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INSTITUTET FÖR VATTEN- OCH LUFTVÅRDSFORSKNING

MEASUREMENTS OF NITROUS ACID IN THE CITY OF GOTHENBURG

Åke Sjödin, Martin Ferm and Peringe Grennfelt

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Rapportens titel och undertitel/Title and subtile of the report

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Sammanfattning/Summary

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nitrous acid in urban air, denuder technique for, daylight photolysis of
formation paths of, correlation to nitrogen oxides

Summary

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Introduction

Nighttime build up of nitrous acid has been observed recently in moderately or heavily polluted air masses (Harris et al., 1982; Perner and Platt, 1979). It is assumed that this build up triggers an increased production of OH-radicals during early morning hours, due to the rapid, direct photolysis by daylight of nitrous acid:

$$HNO_2 + h\nu \longrightarrow OH\cdot + NO \tag{1}$$

Since the very reactive OH-species is a key intermediate for all photochemical processed in the atmosphere, the great importance of nitrous acid in atmospheric chemistry is no longer brought into question. Despite this, the mechanisms of its formation are still not very well understood.

The backward reaction of the photolysis

$$OH\cdot + NO \xrightarrow{M} HNO_2\cdot \tag{2}$$

requires other OH-sourced than (1) to account for the high HNO_2-concentrations observed at night. This is not likely in the dark unirradiated atmosphere (Harris et al., 1983).

Other mechanisms suggest direct reactions between NO, NO_2 and water vapor to form nitrous acid:

$$NO + NO_2 + H_2O \longrightarrow 2HNO_2 \tag{3}$$

$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3 \tag{4}$$
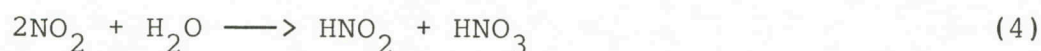
Since the homogeneous rate constant data found in the literature
for these reactions (Kaiser and Wu, 1977; Chan et al., 1976
England and Corcoran 1974, 1975) cannot explain the observed
rapid formation in ambient air, heterogeneous reaction
mechanisms have been suggested (Kessler et al., 1981; Perner,
1980). Therefore, the high NO_x-concentrations in urban air,
especially during wintertime inversion periods, and the relatively
low intensity of sunlight irradiation in northern Europe are
strong arguments for HNO_2 to occur in significant concentrations
and to be the predominant source of OH-radicals.

In this paper we present HNO_2-data from the period winter,
spring and early summer of 1983 (January - May). HNO_2 was
monitored as 12-hours mean values in the city of Gothenburg,
utilizing the denuder technique. The HNO_2 data were evaluated
together with data on NO-, NO_2- and O_3-concentrations as well
as on temperature and reltive humidity in order to investigate
the formation paths and the daylight decomposition of nitrous
acid.

Methods

All measurements were made on the roof of the air monitoring
station governed by the Gothenburg Board of Public Health,
20 m above street level in central Gothenburg.

HNO_2 was determined as 12-hours mean values by sampling from
18 to 6 and 6 to 18 hours local time, respectively. For the
sampling the sodiumcarbonate denuder technique, described in
detail by Ferm and Sjödin (1983), was used. Measurements were
made on weekdays, Monday to Friday, during the period mid of
January to late May, 1983.

A part of the sampling equipment is shown by Figure 1. For each 12-hours sampling period a sampling line consisting of three sodium carbonate denuders connected in series was used. Once a week eight such lines were mounted vertically inside the aluminum box with the denuder inlets outside pointing downwards. To avoid water vapour to condensate on the inside walls of the denuder followed by subsequent destruction of the thin sodium carbonate layer during sampling, the box air was heated well above ambient air temperature by means of a heating fan. Seven of the eight lines were connected to a sequential sampler consisting of a time-relay governing the eight magnetic valves, a vaccume pump with a critical orifice for establishing the sampling flow of about 2 liter per minute and a gasvolumemeter. The last unconnected line represented the blank.

After each sampling cycle, consisting of seven 12-hours samples, the denuders were sealed with Parafilm and brought to the laboratory. Each denuder was analysed for the nitrite content, adjusted for the corresponding blank using the Saltzman spectrophotometric method (Saltzman, 1954).

Since there are three denuders in series for each sampling, it is possible to correct for the artifact formation of nitrite that occurs probably on the glasswalls of the denuders during the sampling.

At a sampling rate of 2.1 liters per minute, ideally 96% of the incoming HNO_2 should be stuck in the first denuder. Obviously, not more than 4% should be seen in the second denuder. If there is more a correction must be made.

Expressed in terms of the nitrite content found in the first and in the second denuder, the corrected HNO_2 value then will be

$$[HNO_2]_{ambient} = 1.085[HNO_2]_{1st} - 1.04[HNO_2]_{2nd}$$

at a sampling rate of 2.1 liters per minute.

At the same station as the HNO_2-samples were taken, continuous measurements of NO, NO_2, O_3, relative humidity and temperature were also made. NO, NO_2 and O_3 were measured by chemiluminescence (Bendix and Meloy Labs). The ambient water vapor concentration was calculated from the measurements of relative humidity and temperature.

Results

The nitrite content found in each denuder, the 12-hours mean values of corrected, ambient HNO_2 and the corresponding values of NO, NO_2, H_2O and O_3 for the whole monitoring period are given in Table 1.

The HNO_2-values vary from below 1 nmole/m^3 up to 50 nmole/m^3. The highest value was observed during the night April 13-14 and reached 51.4 nmole/m^3. The lowest detectable value was 0.5 nmole/m^3. High values, above 30 nmole/m^3, seem to occur preferably on occasions with stagnant air, involving increased NO- and NO_2-levels. As showed by Table 1, the observed HNO_2-levels never exceed 50% of the equilibrium concentrations, calculated from the measured NO, NO_2, temperatur and humidity data and the literature value of the equilibrium constant (Chan et al., 1976) for reaction (3).

Since reaction (4) also might contribute to the formation of the observed HNO_2, the correlations between the HNO_2-concentration and some parameters, like NO , NO_2 and their products with water vapor concentration, were investigated at different NO to NO_2 ratios. From this the relative contribution of reaction (3) and (4) to the HNO_2-formation could be estimated. The results are presented in Table 2 and 3. From these calculations it can be seen, especially at high or moderate NO to NO_2 ratios, that the observed nighttime HNO_2 ocrrelates extremely well with NO, the product of NO-, NO_2- and water vapor concentration, and the calculated equilibrium concentration of HNO_2 from reaction (3) (c.f. Figure 2). Even if all night-values are taken into account

the correlation to $[HNO_2]_{eq}$ is as high as 0.845. The correlations of HNO_2 night means to NO_2 and $NO_2 \cdot H_2O$ were considerably weaker, espeically in the case of very high NO_2 to NO-ratios, i.e. very low NO-levels. For the daytime HNO_2, the correlations to other parameters are relatively weak as seen by Table 2 and 3.

Monthly mean values for the HNO_2-observations made at night and day, respectively, are presented in Table 4. It can be seen that the absolute levels do not differ very much between night and day, but relative to $[HNO_2]_{eq}$ the day levels are about one half of the night levels for January to April, and approximately only one third for the month of May. The highest montly mean is noted for January night observations.

Discussion

The accuracy in the determination of the ambient HNO_2 is lowered by the fact that nitrite, originating from other components than the ambient nitrous aicd, is formed in the denuder during sampling. This can be seen by the elevated nitrite content in the 2nd and 3rd denuder. As mentioned earlier, not more than 4-5% of the nitrite amount should be found in the second denuder, i.e. almost no nitrite should be found in the 3rd denuder at ideal conditions. Laboratory tests show that pure nitrous acid is absorbed according to the expected theory (Figure 3). The amount found in the second and third denuder, as an average when real ambient air is sampled, can also be seen by this figure. Despite the problems with artifact nitrite formation the reproducability of the method in most cases is better than 20-30% (c.f. Figure 4).

In order to investigate some of the mechanisms behind the sampling artifact, the correlations between the nitrite content in the 3rd denuder and some parameters were studied. The results are presented in Table 5 and 6. As in the case of the ambient HNO_2, especially at high NO/NO_2-ratios, there are strong correlations to NO and its product with NO_2 and water vapor. NO_2 alone does not seem to contribute very much to the elevated nitrite levels in the 3rd denuder. At very high

NO_2/NO-ratios or at NO-levels less than 40 nmole/m^3 the nitrite content in the 3rd denuder and the ambient HNO_2 never exceeds 1.0 nmole/m^3 and 4.0 nmole/m^3, respectively. If the artifact HNO_2, represented by the nitrite content in the third denuder, is plotted against the O_3-concentration as in Fgirue 5, it can be seen that O_3 appears to act as an inhibitor. Above 1 µmole/m^3 of ozone the production of HNO_2 in the 3rd denuder is less than 1-2 nmole/m^3. Since high O_3-concentrations correspond to low NO-concentrations and vice versa, it is not clear if this is a real inhibiting effect of ozone alone, or simply low NO-levels or both. However, the same mechanism seems to be responsible for the main part of the nitrite production that occurs in the denuder during sampling as for the observed ambient HNO_2. The strong correlation of these parameters to NO are arguments for reaction 3

$$NO + NO_2 + H_2O \longrightarrow 2HNO_2 \qquad (3)$$

to be the main contributor to the observed urban HNO_2 at night.

Several authors have investigated the kinetics of this reaction in laboratory experiments (England and Corcoran, 1975; Chan et al., 1976; Kaiser and "u, 1977). As seen by Table 7 the observed ambient HNO_2-levels i our and other measurements could be explained by heterogeneous reaction mechanism which has been suggested earlier (Perner and Platt, 1979; Kessler et al., 1981; Karris et al., 1982) Heterogeneous reactions would also account for the rapid formation of HNO_2 that seems to occur on the denuder walls during sampling.

Although the differences between the observed nighttime and daytime HNO_2 realtive to the calculated equilibrium values, as seen by Table 1 and 4, show that there is a daytime decomposition of nitrous aicd, the time resolution (12 hours) of our measurements is not suffcient to make estomations on the production rate of OH-radicals under varying conditions.

The sunlight intensity at daytime during the measurement period has neither been the subject for our investigations.

However, even in the month of January, when the time period between sunrise and sunset is not longer than 6-8 hours and the solar angle at noon is very low at our latitude, there seems to be a marked daytime decomposition of HNO_2. Since the rate of the thermal decomposition of HNO_2 (the backward reaction of (3)) and other possible sinks of HNO_2 should not depend on light conditions, the observed daytime decomposition could only be attributed to the direct photolysis:

$$HNO_2 + h\nu \longrightarrow NO + OH\cdot \qquad (1)$$

The observed variation in the degree of daylight decomposition of HNO_2 might then depend on the frequency and/or the thickness of the cloudlayers.

If the alternative photolytical process ($\lambda < 366$ nm)

$$HNO_2 + h\nu \longrightarrow H\cdot + NO_2 \qquad (5)$$

is considered to be almost negligible (Cox, 1974), and since there are more effective sinks for OH than the backward reaction of (1), there is a net production of hydroxyl radicals available for a variety of constituents in rapid reactions, possibly increasing the photochemical activity in the irradiated Gothenburg atmosphere. The role of HNO_2 as a possible photochemical promotor under different conditions in polluted air masses in Scandinavia will be the subject for further investigations.

Date	NO_2^--content in denuders resp. 1st.	2nd.	3rd.	Calculated ambient $[HNO_2]$	$[NO]$	$[NO_2]$	$[H_2O]$	$[O_3]$	T	$[HNO_2]_{eq.}$	$[HNO_2]$-ambient $/ [HNO_2]$-eq.
	nmole/m³			nmole/m³	μmole/m³	μmole/m³	mole/m³	μmole/m³	K	nmole/m³	
Jan 11	7.9	3.0	1.3	5.5	0.52	0.82	0.33	0.26	282	104.2	0.053
12	5.2	1.5	0.6	4.1	0.22	0.74	0.28	0.52	281	61.4	0.067
13	16.8	7.5	4.1	10.4	0.39	0.82	0.31	0.38	281	90.1	0.115
13-14	8.9	0.5	0.5	9.1	0.19	0.44	0.38	0.85	278	55.4	0.164
26-27	26.6	8.2	1.7	20.3	0.36	0.52	0.24	0.60	280	62.6	0.324
28	35.4	8.1	2.2	30.0	0.58	0.82	0.25	0.47	280	101.7	0.295
28-29	11.7	3.5	0.2	9.1	0.05	0.30	0.30	0.73	280	19.8	0.450
29	7.6	2.1	1.3	6.1	0.13	0.38	0.25	0.80	279	33.2	0.184
31-01	41.8	9.7	—	35.3	2.57	0.84	0.20	0.22	275	222.9	0.158
Feb 01	7.2	1.0	0.6	6.8	0.40	0.62	0.25	0.44	276	81.8	0.083
1-2	7.7	1.4	0.3	7.3	0.18	0.45	0.20	0.49	275	42.9	0.170
3	55.0	28.2	19.5	30.4	9.05	1.86	0.20	0.13	274	638.3	0.048
3-4	20.7	4.6	2.0	17.7	1.03	0.71	0.19	0.40	273	133.9	0.132
7-8	5.6	1.3	0.7	4.7	0.09	0.36	0.15	0.64	268	29.6	0.159
8	8.9	2.0	0.9	7.6	0.27	0.50	0.13	0.59	268	56.1	0.136
8-9	4.6	2.5	1.5	2.4	0.05	0.36	0.14	0.64	268	22.9	0.105
9	18.2	7.5	2.8	12.0	0.82	0.77	0.18	0.27	268	141.2	0.085
10	19.7	8.3	1.9	12.7	1.61	0.94	0.25	0.09	272	229.2	0.055
14-15	25.9	8.2	2.1	19.6	0.58	0.76	0.22	0.40	273	111.9	0.175
15	27.2	7.7	4.5	21.5	1.11	1.02	0.25	0.22	274	185.0	0.116
17-18	21.4	6.3	2.5	16.7	0.40	0.79	0.29	0.40	276	99.7	0.168
Mar 01	20.4	6.8	2.3	15.1	0.27	0.40	0.24	0.49	273	57.9	0.261
1-2	18.4	7.6	5.4	12.1	0.13	0.40	0.29	0.35	272	45.7	0.265
2	23.3	9.1	5.6	15.8	0.71	0.49	0.30	0.18	276	106.0	0.149
2-3	1.1	0.4	0.4	0.8	0.35	0.35	0.27	0.35	276	59.7	0.013
3	2.6	0.3	—	2.5	0.27	0.44	0.27	0.71	275	60.7	0.041
7-8	8.3	1.7	1.5	7.2	0.04	0.22	0.33	0.96	278	17.0	0.424
8	3.9	0.7	1.1	2.5	0.13	0.26	0.38	0.78	280	33.6	0.074
8-9	1.8	0.9	1.2	1.0	0.09	0.13	0.37	1.26	280	18.7	0.053
9	3.3	1.5	1.1	2.0	0.09	0.26	0.41	0.82	281	28.6	0.070
9-10	2.8	0.5	1.4	2.5	0.04	0.17	0.39	1.22	280	16.2	0.154
10	9.4	2.4	0.7	7.7	0.13	0.26	0.35	0.74	280	32.3	0.238
10-11	8.1	2.1	—	7.0	0.05	0.15	0.30	1.06	277	14.3	0.490
14-15	16.0	4.7	2.4	12.5	0.08	0.26	0.39	0.58	280	26.4	0.474
16	7.6	2.4	1.2	5.8	—	—	—	—	279	—	—
16-17	14.0	1.0	0.8	14.2	0.45	0.72	0.34	0.63	279	100.6	0.141
17	13.8	3.1	3.9	11.8	0.63	0.77	0.31	0.23	278	125.9	0.094
17-18	14.0	4.7	2.0	10.3	0.26	0.57	0.37	0.04	279	71.1	0.145
28-29	10.4	2.6	1.8	8.6	0.31	0.53	0.31	0.88	276	74.2	0.116
29	9.3	2.4	1.3	7.6	0.40	0.62	0.27	0.93	276	85.1	0.089
29-30	13.4	3.7	3.1	10.7	0.31	0.62	0.29	0.66	276	77.8	0.138
30	13.8	3.7	2.3	11.1	0.44	0.79	0.30	0.53	276	106.0	0.105

<u>Table 1.</u> Measured concentrations of HNO_2, NO, NO_2, H_2O and O_3 at the air monitoring station in central Gothenburg. The equilibrium concentrations of HNO_2 were calculated from NO, NO_2, relative humidity and temperature data and the equilibrium constant of reaction (3) reported by Chan <u>et al.</u> (1976).

Date	NO$_2^-$-content in denuders resp.			Calculated ambient							[HNO$_2^-$] ambient / [HNO$_2$]$_{eq.}$
	1st.	2nd.	3rd.	[HNO$_2$]	[NO]	[NO$_2$]	[H$_2$O]	[O$_3$]	T	[HNO$_2$]$_{eq.}$	
	nmole/m^3			nmole/m^3	μmole/m^3	μmole/m^3	mole/m^3	μmole/m^3	K	nmole/m^3	
Apr 05	12.4	2.6	1.6	10.8	2.38	0.88	0.22	0.71	277	216.8	0.050
5-6	6.2	2.0	1.4	4.6	0.22	0.53	0.25	1.10	276	56.0	0.082
6-7	3.7	1.6	1.6	2.4	0.52	0.57	0.28	1.13	280	85.0	0.028
7	9.9	4.0	1.6	6.6	0.62	0.86	0.34	0.74	278	131.8	0.050
7-8	2.8	1.2	1.2	1.8	0.04	0.48	0.31	1.32	277	24.7	0.073
11-12	29.1	5.3	2.6	26.1	0.79	1.23	0.28	0.57	277	166.7	0.157
12	4.9	3.0	3.2	2.2	0.62	0.84	0.21	0.88	277	105.4	0.021
12-13	12.2	1.9	1.5	11.3	0.09	0.71	0.23	0.71	276	40.3	0.280
13	18.3	3.4	2.4	16.3	0.75	0.66	0.22	0.71	276	108.5	0.150
13-14	62.1	15.4	5.4	51.4	2.57	1.20	0.23	0.27	275	285.5	0.180
14	45.1	6.9	4.1	41.8	3.06	1.22	0.31	0.48	279	326.3	0.128
14-15	21.5	4.2	1.9	19.0	0.17	0.79	0.35	0.79	280	64.0	0.297
18-19	5.6	1.5	1.7	4.5	0.04	0.40	0.34	1.33	283	19.1	0.236
19	4.6	2.6	1.7	2.3	0.20	0.65	0.30	1.14	286	49.2	0.047
19-20	3.2	1.5	0.7	1.9	0.03	0.31	0.29	1.46	284	13.6	0.140
20	14.0	4.8	3.0	10.2	0.78	1.09	0.35	0.54	280	161.0	0.063
20-21	21.0	9.4	2.8	13.0	0.52	0.85	0.30	0.43	278	113.0	0.115
21	6.9	2.0	1.4	5.4	0.65	0.59	0.32	0.85	283	94.8	0.057
21-22	2.1	1.1	0.9	1.1	0.43	0.29	0.30	1.68	286	47.9	0.023
26-27	29.7	11.2	3.2	20.6	0.65	1.27	0.40	0.29	283	155.2	0.133
27	11.0	4.5	2.0	7.3	0.43	0.54	0.42	1.04	287	75.4	0.097
27-28	1.8	0.8	0.8	1.1	0.02	0.25	0.39	1.54	285	11.5	0.096
28	2.9	1.0	0.8	2.1	0.27	0.67	0.40	1.09	283	72.5	0.029
28-29	5.1	1.3	1.1	4.2	0.06	0.54	0.37	1.36	283	29.6	0.142
May 02-3	2.7	1.4	1.0	1.5	<0.01	0.40	0.37	1.31	283	8.5	0.177
3-4	23.7	8.0	3.3	17.4	0.59	0.82	0.41	0.36	279	135.0	0.129
4	9.9	2.5	2.1	8.1	0.49	0.68	0.31	0.68	281	91.9	0.088
4-5	23.4	16.2	7.0	8.5	1.00	1.04	0.31	0.47	280	167.4	0.051
5	18.0	6.0	2.9	13.3	1.55	0.91	0.25	1.05	281	170.1	0.078
16-17	21.8	3.4	2.2	20.1	0.08	0.62	0.62	0.63	288	41.3	0.487
18	29.2	3.3	1.0	28.3	1.18	0.92	0.52	0.63	288	176.3	0.161
18-19	1.4	1.0	1.2	0.5	<0.01	0.28	0.42	1.87	284	8.3	0.060
19	2.9	2.4	1.5	0.7	0.10	0.60	0.46	1.68	288	39.2	0.038
24-25	3.3	0.1	0.9	3.5	<0.01	0.39	0.34	1.65	287	7.6	0.461
25	4.1	2.2	2.7	2.2	0.13	0.80	0.32	1.00	287	43.8	0.050
25-26	2.5	0.0	0.4	2.5	<0.01	0.31	0.46	1.52	288	7.4	0.338
26	6.8	4.8	3.1	2.4	0.22	0.79	0.43	0.73	287	66.0	0.036
26-27	12.6	0.4	0.7	13.3	0.06	0.55	0.53	0.88	286	59.5	0.224

Table 1. continued.

x_2	r_2			
	night values		no restrictions (n=43)	day values
	$q_2>1.00$ (n=4)	$q_2>0.500$ (n=17)		no restrictions (n=36)
[NO]	0.948	0.831	0.806	0.595
[NO]·[NO$_2$]·[H$_2$O]	0.982	0.857	0.829	0.598
[HNO$_2$]eq	0.990	0.879	0.845	0.686

Table 2. Correlation coefficients (r_2) for the plots of ambient [HNO$_2$] against the parameters x_2, calculated with different restrictions in the ratio [NO]/[NO$_2$] (q_2).

x_3	r_3			
	night values		no restrictions (n=43)	day values
	$q_3>10.0$ (n=8)	$q_3>2.00$ (n=27)		no restrictions (n=36)
[NO$_2$]	0.441	0.645	0.745	0.599
[NO$_2$]^2·[H$_2$O]	0.389	0.773	0.615	0.611

Table 3. Correlation coefficients (r_3) for the plots of ambient [HNO$_2$] against the parameters x_3, calculated with different restrictions on the ratio [NO$_2$]/[NO] (q_3).

Month	$[HNO_2]$ nmole/m^3		$[HNO_2]/[HNO_2]_{eq}$	
	day	night	day	night
January	11.2	18.5	0.143	0.277
February	15.2	11.4	0.087	0.152
March	8.2	7.9	0.125	0.219
April	10.5	11.6	0.069	0.142
May	9.2	8.4	0.075	0.241
Period mean + standard deviation	10.5±9.3	10.7±10.2	0.097±0.065	0.194±0.134

Table 4. Monthly means of the observed HNO_2: Absolute values and values related to the calculated equilibrium concentrations according to reaction (3). K_3-data from Chan et al. (1976).

x_5	r_5			
	night values			
	$q_5 > 1.00$ (n=3)	$q_5 > 0.500$ (n=16)	no restrictions (n=42)	all values (n=75)
$[NO]$	0.999	0.913	0.880	0.852
$[NO] \cdot [NO_2] \cdot [H_2O]$	0.996	0.920	0.891	0.862

Table 5. Correlation coefficients (r_5) for the plots of the amount of nitrite in the 3rd denuder against the parameters x_5 with different restrictions in the ratio $[NO]/[NO_2]$ (q_5).

x_6	r_6		
	night values		
	$q_6 > 10.0$ (n=8)	$q_6 > 2.00$ (n=35)	all values (n=75)
$[NO_2]$	0.471	0.402	0.660
$[NO_2]^2 |H_2O|$	0.410	0.384	0.590

Table 6. Correlation coefficients (r_6) for the plots of the amount of nitrite in the 3rd denuder against the parameters x_6 with different restrictions in the ratio $[NO_2]/[NO]$ (q_6).

$|NO|$ $\mu mol\ m^{-3}$	HNO_2-formation rate $nmol\ m^{-3}hr^{-1}$		Ref.
	observed in this study*	calculated from literature	
		0.001	1
0.1	0.1-1.7		
		0.01	2
		0.01	1
1.0	0.7-2.2		
		0.11	2
		0.04	1
3.0	2.1-4.3		
		0.33	2

Table 7. Estimated formation rates of HNO_2 according to reaction 3 at different NO-concentration. $[NO_2]$ = 1 $\mu mol/m^3$ and RH = 75%. References: 1 = Chan et al., 1976, 2 = England and Corcoran, 1975.

*) at NO-, NO_2 and RH-levels approxiamte to the ones listed.
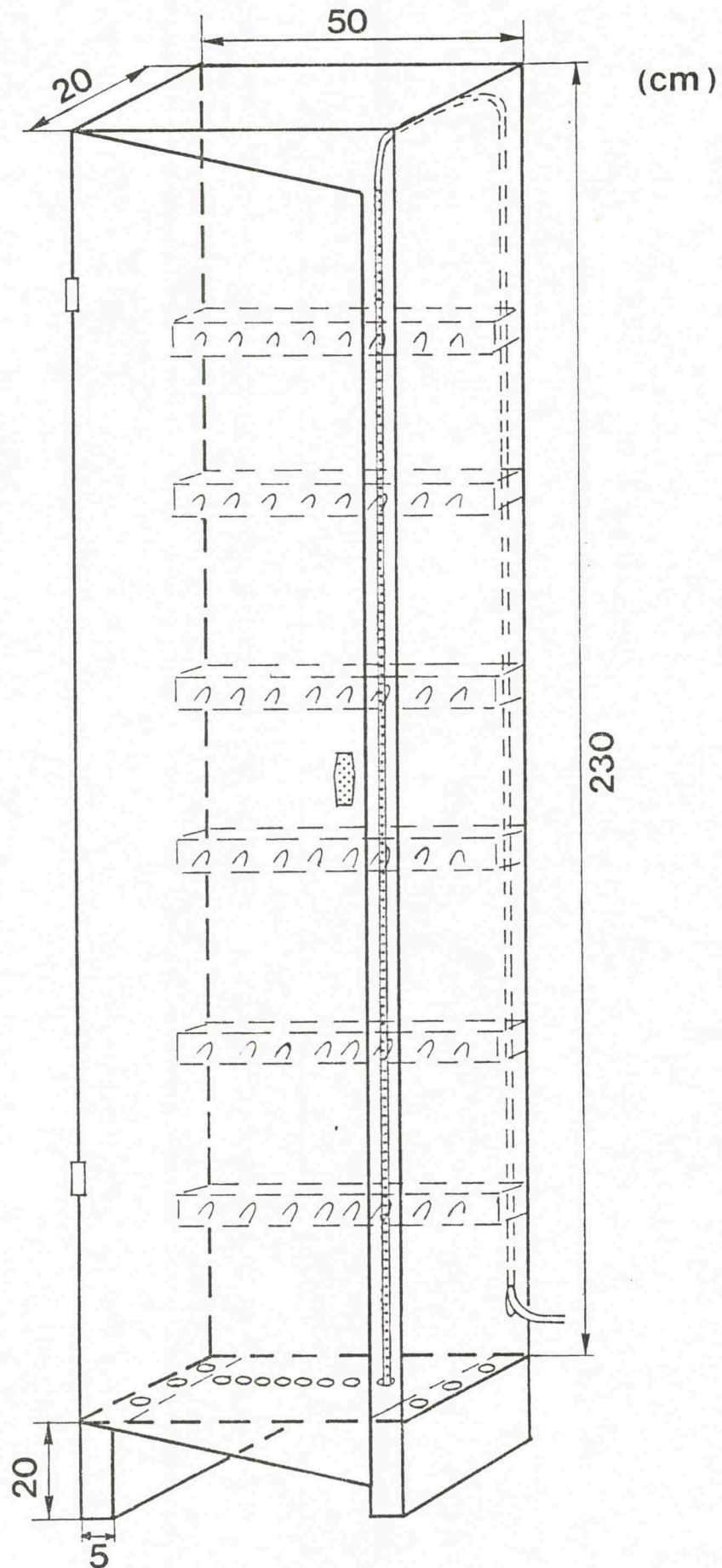
Figure 1. Isolated aluminumbox in which denuders are mounted
and heated over ambient temperature, during sampling.
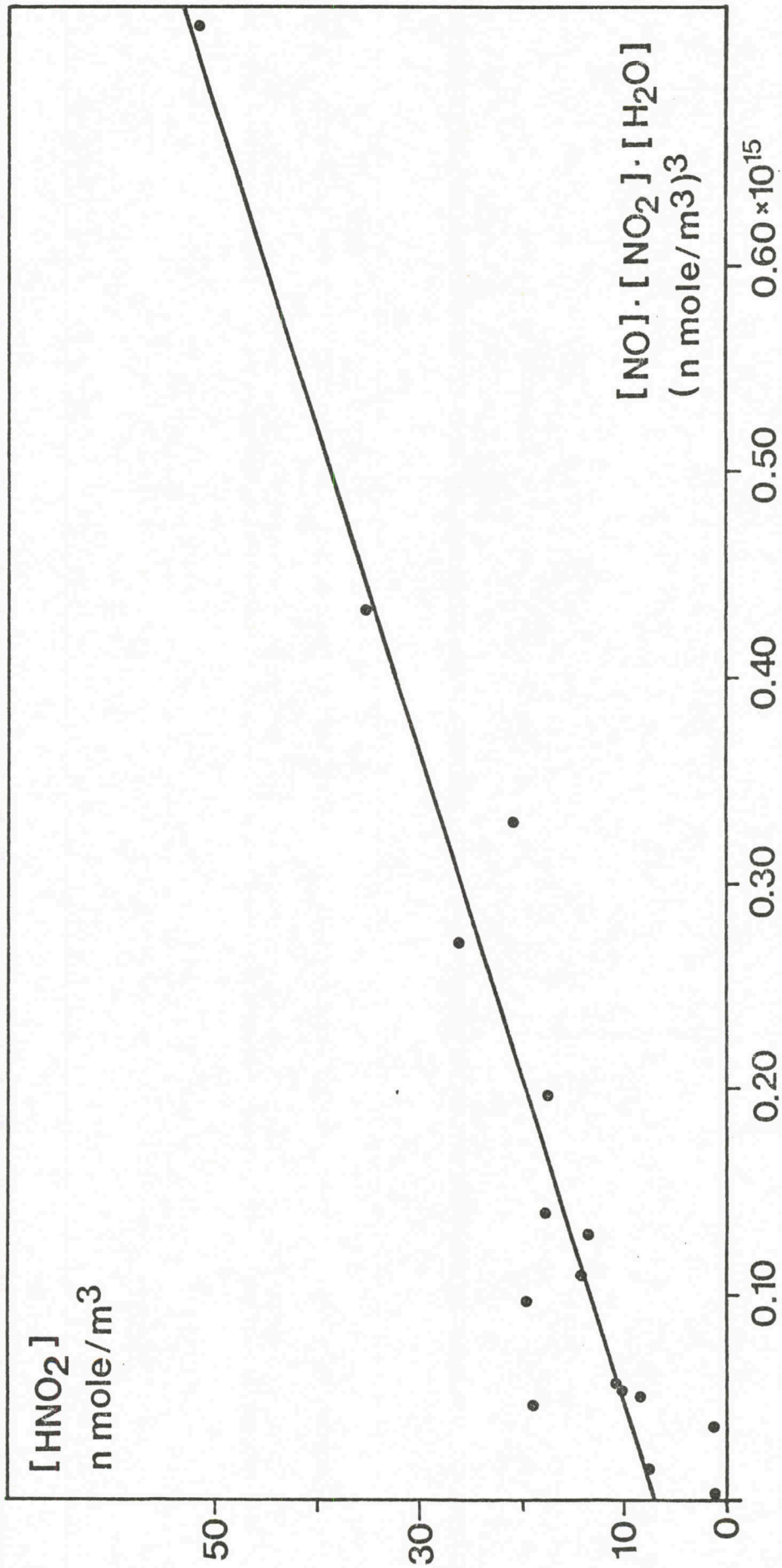
Figure 2. Observed ambient HNO_2 mean concentrations at night as a function of $[NO] \cdot [NO_2] \cdot [H_2O]$ at NO/NO_2-ratios exceeding 0.50
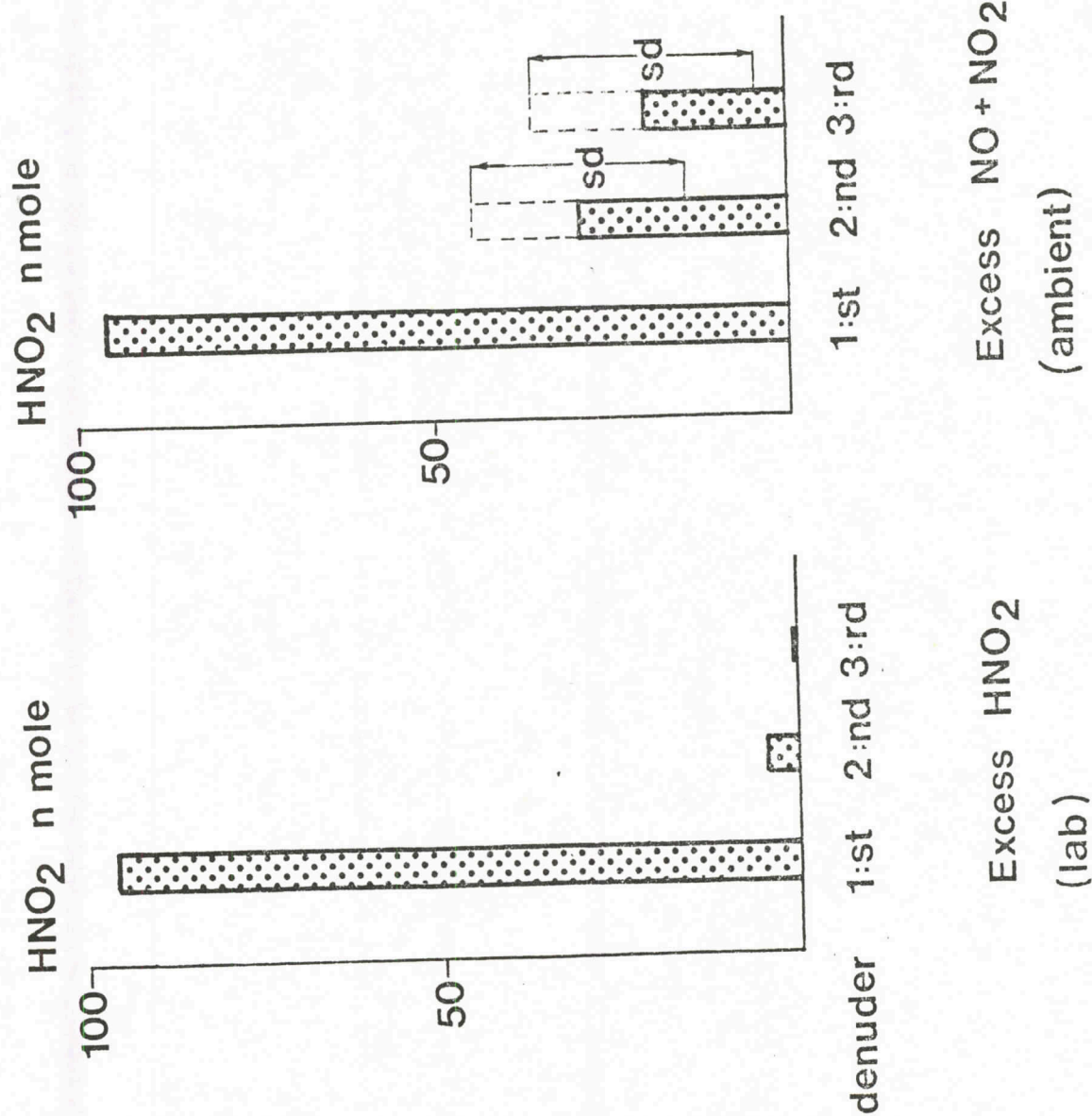
Figure 3. Distribution of sorbed HNO_2 in a sampling line consisting of three sodium carbonate denuders in series at ideal (excess HNO_2) and ambient conditions.
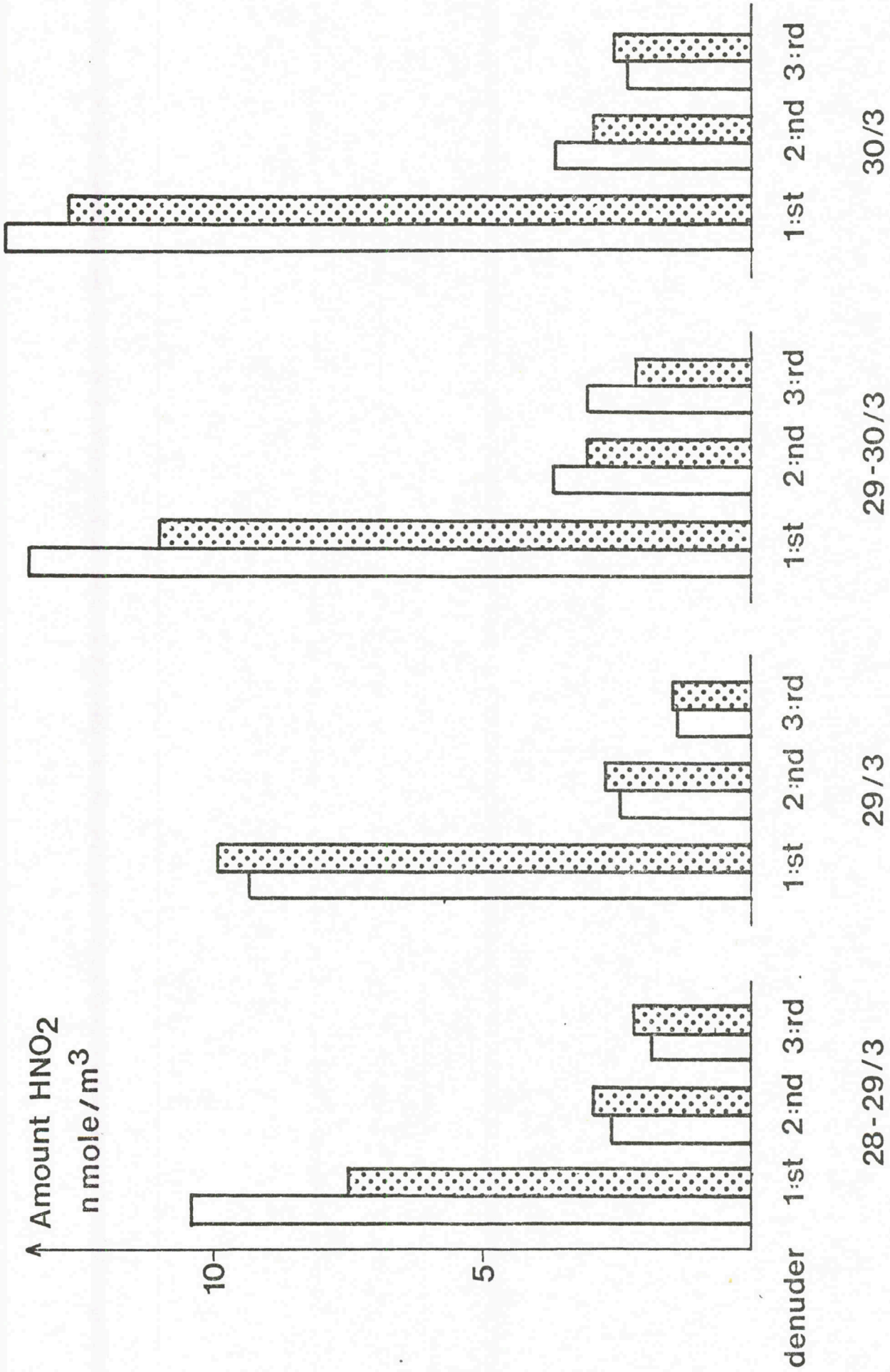
Figure 4. Reproducability within the method. Results from parallell sampling of HNO_2 using three sodium carbonate denuders in series.
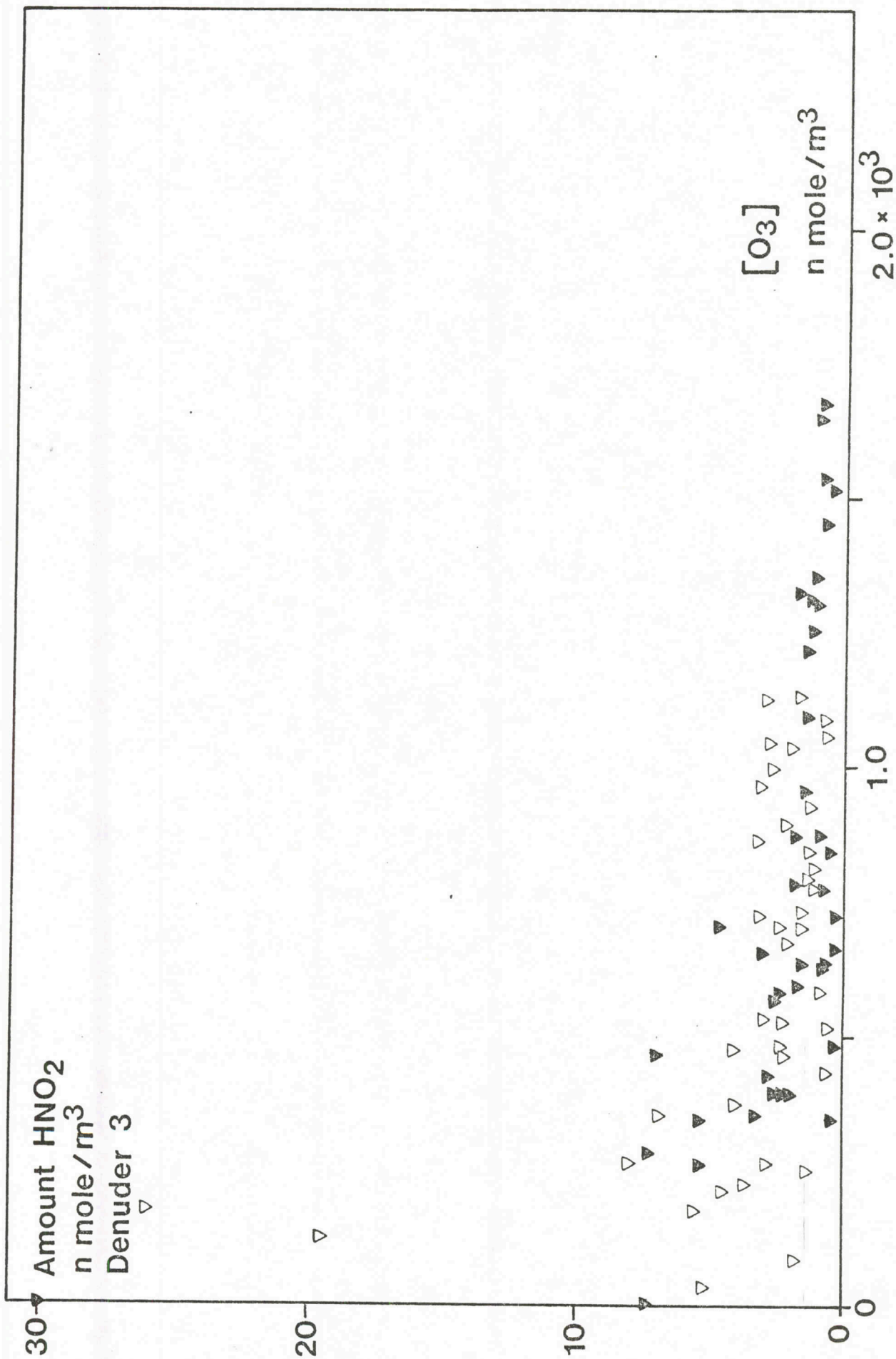
Figure 5. Observed nitrite content in the 3rd denuder expressed in nmole/m^3 as a function of ambient O_3 concentrations.

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