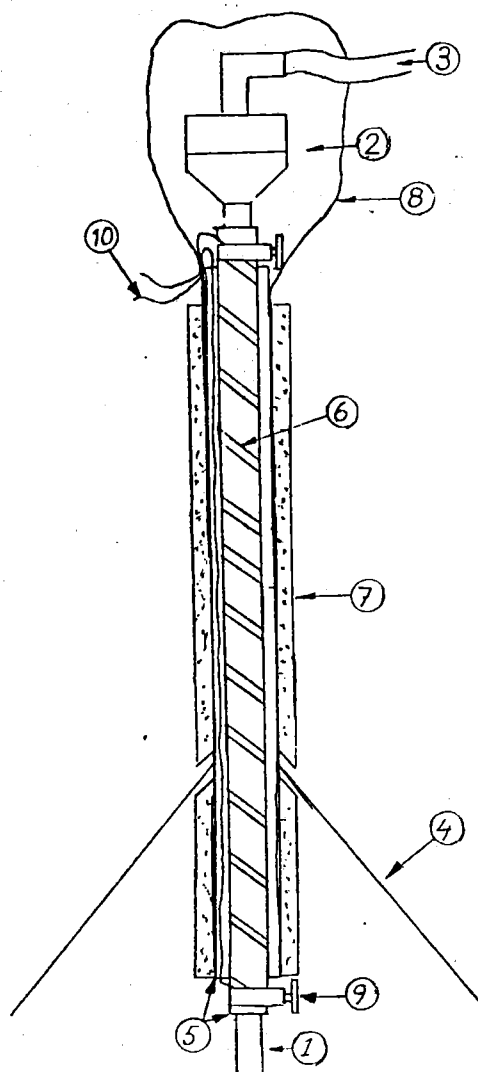


Figure 2. Sampling equipment for the analysis of HNO_2 during periods with rain or fog.

The equipment consists of 1) denuder 2) impregnated filter in a filter holder 3) outlet leading to pump and gasmeter 4) funnel made of polyethylene ϕ 250 mm 5) glass tube 6) metal band 7) isolation 8) plastic bag 9) clips 10) cord for the metal band.

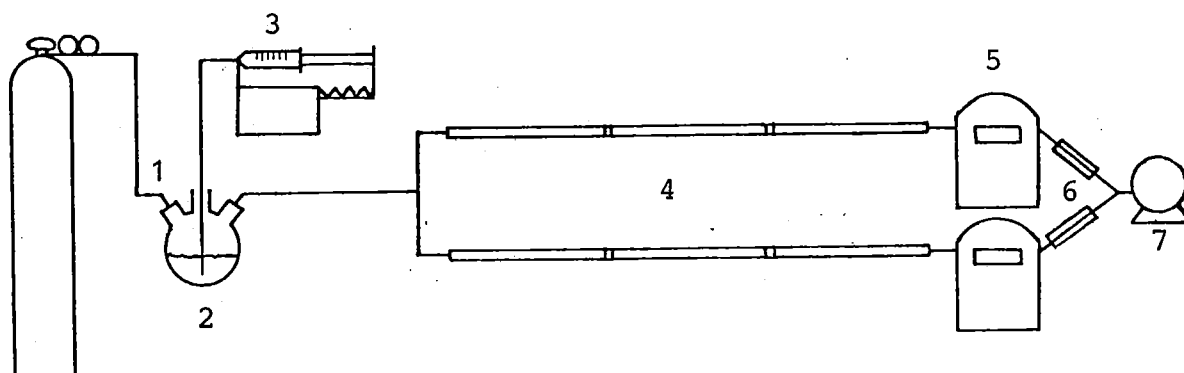


Figure 3. Apparatus for production and parallel sampling of gaseous nitrous acid.

- 1 clean air inlet
- 2 reaction vessel with dilute H_2SO_4
- 3 infusion pump for adding of NaNO_2 (aq)
- 4 three Na_2CO_3 -denuders in series
- 5 gas volume meters
- 6 critical orifices
- 7 membrane pump

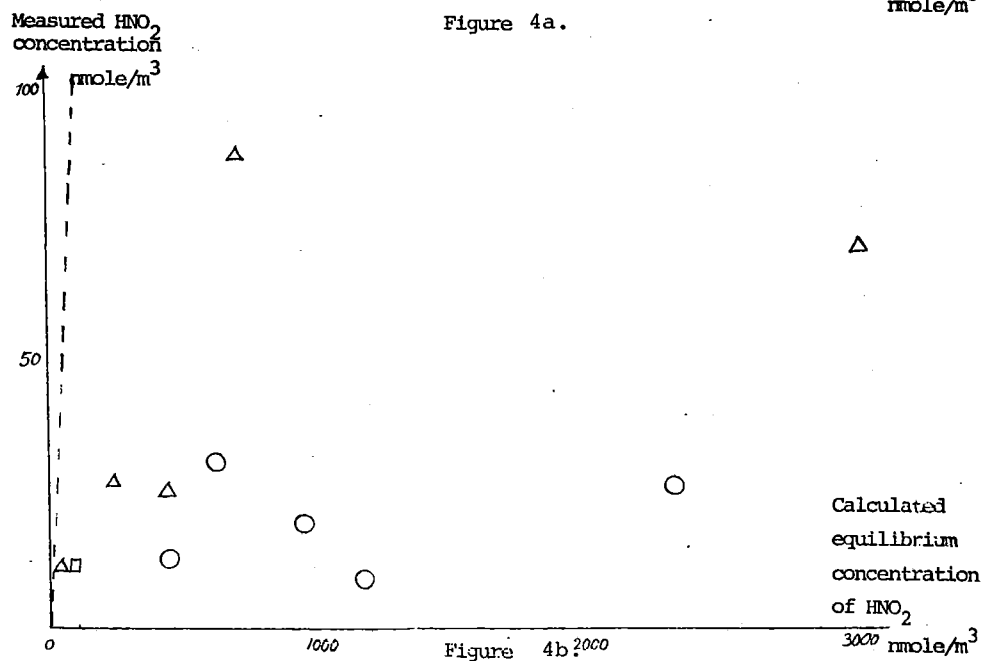
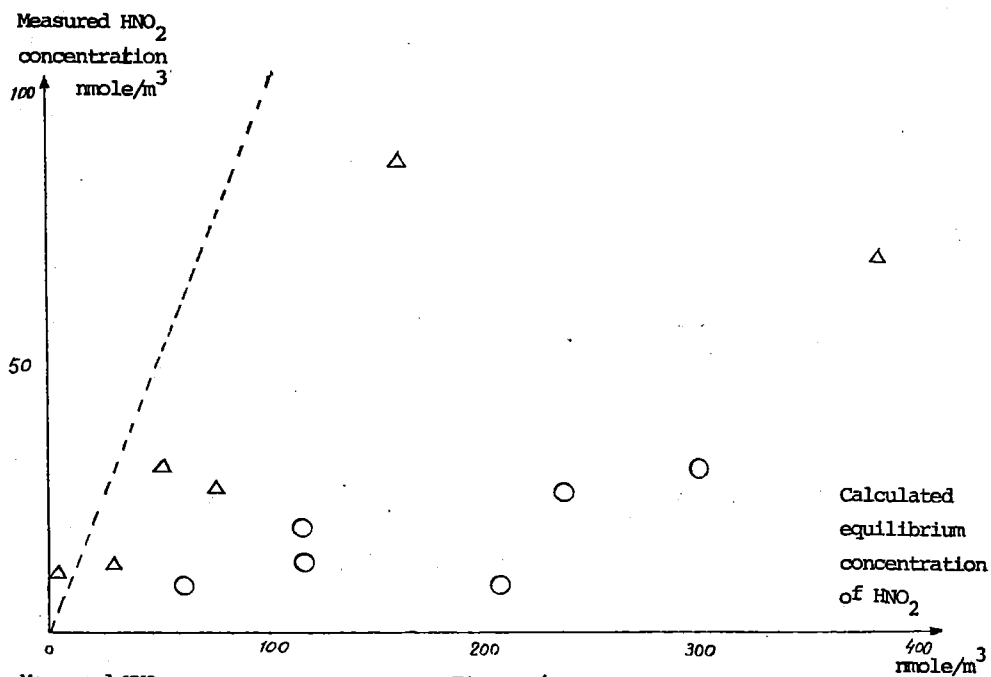
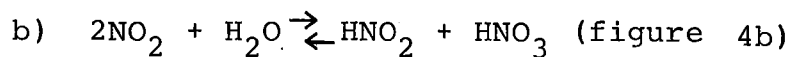
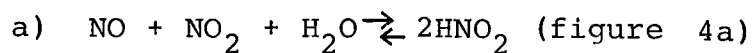


Figure 4. Measured HNO₂ concentrations against calculated equilibria values for the reactions



△ = sampling time 18-06

○ = " " 06-18

□ = " " 06-06

Dotted line represents $x = y$

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