Use of ion chromatography for monitoring atmospheric pollution in background networks

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Abstract

The results of the application of the annular denuder–filter pack technique coupled with ion chromatography to the determination of atmospheric pollutants in semi-polluted and background areas are reported. The coupling of these techniques reveals a viable solution for the precise and accurate measurement of atmospheric pollutants, with discrimination of the gaseous and the particulate phase and without any mutual interconversion during the sampling phase. The sensitivity is appropriate for the determination of pollutants related to both the acid deposition and the photochemical smog phenomenon, even in semi-remote and remote areas. An interpretation of the field results in terms of chemical properties of the atmosphere is given. © 1999 Elsevier Science B.V. All rights reserved.

1. Introduction

The knowledge of the distribution of atmospheric pollutants between the gaseous and the particulate phase is a very important goal for the environmental analytical chemist: gases and particles, in fact, are very different in terms of adverse effects to the human health and to the ecosystem, and generally have different formation pathways and removal processes. Particularly for compounds which are present in the atmosphere in both the gaseous and the particulate phases and which undergo an easy interconversion between the two forms (sulphur dioxide, sulphuric acid and sulphates, nitric acid and nitrates, ammonia and the ammonium ion and a variety of medium- to high-molecular-mass organic compounds) a method which allows not only the separation of the different chemical compounds but also the discrimination of the two phases is strongly needed; obviously, the latter cannot be given by any analytical step but must be obtained in the course of the sampling step.

A viable solution to this problem was given in the early 1980s with the introduction of the diffusion denuder technique, aimed at the determination of gaseous atmospheric pollutants without any bias due to the interference of particulate compounds [1–5]. In the last two decades this technique has been improved and refined, to reach a high degree of reliability, and has been successfully employed in background networks such as the EMEP network (Co-operative Programme for Monitoring and Evaluation of the Long-Range Transmission of Air Pollutants in Europe) [6]. The results reported in this paper refer to the determination of the pollution levels in semi-remote and remote areas, and clearly show how the application of the ion chromatography (IC) and the diffusion denuder–filter pack techniques

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to the determination of inorganic pollutants can yield very valuable results in terms of comprehension of the physico–chemical mechanisms which lead to pollution phenomena.

2. Experimental

The performances of diffusion denuders take advantage of the noticeable difference existing between the diffusion coefficients of gases and particles (several orders of magnitude). When gaseous pollutants are drawn through a denuder, they diffuse towards the denuder walls, which are coated with a chemical suitable for the retention of a specific pollutant or group of pollutants. Particles, instead, proceed unaffected along the device and may be recovered downstream. Annular denuders consist of two coaxial tubes, the inner one closed at both sides, which forms an annular channel; the walls of the channel are coated with the chemical able to act as a sink for the pollutants to be collected [7]. The advantages of the annular geometry with respect to the old hollow tube geometry consist, among others, in the higher operative flow-rate, higher operative capacity and lower dimensions. A low dimension of the devices permit the use of more denuders set in series, allowing the determination of more pollutants at the same time and the implementation of an internal Quality Control Procedure on the collected data [7–9].

Denuders are made of Pyrex glass and have the following dimensions: length: 200 mm, outer diameter: 33 mm; inner diameter: 30 mm. The sampling line (Fig. 1) was composed as follows:

- Two annular denuders coated with a 0.05% (w/w) NaCl in methanol–water (80:20) solution
- Two annular denuders coated with a 1% $Na_2CO_3 + 1\%$ (w/w) glycerol in methanol–water (50:50) solution
- One annular denuder coated with a 1% (w/w) H_3PO_3 in methanol–water (90:10) solution
- One cyclone having a granulometric cut size of 2.5 μm at the operative flow-rate of 15 l/min
- One PTFE (Teflon) filter of 0.8 μm pore size
- One nylon filter of 0.8 μm pore size
- One paper filter impregnated with a 1% (w/w) H_3PO_3 in methanol–water (90:10) solution

This sampling line allows the determination of the following compounds: nitric acid, sulphur dioxide and ammonia in the gaseous phase, nitrate, sulphate, ammonium, sodium, calcium, potassium and magnesium in the particulate phase (coarse and fine fractions). In some cases the NaCl coating was replaced with a NaF coating, allowing also the determination of hydrochloric acid and particulate chloride. Details on the choice of a proper denuders coating and on the coating procedures are reported elsewhere [10,11].

For the sampling phase, the denuder lines were placed inside specifically designed thermoinsulated housings (ADS7, D.A.S., Palombara Sabina, Rome, Italy) which are able to accommodate up to seven lines, allowing, for networks requiring daily determinations, up to one week of unattended operations. The housings are heated during the winter to avoid water condensation, and ventilated during the summer to avoid excessive heating of the denuders and filters. The sampling is operated by a control and sampling Unit (Sequair 92/A, D.A.S.) which directly
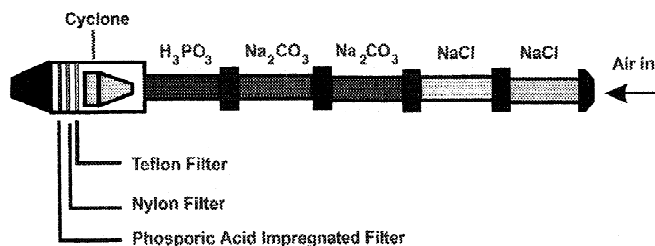

Fig. 1. Scheme of the annular denuders–filter pack sampling line for the determination of gaseous and particulate inorganic pollutants.

and sequentially activates the sampling phase on the denuders lines; the sampling lines which are not "on sampling" are tightly sealed by means of gates automatically run by the sampling unit, in order to avoid any contamination of the samples due to passive diffusion of pollutants. The sampling unit is able to control, in real time, the fluidodynamic conditions of the sampling, providing an appropriate adjustment of the inlet flow-rate, which is able to counterbalance the pressure drop increase due to the filter loading; as a result, a constancy of the flow-rate better than 0.5% is assured. The value of the sampled air volume is given with a 2% accuracy and 1% precision.

After the sampling, the denuders and filters are extracted by means of appropriate water solutions and the extracts are analysed by IC for their ionic (chloride, nitrite, nitrate, bromide, phosphate, sulphate) or cationic (sodium, ammonium, potassium, calcium, magnesium) content. The analyses were carried out by an IC system (DX100 and DX 500, Dionex, Sunnyvale, CA, USA) equipped with a 50-μl sampling loop and a AG12A pre-column and AS12A column for anion determination (eluent: 3.1 mM Na$_2$CO$_3$+0.3 mM NaHCO$_3$; flow-rate: 1.4 ml/min) and a CG12 pre-column and CS12 column for cation determination (eluent: 20 mM methanesulphonic acid; flow-rate: 1.0 ml/min).

The experimental results reported in this paper refer to two monitoring stations: the first one is placed in Montelibretti, a semi-rural location about 30 km north-east of Rome, part of the EMEP program, which addresses the evaluation of the concentration and deposition of atmospheric pollutants over Europe and the evaluation of their long-range transport. The second measurement site is located in Magorno, in the southern part of Italy, and can be considered as a background station. The measurements were carried out between 1995 and 1997; denuder measurements have been added with ozone and nitrogen dioxide continuous measurements and with the monitoring of meteorological parameters and of natural radioactivity; this latter determination allows to evaluate the mixing properties of the lower troposphere, which are of primary relevance for the interpretation of pollution phenomena [12,13].

3. Results and discussion

3.1. The sampling line

The part of the system depicted in Fig. 1 which is devoted to the determination of gaseous pollutants is composed of two NaCl-, two Na$_2$CO$_3$- and one H$_3$PO$_3$-coated denuders, for the measurements of the air concentration of HNO$_3$, SO$_2$ and NH$_3$, respectively. This configuration offers interesting possibilities not only in terms of accuracy and precision of the measurements, but also in terms of quality control of the data generated by the system, since the use of pairs of denuders coated with the same chemical allows to control the reliability of the determined amounts of analyte [8,11].

The first NaCl-coated denuder collects the incoming nitric acid with collection efficiency higher than 99.5% at the operative flow-rate of 15 l/min [5,8,10]. The back-up NaCl denuder allows one to correct, by difference, the nitric acid determination for the possible small nitrate amount due to the impact and turbulent diffusion deposition of particulate matter and to the retention of low reactivity interfering species [8,11]. Additionally this denuder constitutes an operative check of the performances of the system, since the amount recovered on this device must be coherent with the theoretical amount predicted on the basis of the knowledge of the operative conditions and of the theoretical behaviour of the geometry and coating.

In the case of nitric acid, the amount recovered on the back-up denuder can be due to the following [5,8,9]: (1) nitric acid collection: at the flow-rate of 15 l/min, about 0.5% of the atmospheric HNO$_3$; (2) particulate nitrate deposition: about 1–2% of the total incoming nitrate; (3) nitrogen dioxide retention: this nitrate amount is proportional to nitrogen dioxide air concentration ($K \approx 5 \cdot 10^{-3}$ m^3 on a 24-h sampling basis) and (4) blank values: in the order of 0.10 μg nitrate/denuder.

The ion chromatograms reported in Fig. 2 show the analyses of two NaF denuders from a typical 24-h sampling carried out in Montelibretti. During this sampling period, particulate nitrate and nitrogen dioxide concentration were 5.8 and 19.2 μg/m^3, respectively (sampling volume was 21.6 m^3). On this

Main NaF-coated denuder
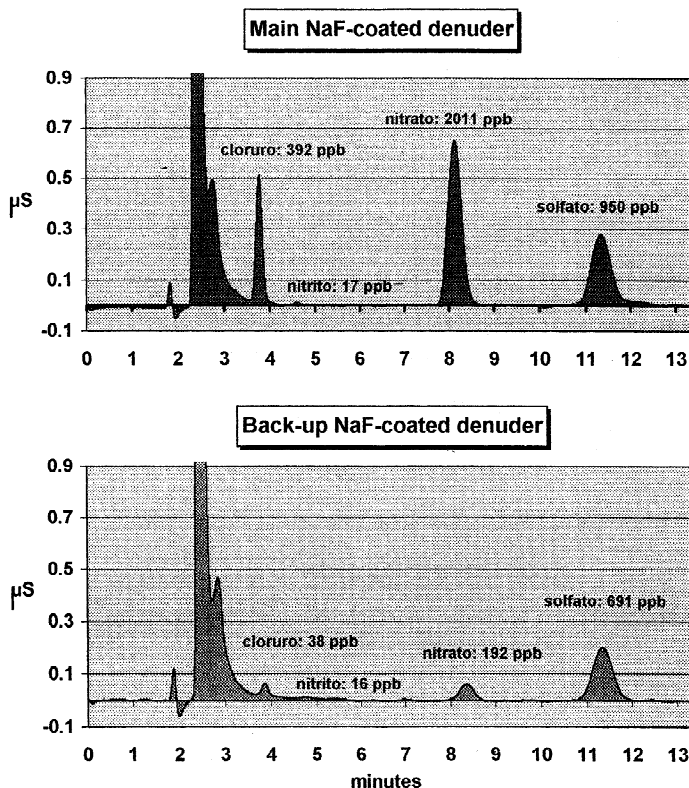

Back-up NaF-coated denuder

Fig. 2. Chromatograms of the analyses of the extracts from the first couple of denuders of the sampling line, coated with NaF. Extraction volume was 10 ml, sampling volume 21.6 m^3, sampling time 24 h. Hydrochloric acid and nitric acid concentration results to be 0.16 and 0.84 $\mu g/m^3$, respectively.

basis, one would expect to find on the back-up denuder about 0.1 μg due to the 99.5% collection efficiency of the first denuder, from 1.25 to 2.50 μg due to the particulate nitrate retention and about 0.1 μg due to the interference of nitrogen dioxide, plus 0.1 μg due to blanks. Thus, the nitrate amount really found on the back-up denuder, 1.92 μg, is in good agreement with the predicted amount (from 1.55 to 2.80 μg). This indicates that the calculation of atmospheric nitric acid concentration, performed by subtracting the nitrate amount found on the back-up denuder from the amount found on the main one, provided reliable results. Otherwise, any noticeable disagreement between the recovered and the predicted amounts would have implied the existence of a bias.

Similar considerations can be made for the determination of hydrochloric acid on NaF-coated denuders (0.38 μg of chloride on the back-up denuder of Fig. 2) and for the determination of sulphur dioxide on Na$_2$CO$_3$-coated denuders; in these two cases, however, interferent compounds are negligible, and the amount recovered on the second denuder can be attributed to particulate deposition and blank values only. In the case of ammonia determination, instead, it is sufficient to use only one H$_3$PO$_3$-coated denuder, since also the deposition of particles can be generally considered to be negligible (ammonium particles are mainly in the lower granulometric size range); it follows that the amount collected on the denuder should be only corrected for the blank value, which is independent of the atmospheric condition of each sampling.

The filter pack, comprised of one PTFE, one nylon and one phosphorous acid impregnated filter, is devoted to the determination of pollutants in the

Table 1

Detection and quantitation limits for pollutants determination by the annular denuder–filter pack system

	Cl^-	NO_2^-	NO_3^-	SO_4^{2-}	NH_4^+	Na^+	K^+	Mg^{2+}	Ca^{2+}
LOD $(\mu g/ml)$[a]	3	5	10	15	5	1	5	2	5
LOQ $(\mu g/ml)$[b]	10	15	30	45	15	3	15	6	15
MDC 1 h (ng/m^3)[c]	30	50	100	150	50	10	50	20	50
MQC 1 h (ng/m^3)[d]	100	150	300	450	150	30	150	60	150
MDC 24 h (ng/m^3)[c]	1.5	2.5	5	7	2.5	0.5	2.5	1	2.5
MQC 24 h (ng/m^3)[d]	4.5	7.5	15	20	7.5	1.5	7.5	3	7.5

[a] LOD: Limit of detection.
[b] LOQ: Limit of quantitation.
[c] MDC 1 h and 24 h: Minimum detectable concentration on 1-h and 24-h sampling at the flow-rate of 15 l/min.
[d] MQC 1 h and 24 h: Minimum quantitable concentration on 1-h and 24-h sampling at the flow-rate of 15 l/min.

particulate phase; this specific configuration is devised in order to take into account nitric acid, hydrochloric acid and ammonia possibly evolved from ammonium nitrate and ammonium chloride particles retained on the PTFE filter (the nylon filter retains the acids and the impregnated filter retains ammonia). The evolution of gaseous compounds from these salts is dependent on the thermodynamic conditions during the sampling (temperature and relative humidity) and it is thus unpredictable "a priori".

3.2. Sensitivity and reproducibility

Detection and quantitation limits for the determination of pollutants concentration by means of the annular denuder–filter pack sampling line described above are reported in Table 1. The limits of detection (LODs) and of quantitation (LOQs) refer to the analytical limits for the IC determination of the various ions in the denuder coating matrix. The minimum detectable concentration (MDC) and minimum quantitable concentration (MQC), instead, refer to the minimum concentration of pollutant which the technique is able to detect and to quantify in the atmosphere, and include the overall imprecision and inaccuracies of the system, such as field blank values. Particularly, in the case of sulphate and ammonium determinations, the MDC and MQC values reported in Table 1 are obtained only when a particular care is used to get low values of the field blanks. These limits make the technique suitable even for very short-term measurements (1 h) in slightly polluted sites, or for medium-term determinations (6–12 h) in very remote atmospheres, such as Arctic or Antarctic regions [14].

Table 2 shows the results of pairs of 24-h measurements carried out by placing side-by-side sampling lines in the sampling station of Montelibretti. The data indicate that the reproducibility of the

Table 2

Reproducibility of the annular denuder–filter pack system: results of side-by-side 24-h samplings

	Replicate measurements												SD
	1		2		3		4		5		6		
	a	b	a	b	a	b	a	b	a	b	a	b	
Nitric acid $(\mu g/m^3)$	0.30	0.27	0.28	0.30	0.10	0.11	1.00	0.91	1.97	1.91	1.59	1.64	3.79
Sulphur dioxide $(\mu g/m^3)$	1.12	1.18	1.40	1.47	1.56	1.48	2.21	2.31	3.67	3.60	2.34	2.67	2.12
Ammonia $(\mu g/m^3)$	1.14	1.19	1.70	1.66	2.54	2.38	2.01	2.09	1.81	1.89	2.21	2.13	1.48
Particulate nitrate $(\mu g/m^3)$	1.08	1.10	1.03	0.94	1.76	1.76	1.86	1.94	2.37	2.44	2.43	2.34	1.43
Particulate sulphate $(\mu g/m^3)$	1.68	1.64	1.78	1.82	1.93	1.79	3.40	3.66	5.39	5.56	7.92	7.78	1.91
Particulate ammonium $(\mu g/m^3)$	0.94	0.91	1.02	1.09	1.26	1.21	1.59	1.45	2.59	2.78	3.12	3.18	2.53

overall system is satisfactory, since the relative standard deviation (RSD) for all the examined compounds is in the range 2–5%.

3.3. Atmospheric studies

The time trend of nitric acid and particulate nitrate measured with resolution time of 1 h in the site of Montelibretti is reported in Table 3. These data constitute an interesting example of how high time resolution measurements of gaseous and particulate compounds can be of help in the interpretation of pollution phenomena. The time trend of Table 3 shows an increase in the atmospheric concentration of nitric acid during morning hours, with a maximum between 2:00 and 3:00 p.m., and a new sharp peak between 4:00 and 5:00 p.m.; these very fast events would have been neglected by measurements having longer integration times. The latter relative maximum has to be attributed to pollution transport from the city of Rome, which superimposes to the local

Table 3
Time trend of nitric acid, evolved particulate nitrate and of their sum in Montelibretti on 21 June 1997

Start time	Nitric acid ($\mu g/m^3$)	Evolved particulate nitrate ($\mu g/m^3$)	Sum ($\mu g/m^3$)
1:00 a.m.	0.8	2.0	2.8
2:00 a.m.	0.6	1.8	2.4
3:00 a.m.	0.7	1.7	2.4
4:00 a.m.	0.9	2.2	3.1
5:00 a.m.	0.8	2.0	2.8
6:00 a.m.	0.7	3.0	3.7
7:00 a.m.	0.9	3.2	4.1
8:00 a.m.	1.2	4.2	5.4
9:00 a.m.	2.2	6.9	9.1
10:00 a.m.	2.8	5.1	7.9
11:00 a.m.	3.5	2.4	5.9
12:00 a.m.	4.2	2.0	6.2
1:00 p.m.	5.0	1.7	6.7
2:00 p.m.	5.3	1.6	6.9
3:00 p.m.	4.8	1.4	6.2
4:00 p.m.	5.2	0.6	5.8
5:00 p.m.	4.4	0.7	5.1
6:00 p.m.	3.6	0.9	4.5
7:00 p.m.	2.0	0.7	2.7
8:00 p.m.	1.3	0.8	2.1
9:00 p.m.	1.2	1.0	2.2
10:00 p. m.	1.0	1.4	2.4
11:00 p.m.	0.6	1.3	1.9
12:00 p.m.	0.7	1.5	2.2

photochemical production: the Montelibretti station is downwind to the city of Rome when the sea-breeze blows, and this causes an increase in photo-chemical pollutants, such as ozone, nitric acid and peroxyacetylnitrate, when the air masses are transported from Rome to the measurement station.

The study of the temporal trend of evolved nitrate (that is the nitrate amount recovered on the nylon filter, which constituted more than 90% of the fine nitrate fraction during the whole duration of the day) shows that the maximum evolution of nitric acid from the collected ammonium nitrate is observed between 9:00 and 10:00 a.m., while a decrease is observed during the period of maximum increase in nitric acid concentration. These observations highlight how during the very first hours after sunrise nitric acid is released from ammonium nitrate particles in the course of the sampling, that is when particles are exposed to an air flow free from any gaseous nitric acid. In the following hours, the further increase in ambient temperature and decrease in relative humidity permit the evolution of nitric acid also from atmospheric ammonium nitrate particles, which can be considered, in these conditions, to be the main responsible for the daytime increase of nitric acid concentration. The time trend of the sum of nitric acid and evolved nitrate shows a somehow constant value during daytime hours, which is consistent with the above interpretation of the results in terms of nitrogen transfer between the two phases.

This general trend was confirmed by the data gathered during several intensive field campaigns carried out in Montelibretti during 1997: ammonium nitrate is generally the main constituent of the fine nitrate fraction, and the evolution of nitric acid from ammonium nitrate collected on the PTFE filter precedes in time the increase in atmospheric nitric acid concentration and the simultaneous decrease in ammonium nitrate concentration.

Atmospheric measurements having longer integration time (e.g., 24-h) are obviously not able to give information about the fine structure of temporal trends, but allow to construct a general picture of pollution trend over a time scale of years. The comparison between the two-year time trends of nitric acid and particulate nitrate recorded in Montelibretti and in the background measurement station

of Magorno on a daily basis (years 1995 and 1996), show, for example, that Magorno can be considered as a remote location, where nitric acid and particulate nitrate average concentrations rarely exceed the value of 1 $\mu g/m^3$ and 3 $\mu g/m^3$, respectively. In the case of the Montelibretti site, instead, the short distance between the station and the city of Rome causes the average concentration levels of nitric acid and particulate nitrate to reach higher values, up to 3 $\mu g/m^3$ and 10 $\mu g/m^3$, respectively. The temporal trend of nitric acid and particulate nitrate along the year is very similar in the two locations and during the two examined periods. Nitric acid shows higher values during the summer and minima during the winter, which is the expected behaviour for a pollutant of mainly photochemical origin. Particulate nitrate, instead, shows minimum values during the summer and maxima during the winter; this behaviour can be explained, again, on the basis of the interconversion between gaseous ammonia and nitric acid and particulate ammonium nitrate, which is the main component of fine nitrate particles. The typical thermodynamic conditions of Mediterranean areas during summer periods, high temperature and a low relative humidity, favour, in fact, the evolution of the gaseous species from ammonium nitrate.

The interconversion between the gaseous and the particulate phases of nitrate species is further evident when the data are averaged according to a three-period division of the year. In Montelibretti the ratio between the average value in the period May–August and the average value in the remaining periods (January–April and September–December) ranges between 3.5 and 4 for nitric acid and between 0.5 and 0.6 for particulate nitrate, while it is close to unity for the sum of gaseous nitric acid and particulate nitrate. In the less polluted site of Magorno, the differences are less distinct but in the same direction: for nitric acid the ratio between the summer period and the remaining periods ranges between 1.3 and 1.6, while it is around 0.8 for particulate nitrate; the sum is, again, close to unity.

4. Conclusions

The coupling of the annular denuder sampling technique with IC reveals a valuable solution to the problem of a precise and accurate measurement of atmospheric inorganic pollutants, with discrimination of the gaseous and the particulate phase. The sensitivity of the technique makes it possible to determine the atmospheric concentration of these compounds with a low time resolution, allowing to carry out a detailed interpretation of pollution phenomena.

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