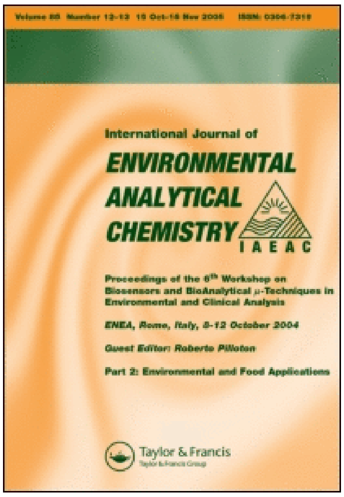

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Continuous Monitoring of Atmospheric HCl, HNO_2, HNO_3 and SO_2 by Wet-Annular Denuder Air Sampling with On-Line Chromatographic Analysis

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CONTINUOUS MONITORING OF ATMOSPHERIC HCl, HNO_2, HNO_3 AND SO_2 BY WET-ANNULAR DENUDER AIR SAMPLING WITH ON-LINE CHROMATOGRAPHIC ANALYSIS

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An automated system for the collection, in-line preconcentration and analysis of acidifying atmospheric gases is described. Collection of HCl, HNO_2, HNO_3 and SO_2 from ambient air is carried out with an annular wet denuder. After addition of an internal standard to the sample flow and conductivity suppression, preconcentration of the sample flow is performed by pumping a measured volume of the sample flow through an anion exchange concentrator column. Following the concentration step, the anions of the corresponding acids are analyzed by ion chromatography with conductivity detection.

The manifold described with two sample loops and two concentrator columns operating in parallel allows automated collection and analysis of two air samples per hour.

A computer programme has been developed for automated performance. It allows the system to run unattendedly during extended periods as all the functions, including data processing, are computer-controlled.

Factors affecting the performance are reported. The detection limits achieved are 5.4, 12 and 17 ng/m^3 for HCl, HNO_2, HNO_3 and SO_2 respectively, with relative standard deviations better than 4% at 1–2 µg/m^3. Ambient measurements for Petten, The Netherlands, are presented which show the capability of the system for continuous monitoring of atmospheric acidifying gases.

KEY WORDS: Air, sampling, wet-annular denuders, acidifying gases, chromatographic analysis.

INTRODUCTION

The increasing scientific and public concern about the fate, transport and adverse effects of atmospheric pollutants has promoted the development of methods for air quality control. The role of compounds such as sulphur dioxide, nitric and nitrous acids and hydrochloric acid on the acidification of natural environment and its effect on ecosystems have been described[1,2].

Several methods have been developed for collection and on-line analysis of acidifying compounds in ambient air. In this type of work, in general, automation of sampling procedures and on-line analysis offer better reproducibility while reducing risks of contamination and sample manipulations. It is especially advisable when unstable compounds (e.g., HNO_2) are to be determined.

Diffusion-based sampling devices such as denuders and diffusion scrubbers are commonly used because these methods allows separation of gaseous and particulate matter during sampling. Computer-controlled thermodenuders, based on thermal sorption/desorption cycles, have been applied for the determination of nitric acid, ammonia and ammonium nitrate, sulfuric acid and ammonium sulfate in ambient air[3-5]. Automated operation of membrane-based diffusion scrubbers in which the gaseous analytes diffuse across an inert porous membrane and are trapped by an absorber liquid in countercurrent flow, has also been described[6,7]. However, the air sampling rates and collection efficiencies of diffusion scrubbers are relatively low and variable, the collection efficiencies decreasing in time due to particle deposition on the membrane. These problems are overcome with wet denuders. Single-tube wet denuders have been coupled to ion chromatographs (IC) for analysis of SO_2[8]. They consist of a cylinder with an absorbing solution flowing down along the inner wall of the cylinder, thus providing a continuously renewed absorbing liquid film, with a countercurrent air flow. The liquid is collected at the bottom of the denuder tube and analyzed by IC. This approach allows automated performance of the sampling/preconcentration/analysis cycle, but some of its features makes it less suitable for continuous measurement systems. The problem of obtaining and keeping a continuous and smooth wetted absorbing film, the relatively low sampling flow allowed (2 l/min) and the variable evaporative losses in the denuder influenced by air temperature and humidity are some drawbacks. It has already been show that most of these drawbacks can be overcome by using annular or parallel plate wet denuder devices[9].

Annular wet denuders solve the problem of uniform wall wetting while allowing high air sampling flow up to 30 l/min. They have been used successfully for ambient measurements of NH_3, HNO_3, HNO_2, SO_2 and H_2O_2. A fully automated annular wet denuder for atmospheric ammonia has been described[10]. Ammonia is collected from air in an absorbing solution in the denuder at low pH, and in-line isolated from the denuder sample stream by diffusion through a gas-permeable membrane after addition of alkaline solution to the sample stream. After diffusion, ammonia is collected in a countercurrent aqueous stream and on-line analyzed by conductivity detection.

In this paper an automated system for the collection, on-line perconcentration and analysis of atmospheric HCl, HNO_2, HNO_3 and SO_2 is described. The compounds are collected from air using an annular wet denuder operating in the continuous-flow mode with sodium carbonate as absorbing solution. After addition of an internal standard to the denuder sample stream and removal of carbonate, a known volume of the stream is concentrated using an anion exchange concentrator column and subsequently analyzed by ion chromatography with electronically suppressed conductivity detection.

Using the manifold with two sample loops and two concentrator columns operating in parallel, two samples per hour can be collected and analyzed, each sample corresponding to 30 min of air sampling. The computer software has been designed for control of the experimental steps as well as for data acquisition, data calculation and representation.

The system can be run unattendedly during extended periods of time which shows its capability for use in field experiments.

EXPERIMENTAL SECTION

Reagents

The absorbent solution in the annular denuder is a 0.001 M sodium carbonate solution. Three mobile phases were tested for chromatographic separation of the anions of interest: (a) p-hydroxybenzoic acid 1.5 × 10^{-4} M, adjusted to pH 7.5 with sodium hydroxide; (b) phthalic acid (0.05 M)/acetonitrile (95/5, v/v, pH 4.2); (c) 2,6-pyridine dicarboxylic acid (0.0005 M)/acetonitrile (98/2, v/v) adjusted to pH 5.2 with sodium hydroxide.

Stock solutions of the anions were prepared from their corresponding sodium salts, except for sulphate which was prepared from concentrated sulphuric acid. All reagents used were of analytical grade.

Apparatus

The chromatographic system consisted of a Model 690 ion chromatograph, a HLPC pump and a Super-Sep analytical column (100 × 4.6 mm); all these components from Metrohm (Herisau, Switzerland). Two types fo anion exchange concentrator columns were tested: (a) Hamilton PRP-X100 (20 × 5 mm), and (b) Zipax SAX (50 × 4 mm, home-packed).

Carbonate was transformed into carbonic acid using a Dionex micromembrane suppressor system AMMS (Dionex, Sunnyvale, CA, USA) operating with 0.001 N H_2SO_4 which was continuously regenerated using a Dionex AutoRegen Anion System. Initially carbon dioxide was eliminated from the liquid stream using microporous membrane tubing (GORE-TEX TA 001, 325 cm × 1 mm i.d., 50% porosity, 2.0 μm maximum pore size).

Solutions were directed with an eight- and a ten-port electrically actuated valve (Valco Instruments, Houston, TX, USA), two peristaltic pumps and a Metrohm Model Dosimat 665 syringe pump.

Control of the syringe pump and the valves as well as data acquisition were performed via a 286 Tulip computer coupled to a home-built laboratory interface equipped with an analogic-to-digital converter.

Continuous-flow annular wet denuder

The annular wet denuder has been previously described[11]. An output flow of the absorbing solution of 0.7 mL min^{-1} ensured complete renewal of the denuder solution within 30 min. The level of the liquid in the denuder was kept constant by means of an infrared sensor with electrical feedback to start and stop the peristaltic pump.

System configuration and operation

In order to achieve automated on-line air sampling, preconcentration and analysis at 30 min intervals, a system based on two sample loops and two concentrator columns was designed. The set-up is shown in Figure 1.

The solution flowing out from the denuder was divided by means of a two-way splitter. Part of the solution was mixed with an aqueous bromide stream used as internal standard and directed to fill one of the sample loops. A flow rate of 0.2 ml/min ensures that the analyzed sample corresponds with approx. 30 min air sampling.

After addition of internal standard to the sample flow, the sample was passed through an anion micromembrane suppressor (AMMS)[11]. The aim was the transformation of carbonate to bicarbonate and carbonic acid. This was necessary because the efficiency of the preconcentration step was dramatically decreased in the presence of high

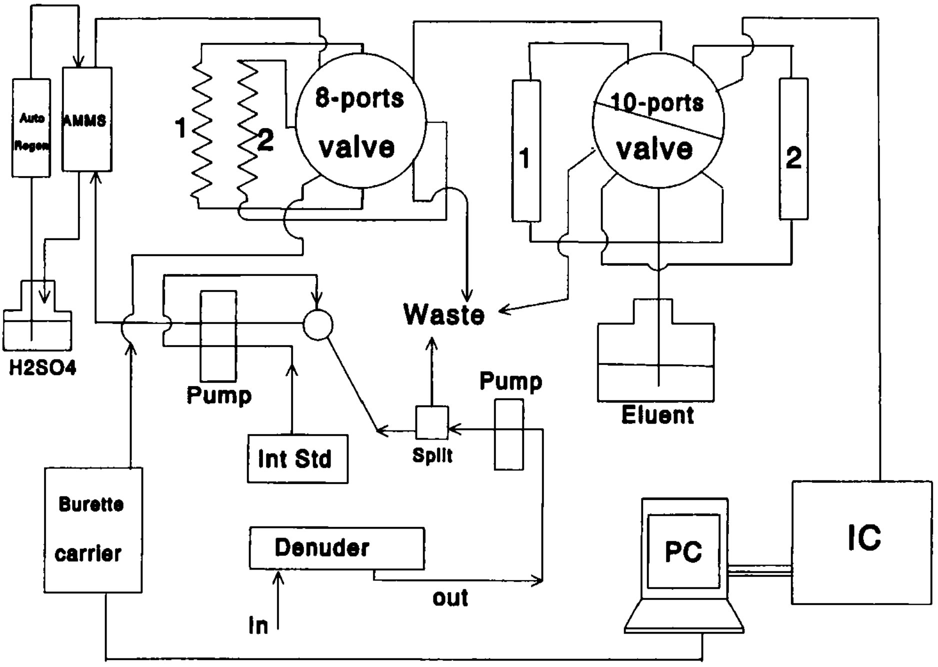

Figure 1 Schematic diagram of the automated wet annular denuder system including sample concentration and ion chromatographic analysis.

concentrations of carbonate, because most of the functional groups in the concentrator column were occupied by carbonate ions. A high concentration of carbonate also had an adverse effect on the chromatographic separation as it caused a severe change of pH and disrupted the equilibrium in the analytical column, leading to poorly defined peaks in the chromatogram and baseline drifting. After suppression, bicarbonate and carbonic acid in the sample stream were initially removed using gas-permeable tubing, thereby shifting the equilibrium to carbon dioxide:

$$HCO_3^- \rightleftarrows H_2CO_3 \rightleftarrows CO_2 \qquad (1)$$

However, it was observed that bicarbonate and carbonic acid did not interfere in the preconcentration and chromatographic separation processes as they were less retained than the anions of interest. Therefore, their removal was not necessary and the permeable tube was eliminated from the manifold shown in Figure 1.

After suppression, a preconcentration step was performed (Figure 2). When the system is in position 2A, the sample is directed to loop (2) and simultaneously, the content of loop (1) is directed to the concentrator column (1) using the syringe pump. Subsequently, the ten-port valve is switched and the concentrated sample (1) is eluted from the concentrator column to the analytical column (Figure 2B).

After 30 min, loop (2) is filled and the eight-port valve is switched (Figure 2C). In this position, the content of loop (2) is transferred to the concentrator column (2), while loop (1) is filled with sample during the next 30 min. Sample (2) concentrated in column (2), is then eluted to the analytical column in the backflush mode. The procedure is repeated in a cyclic way.

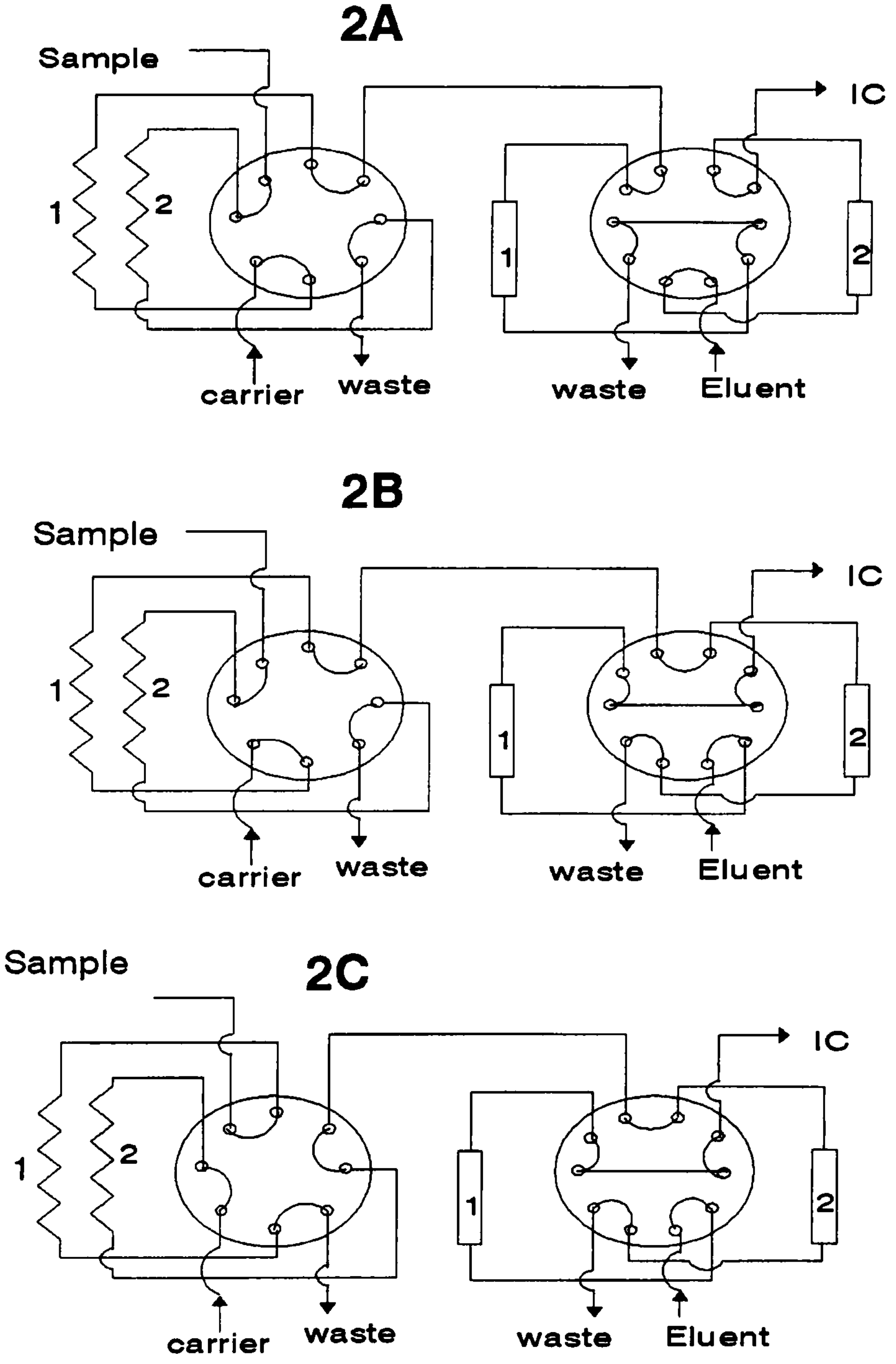

Figure 2 Connections and flow paths at different stages of the concentration process. (A) Sample (1) is concentrated into concentrator column (1) while loop (2) is loaded with sample (2) flowing from of the denuder. (B) The content of concentrator column (1) is eluted to the analytical column. (C) Sample (2) is concentrated into concentrator column (2) while loop (1) is refilled with a new sample from the wet denuder.

Internal standard addition

Calibration via internal standard addition to each denuder sample allows for compensating possible differences in performance between the two concentrator columns. Bromide was used as it is stable under field conditions; it elutes in an 'empty' part of the chromatogram and atmospheric concentrations of hydrogen bromide are negligible.

A known amount of bromide was added to the denuder sample flow on a continuous basis. Other approaches such as the addition of internal standard either in the carrier stream or to the denuder absorbing solution were not satisfactory. With the first option, a double peak was observed in the chromatogram, probably due to the fraction of the carrier that does not enter the concentrator column. With the second option, there was an uncertainty with regard to the concentration of the internal standard in the denuder solution due to variations in the evaporation rate of the absorbing solution.

Software

The software for automated operation of the system, data acquisition and calculations was written in Quickbasic and compiled. The programme structure is modular in order to ease further modifications and enlargement.

With the user-defined parameters for experimental procedure and calculations, the programme allows automated performance without external assistance. Experimental data are collected at a 1 Hz sampling frequency and simultaneously presented on computer screen. At the end of each run the data are stored and calculations are automatically carried out.

Data treatment

Data treatment includes detection of negative and positive peaks, calculation of the baseline and signal integration for the determination of peak heights or peak areas. It also allows quatitative determination based on the signal ratio between the selected peaks and the internal standard.

The peak detection subroutine is based on the use of first and second derivatives of experimental data in order to find the limits of the peaks as well as their extreme position (maximum or minimum). The derivatives are calculated using the Savitzky-Golay algorithm[12]. Once the peak limits and the baseline have been calculated, the peak heights and areas are determined for each anion. From these, the concentration of the anions in the sample are calculated by comparison with the bromide peak. Calculations based on peak areas were preferred. When using peak heights, sensitivity for the most retained anions becomes less good due to band broadening.

RESULTS AND DISCUSSION

Sample preconcentration

The influence of the duration of the concentration step was studied. A relatively high sample flow reduced the effectiveness of the concentration procedure because the anions are not totally retained. The optimum sample flow in terms of sample recovery and concentration time was found to be 1 ml/min for both types of concentrator columns.

The retention of the anions was also influenced by the 'washing effect' due to the sample and the carrier. To study the washing effect, small volumes (40 µL) of a concentrated standard containing a mixture of 7.5 mg/kg of each Cl^-, NO_2^- and NO_3^-, and 15 mg/kg of SO_4^{2-} in 10^{-3} M sodium carbonate was injected in the concentrator column and subsequently eluted with increasing volumes of deionized water. Washing was carried out in the direction of the sample loading. After washing, the content of the concentrator column was transferred to the analytical column in the backflush mode and analyzed. Figure 3 shows the results obtained with the Hamilton column. From Figure 3 it is evident that the washing effect is significant, especially for the weakly bound anions such as chloride and nitrite. For these anions, the recoveries decreased below 10% when washing with more than 5 mL of water. Similar results were obtained for the concentrator columns filled with Zipax SAX material. Because of the washing effect, the sample loop volume was limited to 5 mL and the carrier volume was 5.5 mL, as a small extra volume of carrier is needed to ensure that the total sample in the loop is transferred to the concentrator column.

The concentrator columns were used for extended periods of time. A significant decrease in capacity of Hamilton columns was observed after one week of continuous

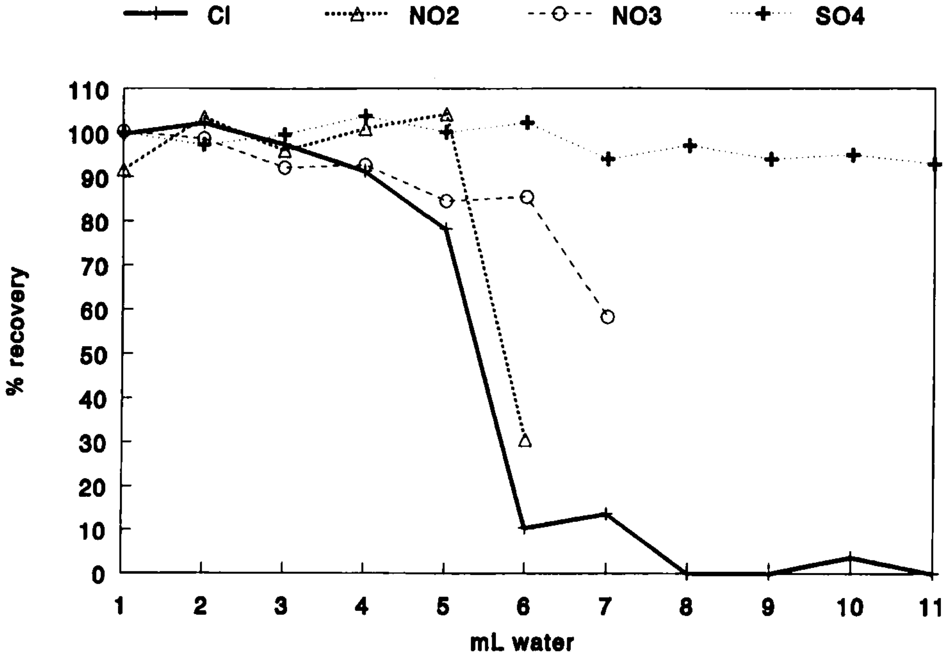

Figure 3 Washing effect due to the injection of large sample volumes. 40 µL of a standard solution containing 7.5 mg/kg of each chloride, nitrite and nitrite, and 15 mg/kg of sulphate in 10^{-3} M sodium carbonate were injected and subsequently washed with increasing volumes of deionized water at 1 ml/min. The concentrator column was a Hamilton PRP-X100.

operation. After one week of operation, differences up to 10% in capacity were observed between two Hamilton columns working in parallel. Zipax-based columns did not show such a significant decrease in capacity after one week of operation.

Choice of eluent

Several eluents were tested in order to optimize the transfer of the anions from the concentrator column to the analytical column and the subsequent conductivity detection. One should realize that the concentrator column is equilibrated with eluent before sample loading. Therefore, the optimal eluent should be weak enough to allow quantitative binding of the anions during the preconcentration step but strong enough to achieve quantitative elution of the retained ions to the analytical column. In this work, the performance of p-hydroxybenzoic acid, phthalic acid and 2,6-pyridine dicarboxylic acid were evaluated. Unless mentioned all tests were made using the Hamilton concentrator columns.

With p-hydroxybenzoic acid (pH 7.5) good performance was obtained during the concentration and separation steps as long as the samples were free from phosphate. However, in the presence of phosphate an increase in backpressure on the concentrator column was observed after only 2 days, together with a sharp decrease in peak separation. After rinsing the concentrator column overnight with hydrochlotic acid, it could be used again. Because the regeneration of the analytical column should be carried out every 1–2 days, this eluent is clearly unsuitable to be used in field campaigns.

With *phthalic acid* (pH 4.5) all anions were eluted within 7 min. However, the separation between early eluting anions, i.e., chloride and nitrite, was insufficient. A lower pH improved the separation between these anions but a large system peak eluted after sulphate and over 10 min were needed to reach equilibrium in the column before the next sample could be injected.

2,6-Pyridine dicarboxylic acid proved to be an effective eluent, with low background conductivity, good resolution of early eluting peaks which were also clearly separated from the injection peak. The most suitable eluent pH, flow-rate and concentration were 5.2, 1.5 mL min^{-1} and 5 × 10^{-1} M, respectively. It is noteworthy that careful adjustment of the eluent pH is necessary in order to resolve the late eluting system peak from sulphate without increasing the time neede for re-equilibration of the columns.

Figure 4 shows a chromatogram recorded for 5 mL of a standard mixture containing 50 μg/kg of each anion in 10^{-3} M sodium carbonate, with 2,6-pyridine dicarboxylic acid as eluent. The sample was concentrated on a Hamilton PRP-X100 column at 1 ml/min.

Calibration graphs

Calibration graphs were obtained by injecting 5 mL of standard solutions in 10^{-3} M sodium carbonate, with different concentrations of the anions and a constant concentration of bromide. Samples were concentrated using deionized water as carrier and 2,6-pyridine dicarboxylic acid was used as eluent. From the resulting chromatograms, peak areas were calculated and the peak area ratios to bromide, after blank subtraction, were plotted versus the concentration of the anions in the standard solutions. The graphs obtained showed a linear response up to at least 150 μg/kg of chloride and 300 μg/kg of fluoride, nitrite, nitrate and sulphate.

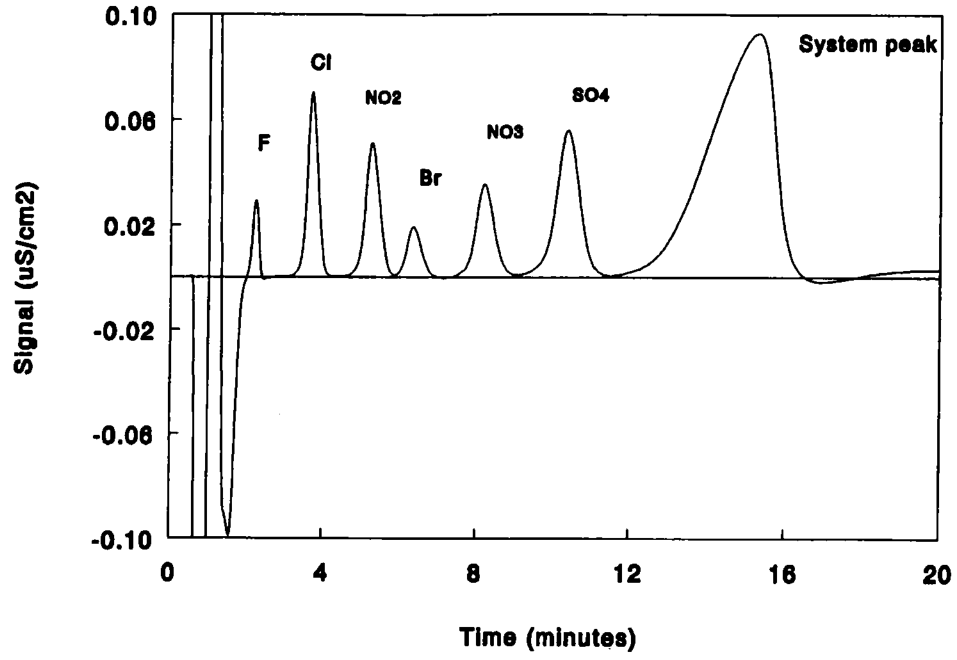

Figure 4 Chromatogram obtained for a 5 ml sample after concentration. Sample, 5 mL of a solution containing 50 µg/kg of chloride and 100 µg/kg of each fluoride, nitrite, nitrate and sulphate in 0.001 M sodium carbonate. Concentrator column, Hamilton PRP X-100 (20 × 4.6 mm i.d.); loading flow rate, 1 ml/min; carrier, deionized water. Eluent for chromatographic separation, 2,6-pyridine dicarboxylic acid, pH 6.5 at 1.5 ml/min.

For quantification a correction factor for each anion, $F_x(i)$, is used because the specific conductivity and that of the internal standard are different. The correction factor was obtained from the measured peak areas:

$$F_x(i) = \frac{A_{IS}*C_i}{[A_i - A_0]*C_{IS}} \qquad (2)$$

in which A_i and A_{IS} are the peak areas of the anions and internal standard, respectively, and C_i and C_{IS} the corresponding concentrations. A_0 is the signal of a blank (0.001 M sodium carbonate).

When $(A_{IS}/[A_i - A_0])$ is plotted versus (C_{IS}/C_i) the slope of the plots obtained for each anion gives the corresponding $F_x(i)$. These were then used to calculate the concentration of the anions in the sample:

$$C_i = \frac{[A_i - A_0]}{A_i} * F_x(i) * C_{IS} \qquad (3)$$

Precision and detection limits

In order to determine the precision, a series of 30 injections of 5 mL of a standard solution in 10^{-3} M sodium carbonate, containing 50 µg/kg of chloride, 100 µg/kg of each fluoride, nitrite, nitrate and sulphate, and 40 µg/kg of bromide were analyzed. The results are given in Table 1, together with the detection limits, defined as 3x the standard deviation of a solution of 0.001 M sodium carbonate. The detection limits for the determination of the compounds in air, using the system shown in Figure 1, are also given in the table. The precision for fluoride is relatively poor because of the fluoride peak overlap with the injection peak. Probably, the difference in performance between the two concentrator columns working in parallel also contributes to the higher standard deviations for fluoride and chloride measurements because the early eluting peaks are most sensitive to the washing effect (see above).

Sampling and analysis of ambient air

Analysis of ambient air was carried out at Petten for prolonged time periods using the system shown in Figure 1. Air was sampled at 12 m height with 30 min intervals. The result for June 30th and July 1st, 1992 are shown in Figure 5. This was a period of photochemical smog, with high concentrations of HNO_3 during daytime on June 30th (7–9 µg/m^3). This smog event warrants the interpretation of the reported HNO_2 and HNO_3 concentrations since high NO_2 concentrations typically observed during photochemical smog periods (NO_2 is the major precursor of HNO_3 via reaction with hydroxy radical) may lead to artefact formation of HNO_2 and HNO_3 in the denuder via reaction of NO_2 (aq) with sulphite in the denuder absorbing liquid. Also, a risk of oxidation of NO_2^- to NO_3^- via ozon exists especially during smog periods. Such interfering reactions will be the subject of further study. The typical pattern of HCl probably arises from differences in performance of both concentrator columns. The effect of such differences will be most pronounced for early eluting compounds and are not totally compensated for by the internal standard, bromide.

Table 1 Precision and detection limits of the automated wet annular denuder[1].

Anion	*R.S.D. (%) (n = 30)*	*LOD (ng ml^{-1} denuder solution*	*LOD (ng m^{-3} ambient air)*
Fluoride	6.3	3.8	89
Chloride	3.8	0.23	5.4
Nitrite	1.7	0.52	12
Nitrate	2.1	0.52	12
Sulphate	2.3	1.1	17(SO_2)

[1] Precision determined after 30 successive injections of a 5 mL sample containing 50 µg/kg chloride, 100 µg/kg of each fluoride, nitrite and sulphate and 40 µg/kg of bromide (internal standard) in 0.001 M sodium carbonate. Eluent for chromatographic separation was 2,6-pyridine dicarboxylic acid, pH 5.2 at 1.5 ml/min. The limit of detection (LOD) is calculated as 3x the standard deviation of a blank chromatogram of 0.001 M sodium carbonate. The detection limits are also calculated for ambient air concentrations, for an air sampling flow of 30 L/min and assuming quantitative collection of the gases in the denuder absorbing phase.

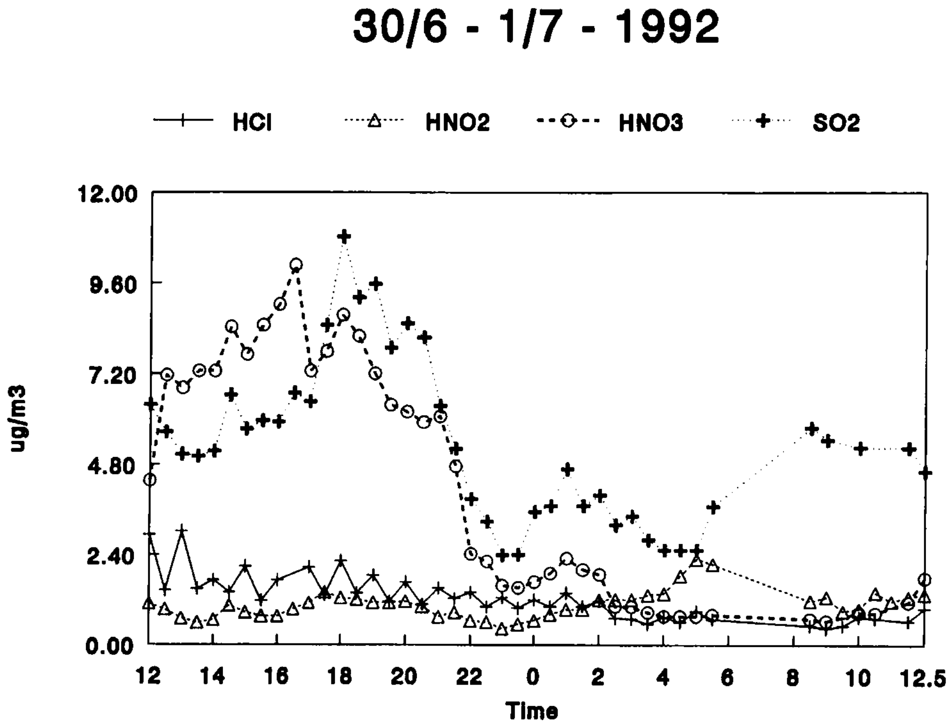

Figure 5 30 min ambient concentrations of HCl, HNO_2, HNO_3 and SO_2 measured with automated wet-annular denuder with in-line preconcentration and ion chromatographic analysis. Data obtained during a photochemical smog period at Petten on June 30th and July 1st, 1992.

CONCLUSIONS

A versatile instrument has been developed for the measurement of atmospheric HCl, HNO_2, HNO_3 and SO_2 at 30 min intervals with adequate sensitivity and good precision, to be used in remote, relatively non-polluted areas. Further optimization of the method in terms of sample throughput and sensitivity can be obtained if measurement of early eluting chloride is not required. The most critical aspect of the procedure was the performance of the concentrator columns. A rapid increase in backpressure over the concentrator columns and drastic changes in anion concentrating capacity were sometimes observed. Future developments of the instrument will be directed to the use of new column technology (Dionex IonPac AS-12A analytical column) to improve the separation of fluoride and chloride from the injection peak. In addition, the interfering reaction between NO_2 (aq) and sulphite which produces artefact HNO_2, will be studied.

Acknowledgements

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