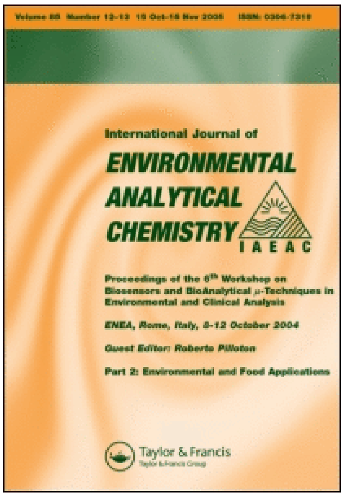

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MEASUREMENT OF ATMOSPHERIC NITRIC ACID IN GAS PHASE AND NITRATE IN PARTICULATE MATTER BY MEANS OF ANNULAR DENUDERS

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A denuder technique for the determination of nitric acid and particulate nitrate is described. The technique relies on the use of four annular denuders set in series followed by a downstream filter-pack, and allows the reliable and accurate measurement of gaseous nitric acid, coarse nitrate and fine nitrate, even in the presence of high concentration levels of other nitrogen gaseous species and in case of high particulate to gaseous phase ratio. Field data collected by using the described system in extreme conditions, ranging from very polluted areas to extremely remote sites, are discussed. The data are analyzed in terms of mass distribution of the analyte on the different stages of the set-up; time resolution, minimum detectable concentration and precision of the measurements are also discussed.

KEY WORDS: Atmospheric pollution, diffusion techniques, annular denuders, nitric acid, particulate nitrate.

INTRODUCTION

The measurement of the air concentration of nitric acid is a fundamental step for the comprehension of the atmospheric mechanisms which regulate secondary atmospheric pollution. Some specific characteristics of this species, in fact, make it an essential link in several pollution mechanisms:

- due to its high deposition velocity and its solubility in water, nitric acid is a main component of acid dry and wet deposition;
- due to its equilibrium with ammonium nitrate, which is regulated by the thermodynamic conditions, nitric acid can be transported to very long distances under the form of particulate nitrate and then released again into the gaseous phase; thus, high nitric acid concentrations can be measured also in areas which are relatively far from primary pollution sources;

- due to its formation pathway, which is mainly the homogeneous reaction between nitrogen dioxide and the OH radical, nitric acid is involved in photochemical air pollution as a fundamental link in the chain which connects the primary emitted NO to the final oxidation product NO^-_3.

For these reasons, the accurate and precise measurement of gaseous HNO_3 and particulate NO^-_3 is necessary for a correct interpretation of pollution field data; thus, a measuring technique which does not disturb the partitioning of these compounds existing in the atmosphere at the time of the sampling is essential.

The existing measuring techniques for HNO_3, developed in the last decades, can be grouped into three main categories: i) direct spectroscopic systems; ii) filter-pack accumulation methods; iii) denuder accumulation methods.

The techniques of the first group, which include the long path Fourier transform IR spectrometry (FTIR)[1] and the tunable diode laser absorption spectrometry (TDLAS)[2], are generally considered as an absolute approach. However, both techniques are obviously unable to measure particulate nitrate; in addition, FTIR suffers from a still too high detection limit (4 ppb) which prevents its use in most areas[3], while TDLAS results can be heavily biased by losses of HNO_3 on the sampling line and optical cell[4].

Filter-pack methods, which have been up to now extensively used in most measuring networks and pollution studies, have been demonstrated to suffer from a number of bias, namely, gas-particle and particle-particle interactions on the filter surface and interconversions between the gaseous and the solid phases[5–8]. The latter are particularly significant for the HNO_3-NH_4 NO_3 system, whose equilibrium can be easily disturbed by small changes in the thermodynamic conditions occurring during the sampling (e.g. evolution of nitric acid and ammonia due to temperature increase and/or relative humidity reduction, which results in the underestimation of particulate NH_4 NO_3 and overestimation of gaseous HNO_3).

Denuder techniques in different configurations (tubular and annular denuders[9–15], thermodenuders[16–17]), which are starting to replace filter-pack methods for many compounds, couple an high sensitivity with a good reliability in the discrimination between the gaseous and the particulate phase (residence time in the denuder is of the order of seconds, thus the adjustment of the partition equilibrium is negligible[9,11,15]). Criticisms reported in the literature to the application of this method to the measurement of HNO_3 include possible losses of the gas on the walls of the pre-impactor or, if a pre-impactor stage is not used, large particles deposition on the denuder walls[18], and artifacts due to the undesired measurement of interferent species (it should be stressed that these artifacts, in principles, can also be attributed to filter-pack methods making use of the same coating layer[19]).

We discuss here the features and the performances of a denuder method for the simultaneous measurement of HNO_3 and particulate nitrate, which relies on the use of annular denuders and downstream filters. We report some data obtained during a number of field studies carried out in locations ranging from extremely remote sites to highly polluted areas. The interpretation of field data is carried out in terms of the analysis of the nitrate mass distribution on the different stages of the set-up.

EXPERIMENTAL

Gaseous nitric acid was collected by using a sampling train composed of four annular denuders set in series and two downstream filters. Annular denuders are made of pyrex glass and have the following dimensions: outside diameter 3.3 cm; inside diameter 3.0 cm; length 20 cm. The devices are specially designed so as to assure the same fluidodynamic conditions at the inlet of each denuder in spite of its position in the sampling train. A polyethylene cyclone, having a cut size of 2.5 μ at the flow rate of 15 l min^{-1}, and a polyethylene filter holder are placed downstream of the denuders.

The denuders cleaning procedure is as follows: at their first usage after a long period, the denuders are kept for a few hours in a basic solution (0.1% NaOH in water), then rinsed several times with distilled water and rinsed once again with distilled water. If they are continuously used, the first step is unnecessary. After rinsing, the denuders are dried with a gentle flux of very clean air and are closed with caps. The filters cleaning procedure is as follows: Nylon filters (Nylasorb 1 μm, 47 mm, Gelman Sciences) are extracted twice for 5 minutes in ultrasonic bath by using an alkaline solution (same as for sample extraction); then they are rinsed several times with distilled water, rinsed again for 5 minutes in ultrasonic bath and placed inside plastic containers which have been cleaned with the same procedure. The containers are left open in the oven at the temperature of about 50°C until the filters are dried (a couple of minutes are generally sufficient). Teflon filters (Teflo w/ring 1 μm, 47 mm, Gelman Sciences) are used as such.

Denuder coating solutions were as follows:

- NaCl coating: 0.2% (w/v) NaCl in methanol;
- Na_2CO_3 coating: 1% Na_2CO_3 + 1% glycerol (w/v) in water-methanol 1:1 solution;
- citric acid coating: 1% (w/v) citric acid in methanol;

Extraction solutions (8 mls for denuders and filters, 5 ml for the cyclone) were as follows:

- distilled water for citric acid coated denuders;
- distilled water containing 0.037% H_2O_2 for NaCl and Na_2CO_3 coated denuders;
- alkaline solution (0.25 g/l Na_2CO_3 + 0.25 g/l $NaHCO_3$) for the cyclone and for the Teflon and the Nylon filters.

The anionic content of the denuders and filters was analyzed by ion chromatography (Dionex IC mod. DX100).

During the field campaigns, the sampling lines were placed in a temperature controlled housing, able to accommodate up to 7 sampling set-ups (ADS7, D.A.S., Palombara Sabina, Italy). The housing is directly operated by a microprocessor controlled automatic sampler (Sequair 92/A, D.A.S., Palombara Sabina, Italy), which selects, in sequence, the sampling train which goes "on sampling". The sampling lines which are not operating are tight to outside atmosphere. The automatic sampler is able to control, in real time, the fluidodynamic conditions of the sampling step, providing an appropriate adjustment of the inlet flow rate; as a result, a constancy of the inlet flow rate better than 0.5% and a precision in the determination of the sampled volume better than 1% is obtained.

Sampling flow rate was 15 l/min in the case of the Montelibretti campaign, 12 l/min^{-1} in all the other cases.

Field studies, programmed in order to verify the performances of the technique in different environmental conditions, were conducted as follows:

- Roma: during September 1991, in a measuring unit placed on the roof of a building in the centre of the city; sampling time: 4 hours;
- Montelibretti: during August 1992, in the C.N.R. pilot station placed in Area della Ricerca di Roma, which is located about 30 Km NE from the city of Rome; sampling time: 1 hour;
- Milano: during February 1991, in a measuring unit placed at ground level in the centre of the city; sampling time: 4 hours;
- Himalaya: during September and October 1991 in Italian Pyramid Laboratory placed in the Nepal's Sagarmatha National Park, 5050 m above sea level, in the framework of the Ev-K^2-CNR project; sampling time: 24 hours;
- Antarctica: during January and February 1991 in the Italian base of the Terranova Bay in the framework of the National Program for Antarctic Researchs; sampling time: 48 hours.

Description of the method

Several coatings may, in principle, be able to collect nitric acid. Among these, sodium carbonate, sodium fluoride and sodium chloride are all good sinks for nitric acid and have been extensively used (20–21). Previous experimental work showed that all three coatings suffer from the small direct interference of nitrogen dioxide (the interference on Na_2 CO_3-coatings is one order of magnitude higher than on NaCl- and NaF-coatings); an additional interference also occurs on sodium carbonate when NO and NO_2 are both present in the atmosphere[15]. The collection of these species yields nitrite ion, which, during the sampling, can be oxidized to nitrate ion, causing a positive interference in the determination of HNO_3. In the case of NaF- and NaCl- coatings the interference is negligible. In the case of the Na_2 CO_3-coating, instead, the necessary correction of this artifact can be obtained by using the differential technique, as described in previous papers[12,15] (NO and NO_2 can be regarded as low reactivity interferents, thus their mass distribution along two denuders is fairly constant).

Previous studies also showed that carbonate coatings are a good sink for nitrous acid; the resulting nitrite ion can, again, undergo an oxidation process during the sampling, yielding a nitrate amount which positively interferes with the determination of HNO_3[15]. Besides, the retention of NO_2 on this coating is greatly enhanced when high amounts of SO_2 are also collected (highly polluted atmospheres)[22]. For these reasons, carbonate coatings are clearly inappropriate for an accurate determination of nitric acid. Sodium fluoride coatings also show a certain variable activity in the retention of nitrous acid, which probably undergoes a reversible adsorption process on the fluoride surface[15]. As a consequence, sodium chloride was chosen as denuder coating in our sampling system. Sodium fluoride can be only used in areas where the concentration of nitrous acid is supposed to be low, when the air concentration of hydrochloric acid has to be determined (paper in preparation).

The set-up used for the measurement of the atmospheric concentration of nitric acid is

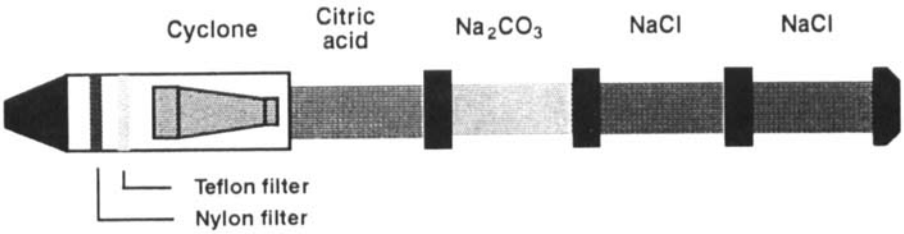

Figure 1 Annular denuder set-up used for the measurement of nitric acid and particulate nitrate atmospheric concentration.

depicted in Figure 1. The system is composed of two NaCl-coated annular denuders, one Na_2CO_3-coated and one citric acid-coated annular denuder set in series, followed by a cyclone and a Teflon-nylon filter-pack.

At the flow rate of 12 l/min, more than 99% of the incoming nitric acid is collected on the first NaCl-coated denuder. The second NaCl-coated denuder, beside being an operative check of the performances of the sampling set-up, allow to correct the nitric acid value for the possible small nitrate amount due to the impact and turbulent diffusion deposition of particles. In fact, provided that the fluidodynamic conditions at the inlet of the first and second denuder are the same, a very similar particulate distribution will occurr on the two denuders; thus, the calculation of the difference between the analyte masses determined on the two denuders (Absolute Differential Technique[14]) permits a reliable determination of gaseous nitric acid even in the presence of very high amounts of particulate nitrate (a field validation of these assumptions is reported in the experimental section).

The Na_2CO_3 and the citric acid-coated denuders are used to remove nitrous acid and ammonia, respectively, from the air stream before it reaches the filter-pack. Nitrous acid, in fact, could be retained on the nylon filter and oxidized to nitrate, causing a positive bias in the determination of the evolved ammonium nitrate[19], while ammonia could be responsible of undesired reactions on the particulate matter collected on the Teflon filter.

The polyethylene cyclone, which allows the retention and successive analysis of coarse particulate nitrate, is placed downstream of the denuders so as to avoid any adsorption of nitric acid on the cyclone walls (the transmission of nitric acid has been demonstrated to be affected by the materials which come in contact with the air stream[23]).

Fine particulate nitrate is collected on the Teflon filter. The back-up nylon filter has the purpose of collecting the nitric acid amount possibly produced during the sampling because of the dissociation of particulate ammonium nitrate collected on the Teflon filter. This process, although enhanced by the removal of nitric acid and ammonia on the denuders, depends on the termodynamic conditions of the sampling (it is favoured by high temperatures and low relative humidities); thus, the amount of nitrate recovered on the nylon filter does not necessarily coincide with the total amount of ammonium nitrate originally present in the atmosphere. However, the atmospheric concentration of ammonium nitrate can be determined, after the sampling, by passing clean air through the Teflon filter and by recovering the resulting nitric acid on the same nylon filter used during the sampling (or on another suitable denuder or filter set downstream of the desorption system). Laboratory investigations have shown that the Teflon filter can be heated, in order to speed the process up; at the temperature of 70°C only the volatilization of ammonium nitrate and ammonium chloride occurres, while sulfuric acid and related ammonium salts are stable[24].

RESULTS AND DISCUSSION

Detection limits

The detection limits of the described technique depends on a variety of parameters, among which the value of the "laboratory blanks" and those of "field blanks" for the various components of the set-up. While laboratory blanks depends on the purity of the coating solutions, on the filters and denuders cleaning procedure and on the absence of releases from the materials which came in contact with the denuders and filters themselves (caps, connections, gaskets, etc.), the values of field blanks greatly depend on the performances of the denuder housing.

With an analytical detection limit of 0.01 μg/ml and an extraction volume of 8 ml, the minimum detectable nitrate amount is 0.08 μg/device. With the cleaning procedure reported above, the values of laboratory blanks for all the components of the sampling set-up (NaCl- or NaF-coated denuders, Teflon filters and Nylon filters) were below the minimum detectable nitrate amount. During the measurement campaign of Milano, field blanks have been also evaluated, that is, complete set-ups have been prepared, kept in the field for a period equivalent to the sampling time, then extracted and analyzed. The results showed that in the great majority of the cases field blank values were of the same order of magnitude as the analytical detection limits, that is, there were no significative difference between laboratory and field blanks; this indicates that the denuder housing was tight to outside atmosphere.

Blank values of this order of magnitude allowed to stress the minimum sampling time of this system to 1 hour, obtaining, for the flow rate of 15 l/min, the detection limit of 0.1 μg/m^3 and the quantitation limit of 0.3 μg/m^3 (detection limit is calculated as three times the standard deviation, quantitation limit is calculated as ten times the standard deviation[25]); this made it possible to follow the variation in the concentration of nitric acid and nitrates of polluted atmospheres with very low resolution time (Montelibretti campaign). On the other hand, on a 24-hour basis, at the flow rate of 12 l/min, the quantitation limit is about 0.01 μg/m^3, which made it possible to perform measurements of nitric acid and nitrates in background atmospheres (Himalaya and Antarctica). The values of field blanks obtained in the course of these field studies confirmed the reliability of the system.

Field studies

The results of some measurements carried out during the field studies of Roma and Milano are reported, as a 4 hours trend, in Figure 2. Sampling periods were as follows: 3.00 to 7.00;

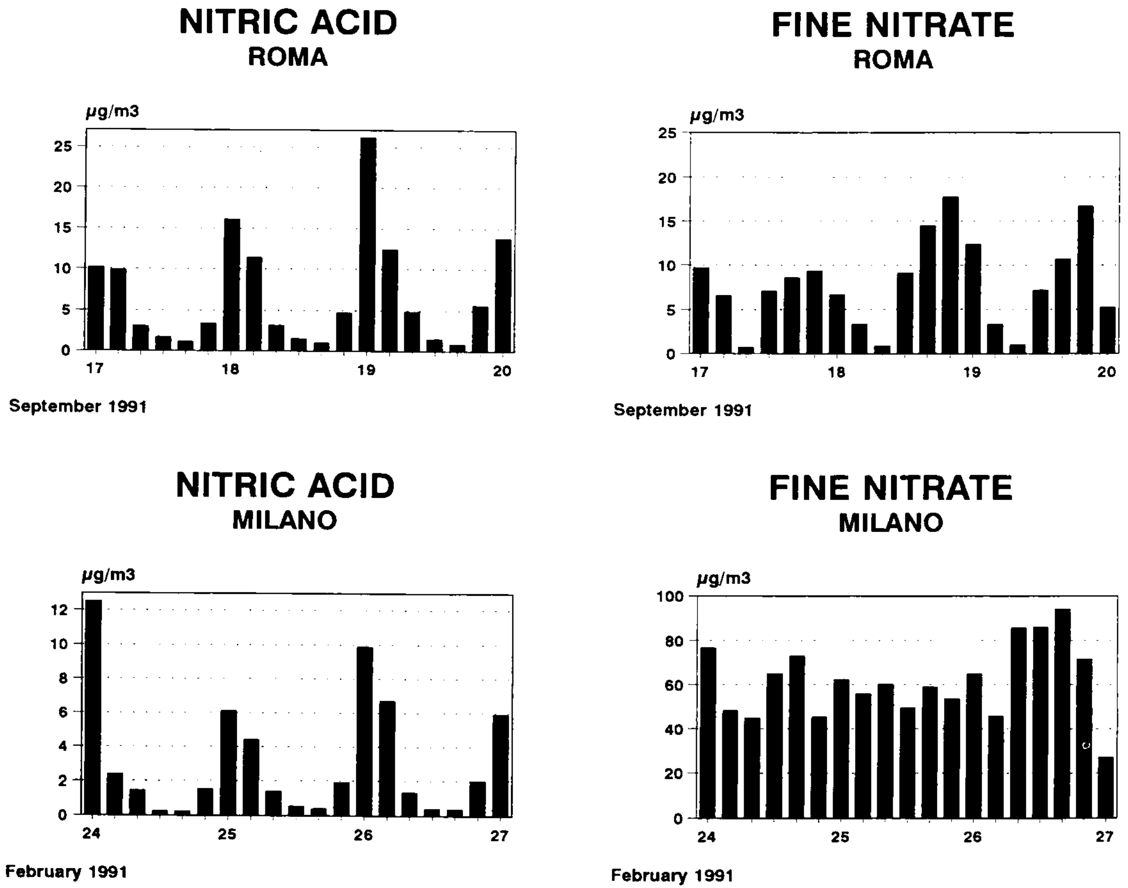

Figure 2 Temporal trend of nitric acid and fine nitrate concentration measured during the field studies of Roma and Milano. Sampling time: 4 hours; detection limit: 0.03 µg/m^3.

7.00 to 11.00; 11.00 to 15.00; 15.00 to 19.00; 19.00 to 23.00; 23.00 to 3.00. In all figures, the date corresponds to the period around midday (11.00 to 15.00). The data clearly indicate that, on both locations, nitric acid exhibits, as expected, a temporal trend with maxima during daytime (typically during the period 11.00 to 15.00) and minima during the night. Fine nitrate concentration measured in Rome also show a well-defined trend with minima during the evening (typically during the period 19.00 to 23.00) and maxima during the early morning. This behaviour is related to the strong vertical mixing which usually occurres in this area during the afternoon. Differently, during the period of the Milano campaign the Po valley was characterized by stagnant meteorological conditions, which resulted in much less pronounced variations of fine nitrate concentration in the Milano area.

From Figure 2 it clearly results that in the field study of Roma nitric acid and nitrate concentrations were of the same order of magnitude. During the Milano campaign, instead, the ratio between particulate nitrate and nitric acid was extremely high (up to more than 300). This situation constituted a very good chance for checking both the ability of the denuders to pass particles and the field performances of the described technique in the measurement of very low HNO_3 concentrations in case of high concentrations of particulate nitrate.

By theory, particulate nitrate causes a potential error in the determination of nitric acid carried out by means of annular denuders; this is expressed by equations [1] and [2], which describe the nitrate distribution pattern on two NaCl-coated denuders set in series (assuming that the operative conditions allow a HNO_3 removal efficiency close to unity):

$$A_1 = A\int + \alpha_1 A_p + B_1 \qquad [1]$$

$$A_2 = \alpha_2 (1 - \alpha_1) A_p + B_2 \qquad [2]$$

where: A_1 and A_2 are the nitrate amounts collected on the two denuders; $A\int$ and A_p are the inlet amounts of HNO_3 (expressed as nitrate) and particulate nitrate, respectively; α_1 and α_2 are the mass removal efficiency of particulate nitrate on the two denuders; B_1 and B_2 are the two values of nitrate blanks.

If we subtract A_2 from A_1 (A.D.T., Absolute Differential Technique), we get:

$$A_1 - A_2 = A\int + A_p (\alpha_1 - \alpha_2 + \alpha i l \alpha_2) + B_1 - B_2$$

thus, the error in the determination of HNO_3 by means of the A.D.T. is the sum of two terms: a first one $(B_1 - B_2)$ due to blanks, and a second one, $A_p (\alpha_1 - \alpha_2 + \alpha_1\alpha_2) = A_p.\Omega$, due to particle collection. As reported above, in these field studies blank values were of the same order of magnitude as the analytical detection limits, thus the error due to the amount $(B_1 - B_2)$ can be neglected. As regards the estimate of Ω, theoretical considerations and experimental studies[26–28] indicate that when the fluidodynamic conditions at the two denuder inlets are very similar, the following values are expected:

$$\alpha_1 \approx \alpha_2 << 10^{-1} \qquad [3]$$

Table 1 Concentration and analytical data of the Milano campaign.

DATE 1991	TIME	HNO3 μg/m3	COARSE NO3- μg/m3	FINE NO3- μg/m3	SAMPLED VOLUME m3	NaCl1 NO3- μg	NaCl2 NO3- μg	Na2CO3 NO2- μg	Na2CO3 NO3- μg	Cyclone NO3- μg	Teflon NO3- μg	Nylon NO3- μg
Feb.24	11-15	12.52	6.07	76.57	2.75	37.9	4.3	49.3	11.8	16.7	127.6	82.9
Feb.24	15-19	2.38	3.22	48.34	2.72	8.8	2.5	24.5	4.9	8.8	60.3	71.2
Feb.24	19-23	1.45	3.35	44.75	2.88	6.2	2.1	63.7	10.3	9.7	67.9	61.0
Feb.24	23-03	0.26	3.49	65.02	2.83	2.4	1.7	108.1	23.9	9.9	137.6	46.4
Feb.25	03-07	0.22	3.71	72.89	2.82	1.9	1.3	89.9	17.3	10.5	179.3	26.2
Feb.25	07-11	1.53	3.73	45.41	2.90	6.6	2.2	68.9	22.1	10.8	109.7	22.0
Feb.25	11-15	6.12	4.62	62.35	2.85	19.7	2.7	26.0	8.7	13.2	94.6	83.1
Feb.25	15-19	4.40	4.46	55.67	2.83	14.1	2.0	39.8	14.5	12.6	57.1	100.5
Feb.25	19-23	1.42	4.29	60.14	2.83	5.6	1.7	90.4	16.6	12.1	107.2	63.0
Feb.25	23-03	0.54	3.96	49.47	2.78	2.7	1.2	112.3	30.3	11.0	102.5	35.0
Feb.26	03-07	0.40	4.13	58.95	2.76	2.1	1.1	99.8	26.1	11.4	134.1	28.6
Feb.26	07-11	1.91	4.75	53.66	2.88	9.2	3.9	103.3	26.2	13.7	126.2	28.3
Feb.26	11-15	9.90	5.44	64.80	2.77	30.8	4.2	55.7	18.1	15.1	76.8	102.7
Feb.26	15-19	6.71	4.70	45.87	2.72	20.2	2.4	31.2	6.7	12.8	29.6	95.2
Feb.26	19-23	1.35	4.20	85.71	2.80	6.0	2.3	93.4	13.4	11.8	158.1	81.9
Feb.26	23-03	0.40	4.25	85.80	2.83	2.6	1.5	139.0	19.0	12.0	174.2	68.6
Feb.27	03-07	0.38	4.64	94.00	2.80	2.3	1.3	125.6	17.2	13.0	236.3	26.9
Feb.27	07-11	1.99	5.13	71.56	2.89	7.6	1.9	124.3	15.2	14.8	181.1	25.7
Feb.27	11-15	5.92	2.94	26.93	2.83	18.1	1.8	14.3	1.4	8.3	11.5	64.7

Table 2 Calculation of an upper limit for the error in the measurement of nitric acid by means of the Absolute Differential Technique.

DATE 1991	*TIME*	A_1	A_2	A^*_p	A_1/A^*_p	A_2/A^*_p	Ω_{max}
24/2	23-03	2.4	1.7	195.6	0.012	0.009	$3\cdot10^{-3}$
25/2	03-07	1.9	1.3	217.3	0.009	0.006	$3\cdot10^{-3}$
25/2	23-03	2.7	1.2	149.7	0.018	0.008	$1\cdot10^{-2}$
26/2	03-07	2.1	1.1	175.2	0.012	0.006	$6\cdot10^{-3}$
26/2	23-03	2.6	1.5	256.3	0.010	0.006	$4\cdot10^{-3}$
27/2	03-07	2.3	1.3	277.5	0.008	0.005	$3\cdot10^{-3}$

Atipically, we have $\alpha \approx 2 \div 3\cdot10^{-2}$ and Ω of the order of 10^{-3}. Condition [3] holds only if there are no fluidodynamic perturbations at the first denuder inlet, which could be due, for example, to high speed of the wind.

The validity of assumption [3] can be checked through the analysis of the experimental data set; nitrate deposition data on the sampling line allow, in fact, to determine a value Ω_{max} which is an overestimation of the true value of Ω.

From relationships [1] and [2] we get:

$$A_1/A_p > \alpha_1 \geq \alpha_2 > A_2/A_p \qquad [4]$$

From the experimental data set of Table 1, a value A^*_p which is a good estimate of A_p can be calculated as follows:

$$A^*_p = A_{FT} + A_{FN} + A_{CY} + A_2 \lesssim A_p$$

where A_{FT}, A_{FN}, A_{CY} are the nitrate amounts collected on the Teflon filter, Nylon filter and cyclone, respectively.

Calculating the values A^*_p for the sampling periods when nitric acid concentration was supposed to be very low (late nighttime periods) and substituting them for A_p into relationship [4] we obtain the data of Table 2. It results that α_1 and α_2 are of the order of 10^{-2}, while the values of Ω_{max} range from $3\cdot10^{-3}$ to 10^{-2}, with an average of $5\cdot10^{-3}$. It is worth stressing that Ω_{max} is an upper limit for Ω, which coincide with the true value of Ω only in the case no nitric acid was present in the atmosphere at the time of the sampling, a condition which is quite unrealistic. By using the A.D.T., which is based on the condition $\alpha_1 = \alpha_2$, the determination of HNO_3 during the Milano campaign could be, at most, affected by a sistematic error of: $A_p \cdot \Omega_{max}$ (upper limit).

The data of Table 1 show that the deposition of particulate nitrate on the second NaCl denuder ($\alpha_2(1 - \alpha_1)A_p$), expressed as percentage of the total amount of nitrate collected in the cyclone and the filters never exceeded 2.3%. By applying the Absolute Differential Technique it was possible to take into account this small interference and to measure HNO_3 concentration down to 0.2 $\mu g/m^3$ (nighttime values), with the limitations reported above, even in the presence of particulate nitrate concentration two orders of magnitude higher.

The comparison between the nitric acid concentration data obtained by applying the Absolute Differential Technique and the data which should have been obtained if only one denuder had been used is reported in Figure 3a. As shown, the results yielded by the One Denuder Technique are clearly affected by a positive error which makes this technique unaccurate[14]; in the case of an high particulate nitrate to nitric acid ratio, for example during nightime hours, the error increases, causing the technique to be unreliable: in the case of the Milano campaign, the per cent difference between the two determinations would have reached values of more than of 200% (Figure 3b).

The ratio of ammonium nitrate which evolved from the Teflon filter during the sampling to the total amount of fine nitrate is reported in Figure 4. As expected, the evolution of nitric acid is higher during the day, when the temperature and relative humidity conditions favour the evolution process.

All the concentration and analytical data of the Milano campaign are reported in Table 1. The analysis of the nitrate mass distribution over the collecting media shows, again, that nitrate is present on both the NaCl-coated denuders, with the pattern discussed above, and on the Na_2CO_3-coated denuder. This last amount, however, comes from the small direct interference of nitrogen oxides and from the oxidation of nitrite, which is mainly due to the collection of nitrous acid[15] (maximum nitrite amounts are during nightime hours). The attribution of these amounts to gaseous interferent compounds is also supported by the observation that the nitrate amounts recovered on the Na_2CO_3 denuder greatly exceed those found on the second NaCl denuder. These results confirm that Na_2CO_3-coated denuders would have been inappropriate for the determination of nitric acid.

During the Roma campaign, a temporal self-consistency test has been carried out, that is, 24-hour samplings have been performed side by side to the 4-hour main sampling line. The comparison between the results of the 24-hour samplings and the average of the results of the six 4-hour samplings is reported in Table 3. The temporal self-consistency test constitutes an useful tool for evaluating the reliability of accumulation methods in real operative conditions and for underlining possible artifacts which are dependent on the sampling duration[8]; the fulfillment of this test, which acts as a quality indicator, is a pre-requisite for considering a method as accurate.

The data of Table 3 show that the technique exhibited a very good self-consistency for nitric acid and nitrate concentrations. The results of the 24-hour determinations, in fact, cannot be statistically distincted from the averages of the six 4-hour samplings.

The analysis of the nitrate mass distribution over the collecting media allows to make some important remarks:

- the nitrate content of the second NaCl denuder is very low, and this agrees with a very small deposition of particulate matter and with the theoretical efficiency of the first NaCl denuder of 99.5%;
- the nitrite and nitrate amounts recovered on the Na_2CO_3 denuder are individually not self-consistent; this nitrate amount, in fact, is mainly due to the conversion of nitrite, which occurres during the sampling as an action of atmospheric oxidants; this phenomenum is a function of the nitrite amount collected and, thus, its extent depends on the sampling duration[8]. The data show that the conversion of nitrite to nitrate occurred at a greater extent in the 24-hour sampling, because in the first hours of the morning the oxidative process could act on the considerable nitrite amount collected during the night. If these nitrate amounts are converted to equimolar amounts of nitrite and added to the nitrite amount recovered on

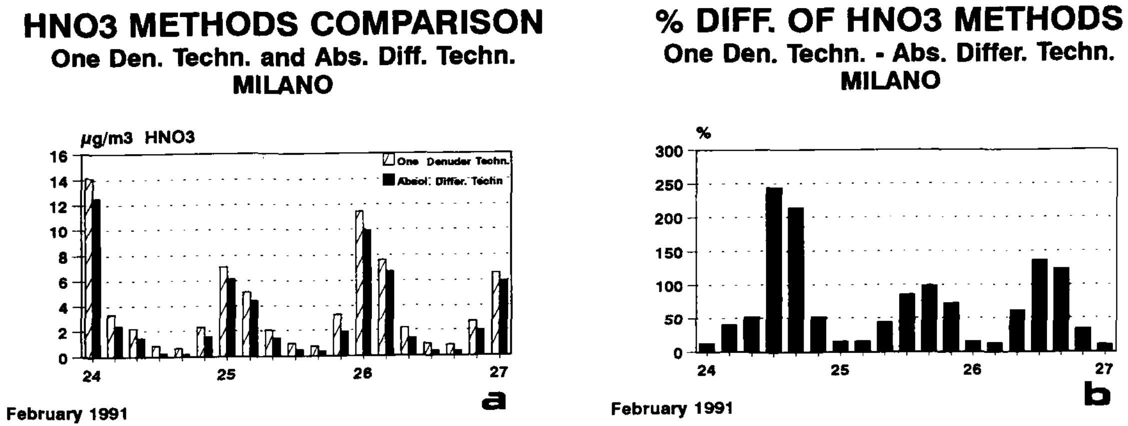

Figure 3 Comparison between the One Denuder Technique and the Absolute Differential Technique in the determination of nitric acid in the presence of high particulate nitrate levels (field study of Milano). a: comparison of the measured HNO_3 concentrations; b: per cent difference in the measurement of HNO_3 concentration.

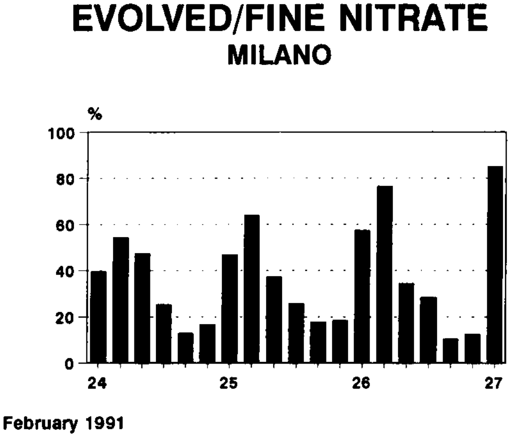

Figure 4 Ratio of nitric acid evolved from the Teflon filter, and recovered on the back-up Nylon filter, to the total fine nitrate amount: temporal trend during the field study of Milano.

the denuder, a good self-consistency is achieved (the little difference in the sampling volumes must be taken into account);

- the nitrate amounts collected on the teflon and the nylon filters are individually not self-consistent since the evolution process which causes the partitioning between the two filters is, again, a function of the total amount collected[8]. As expected, the sum of the amounts recovered on the two filters, expressed as concentration, exhibits a very good temporal self-consistency.

The self-consistency data reported in Table 3 also allow to estimate an upper limit for the reproducibility of the system. This limit, which takes into account not only the analytical standard deviation but the overall uncertainty of the sampling and analytical procedure, has been estimated to be of the order of $\sigma = 0.05$ µg/m^3.

The data of the field studies of Himalaya (24-hour sampling) and those of Antarctica (48-hour sampling) are shown in Figure 5. In remote areas, particles interference in the determination of nitric acid is usually negligible, because of the very low particulate nitrate concentration values which occur in these sites. Attention has to be paid, however, to the occurrence of high wind speed, which could invalidate assumption [3]. For some determinations of the Antarctica field study, wind speed was between 10 and 20 m/sec; thus consideration has to be given to the possibility that condition [3] was not satisfied and that an excess value was obtained for nitric acid concentration. For these reasons, some of the nitric acid data of the Antarctica campaign (identified in figure 5 with an asterisk) constitute an upper concentration limit. In order to minimize this problem, the performances of an appropriate wind shield to be used in case of high wind speed is under study.

From the data in Figure 5 it results that the described method allowed to evaluate nitric acid concentrations which never exceeded 0.25 µg/m^3, and particulate nitrate concentrations which were below 0.6 µg/m^3. The method allowed to evaluate the partitioning of nitrate between the gaseous phase and the two granulometric fractions of the particulate phase: in the case of Himalaya, fine nitrate fraction was predominant with respect to nitric acid and,

Table 3 Results of the temporal self-consistency test carried out during the Roma campaign: concentration and analytical data.

DATE 1991	TIME	HNO3 µg/m3	NO3- µg/m3	SAMPLED VOLUME m3	NaCl1 NO3- µg	NaCl2 NO3- µg	Na2CO3 NO2- µg	Na2CO3 NO3- µg	Teflon NO3- µg	Nylon NO3- µg	Total NO3- µg
Sep.17	11-15	10.16	0.62	2.72	27.1	0.2	5.3	4	1.4	0.2	1.7
Sep.17	15-19	9.85	6.52	2.71	26.4	0.4	4.8	3.2	17.6	0.1	17.7
Sep.17	19-23	3.04	0.69	2.80	8.3	b.d.l.	16.4	1.6	1.7	0.2	1.9
Sep.17	23-03	1.70	7.04	2.84	5.0	0.3	39	2.4	6.2	13.8	20.0
Sep.18	03-07	1.11	8.56	2.87	3.4	0.3	17.5	1.7	5.4	19.2	24.6
Sep.18	07-11	3.38	9.34	2.86	9.9	0.5	20.8	4.6	5.6	21.1	26.7
4-HOUR	SUM			16.80	80.1	1.7	103.8	17.5	37.8	54.7	92.6
4-HOUR	AVG.	4.79	5.51								
Sep.17-18	24-h	4.78	5.47	17.28	82.0	1.6	74.2	59.4	32.4	62.1	94.5

Sep.18	11-15	16.10	6.65	2.73	43.3	0.5	5	7.2	3.1	15.0	18.2
Sep.18	15-19	11.38	3.39	2.69	30.1	0.3	6.1	3	1.8	7.4	9.1
Sep.18	19-23	3.15	0.89	2.80	8.6	b.d.l.	19.7	1.8	2.1	0.4	2.5
Sep.18	23-03	1.51	9.12	2.85	4.5	0.3	33.7	44.9	7.5	18.5	26.0
Sep.19	03-07	1.00	14.44	2.87	3.3	0.5	27.9	4.4	15.0	26.5	41.4
Sep.19	07-11	4.72	17.77	2.85	14.1	1.0	24.3	4.1	9.8	40.8	50.6
4-HOUR	SUM			16.79	103.9	2.6	116.7	65.4	39.3	108.6	147.8
4-HOUR	AVG.	6.20	8.81								
Sep.18-19	24-h	6.10	8.68	17.30	105.4	2.7	66.6	138.1	21.2	129.0	150.2
Sep.19	11-15	26.05	12.35	2.74	70.4	0.9	7.3	11.7	6.2	27.6	33.8
Sep.19	15-19	12.41	3.33	2.69	32.7	0.2	5.4	3.5	1.4	7.5	9.0
Sep.19	19-23	4.86	1.00	2.79	13.3	0.1	25	2.6	1.6	1.2	2.8
Sep.19	23-03	1.48	7.18	2.84	4.4	0.3	7.7	27.6	5.1	15.3	20.4
Sep.20	03-07	0.82	10.73	2.87	2.7	0.4	28.3	2.9	11.0	19.8	30.8
Sep.20	07-11	5.60	16.70	2.86	16.6	1.0	30	4.7	8.5	39.3	47.8
4-HOUR	SUM			16.79	140.1	2.9	103.7	53.0	33.8	110.7	144.6
4-HOUR	AVG.	8.39	8.61								
Sep.19-20	24-h	8.36	8.68	17.29	143.8	3.0	84.0	82.3	11.1	138.9	150.0

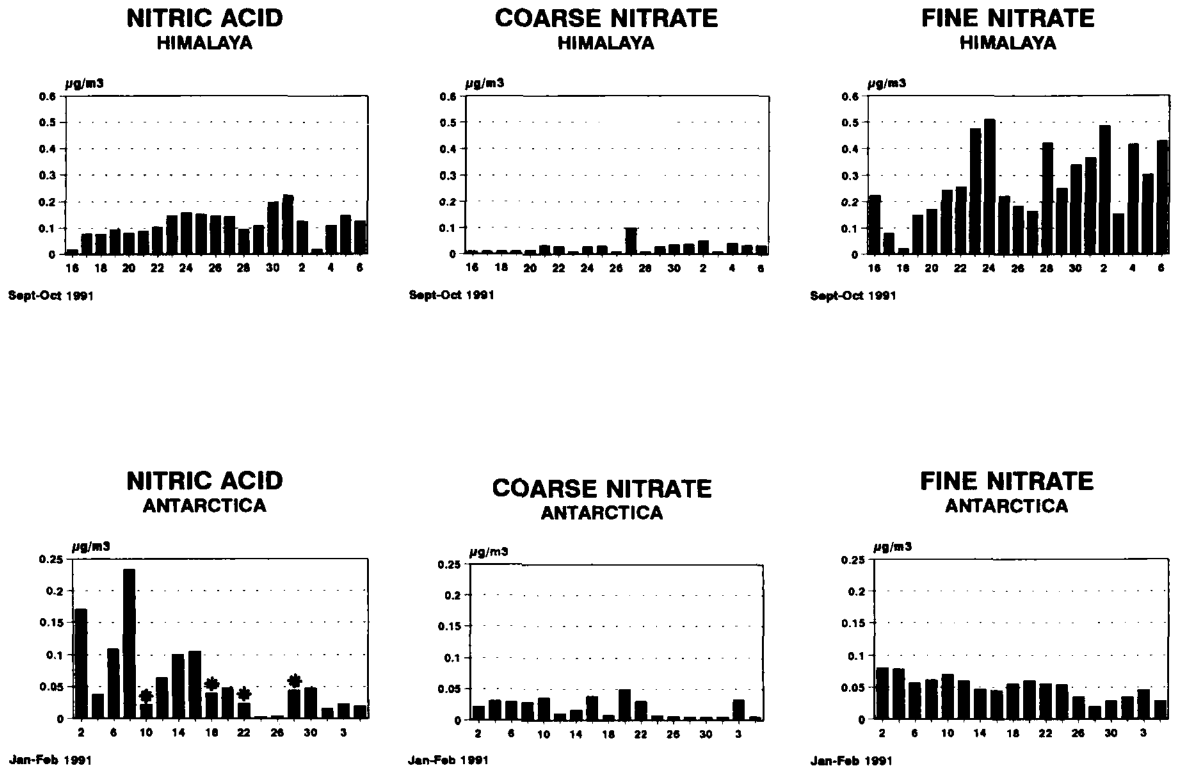

Figure 5 Temporal trend of nitric acid, coarse nitrate and fine nitrate concentration during the field studies of Himalaya (sampling time: 24 hours; detection limit: 0.004 μg/m^3) and Antarctica (sampling time: 48 hours; detection limit: 0.002 μg/m^3).

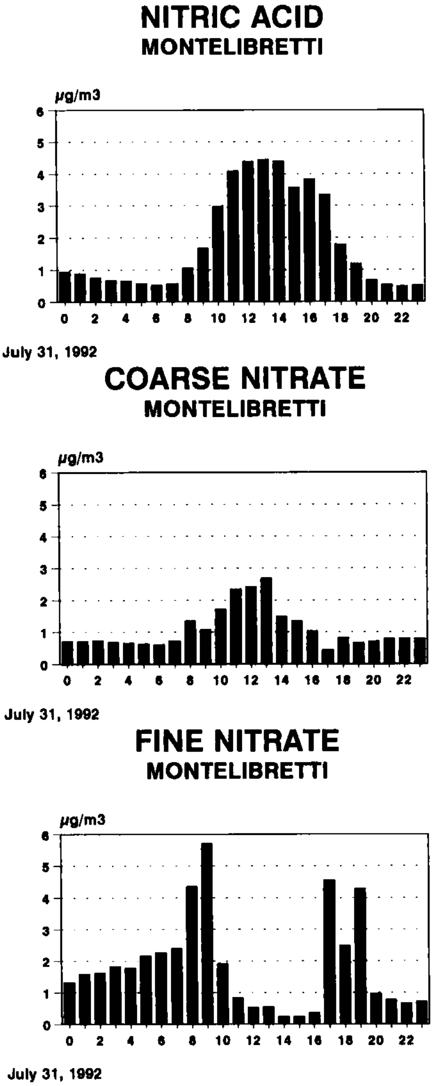

Figure 6 Temporal trend of nitric acid, coarse nitrate and fine nitrate concentration during the field study of Montelibretti (sampling time: 1 hour; detection limit: 0.1 µg/m^3).

at a major extent, coarse nitrate fraction; in the case of Antarctica, nitric acid was the predominant species, while fine and coarse nitrates were considerably lower.

The data of the 1-hour trend carried out during the Montelibretti campaign are reported in Figure 6. In this case, wind speed was always well below 5 m/sec, and thus a detection limit of 0.1 µg/m^3 and a quantitation of about 0.3 µg/m^3 could be obtained by paying only particular care to the denuder cleaning step, which determine the values of blanks. The trends reported in Figure 6 show how the temporal behaviour of nitric acid, fine nitrate and coarse nitrate could be well characterized, also in these extreme time resolution conditions. The reliability of the measurements supported the interpretation of very small variations in nitric acid and nitrate concentration: for example, the two relative maxima in the nitric acid concentration trend could be attributed to local photochemical smog formation (around 1 p.m.), and to transport from the city of Rome (around 4 p.m.), respectively. Coarse and fine nitrate concentrations both show the maximum values during the morning, while the unusual relative maximum of fine nitrate which occurres during the afternoon has to be attributed to a sudden change in the meteorological conditions (paper in preparation).

CONCLUSIONS

The described denuder method for the determination of the atmospheric concentrations of nitric acid and particulate nitrate allows accurate and reliable measurements of these compounds, also in the case of a very high nitrate to nitric acid concentration ratio. The method exhibits high sensitivity, and allows to perform short-time measurements of the nitric acid, coarse nitrate and fine nitrate content and ammonium nitrate fraction of the atmosphere under study at concentration levels ranging from those encountered in extremely remote sites to those typical of heavily polluted areas.

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