Evaluation of Gas Phase and Particulate Components Relevant to Polar Tropospheric Processes

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The measurement of atmospheric trace components relevant to atmospheric chemistry, in gas phase and particulate matter, was carried out in the Antarctica troposphere during the Antarctic summer 1990–91. The determinations were carried out by sampling air through a diffusion denuder/filter pack sampling system, followed by extraction and analysis by ion chromatography. Through the analysis of the mass distribution of anions, an accurate and sensitive method for the measurement of several important species was provided. Results show that sulfur dioxide, nitric acid, sulfates, nitrates and other significant compounds might be well characterized, even at concentration levels as low as a few parts per trillions, thus providing a highly significant and consistent data set for the study of polar atmospheric chemistry.

INTRODUCTION

Tropospheric chemical processes are responsible for the formation of several compounds which might damage vegetation, materials and, in general, the environment. In addition, chemical processes are also responsible for the formation and transformation of compounds in both gas and particulate phase which are relevant to the "Global Change". Sulfur and nitrogen compounds, in addition to hydrocarbons, are the main species involved in tropospheric chemistry. The presence of these species have been clearly shown in polluted urban and industrial atmospheres, where they are present in relatively high concentrations and where they contribute to acid deposition and photochemical pollution phenomena.

Remote sites are characterized by the presence, at trace levels, of the same class of compounds which are found in polluted atmospheres; their presence is due to natural emissions, long range transport or to local anthropogenic activities. Such species evolve into gas phase and particulate components which might be responsible for adverse environmental effects. This is the case of Antarctica, where the presence of atmospheric trace compounds has been recognized. As reported in recent works, in order to characterize the tropospheric

chemistry of Antarctica, a great effort must be taken to measure very tiny amounts of reactive compounds [1,2,3].

Recently, a great deal of attention has been paid to sulfur and nitrogen compounds, since the atmospheric cycles of these two elements are responsible for a large fraction of the chemical processes taking place in troposphere. It is well known that sulfur dioxide is emitted by a large number of sources, including natural emissions, and that it is removed from the atmosphere by means of dry and wet deposition. A very large fraction of sulfur dioxide is oxidized into sulfuric acid and sulfate (mainly ammonium bisulfate and sulfate), which are also removed through wet and dry deposition. Naturally emitted compounds, such as H_2S, DMS or DMSO are also oxidized yielding airborne sulfur dioxide and sulfates[4].

The nitrogen cycle is by far more complex than that of sulfur. Nitrogen is emitted by natural processes mainly as ammonia, while anthropogenic combustion sources mainly emits nitrogen oxide. This is rapidly oxidized by ozone and radicals to nitrogen dioxide, nitric acid, nitrates and other nitrogen containing compounds. Nitric acid is neutralized by ammonia yielding ammonium nitrate aerosols which are in thermodynamic equilibrium with nitric acid and ammonia. As a result, nitric acid can be formed in the vicinity of pollution sources, transported over long distances and dissociated again into nitric acid in remote sites. This mechanism might contribute to dry acid deposition, provided that thermodynamic conditions shift the equilibrium toward the gaseous components.

In order to understand the chemical processes which control the nitrogen and sulfur cycles, a series of measurements of the relevant components in Antarctica has been devised. They include sulfur dioxide and nitric acid in gas phase and sulfates and nitrates in particulate matter and have been carried out by using the annular denuder method. The mass distribution of the analytes in the various stages of the sampling system has also been studied, in order to obtain reliable results on the measurement of atmospheric concentrations of the above components and to explore the feasibility of denuder based techniques to yield reliable data even in very remote sites.

SAMPLING METHOD

Since the expected concentrations are in the parts per trillions range, an analytical accumulation methods must be used, that is, the species of interest must be sampled over a suitable substrate where the molecules are selectively collected. After sampling, the substrate is dissolved and the relevant species analyzed by means of classic analytical methods. When the investigated compounds are acidic, an alkaline substrate can be used; after sampling the substrate can be dissolved in water and the relevant anions determined by means of ion chromatography. As will be shown below, the expected concentrations of the species of interest and the sensitivity of ion chromatography are such that at least 30 cubic meters of air should be collected; that is about 48 h of sampling at a flow rate which ensures efficiencies of collection close to 100%, are needed.

However, since the species of interest are also in particulate phase, a separation between the two phases must be ensured. This can be accomplished through a sampling technique which was developed many years ago and which is based upon the use of annular denuders,

i.e., concentric glass tubes where the surface of the annulus is coated with a suitable substance and through which air is drawn by means of a pump. Gas molecules diffuse to the annular walls where they are collected, while particles proceed along the tube without any disturbance and can be collected by means of a membrane filter. Several works have shown the suitability of this technique and its ability in discriminating the gaseous from the particulate phase [5,6,7,8].

Even though the method is very simple, at least in principle, its use requires a lot of attention, especially if accurate and precise measurements has to be carried out at very low concentration levels, such as in the case of the evaluation of Antarctic troposphere. Indeed[7], several conditions should be met in order to ensure that the measurement is accurate:

 i) The sampling device must ensure a sufficiently high efficiency for the collection of gaseous species.
 ii) The sampling must ensure a complete separation between gas and particles.
 iii) The collection efficiency of particles should be well characterized.
 iv) Gas to particles and particles to gas conversions must be avoided.
 v) Stability of the collected species should be ensured.

In order to fulfill such requirements a dedicated sampling train has been set-up and operated as shown in Figure 1. It consists of a denuder train followed by a filter pack. The denuders train is made up of two NaCl coated denuders (D1 and D2) for the collection of nitric acid, two Na_2CO_3 coated denuders (D3 and D4) for the collection of other acidic components and one denuder coated with citric acid (D5) for the collection of ammonia. After the denuder train, air passes through a cyclone (Cy) which removes particles larger than 2.5 μm in aerodynamic size and then through the filter pack with a front Teflon filter (F1) and a backup nylon filter (F2). A Citric Acid impregnated filter can also be added to the set-up (F3).

The rationale for such a sampling set up has been discussed in a series of works[7,8,9]. In this case, NaCl denuders are used because they efficiently collect nitric acid, while they are almost inert to sulfur dioxide, which can be therefore collected on the carbonate coated denuders. Sulfates and nitrates in particulate matter are collected in the cyclone (coarse
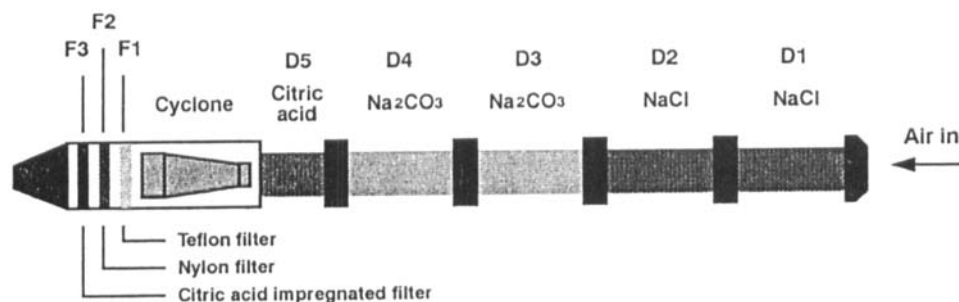

Figure 1 The denuder/filter pack sampling train which was used for the sampling step (Symbols are explained in the text).

fraction) and on the double stage filter pack (Teflon filter) the second Nylon filter is used to recover nitric acid evaporated from the ammonium nitrate particles collected in the Teflon front filter while ammonia can be recovered on the citric acid impregnated filter. Experimental results in other sites seems to indicate that other ammonium salts are evaporated from the Teflon filters, thus the Nylon membrane will also ensure the collection of other anions (chlorides and sulfates)[10].

The denuder coated with citric acid is used in order to remove ammonia from the gaseous stream. However no attempt has been made in order to measure the ammonia concentration due to the variability of field blanks.

The analytical method, as previously stated, requires the extraction of denuders and filters with a proper solution and the analysis by means of ion chromatography. Suppose we measure the ionic specie k, the mass m_k of such ion which is recovered from the diffusion denuder is such that:

$$m_k = \sum E_{,k} \, m_{i,\,k}$$

i.e., it is the sum of the contribution coming from the various species which, after sampling with an efficiency E_i and extraction, yields the ionic species k. Thus, given the species of interest A, the denuder set-up should be such that:

$$E_{A_k} \simeq 1 \quad \text{and} \quad E_{B_k} = E_{C_k} = \ldots.. \ E_{N_k} \simeq 0$$

which means that the efficiency for the species of interest must approach 100%, while the collection efficiency for other interfering species should approach zero, i.e.:

$$m_k = m_{A_k}$$

In other words, the mass distribution of the ions in the denuder line gives figures which are related to the reliability of the sampling hypothesis, that is to the reliability of the measurements carried out.

EXPERIMENTAL

Sampling site

The measurements have been carried out in the Italian base of Antarctica which is located in Terranova Bay. Figure 2 shows the location of the base and the sampling site. All measurements have been carried out during the Antarctica Summer 1990–91. Table 1 identifies the sampling runs, the sampling time periods and the volume of air which has been collected.
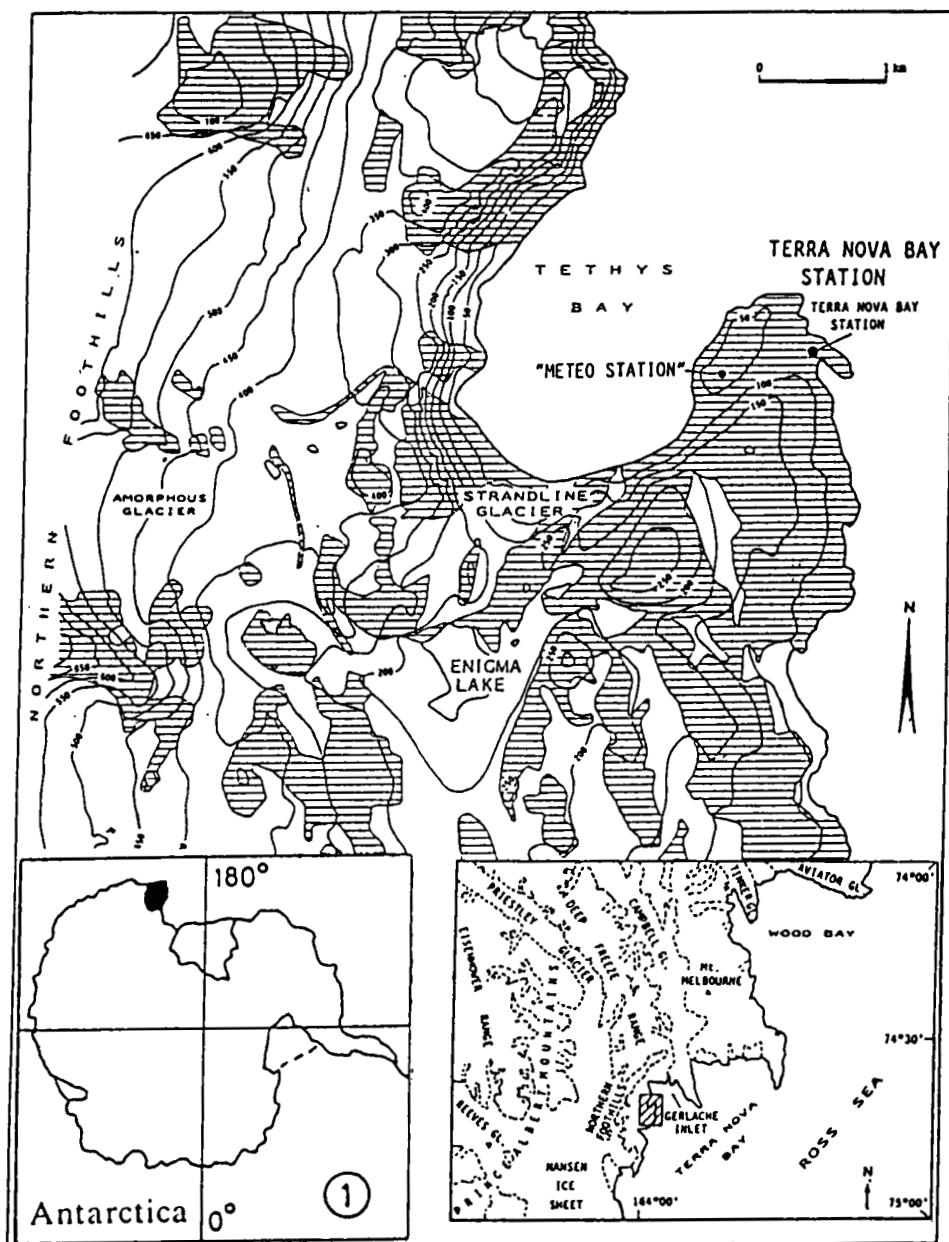
Figure 2 The location of the Italian Base at Terranova Bay with a detail showing the sampling site.

Table 1 Air samples collection during the campaign. Volumes are in standard m^3.

RUN No.	SAMPLING PERIOD	SAMPLED VOLUME
1	Jan 2–4	34.72
2	Jan 4–6	34.57
3	Jan 6–8	34.89
4	Jan 8–10	34.34
5	Jan 10–12	34.59
6	Jan 12–14	34.41
7	Jan 14–16	33.68
8	Jan 16–18	34.40
9	Jan 18–20	33.66
10	Jan 20–22	34.91
11	Jan 22–24	34.79
12	Jan 24–26	34.78
13	Jan 26–28	25.84
14	Jan 28–30	35.03
15	Jan 30–Feb 1	35.24
16	Feb 1–3	35.74
17	Feb 3–5	35.50
18	Feb 5–7	35.58

Sampling elements

Annular denuders used in the experiments have been prepared by using pyrex glass. The length of the denuder was 20 cm; the inner diameter of the outer tube was 33 mm while the outer diameter of the inner tube was 30 mm, yielding an annular space of 1.5 mm.

The cyclone ensures a cut size of about 2.5 μm at a nominal flow rate of 15 L/min and was made by polyethylene. The front filter was made of Teflon (Teflon w/ring 1 μm 47 mm, Gelman Science, Ann Arbor, Mi, USA) and the back-up filter of Nylon (Nylasorb 1 μm, Gelman Science, Ann Arbor, Mi, USA)).

Sampling equipment

The samples have been collected by means of a properly designed electronic sampler (Sequair 92A, D.A.S., Palombara Sabina, Italy). It essentially consists of a microprocessor controlled air sampler where the microprocessor controls all the parameters which define the precision and accuracy of the sampling step. Air was sampled through the denuder line and the standard flow rate is measured by measuring the absolute temperature and the pressure drop across an orifice. The measurement of the external temperature allowed the calculation of the actual sampling flow rate which was then compared with the value selected by the user. According to the change in the in-line pressure drop, the microprocessor adjusted the inlet flow rate by controlling a metering valve placed in line [11]. The operating sampling flow rate was 12 L/min.

The equipment which was transported in Antarctica also includes a meteorological station (LASTEM, Settala Premenugo, Italy) for the collection of the relevant data and a sampler

for particulate matter which was also used to measure the natural radioactivity. This parameter may be correlated to the atmospheric stability and therefore offers the opportunity of having a direct indication as to the mixing properties of the tropospheric boundary layer. The meteorological station was also interfaced to the microprocessor of the sampling device in order to stop sampling if the prevailing winds blow from the base. Fortunately this was a very rare event.

Analytical equipment

Before sampling, the denuders were washed with distilled water and coated with the following solutions:

i)   NaCl Denuders: 0.2% w/v NaCl in methanol
ii) Na_2CO_3 Denuders: 1 % Na_2CO_3 + 1% glycerol (w/v) in water-methanol 1:1 solution
iii) Citric acid Denuders: 1% (w/v) citric acid in methanol.

After sampling, the denuders were extracted with 8 mL of distilled water containing 0.037% H_2O_2, while the cyclone and the filters were extracted with 5 mL and 8 ml respectively of the Dionex eluent solution and the solutions being treated as before. After returning to the laboratory, the solutions were analyzed according to a standard analytical procedure by using a Dionex mod. DX 100 ion chromatograph (Dionex Co, Sunnyvalle, Ca, USA) equipped with a Dionex AS3 column.

RESULTS AND DISCUSSION

Samples were collected for about five weeks extending from Jan 2nd through Feb 7th, 1991. Since every sampling step had a duration of two days, eighteen samples were collected for a total sampled volume of about 34 m^3 per sample. It is worth stressing that all samples were used for the evaluation of the results since no significant contamination was detected.

Blanks

From the analytical point of view, great attention was been paid to blank problems and, since the experience with some component gave poor results, it was decided to not analyze ammonia and chlorides in gas phase and particulate matter. None of the analysis carried out in the Laboratory at Rome after the campaign showed any contamination. As regards nitrate and sulfate, the values of the laboratory blanks were below the minimum detectable amount of the analytical system (0.01 μg/mL). Field blanks were, in general, of the same order of magnitude as the laboratory blanks, showing that the denuder hóusing was airtight to the outside atmosphere.

Table 2 Mass distribution of sulphate ion along the sampling line.

	D1 µgSO4=	D2 µgSO4=	D3 µgSO4=	D4 µgSO4=	Cy µgSO4=	F1 µgSO4=	F2 µgSO4=
1	11.78	1.07	17.87	1.53	4.29	7.03	1.14
2	6.68	1.05	13.84	2.08	3.90	14.25	2.46
3	9.28	0.34	21.34	2.88	3.20	11.94	1.62
4	18.12	0.62	24.18	2.44	2.00	15.90	1.20
5	1.19	0.58	35.54	2.14	1.10	15.89	1.28
6	4.16	0.48	21.50	2.03	3.05	8.67	1.24
7	2.89	0.23	2.98	1.05	1.80	7.84	1.59
8	8.21	0.25	24.94	1.89	2.85	14.81	1.38
9	4.01	0.20	21.68	2.27	2.95	12.40	1.15
10	6.99	0.25	45.31	5.40	15.25	18.40	1.11
11	3.81	0.18	15.16	0.21	7.05	19.43	0.79
12	2.37	0.17	1.93	0.51	4.90	14.55	1.23
13	49.60	1.13	18.05	8.82	33.85	15.25	1.22
14	0.85	0.07	3.71	1.15	3.10	8.13	1.16
15	2.25	0.09	2.85	1.04	3.95	7.25	1.35
16	2.22	0.16	6.90	0.07	5.75	7.18	1.07
17	1.71	0.13	8.02	0.20	8.75	12.48	1.44
18	3.02	0.14	9.55	0.16	2.90	10.00	1.22

Particulate sulfate

The mass distribution of sulfate ion in the denuder line is shown in Table 2. Sulfates were detected at noticeable amounts in the D1 through D4 denuders, in the cyclone and on the filters. Since the minimum detectable amount for this ionic species was about 0.015–0.020 µg SO_4^{2-}/mL, an amount of sulfates on a single sampling element less than 0.15 µg is to be considered negligible. As it is clearly shown in the data set, a substantial amount of sulfate is detected in D1, with negligible amount on D2. This can be explained by assuming that sulfates found on D1 is entirely due to sulfate particulate matter in the large size region which, as it is well known, might be efficiently deposited in the first tract of the sampling line because of aerodynamic deposition. After the first portion of the denuder, a laminar flow is rapidly developed and the deposition of the particles drops to very low values. Indeed, the second NaCl denuder did not show appreciable amounts of sulfates. The hypothesis that giant sulfur-containing particles are collected in the first denuder is also confirmed the by large quantities of the same ion found in the cyclone. The relationship, however, is not very direct since the efficiency for the collection of sulfates in the first denuder is also a function of the wind speed. In fact, there is a clear correspondence between sulfates found in D1 and the wind speed. Clearly, the sulfate in the large particle region is typical of air masses of marine origin. As previously stated, no attempt has been made to measure chlorides, thus no conclusion can be drawn about the characterization of sea-salt and nss (non sea salt) sulfates.

Concentration data for the sulfur containing compounds is reported in Table 3. The maximum concentration (3.5 µg/m^3) has been found in the sample No. 13 (Jan 26–28) which is characterized by very strong northerly winds of marine origin. The data shows that the amount of coarse sulfates, as obtained by adding sulfates found on the first denuder to those

Table 3 Concentration in $\mu g/m^3$ of sulphur-containing compounds.

	SO2 D3+D4	coarse SO4= D1+Cy	fine SO4= F1	evap. SO4= F2	total fine SO4= F1+F2
1	0.372	0.463	0.202	0.033	0.235
2	0.307	0.306	0.412	0.071	0.483
3	0.462	0.358	0.342	0.046	0.389
4	0.516	0.586	0.463	0.035	0.498
5	0.725	0.066	0.459	0.037	0.496
6	0.455	0.210	0.252	0.036	0.288
7	0.080	0.139	0.233	0.047	0.280
8	0.519	0.322	0.431	0.040	0.471
9	0.474	0.207	0.368	0.034	0.403
10	0.967	0.637	0.527	0.032	0.559
11	0.294	0.312	0.558	0.023	0.581
12	0.047	0.209	0.418	0.035	0.454
13	0.693	3.229	0.590	0.047	0.637
14	0.092	0.113	0.232	0.033	0.265
15	0.074	0.176	0.206	0.038	0.244
16	0.130	0.223	0.201	0.030	0.231
17	0.154	0.295	0.352	0.041	0.392
18	0.182	0.166	0.281	0.034	0.315

found on the cyclone, is highly variable. It is worth stressing that the definition of large sulfate particles is ambiguous, as it refers to the particles which are effectively collected. It is well known that the efficiency of particle sampling, in the geometrical configuration typical of the denuder line, inversely depends on the wind speed. Thus, at large wind velocities, the geometric cut in the particle size will be reduced.

Sulfates found in the Teflon filter (fine fraction) do not show a very large variability, as they are generated, as it is well known, by homogeneous oxidation of gas phase sulfur containing compounds (e.g., sulfur dioxide, DMS, DMSO, etc.). The concentration found in Antarctica is about 0.4 $\mu g/m^3$ which is quite consistent with other observations in remote areas. Maxima in the concentration values are typical of northerly winds.

Sulfates in the Nylon filters have been detected at levels which are not very far from the detection limits, but which are still significant from an analytical point of view. The presence of sulfate ions in F2 can only be explained by assuming the evaporation of sulfur compounds from the front Teflon filter. The source and the nature of these compounds are unknown. However, the presence of sulfates on the Nylon filter is a common finding in samplings carried out in other environments such as urban or rural sites, especially when the duration of the sampling step extends over several hours (To be published).

Since the nature of sulfates found on the Nylon filter is not known, the general term "Evaporated sulfates" is used. The concentration is however very small (in most of the cases it is of the order of few tens of nanograms per cubic meter). Clearly, the total concentration of fine sulfates will be obtained by adding the amount found on F1 to that found on F2.

Gas phase sulfur dioxide

The measurement of gas phase sulfur dioxide can be carried out by analyzing the mass distribution of sulfate in the carbonate coated denuder. Indeed, earlier experiments confirm that SO_2 is not collected on sodium chloride, but it is efficiently recovered on the sodium carbonate denuders. The inlet flow rate is such that a collection efficiency better then 95% is ensured, thus negligble amount of sulfur dioxide is expected in the first two NaCl denuders and in the second Na_2CO_3 denuder. Tab. II shows that the sulfate content of D2 is very low (sulfate in D1 is due to particulate matter) while there is a noticeable sulfate amount on the first carbonate element D3, where SO_2 is expected to be found. In order to discuss the source of the sulfate in D3 and D4, it is worth recalling that they are the result of the sum of several contributing sources which might be written, in molar form, as:

$$m_{SO_4^=} = m_{SO_2g} + m_{part} + m_{nr} + m_x$$

where the different terms are defined and discussed as it follows:

i) Gas phase sulfur dioxide ($m_{SO_2\,g}$): In this case most of the gas is collected on the first carbonate denuder (D3).

ii) Deposition of particulate sulfate (m_{part}): The interference from this source should be the same in the second, third and fourth denuder, since the aerodynamic conditions of the inlets are the same. Since there is a small amount of sulfate on the second denuder D2, it is possible to neglect the particulate sulfate contribution in the third denuder and fourth denuder as well.

iii) Other reactive gas-phase sulfate-forming species (m_{nr}): This interference is to be connected with the presence of highly reactive compounds, other than SO_2, which are efficiently collected on the first denuder and which yield sulfates when extracted with water. Since, up to now, the presence of such compounds was not evidenced, this term can be neglected.

iv) Other non-reactive gas-phase sulfate-forming species (m_x): Same as above, but with low collection efficiency. In this case the sulfate mass found on D4 will be approximately equal to that found in D3. The presence of such a species might justify the sulfate content of second carbonate denuder, thus this term does not appear to be negligible. However, if such amounts in the second denuder are to be ascribed to a species collected with very low efficiency, this species should be present at very high concentration levels. Since up to now such species has not been detected, it can be said that this contribution approaches zero as well.

Therefore:

$$m_{SO_4^=} = m_{SO_2g}$$

In this hypothesis, there should be no way to justify the amount of sulfate recovered in the second carbonate denuder. However, early observations on the collection of relatively weak acids such as nitrous, hydrofluoric and sulfur dioxide, demonstrate that when the

sampling step last for a long time, anions may migrate in the direction of the air flow. The extent of this effect depends upon the absolute humidity, temperature etc.. Since the denuders are operating in a thermostated box, the air temperature at the carbonate denuders is higher than that ambient temperature, thus migration is possible. By assuming that the sulfate in the account carbonate denuder is due to displacement of sulfites from the first one, the net amount of SO_2 can be well estimated by adding the sulfate amount in both elements. With this procedures, an upper limit for gas phase sulfur dioxide concentration can be calculated. The results are shown in Table 3.

The amount of sulfur dioxide was never found larger than about 1.0 $\mu g/m^3$ with relative maxima during January. The last week of sampling was characterized by low values which are consistent with the wind direction (Mainly westerly or southerly).

Particulate nitrate (Coarse particles)

As previously stated, no attempt has been made in order to characterize ammonia in gas phase and ammonium ion in particulate matter; NO_2 was not detected either. The extracted denuders and filters has been only analyzed according to nitrite and nitrate, as shown in Table 4a and 4b where the mass distributions of these two ions have been reported.

Table 4b shows that only a small amount of nitrates was found on D1, while the amount detected on D2 approached zero. In this case, the mass of nitrate on the denuder, can be written as:

$$m_{NO_3^-} = m_{HNO_3} \, g + m_{NO_3^-} \, p$$

Table 4a Mass distribution of nitrite ion along the sampling line.

	D1 μg NO2–	D2 μg NO2–	F1 μg NO2–	F2 μg NO2–
1	0.53	0.25	2.17	0.25
2	1.63	0.62	0.01	0.19
3	2.28	0.82	0.16	0.43
4	0.82	2.75	0.11	0.29
5	1.72	0.79	0.44	0.22
6	1.60	0.61	0.16	0.21
7	0.80	0.62	0.47	0.11
8	0.94	0.92	0.18	0.31
9	0.96	3.22	0.25	0.26
10	2.57	0.92	0.27	0.37
11	0.46	3.31	0.22	0.33
12	0.08	0.03	0.06	0.42
13	0.05	0.04	0.10	0.31
14	0.18	0.12	0.15	0.18
15	0.33	0.08	0.03	0.22
16	0.72	0.17	0.07	0.20
17	0.39	0.03	0.10	0.50
18	0.23	0.04	0.01	0.36

Table 4b   Mass distribution of nitrate ion along the sampling line.

	D1 μg *NO3−*	*D2* μg *NO3−*	*D3* μg *NO3−*	*D4* μg *NO3−*	*Cy* μg *NO3−*	*F1* μg *NO3−*	*F2* μg *NO3−*
1	5.77	0.23	0.20	0.41	0.51	2.07	0.70
2	1.25	0.12	0.70	0.79	0.90	1.18	1.52
3	3.71	0.08	1.38	0.57	1.00	0.63	1.33
4	7.79	0.39	0.92	1.55	0.60	1.18	0.91
5	0.72	0.13	2.04	0.77	1.10	1.42	0.98
6	2.15	0.10	19.50	0.35	0.34	1.00	1.05
7	3.30	0.10	1.19	0.64	0.55	0.16	1.40
8	3.53	0.18	1.34	0.74	1.11	0.45	1.09
9	1.31	0.10	1.16	3.18	0.25	0.87	0.98
10	1.62	0.10	2.24	0.83	1.70	0.98	1.12
11	0.80	0.00	0.17	0.07	1.05	0.91	1.03
12	0.10	0.00	0.06	0.08	0.25	0.98	0.88
13	0.10	0.00	0.07	0.07	0.15	0.05	0.84
14	1.51	0.04	0.08	0.27	0.15	0.04	0.65
15	1.61	0.00	0.06	0.08	0.16	0.03	0.96
16	0.53	0.07	0.09	0.28	0.05	0.09	1.13
17	0.78	0.00	0.08	0.15	1.15	0.01	1.60
18	0.67	0.00	0.11	0.03	0.00	0.00	1.00

e.g., the nitrate ions come from the absorption of nitric acid in the gas phase and the deposition of coarse nitrate particulate matter. In this case it is not easy to differentiate the two sources of nitrates as was done for the sulfate. In fact, the chemical reactivity of the substrates ensure that there is no collection of sulfur dioxide in the NaCl denuder. Since a complete absorption on carbonate occurs, a complete separation of the two components is ensured.

For nitrates, it is possible to make some very realistic hypothesis. For instance, the data set shows that the amount of nitrate found on the cyclone is low, thus the concentration of nitrates in the large particle fraction is also very low. This is consistent with the sources of large particulate nitrates, which are generated by the reaction of sea salt (NaCl) with nitric acid. However, since the extent of this reaction depends upon the relative concentration of nitric acid, in remote locations and on aerosols of marine origin the amount of large nitrates is very low.

If this assumption (Case a) is accepted, m_{NO3-p} approaches zero and the concentration of large particles is given by nitrates found on the cyclone as given in Table 4b. If the assumption is not accepted, the amount of large particles will be the sum of that found on the first denuder and on the cyclone (Case b). However, this is an upper limit, since no nitric acid is supposed to be present.

Another approach might make use of the calculations run on sulfates. Since it is possible to accurately evaluate the ratio of sulfate in the first denuder and in the cyclone, by assuming the same size distribution for sulfates and nitrate in the large particle fraction and by using the nitrate data on the cyclone, it is possible to calculate the amounts m_{NO3-p} found on the first denuder and then to obtain the mass of the coarse nitrates as m_{NO3-p} plus $m_{NO3-(cycl)}$, as reported in Table 5a (Case c).

Table 5a Concentration in µg/m3 of particulate nitrate.

	coarse NO3–			fine	evap.	total fine	evap. fract.
	case A	case B	case C	NO3–	NO3–	NO3–	NO3–
	Cy	D1+Cy	Cy*(d1/Cy)SO4	F1	F2	F1+F2	F2/(F1+F2)*100
1	0.015	0.181	0.040	0.060	0.020	0.080	25.3
2	0.026	0.062	0.045	0.034	0.044	0.078	56.3
3	0.029	0.135	0.083	0.018	0.038	0.056	67.9
4	0.017	0.244	0.158	0.034	0.026	0.061	43.5
5	0.032	0.053	0.034	0.041	0.028	0.069	40.8
6	0.010	0.072	0.013	0.029	0.031	0.060	51.2
7	0.016	0.114	0.026	0.005	0.042	0.046	89.7
8	0.032	0.135	0.093	0.013	0.032	0.045	70.8
9	0.007	0.046	0.010	0.026	0.029	0.055	53.0
10	0.049	0.095	0.022	0.028	0.032	0.060	53.3
11	0.030	0.053	0.016	0.026	0.030	0.056	53.1
12	0.007	0.010	0.003	0.028	0.025	0.053	47.3
13	0.006	0.010	0.009	0.002	0.033	0.034	94.4
14	0.004	0.047	0.001	0.001	0.019	0.020	94.2
15	0.005	0.050	0.003	0.001	0.027	0.028	97.0
16	0.001	0.016	0.001	0.003	0.032	0.034	92.6
17	0.032	0.054	0.006	0.000	0.045	0.045	99.3
18	0.000	0.019	0.000	0.000	0.028	0.028	100.0

Particulate nitrate (Fine fraction)

The particulate nitrate fine fraction is collected on the front Teflon filter and in the Nylon filter. Results are also shown in Table 5a, which reports the equivalent concentrations found on the two elements and their sum. The amount of nitrates collected on the back-up Nylon filter is statistically larger than the one measured on the front filter, and this is an indication that a noticeable amount of nitrate is in the form of ammonium nitrate. This species, in fact, dissociates into nitric acid and ammonia, especially at low absolute humidities and relatively high temperatures, conditions which are easily met during the sampling in the denuder line. Table Va also shows the fraction of evolved nitrates which is, especially at the end of the sampling period, very close to 100%. This result is also typical of polluted areas. It should be stressed that nitric acid might be evolved from the Teflon filter also through the reaction of nitrate with acidic particle (e.g. H_2SO_4), thus the proof that the evolved nitrates are given by ammonium salts can only be obtained by also analyzing the evolved ammonia.

Gas phase nitric acid

The concentration of this species is obviously complementary to that of the large particulate nitrate found in the first denuder, thus, as discussed before, three cases can be defined.

Case a): No large particles are intercepted by the first denuder so that all nitrates are to be ascribed to HNO_3. This is the upper limit for the concentration of nitric acid as determined by means of the denuder technique.

Case b): In this case nitric acid is absent (C=0) and this is clearly a lower limit.

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Table 5b   Concentration in ug/m3 of gas phase nitric acid.

	case A D1	case B	case C D1-Cy*(d1/Cy)SO4=
1	0.166	0.000	0.126
2	0.036	0.000	−0.008
3	0.106	0.000	0.023
4	0.227	0.000	0.069
5	0.021	0.000	−0.014
6	0.062	0.000	0.049
7	0.098	0.000	0.072
8	0.103	0.000	0.010
9	0.039	0.000	0.029
10	0.046	0.000	0.024
11	0.023	0.000	0.007
12	0.003	0.000	−0.001
13	0.004	0.000	−0.005
14	0.043	0.000	0.042
15	0.046	0.000	0.043
16	0.015	0.000	0.014
17	0.022	0.000	0.016
18	0.019	0.000	0.019

Case c): In this case the evaluation of the two different contributions is required, by assuming a similar distribution of large sulfates and nitrates.

These data are reported in Table 5b. In conclusion, the most probable value for the concentration of nitric acid might be evaluated as an intermediate value for the case c) and a). Data show that the amount of nitric acid is extremely low, being well below 0.5 ug/m^3. In fact, nitric acid is mainly generated through the reaction of NO_2 with OH radicals or through the thermal dissociation of ammonium nitrate. The very low amounts of the two components are such that only sub parts per billions levels of HNO_3 are expected. Clearly, the accuracy in the measurement of HNO_3 can be improved through a better separation of gas phase and particulate matter according to a procedure which is now being tested and which will be used in the next campaigns.

Figure 3 shows the trend of nitric acid and sulfur dioxide, as well as the measurements of the natural radioactivity, shown in order to have a crude evaluation of the mixing properties of the atmosphere. It can be seen that nitric acid correlates very well with atmospheric stability. Sulfur dioxide has a similar trend which includes however three maxima, corresponding to days characterized by northerly winds (Jan. 8, 20 and 26th). The increase in the sulfur dioxide concentration, as well as the increase in the levels of fine sulfate, is related to the presence of the Melbourne volcano which is located about 50 Km north from the Italian Base.

Other gas phase nitrogen compounds

The denuder analysis was able to detect nitrites and nitrates on the carbonate denuders. The source of the these ions, in this case, has not been investigated. However, in general, they
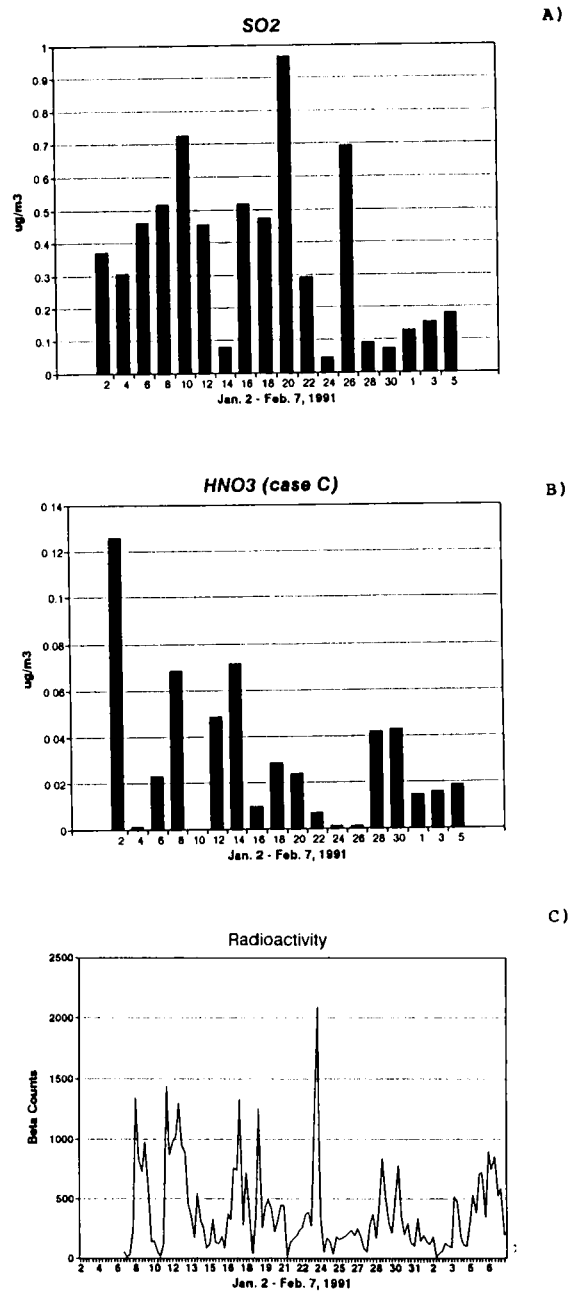
Figure 3 Temporal trend of the concentrations of sulfur dioxide (A) and nitric acid (B), as measured by means of annular denuder/filter pack. Natural radioactivity (C) is also shown for the same sampling period.

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can be attributed to the absorption of NO_2 which, on alkaline substrates, is reduced to nitrite, Subsequently, nitrites can be oxidize to nitrates. Since the collection efficiency for NO_2 is low, the mass distribution of NO_2^- and NO_3^- are almost the same in the two denuders[7]. These data were not used for the evaluation of any components.

Particulate chloride

Problems concerning with blanks and contamination did not allow the measurement of gas phase hydrogen chloride and large particulate chlorides collected in the cyclone; thus only the amount of chlorides found on the Teflon and Nylon filters have been reported. Large amount of particulate chlorides have been found during the third week of sampling (Samples 9 to 14) with a trend which is very similar to that observed for fine sulfate. However, the amount collected on F2 is quite large, as in the case of nitrates. Even in this case, the collection of evolved ammonia might be a decisive test in understanding the source of evolved chloride (Ammonium chloride dissociation or displacement of hydrogen chloride by sulfuric acid). The presence of relevant amounts of evaporated chlorides is not unexpected, since substantial amounts of ammonium chlorides have been already identified in some non-polluted areas[10].

Table 6 shows the chloride ion masses found on filters and the relative concentration of chlorides. It should be stressed that the the presence of evaporated chloride on F2 might be due to the reaction of fine sodium chloride with sulfuric acid or ammonium bisulfate. Such a doubt might find a proper answer during next campaigns where ammonia in the elements of the sampling line will also be measured.

Table 6 Mass distribution of cloride ion and concentration in ug/m3 of particulate cloride.

	F1 $\mu g Cl-$	F2 $\mu g Cl-$	fine Cl^- $\mu g/m^3$ F1	evap. Cl^- $\mu g/m^3$ F2
1	2.47	7.79	0.071	0.224
2	8.02	6.20	0.232	0.179
3	2.55	6.00	0.073	0.172
4	3.86	2.97	0.112	0.086
5	1.77	2.29	0.051	0.066
6	2.23	2.00	0.065	0.058
7	0.85	5.33	0.025	0.158
8	2.20	2.55	0.064	0.074
9	5.12	3.67	0.152	0.109
10	8.45	4.28	0.242	0.123
11	6.45	4.38	0.185	0.126
12	9.51	3.24	0.273	0.093
13	10.86	4.32	0.420	0.167
14	5.04	4.90	0.144	0.140
15	4.86	3.92	0.138	0.111
16	3.95	4.00	0.111	0.112
17	8.73	3.26	0.246	0.092
18	3.20	3.22	0.090	0.091

CONCLUSIONS

Data obtained from this preliminary campaign clearly demonstrate the feasibility of the diffusion denuder technique in obtaining reliable data about the concentration of minor components in gas phase and in particulate matter in the Antarctica troposphere. Gas phase sulfur dioxide can be measured in a sufficiently accurate manner to levels as low as a few nanograms per cubic meter, while nitric acid and nitrates may be well characterized and measured. The uncertainty derived from the imperfect separation between the gaseous and particulate phases may be reduced to a minimum by properly analyzing the mass distribution of the relevant ions along the sampling line.

Additional information on the chemical properties of polar tropospheres can be inferred by performing other measurements which were not planned for this campaign. For instance, the measurement of ammonia in the fifth denuder, coupled to ammonium found on the cyclone, filters and on a third back-up filter allow the study of many other compounds, while the determination of hydrogen chloride may significantly contribute to the study of dry and wet acid deposition in remote areas. Such measurements will be carried out during the next sampling campaigns.

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