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Short communication

Carbon-coated annular denuders and ion chromatographic measurements for the determination of nitrogen-containing species (NO_2 and NO_y) in remote atmospheres

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Abstract

Nitrogen oxides play a major role in determining the chemical properties of the atmosphere. Measurements of these species in remote areas are rare, although their relevance is well established. This is particularly true for polar sites. In order to fill this gap, an annular diffusion denuder system, with an alkaline carbon surface, for the simultaneous collection of nitrogen dioxide (NO_2) and peroxyacetyl nitrate and other organic nitrates has been developed. In the collection stage, nitrogen dioxide (NO_2) and NO_y yield nitrite (NO_2^-) and nitrate (NO_3^-) ions, respectively. These are extracted after sampling and analysed by ion chromatography. The experimental set-up was tested during two expeditions carried out in sites located in Arctic and Antarctica. The Arctic concentrations were found between 10 and 170 ng m^{-3} for NO_2 and between 100 and 600 ng m^{-3} for NO_y while in Antarctica concentrations were found between 10 and 300 ng m^{-3} for NO_2 and between 300 and 700 ng m^{-3} for NO_y .

Results obtained from these expeditions demonstrate that the minor components may be measured at levels as low as a few nanograms per cubic meter in remote atmospheres using the suggested technique. The reported concentrations are to be considered among the first observations of gas phase nitrogen compounds in polar areas. © 1999 Published by Elsevier Science B.V. All rights reserved.

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1. Introduction

Nitrogen oxides, especially NO_2 , play a very important role in determining the chemical properties of the atmosphere [1]. In fact, these species cause changes in the oxidizing properties of the atmosphere due to their ability to generate ozone when reacting with non-methane hydrocarbons (NMHCs) [(NMHCs + $\text{NO}_x + h\nu \rightarrow \text{O}_3 + \text{peroxyacetyl nitrate (PAN)} + \text{HNO}_3 + \text{etc.}$)]. They produce nitrous acid

through a heterogeneous reaction with vapour water ($2\text{NO}_2 + \text{H}_2\text{O} \rightarrow \text{HONO} + \text{HNO}_3$) and participate to a chain reactions that leads to the formation of nitric acid, peroxyacetyl nitrate and particulate nitrates.

Therefore, the determination of NO_2 is essential to clarify the temporal evolution of the most significant atmospheric components. However, such measurements in remote areas are rare since several analytical problems are involved [2]. In fact, the concentrations of minor components in remote areas are very low, thus reliable results need highly sensitive and interference free analytical method. Many com-

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mercial instruments are available for the monitoring of such pollutants. However, their sensitivity is not adequate for such measurements, especially when concentrations are low. In addition, a simultaneous measurement of the atmospheric concentration of pollutants either in the gas or in the particulate phase without any cross-interference, is often required. The recent development of the annular denuder technique has allowed a precise measurement of several components of extreme importance for the knowledge of atmospheric processes at polar sites. Among them, the annular denuder sampling technique allows the determination of the nitrogen dioxide (NO_2) and peroxyacetyl nitrate PAN and other organic nitrates ($\text{NO}_y \equiv \text{NO}_x + \text{PAN} + \text{HNO}_3 + \text{RONO}_2 + \text{N}_2\text{O}_5 + \dots$). The term NO_y commonly denoted the odd nitrogen oxides, where PAN and alkyl nitrates have been reported to contribute 70–80% to NO_y [3].

2. Materials and methods

The annular denuder sampling technique is one of the most important methods for collecting gaseous and particulate species in a selective way at very low levels of concentrations. The diffusion denuder technique was described in several papers [4,5]. The performance of a denuder is based on the very high difference in the penetration efficiency exhibited by gases and particles when air is drawn through the device under laminar flow conditions. In fact, particles passing through the tube have a much lower diffusion rate than gaseous compounds by several orders of magnitude. For these reasons, particles proceed unaffected along the tube and can be collected at the end of the sampling train by a set of filters. The gaseous molecules diffuse onto the walls of the denuder. Since the walls are coated with a proper chemical substance, the gaseous molecules are restrained selectively by a chemical reaction in the layer (sometimes by a physical absorption). A second denuder (back-up denuder) is usually placed afterward to assure the quality control of the measurement through the collection efficiency on the first one. The denuders employed were made of Pyrex glass, 20 cm in length, 3.0 cm (inside) and 3.3 cm (outside) in annulus diameter. The operating flow-rate utilized during the field studies was 12 l min^{-1} . The measurement of NO_2 and NO_y were performed

by means of alkaline carbon coated denuders [6]. The collection efficiency (E) for NO_2 and NO_y on annular denuders is calculated by:

$$E = 1 - \frac{b}{a}$$

where a and b are the amounts of nitrite (for NO_2) and nitrate (for NO_y) on the first and second denuder, respectively. The calculated efficiency was above 99% for both species. The interference due to NO was considered negligible according to previous studies by De Santis et al. [6].

After sampling, the denuders were extracted by shaking for 1 min with 10 ml of distilled water. After centrifugation, the supernatant was injected into the ion chromatograph DX 100 and 500 (AS12 separation column, AG12 precolumn and a 150 μl sampling loop) by applying NaHCO_3 – Na_2CO_3 eluent isocratic procedure. For the chromatographic analysis it was employed an alkaline standard solution of Cl^- , NO_3^- , NO_2^- and SO_4^{2-} (1000 mg l^{-1} , Merck). The control samples, consisting of 100 ng ml^{-1} calibration solution, were regularly analysed in order to re-calibrate the ion chromatograph. The variation in the concentration of the control samples is generally of the order 0.5–1%. The concentrations of NO_2 and NO_y were calculated from the nitrite and nitrate amount, respectively. The ion chromatography (IC) detection limits for both measured ions were always below the respective levels of sample blanks. The detection limit of this technique depends on various parameters such as the value of laboratory blanks and of the field blank. The lower detection limit (LOD), the lowest concentration of an analyte that the analytical process can reliably detect, is located 3σ above the measured average blank. It was evaluated by running operational blank analyses. The limit of quantification (LOQ) is 10σ above the blank. For nitrite it was found that LOD and LOQ are 4 and 13 ng ml^{-1} , respectively, while for the nitrate they are 6 and 20 ng ml^{-1} , respectively. These are corresponding to atmospheric concentrations of 2.3 and 4.3 ng m^{-3} for NO_2^- and NO_3^- , respectively (24 h samplings at flow-rate of 12 l min^{-1} and an extraction volume of 10 ml).

3. Results

The experimental set-up was tested during a field

study carried out in the Arctic troposphere, at the Zeppelin station near Ny-Alesund, Svalbard Islands, (78° 55' N, 11° 53' E) from 27 May to 12 June 1997 [7]. The Arctic concentrations found at this location were ranging between 10 and 170 ng m⁻³ for NO₂ and between 100 and 600 ng m⁻³ for NO_y, as it is shown in Table 1. How Nitrogen Dioxide is transported into the Arctic is still matter of speculation. Besides transport with air masses from polluting sources, a chemical mechanism for their formation may be postulated. In fact, photochemistry and chemical reactions in the atmosphere convert most of nitrogen oxides into odd nitrogen species (NO_y). The reduced temperatures in the polar regions increases the lifetime of NO_y so that they may act as sources of NO_x through thermal decomposition. Since this is occurring at low rates, nitrogen oxides concentrations are function of the amount of NO_y present in the atmosphere. This is also confirmed by a NO₂/NO_y molar ratio which is usually less than unity. On the other hand, on 10–12 June concentrations as high as 700 ng m⁻³ of NO₂ were sometime observed (see

on 10–12 June). This is probably due to an event of local pollution. This was also confirmed by a higher NO₂/NO_y molar ratio of 5.

Another expedition was carried out in the Antarctica troposphere, at Italian Base Terra Nova Bay (74° 41' 42" S, 164° 05' 36" E), from 9 to 28 December 1997. In this field study the concentration of NO₂ in the range of 10–300 ng m⁻³ and of NO_y in the range of 300–700 ng m⁻³ were found (Table 2). These concentrations are somewhat higher than expected for such site. These results are probably caused to local phenomena of pollution coming from activities carried out in the Antarctica base itself.

4. Conclusions

The measurement of atmospheric nitrogen compounds is a very important step to understand the chemical and physical evolution of atmospheric pollutants in polar areas. Results obtained from these field studies demonstrate, in a sensible and accurate

Table 1
NO₂, NO_y and NO₂/NO_y data collected in Arctic

Day (May–June 1997)	NO ₂ (ng m ⁻³)	NO _y (ng m ⁻³)	NO ₂ /NO _y (molar ratio)
27–28	29.85	474.37	0.05
28–29	27.54	338.37	0.06
29	73.91	594.61	0.09
29–30	12.20	488.70	0.02
30–31	60.24	267.36	0.17
31–1	109.61	162.79	0.50
1–2	170.92	307.12	0.41
2–3	36.32	274.74	0.10
3	31.53	214.50	0.11
3–4	41.53	240.96	0.13
4	31.05	597.47	0.04
4–5	68.93	467.14	0.11
5	34.98	210.35	0.12
5–6	32.32	242.88	0.10
6	59.91	210.41	0.21
6–7	44.34	210.77	0.16
7	46.98	325.37	0.11
7–8	43.27	267.37	0.12
8	37.15	596.59	0.05
8–9	57.49	337.92	0.13
9–10	68.28	158.45	0.32
10	63.66	330.29	0.14
10–11	693.78	199.42	2.58
11	694.65	101.17	5.09
11–12	468.00	124.20	2.80

Table 2
NO₂, NO_y and NO₂/NO_y data collected in Antarctica

Day (December 1997)	NO ₂ (ng m ⁻³)	NO _y (ng m ⁻³)	NO ₂ /NO _y (molar ratio)
9–10	285.99	473.06	0.45
10–11	98.39	390.36	0.19
11–12	218.90	306.49	0.53
12–13	193.94	622.27	0.23
13–14	427.44	496.01	0.64
14–15	88.54	379.13	0.17
15–16	200.19	434.02	0.34
16–17	127.90	589.65	0.16
17–18	130.16	468.68	0.21
18–19	620.73	525.87	0.88
19–20	173.75	473.75	0.27
20–21	225.72	701.20	0.24
21–22	35.57	302.18	0.09
22–23	224.74	539.85	0.31
23–24	80.81	382.24	0.16
24–25	201.51	403.22	0.37
25–26	275.91	313.71	0.65
26–27	132.99	318.57	0.31
27–28	196.27	315.97	0.46

manner, that the minor components may be measured at levels as low as a few nanograms per cubic meter in remote atmospheres using the denuder technique. The reported concentrations are to be considered among the first observations of gas phase nitrogen compounds in polar areas and contribute significantly to the physico-chemical processes occurring in such sites.

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