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EVALUATION OF A DENUDER METHOD FOR AMBIENT NO₂ MEASUREMENTS AT PPB LEVELS

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A thorough investigation on the denuder method for ambient NO₂ determination, based on the reaction with phenoxide ions has been made. A thermostatted sampling unit comprising an annular denuder coated with alkaline eugenol and a nylon pre-filter has been found to be suitable for ensuring quantitative sample collection and preventing interferences from nitrous acid as well as from gaseous and particulate nitrate. Results of laboratory and field tests concerning the effect of humidity on collection efficiency, the oxidation of nitrite on the wall by O₃/oxidants and the reliability of the method are reported and discussed.

KEY WORDS : annular denuder, nitrogen dioxide, alkaline eugenol, ion chromatography.

INTRODUCTION

NO₂ plays an essential role in the acid deposition chemistry as well as in the photochemistry of the atmosphere. Its concentrations levels, however, rarely exceed 10 ppb in relatively unpolluted areas, where monitoring receptor sites are located. Commercial chemiluminescent analyzers based on the catalytic reduction of NO₂ to NO prior to reaction with ozone offer a detection limit of a few ppb for NO₂; then, they are of limited significance in remote environments. In addition, other nitrogenous species, like HNO₂, HNO₃ and peroxyacetyl nitrate (PAN), interfere in the NO₂ measurements¹⁻³.

A more selective technique to convert NO₂ to NO involves UV photodissociation, which prevents interferences from HNO₃ and PAN and allows to achieve a higher sensitivity with the reaction chamber operating at reduced pressures⁴. The determination of NO₂ by its chemiluminescent reaction with luminol is a rapid and sensitive system of measuring NO₂, although it is still subject to O₃ and PAN interferences⁵. Moreover, several corrections are necessary in order to obtain accurate NO₂ data at low concentrations, where a non linear response has been found⁶.

In routine measurements the real-time NO₂ readings produced by spectrochemical

analyzers must be integrated over a suitable time period. Therefore, when one needs NO₂ concentrations averaged over 12 or 24 hours, the availability of simple and reliable integration techniques appears convenient. In particular, the coupling of denuder sampling and ion chromatographic analysis offers undeniable advantages in terms of collection efficiency and detection limit⁷.

The performances of alkaline guaiacol-coated annular denuders for NO₂ collection have already been outlined⁸ and confirmed in a recent investigation⁹. Nevertheless, when analyzing the results of several field measurements of NO₂ by denuder, we observed that a fraction of nitrite produced by reaction of NO₂ with phenoxide ions, was converted to nitrate during sampling. Oxidation was primarily observed (20-50%) during long sampling periods (24 h or more) in summertime, when the occurrence of photochemical pollution episodes was frequent.

Whenever nitrite plus nitrate have to be taken into account to calculate NO₂ concentration, the latter may be overestimated if gaseous and particulate nitrate are not selectively removed upstream of the denuder. For this reason we placed a nylon filter in front of a denuder coated with alkaline eugenol (4-allyl-2-methoxyphenol) to collect NO₂. This sorbent was chosen to reduce nitrite oxidation by taking advantage of the ozone attack to olefinic bond in allyl groups¹⁰.

Results of laboratory tests and field experiments carried out to evaluate the performances of this NO₂ sampler are discussed below.

EXPERIMENTAL

Apparatus

Pyrex annular denuders, 22 cm in length, 1.0 and 1.3 cm in annulus diameters, were used as NO₂ sampling devices. Inner and outer walls of the annular space were sandblasted for better retention of the coating solution and larger loading capacity. Coating was achieved with a 5% eugenol - 2.5% NaOH (w/v) methanolic solution. A smooth coating film was obtained by passing clean air through the denuder to facilitate solvent evaporation.

Filter papers (47 mm Whatman No. 41) and nylon filters (47 mm Gelman Nylosorb, 1 μm pore size) were washed with deionized water and carbonate buffer prior to water, respectively. After drying the former were impregnated with 2% Na₂CO₃- 1% glycerol (w/v) solution and dried in a vacuum desiccator; the latter were kept in a desiccator until used.

A temperature-controlled permeation tube and a variable-current mercury lamp in a gas-phase dilution system (Monitor Labs, Model 8500) were used as NO₂ and O₃ sources, respectively.

Clean dry air carrying NO₂ and/or O₃ was diluted in a mixing chamber with additional air at varying humidities and flowrates. Relative humidity (rel.hum.) was adjusted to 30-60% either by passing the air through a silica gel bed or using room air humidity. High humidities (rel.hum. >85%) were obtained by drawing pre-humidified air through a tube of wet cotton wool. Rel.hum. values were determined with a Digitek hygrometer Model DP4.

Field samples were collected with a sampling train consisting of a nylon filter inserted

in a PTFE filter holder and two alkaline eugenol-coated denuders, in sequence. Connections were realized with threaded PTFE couplers.

The sampling train was contained in a metal case thermostated at 27°C to avoid water condensation on denuder walls and subsequent dripping of the coating layer. The sampling unit was operated by an electronically controlled sequential sampler (Sequair 92, Gruppo Flow). All samples were collected at Montelibretti (30 km NE of Rome) between November 1990 and March 1991.

Procedure

Nylon filters were extracted for 20 min in an ultrasonic bath with ion chromatographic eluant (3 mM NaHCO₃/2.4 mM Na₂CO₃). Na₂CO₃/glycerol-coated Whatman No. 41 filters as well as NaOH/eugenol-coated denuders were extracted with deionized water.

A Dionex ion chromatograph Model 4000i equipped with a 250 mm x 4 mm I.D. HPLC-AS3 column and interfaced to an IBM AT Personal Computer was used to determine NO₂⁻ and NO₃⁻ in all extracts.

RESULTS AND DISCUSSION

NO₂ Collection efficiency

The collection efficiency, *E*, of NO₂ in an alkaline eugenol-coated annular denuder was checked at different air flow rates by sampling dry and humidified atmospheres of NO₂. Measurements of NO₂ upstream and downstream of the denuder were performed with a NO_x chemiluminescence analyzer (Environnement, France, Model AC30M). The signal of this analyzer was found not to be affected by the presence of eugenol vapours in the air stream, whilst several tests provided evidence of their negative interference in NO₂ detection by a luminol-based chemiluminescence monitor (Luminox Model LMA-3, Scintrex, Canada).

Table 1 Efficiency (*E*%) of NO₂ removal for alkaline eugenol-coated annular denuders (22 cm in length, 1.0 cm and 1.3 cm in annulus diameters). T: 20°C; test duration: 1 h

NO ₂ conc. (ppb)		Air flowrate (l min ⁻¹)	E%		Rel. hum. (%)
upstr.	downstr.		exp.	calc.	
195-198	1-2	4.3	98.2	99.4	35
110-113	5-6	7.5	95.1	95.0	35
197-199	2-3	4.3	98.7	99.4	60
114-117	7-8	7.5	93.5	95.0	60
196-200	6-10	4.3	96.0	99.4	>85
112-115	12-17	7.5	87.2	95.0	>85

Table 2 Nitrite-to-nitrate oxidation on alkaline eugenol- and guaiacol-coated annular denuders during NO₂ absorption in the presence of ozone.

NO ₂ conc. (ppb)	O ₃ conc. (ppb)	NO ₂ ⁻ (μg)		NO ₃ ⁻ (μg)		α(%)	
		AE	AG	AE	AG	AE	AG
120	60	48.0	46.1	1.0	2.3	1.6	3.6
120	180	46.3	44.5	2.7	6.1	4.0	9.2
120	360	44.5	42.3	4.7	10.3	7.3	16.4

T = 20°C. rel.hum., 50-55%; air flow rate, 2 l min⁻¹; test duration, 1 h. AE = alkaline eugenol; AG = alkaline guaiacol; α, conversion factor.

At rel.hum. ranging from 35 to 60% the denuder was very effective in NO₂ removal and rel.hum. variations had no effect on collection efficiency. The experimental data of Table 1 agree nicely with those calculated from the equation found for alkaline guaiacol-coated denuders⁸.

A considerable increase in humidity (rel.hum. >85%) decreased the retention of NO₂ after 1 hour, possibly because of coating losses.

In all chromatograms only a nitrite peak was observed, indicating a NO₂ gas to NO₂⁻ ion stoichiometric factor equal to unity.

Loading capacity

The operative capacity of a denuder depends both on the operative conditions and the initial value of E¹¹. Particularly, it increases sharply with the initial denuder efficiency. We measured the breakthrough loading of NO₂ at a flowrate (2 l min⁻¹) ensuring asymptotic conditions (E > 99.9%) with a dry (rel.hum., 30-35%) air-NO₂ mixture. Continuous measurements of denuder effluent showed that more than 270 μg of NO₂ were absorbed without a detectable increase in the NO₂ analyzer signal. Furthermore, 660 μg of NO₂ were collected on the denuder until the efficiency dropped to 95.0% of the initial value.

Blank and sample stability

Three coated denuders were extracted and analyzed; another set was capped immediately and extracted after one week. In all samples, blank values of nitrite (as well as nitrate) were below the detection limit of the analytical method (0.02 μg NO₂⁻ per ml) corresponding in principle to a minimum detectable concentration in air of 0.1 μg NO₂ m⁻³ for 12 h sampling at 3 l min⁻¹. In addition, neither nitrite losses nor overlapping degradation peaks were observed in chromatograms of extracts stored in the dark and analyzed one week after denuder exposure to NO₂.

Nitrite oxidation

The occurrence of nitrite-to-nitrate conversion due to ozone during sampling was tested by exposing two annular denuders, coated with alkaline eugenol (AE) and alkaline guaiacol (AG), respectively simultaneously for 1 h to O_3 (60-360 ppb)/ NO_2 (120 ppb)/air mixtures. The results of this experiment are summarized in Table 2. As expected, the percentage of nitrite-to-nitrate conversion increased with O_3 concentration, especially on the guaiacol coating. A conversion factor, α was calculated on a molar basis from the ratio between nitrate and nitrate plus nitrite. Since nitrite oxidation also occurred, although to a lesser extent, on the alkaline eugenol coating, we decided to remove interfering gaseous and particulate nitrate during field NO_2 measurements by placing a nylon filter in front of the denuder¹². Nylon also exhibits a substantial activity in collecting nitrous acid (see below).

PAN interference

Results of a detailed study on PAN absorption as nitrite in alkaline eugenol-coated annular denuders indicated some removal of PAN (6-8%) at 3 l min^{-1} on denuders of the same size as those used here¹³.

Advantages and limitations of nylon filters

Nylon is a perfect sink for HNO_3 and a fair sorbent for HNO_2 . A collection efficiency of 80% was measured¹⁴ at 2 l min^{-1} for HNO_2 on nylon filters and a progressive conversion of nitrite to nitrate was observed in the presence of ozone^{14,15}. Due to its reversible absorption on nylon, HNO_2 may be partially blown off the filter before a substantial oxidation takes place.

In order to roughly estimate how much atmospheric HNO_2 is retained on nylon filters, we used two filter packs in parallel samplings of ambient air at 3 l min^{-1} for 18 h. Each filter pack contained a NaCl-impregnated filter (to collect HNO_3 and nitrate particles without affecting the passage of HNO_2 and NO_2)⁷ and a Na_2CO_3 /glycerol coated paper filter (Whatman No. 41) to collect HNO_2 escaped from a nylon filter placed in between. One of the two samplers was preceded by an eugenol-coated annular denuder to quantitatively trap atmospheric ozone and transmit HNO_2 and NO_2 . After sampling, the mass distribution of nitrite and nitrate on the last two filters of each line was examined. In the absence of ozone, nitrate was negligible compared to nitrite on both filters; however, only 27% of total nitrite ($4.8 \mu\text{g}$) was found on the nylon filter. In the presence of ozone (up to 40 ppb), the nitrite to nitrate ratio was inverted, but 74% of the $NO_2^- + NO_3^-$ amount was found on the nylon filter. Anyway, due to the high NO_2/HNO_2 concentration ratios usually encountered in non-urban atmospheres, the partial and variable uptake of HNO_2 by nylon filters should not present a problem for NO_2 determination by the denuder technique.

It is worth noting that NO_2 is slightly absorbed on nylon filter¹⁴ with a surface removal constant on the order of $1 \cdot 10^{-4} \text{ ms}^{-1}$. Supposing that 10 ppb of NO_2 is passed through a nylon filter for 24 h, interfering nitrite plus nitrate (as NO_2^-) would be $0.2 \mu\text{g}$. This means a NO_2

loss of only 0.25% at a 3 l min⁻¹ sampling flow rate.

On the basis of experimental results, nylon filters were preferred to Na₂CO₃/glycerol-coated Whatman No. 41 filters to discriminate between NO₂, and HNO₂ plus HNO₃. Although HNO₂ is irreversibly absorbed on Na₂CO₃/glycerol-coated surfaces, where NO₂ is still less retained than on nylon, the concomitant absorption of SO₂ as sulphite can cause a remarkable increase in NO₂ retention¹⁶. This interaction does not take place on nylon, where SO₂ is poorly retained and partially converted to sulphate^{17, 18}.

Field testing

Several NO₂ field measurements were made to check the denuder behaviour under variable meteorological conditions.

A first series of experiments (Table 3) involved the running of two parallel sampling trains, of which one was not thermostatted, to verify the effect of humidity condensation on NO₂ collection efficiency. NO₂ collection efficiency of unheated denuders was found to be strongly dependent on humidity, while thermostatted denuders were not appreciably affected by high rel.hum. values and showed efficiencies approaching those obtained in laboratory tests.

The oxidation of nitrite to nitrate did not proceed to a significant extent in wintertime; values of the conversion factor, α , varying from 0.8 to 4.1% were measured on the first denuder, while nitrate was never detected on the second denuder.

In a second series of measurements, performed at 2-3 l min⁻¹ with thermostatted units, parallel samples were taken to assess the reproducibility and reliability of the method. Table 4 shows the results of the analysis of 14 duplicate samples. A relative standard deviation of $\pm 7.6\%$ was obtained with these data.

NO₂ concentrations resulting from 24-h samplings were also compared with those averaged from two consecutive 12-h samplings. The results, expressed as a ratio, R, between

Table 3 NO₂ removal field tests with two pairs of alkaline eugenol-coated annular denuders running in parallel

Exp.No.	Unit	Date	Hours	Air Flow (l min ⁻¹)	Rel.hum (%)	Temp. (°C)	Ion Content (μg)			E%		$\alpha\%$
							1st den NO ₂ ⁻	2nd den NO ₂ ⁻	NO ₃ ⁻	meas.	calc.	
1	A*	26-27.11.90	18.00-20.00	7.0	83-100	9-16	39.6	1.6	9.9	75.7	96.0	2.9
	B			7.1			58.2	2.2	3.7	93.6	95.8	2.7
2	A*	28-29.11.90	13.00-12.00	6.3	65-100	6-13	125.4	1.7	25.9	79.5	97.1	1.0
	B			6.3			166.9	1.8	10.8	93.6	97.1	0.8
3	A*	03-04.12.90	12.00-12.00	4.2	37-68	0.10	132.6	3.2	1.3	99.0	99.6	1.8
	B			3.9			169.9	4.4	1.4	99.2	99.5	1.9
4	A*	05-06.12.90	15.00-09.00	3.5	48-98	-3-6	69.2	4.0	7.6	89.6	99.8	4.1
	B			3.0			75.3	2.7	1.0	98.7	99.9	2.6
5	A*	06-07.12.90	16.00-10.00	5.2	43-90	2-7	120.4	1.7	10.0	92.7	98.6	1.0
	B			4.9			114.8	3.3	3.5	97.0	98.9	2.0
6	A*	09-10.12.90	16.00-10.00	7.3	66-100	6-10	128.0	5.2	21.2	84.0	95.5	2.9
	B			7.5			159.6	7.9	8.6	94.8	95.0	3.5
7	A*	12-13.12.90	16.00-10.00	10.1	42-67	2-7	254.3	7.7	35.3	87.0	90.2	2.2
	B			10.1			275.5	10.5	29.9	89.5	90.2	2.7

* = not thermostatted

Table 4 Duplicate measurements of NO₂ concentrations in air with two thermostatted annular denuder systems operating in parallel at 2 l min⁻¹.

Date	Sampling interval (h)	NO ₂ conc. (µg ⁻³)	
		Unit A	Unit B
16-17.12.90	16.00-10.00	21.3	22.9
18-19.12.90	16.00-10.00	16.2	17.9
20-21.12.90	16.00-10.00	18.1	21.0
08-09.01.91	16.00-10.00	27.0	25.7
10-11.01.91	16.00-10.00	23.8	22.5
14-15.01.91	16.00-10.00	11.8	14.4
15-16.01.91	16.00-10.00	28.2	25.2
22.01.91	08.00-20.00	14.0	16.2
26.01.91	08.00-20.00	17.7	18.5
31.01.91	10.00-19.00	20.4	18.6
03.02.91	10.00-20.00	23.2	20.6
09.02.91	08.00-17.00	12.4	13.8
18.02.91	08.00-18.00	26.5	24.1
26.02.91	08.00-18.00	15.2	17.0

Table 5 Effect of sampling duration on NO₂ denuder performance and influence of photochemical oxidants on nitrite-to-nitrate conversion.

Date	Unit	Sampling time hours	NO ₂ (ppb)	R 2A/(B ₁ +B ₂)	α (%)	O ₃ max (ppb)	PAN max (ppb)
March 1991							
19/20	A	19.00-19.00	11.5		6		
19/20	B ₁	19.00-07.00	13.4	1.03	4	10	1.5
20	B ₂	07.00-19.00	8.9		10	49	3.1
20/21	A	19.00-19.00	13.5		3		
20/21	B ₁	19.00-07.00	14.1	1.05	-	26	1.6
21	B ₂	07.00-19.00	11.7		10	57	5.8
21/22	A	19.00-19.00	8.7		10		
21/22	B ₁	19.00-07.00	10.6	1.07	6	8	1.1
22	B ₂	07.00-19.00	5.6		10	42	1.6
22/23	A	19.00-19.00	6.0		9		
22/23	B ₁	19.00-07.00	6.3	1.09	4	23	0.8
23	B ₂	07.00-19.00	4.7		8	40	1.2
23/24	A	19.30-19.30	8.7		7		
23/24	B ₁	19.30-07.30	12.7	0.94	3	9	1.0
24	B ₂	07.30-19.30	5.8		12	47	1.9
24/25	A	19.30-19.30	6.3		5		
24/25	B ₁	19.30-07.30	6.0	0.98	4	18	0.6
25	B ₂	07.30-19.30	6.9		10	39	0.8
25/26	A	20.00-20.00	5.2		8		
25/26	B ₁	20.00-08.00	4.6	0.98	3	12	0.4
26	B ₂	08.00-20.00	6.0		9	34	0.7

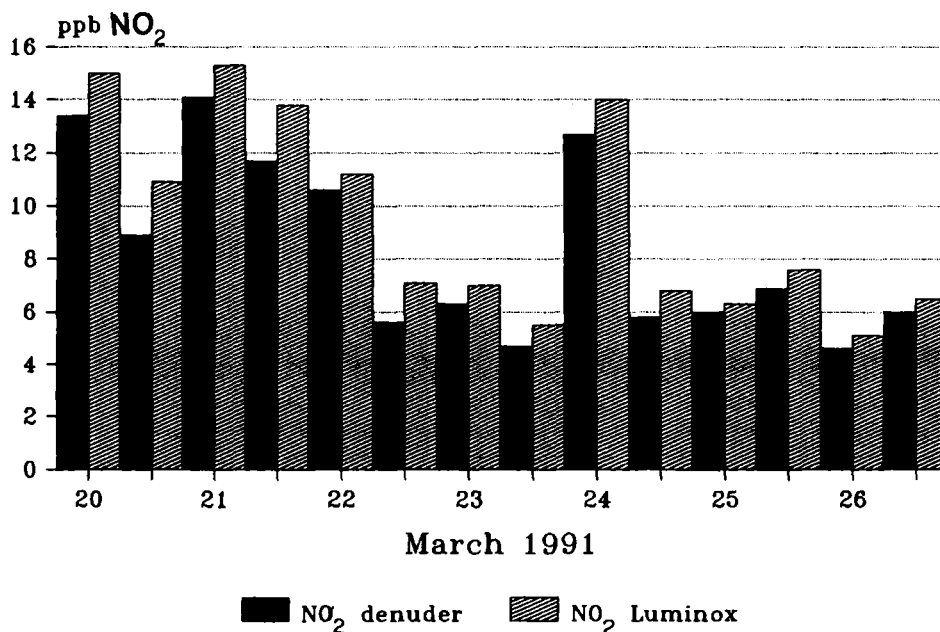


Figure 1 12-h NO₂ concentrations measured in parallel by denuder and LMA-3 Luminox techniques at Montelibretti (Rome).

the extended period and consecutive half-periods, are shown in Table 5. The reliability of the method for 24-h sampling clearly emerges from the R values of around unity. Table 5 also emphasizes an appreciable increase in α values compared to those listed in Table 3, although they did not exceed 12% in the daytime. This fact was ascribed to the presence of higher levels of photochemical oxidants. O₃ and PAN reached hourly maxima of 57 and 6 ppb, respectively, during the week 20-26 March 1991.

Finally, Fig. 1 gives a comparison between 12-h concentrations of NO₂ measured by denuder (DEN) and the corresponding integrated values provided by the Luminox monitor (LUM). The equation for the regression line, expressed in ppb, was: $[\text{NO}_2]_{\text{DEN}} = 0.90 [\text{NO}_2]_{\text{LUM}} - 1.6$. The two methods were highly correlated ($r = 0.99$) in the 5-15 ppb NO₂ range, with the Luminox results averaging 12% higher than those by denuder.

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