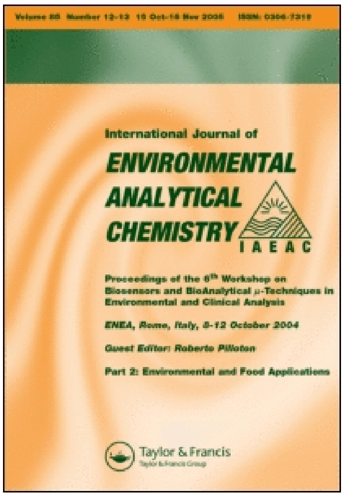

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AN AUTOMATED FIELD INSTRUMENT FOR THE DETERMINATION OF ACIDIC GASES IN AIR

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An automated field instrument is described for the continuous measurement of soluble acidic gases in ambient air. Sampling of the gases is carried out by using a wet-rotating annular denuder filled with an aqueous carbonate absorption solution. After addition of internal standard, the absorption stream from the denuder is led through one of two injection loops of an ion-chromatographic system. Separation is carried out on a Dionex IonPac AS–12A analytical column with suppressed conductivity detection. While one sample is analysed, a parallel injection loop of the chromatograph is filled with a next sample. In this way, air concentrations of HCl, HONO, HNO_3 and SO_2 can be obtained at approximately 20 min intervals. Detection limits are 0.1 $\mu g/m^3$ for HCl and HONO and 0.2 $\mu g/m^3$ for HNO_3 and SO_2. The applicability of the system is demonstrated in a measurement campaign at Petten, The Netherlands.

Keywords: Acidification; acidic gases; wet-denuder; air-sampling; ion-chromatography

INTRODUCTION

Knowledge of the fate of acidic gases is hampered with uncertainty due to insufficient data on the temporal and spatial distribution of acidic gases[1]. To some extent, this is due to the lack of field-instrumentation for simultaneous measurement of these compounds, notably HCl, HONO and HNO_3 with high time resolution, i.e. at 10–30 min intervals. Normally, these compounds are isolated from air using wet-annular denuder sampling with subsequent off-line analysis at the laboratory by ion-chromatography. These off-line procedures are very laborious, especially in view of the many samples which are needed for better understand-

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ing of acid formation and deposition processes. Sample integrity becomes a critical factor due to risks of analyte degradation and sample contamination during transport, storage and handling of the samples.

It has been shown that acidic gases can be measured in ambient air on a continuous base by using wet-denuder air sampling in combination' with on-line ion-chromatographic analysis of the denuder absorption liquid[2–5]. Due to the relatively low diffusity of aerosols in air as compared to gases, aerosols are not trapped in the absorption solution and hence show negligible interference with the analysis of the gases under normal sampling conditions. In this way, detection limits in the low ng/m^3 range have been obtained for SO_2[2–5] and HCl, HONO and HNO_3[5].

In this paper, a modified configuration of the system described in ref. 5 is presented. The most important modifications refer to direct injection of the wet-denuder sample stream onto the analytical column (i.e. without sample preconcentration), the use of formaldehyde in the absorption liquid for reducing interfering reactions and for eliminating adverse effects from bacteria on sample integrity and, finally, the use of a Dionex IonPac AS–12A separation column in combination with post-column conductivity suppression of the eluent. The applicability of the system is demonstrated in a measurement campaign at Petten, The Netherlands.

EXPERIMENTAL

Wet-annular denuder

A detailed description of the rotating wet-denuder for collecting HCl, HONO, HNO_3 and SO_2 from ambient air is given elsewhere[6]. In short, air is pumped at approximately 27 l/min through a horizontally mounted rotating annular denuder device coated with a 1 mM aqueous sodiumcarbonate solution. The long-term precision of the air flow through the denuder is 3 % (R.S.D.).

A small amount of formaldehyde (0.25 ml of an aqueous solution of formaldehyde (37% v/v)) is added to 1.00 liter of the carbonate solution. The role of formaldehyde is two-fold: (1) To prevent adverse effects from bacteria on sample integrity, in particular for nitrite and nitrate and (2) to stabilize sulphite in the sample as methanesulfonic acid, thereby preventing interfering reactions from NO_2 with sulphite (see under *'interferences').*

The absorption solution is pumped through the denuder at 1 ml/min using a peristaltic pump. The amount of solution in the denuder is kept constant by means of an infra-red sensor for active feed-back of the absorption solution pump. Under these conditions, soluble acidic gases are concentrated from about 27 l of air in 1 ml absorption solution each minute.

Chromatographic configuration

A schematic diagram of the ion chromatographic system is given in Figure 1. The denuder stream, further referred to as 'sample stream', is pumped at 1.0 ml/min using a peristaltic pump. An aqueous solution of the internal standard is added at 0.06 ml/min to the sample stream via a 0.5 ml mixing chamber, equipped with magnetic PTFE-coated stirring bar. The flow of both the sample stream and the internal standard stream are monitored with Model FA-110 flow-meters (Bronk-horst Hi-Tec). Flow-rates are archieved by the computer program and used for calculation of analyte and internal standard concentrations. After mixing, a small part of the liquid stream is led at 10 μl/min through one of the injection loops (200 μl each). One of the injection loops is filled with a sample while the content of the second loop is analyzed.

The chromatograph consists of a model 690 Ion-Chromatograph with a Model 697 IC pump and a conductivity detector with electronic compensation of the conductivity background. The detector housing is thermostatted at 35 °C (Metrohm, Switzerland). The ion-chromatograph is equipped with a 10-port injection valve (Valco), a Dionex IonPac AG–12A guard column, a Dionex AS–12A analytical column (100 × 4 mm) followed by a Dionex ASRS–1 self-regenerating electrochemical suppressor. The mobile phase consists of 2.1 mM sodiumcarbonate/0.80 mM sodiumbicarbonate in demineralized water at 1.5 ml/min. All connecting capillaries are from PEEK^{tm} (0.25 mm i.d.).

Calibration

Since the equipment is developed for one-week unattended operation under field conditions, it is essential that standards used for on-site calibration are stable for prolonged periods of time. Preferably, aqueous standards of HNO_2 and sulphite should not be used under these conditions. Furthermore, the calibrant concentrations should be within the range of the anions of interest in the samples. The expected analyte concentrations in the denuder sample stream are in the 5–200 μg/kg range and this is not applicable for use under field conditions in view of standard stability and risk of contamination. Finally, much time will be wasted on measuring individual standard solutions for calibration purposes.

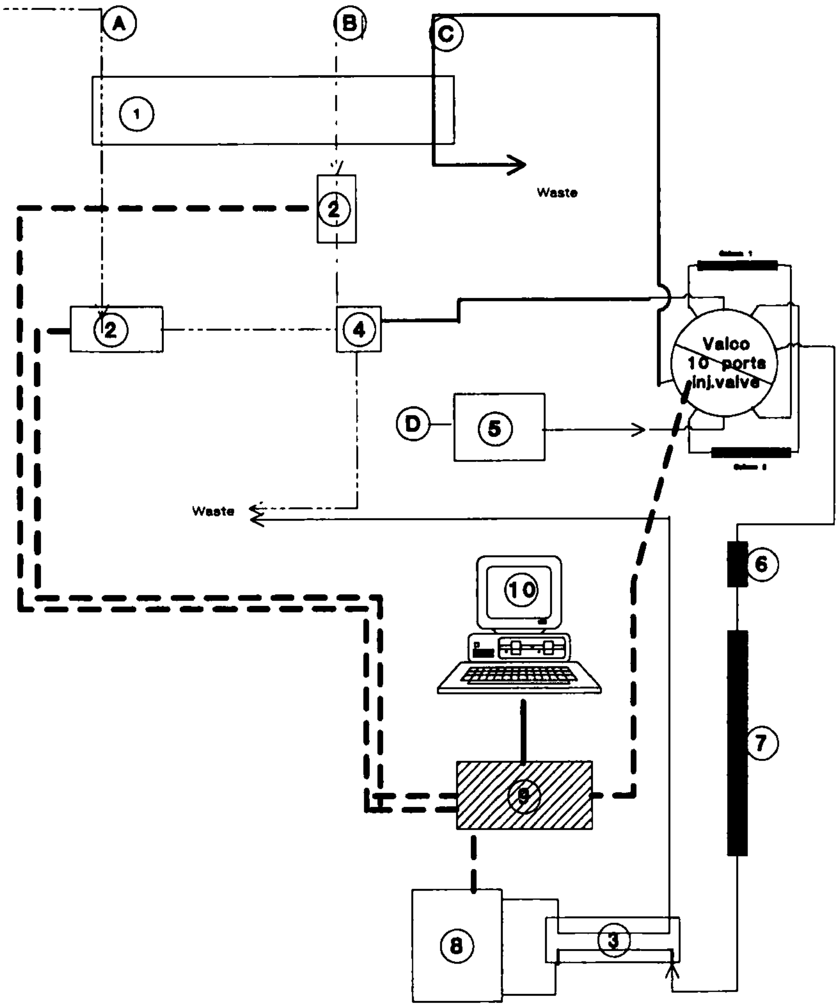

FIGURE 1 Schematic diagram of configuration for the analysis of ambient HCl, HONO, HNO_3 and SO_2 by wet-denuder sampling and on-line ion-chromatographic analysis. 1. peristaltic pump, 2. flowmeter/controller, 3. self-generating suppressor, 4. 0.5 ml mixing vessel, 5. HPLC pump, 6. guard column (Dionex AG-12), 7. analytical column (Dionex AS-12), 8. conductivity detector, 9. laboratory interface (ECN-made), 10. computer. A. sample from denuder (1.0 ml/min), B. bromide 1.5 mg/kg at 0.06 ml/min), C. sample to loop (at 0.010 ml/min), D. mobile phase for ion chromatograph (at 1.5 ml/min).

As an alternative, the use of internal standard addition to the sample stream was found to be very convenient, circumventing the difficulties mentioned above. To this end, an aqueous solution of KBr (1.50 mg/kg) is added to the sample stream at 64 µl/min. Interference from HBr from air is expected to be negligible under normal conditions. This has been confirmed by ambient air sampling, leaving out the bromide standard[5]. In this work, dilution of the sample stream by the internal standard stream is kept to a minimum so that the amount of the analytes put onto the analytical column is not compromised. The exact amount of bromide introduced into the ion-chromatograph is calculated from the bromide concentration of the standard and the flow-rates of both the sample stream and bromide standard stream which are continuously registrated by mass flow meters. The resulting concentration of bromide in the sample stream (84 µg/kg) can be measured with satisfactory accuracy and precision with the ion chromatograph. The precision of the net bromide peak area under the experimental conditions amounts to 0.3% (R.S.D.; n=54).

Calculation of the absolute amount of analyte on the column is then performed by comparing the peak areas of analyte and bromide, using correction factors based on calculation of total amounts of sample from measured conductivity data[10].

In order to check the calculation of analyte concentrations and to determine the system reproducibility and sensitivity, aqueous standard solutions of the anions in 1 mM sodiumcarbonate were analyzed. The standard solutions were introduced via the wet-denuder. In order to test the recovery of the wet-denuder, different SO_2 concentrations in zero air were prepared using a model VE 3M portable calibrator (Environment S.A.) equipped with SO_2 permeation tube. After dilution, the SO_2 stream was transported through the denuder at 27 l/min and subsequently analyzed as the sum of sulphite and sulphate against the internal standard.

Interferences

In wet-denuder air sampling, artefact formation of nitrite can be observed under certain conditions, notably from the aqueous phase reaction between NO_2 and SO_3^{2-}:

$$NO_2\,(aq) + SO_3^{2-}(aq) + OH^- \dashrightarrow HNO_2\,(aq) + SO_3^{2-}\,(aq) \qquad (1)$$

It has been shown that for a bicarbonate wet denuder such artefact formation is negligible if SO_2 and NO_2 concentrations are less than 10 and 15 µg/m^3, respectively[7]. For the present analytical configuration, artefact formation of nitrite was tested by varying the NO_2/SO_2 ratio in the wet denuder air stream. NO_2 and SO_2 were obtained from the permeation device. Mixing of the two gas streams with zero air took place in a 2 l polythene bottle. Before mixing, traces of interfering gases were removed from the zero-air gas stream over a carbonate-impregnated glassfiber filter. NO_2 concentrations were measured with a model CLD 700 NO/NOx chemiluminescence analyzer in NO_2 mode.

Automation

The software for automatic operation of the system, data acquisition of the flow-meters and the conductivity detector and data treatment is written in Quickbasic. Peak detection is based on the use of first and second derivatives which are calculated by using the Savitsky-Golay algorithm[8]. Analyte concentrations are based on net peak areas.

RESULTS AND DISCUSSION

Analytical performance

In Figure 2, the chromatogram for an ambient air sample is given. Complete separation of all analytes of interest is obtained with no interference from bicarbonate of the denuder adsorbent. It was observed that, using the AS-12A column, chloride is separated from the injection system peak which was not the case while using a Dionex AS-9 column. For the latter, chloride was found to elute close to the end of the injection peak and was therefore difficult to be analyzed by conductivity detection. The analysis time per sample is 20 min which includes ion-chromatographic analysis and calculation of air concentrations. Although in principle the time needed for separation may be reduced by using a stronger mobile phase, the total analysis time of 20 min seems to be sufficiently short for most applications. The response time of the system is approximately 60 min, i.e., after starting the air pump of the denuder, 95% of the expected signal for each analyte is observed.

The analytical performance of the system was tested by analyzing standard solutions containing 0–200 μg/kg of the analytes of interest in 1 mM sodiumcarbonate. Solutions were introduced into the system via the wet-denuder. Satisfactory detection limits are obtained in view of the average concentrations of the compounds of interest in air in northwestern Europe, i.e., 0.1 μg/m^3 for HCl and HNO_2 and 0.2 ug/m^3 for HNO_3 and SO_2 (calculated according to detection limit = experimental blanc + 3x standard deviation in blanc). The precision amounts to approximately 10% (relative standard deviation) irrespective of amount of sample put onto the column. This is rather unexpected and further study to elucidate the factors affecting precision is needed. It was found that the sensitivity can further be improved by a factor of 2 (for Cl^- and NO_2^-) to 5 (for NO_3^- and SO_4^{2-}) by increasing the loop volume to 500 μl without deteriorating separation efficiency. The recovery of SO_2 as the sum of SO_3^{2-} and SO_4^{2-} was better than 95%. Response was linear over the full range studied for all analytes.

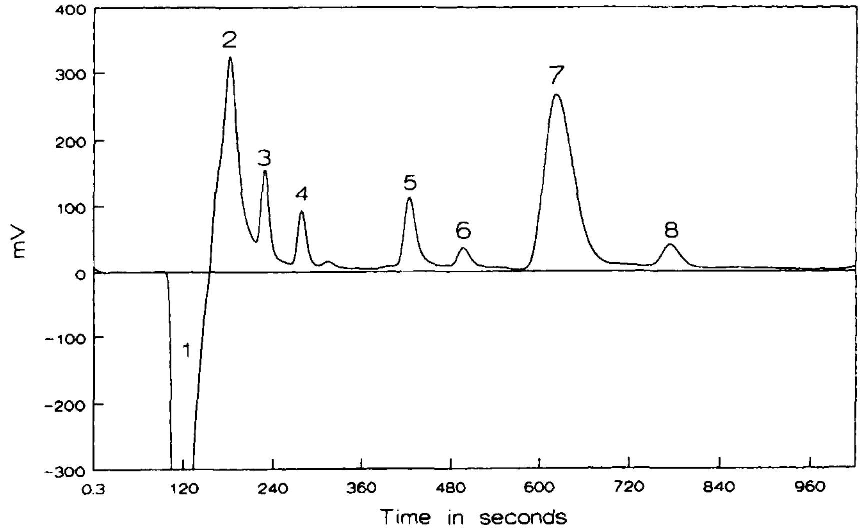

FIGURE 2 Chromatogram of air sample arriving from Eastern France. The air samples were taken at Petten, The Netherlands on 16 January 1995. Peak identification 1. system peak, 2. bicarbonate, 3. Chloride (0.99 μg/m^3), 4. Nitrite (1.05 μg/m^3), 5. Bromide (internal standard), 6. Nitrate (0.80 μg/m^3), 7. Sulfite (15.33 μg/m^3 as SO_2) and 8. Sulfate (0.72 μg/m^3 as SO_2)

Artefact HNO_2 from NO_2 and SO_3^{2-} reaction is observed if no formaldehyde is added to the wet-denuder absorbing liquid. In that case, a distinct effect of NO_2 on the SO_3^{2-}/SO_4^{2-} ratio is found. At NO_2 and SO_2 concentrations of 42.6 and 9.4 μg/m^3 respectively, artefact formation of HNO_2 is equivalent to 0.2 μg/m^3 HONO in air. For The Netherlands $NO_2$and SO_2 concentrations are normally less than 15 and 30 μg/m^3, respectively[9]. Hence, under practical conditions, artefact HNO_2 from reaction (1) is then negligible. Artefact formation of HNO_2 is reduced by a factor of 2.5 in case formaldehyde is used in the denuder absorbing liquid. This can most likely be explained from the observed rapid stabilisation of SO_3^{2-} by complexation with formaldehyde as methanesulfonic acid in liquid phase.

Measurement campaign

In Figures 3a-d, ambient air concentrations of HCl, HONO, HNO_3 and SO_2 are given, recorded from January 13–16, at Petten, The Netherlands. The sampling site is situated at approximately 500 m distance from the North Sea coast. Air trajectory analysis (36 h backwards) reveals that air masses arrived over the southern part of UK (13.01), the Channel region (14.01) and the Continent (Western-France, Belgium from 15.01 – 16.01). Measurements were conducted with the configuration shown in Fig. 1. Formaldehyde was used in the denuder liquid.

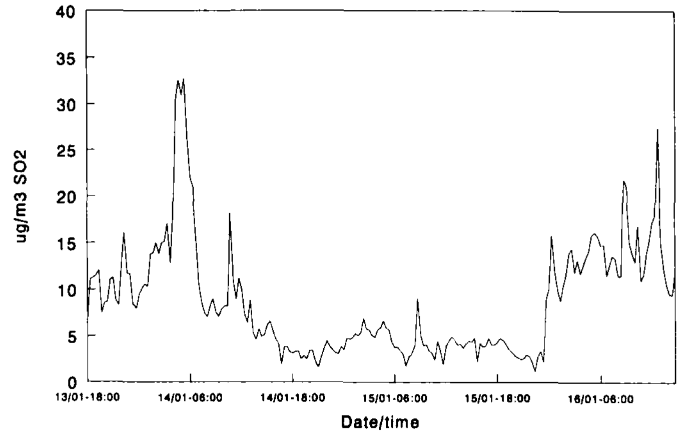

FIGURE 3d

FIGURES 3a-d. Ambient concentrations of HCl (3a), HONO (3b), HNO_3 (3c) and SO_2 (3d) measured using the automated wet-denuder ion-chromatograph at Petten, The Netherlands, January 13–16, 1995

Clearly, it is difficult to explain in detail the observed concentration patterns based on the limited data set available. Nevertheless, some interesting features from these measurements can be seen:

On all days, a clear diurnal variation in HONO is observed, with maximum and minimum concentrations of 1.1 and 0.3 μg/m^3 around 04:00 p.m. and 18:00 a.m., respectively. The observed HONO pattern indicates a rapid photolytic breakdown of HONO which effect is at maximum at around 17:00 a.m.. The maximum HONO concentrations are virtually independent of the origin of the air masses at Petten. This type of pattern indicates that HONO concentrations are determined mainly by local tropospheric chemistry with a relatively constant supply of HONO precursors and a rapid HONO removal from the atmosphere by photolysis during daytime. Alternatively, the HONO pattern may be explained by diurnal variation of the height of the mixed boundary layer with minimum and maximum values in the early morning and the late afternoon, respectively. This latter explanation seems not very realistic since the measurement campaign was conducted in wintertime during which diurnal variations in the boundary layer height are rather small.

No distinct diurnal variation in HNO_3 is found. Contrary to HONO, HNO_3 is not destroyed by photolysis but is removed from the atmosphere via wet- or dry deposition or aerosol formation. HNO_3 concentrations are highly fluctuating in relation to the other compounds. This can be explained from the HNO_3 formation during daytime via oxidation of NO_2 with hydroxyl radical and during nighttime via the heterogeneous reaction of N_2O_5 with water[1]. The deposition velocity of HNO_3 is high compared to the other gases which might explain the complex HNO_3 pattern.

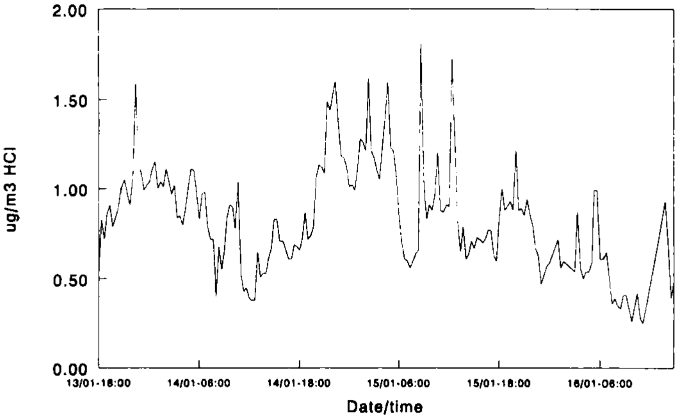

FIGURE 3a

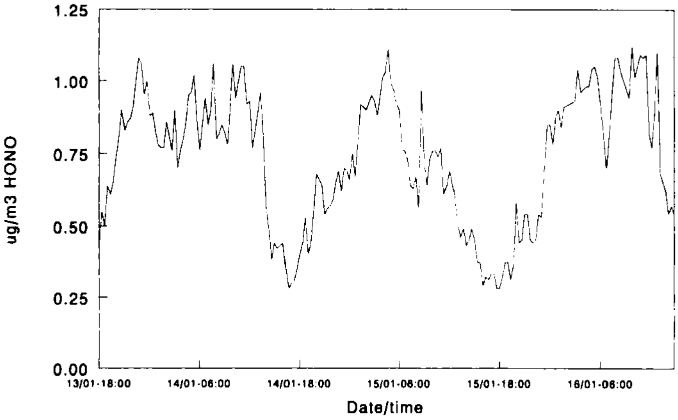

FIGURE 3b

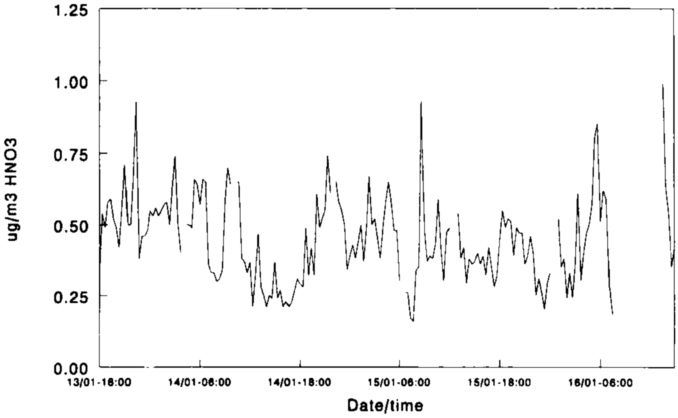

FIGURE 3c

HCl concentrations range from less than 0.20 to 1.9 $\mu g/m^3$. On January 13–15, the HCl pattern shows a clear diurnal pattern with high concentrations during night and low concentrations during daytime. Since the sampling site is very close to the North Sea coast, the observed HCl pattern should be explained, at least partly, by in-situ formation from sodiumchloride ('seasalt'). This is supported by the fact that low HCl is observed on January 14th around midday with air arriving from the area between France and UK, i.e., from the North Sea Channel region. For such air masses, high seasalt concentrations are expected but since the corresponding HONO and HNO_3 concentrations are also very small, HCl-formation from seasalt does not occur to a significant extent. On January 16, purely continental air was collected arriving from Eastern France. In continental air masses seasalt is negligible and HCl diminishes despite the corresponding high HONO and HNO_3 concentrations. The contribution to the measured HCl concentrations arising from seasalt deposition on the denuder wall is probably negligible since most of the mass of the seasalt aerosol is in the submicron to micron fraction.

A complex pattern is obtained for SO_2. The SO_2 concentrations vary from between 2 and 32 $\mu g/m^3$ and must be explained largely by long range transport over anthropogenic source areas : London, France, Belgium and The Netherlands. Low SO_2 is observed in air masses arriving over the North Sea and the western part of France and Belgium (14–15 January). High SO_2 is observed in air masses arriving over UK (13–14 January) and Eastern part of France and Belgium (15–16 January).

CONCLUSIONS

The analytical performance of the configuration described in this paper allows the simultaneous determination of atmospheric HCl, HONO, HNO_3 and SO_2 in air typical for NW-Europe at 20 min intervals without the need for complex preconcentration schemes. It has been demonstrated that interfering formation of HNO_2 in the denuder liquid by $NO_2(aq)$ and SO_3^{2-} is negligible under normal conditions found in The Netherlands especially if formaldehyde is used in the denuder liquid. Formaldehyde was further found to be very effective in preventing adverse effects from bacteria on nitrite and nitrate concentrations. The automated system combines wet-denuder air sampling with on-line analysis by ion-chromatography thereby circumventing problems likely to occur with off-line trace analysis such as sample contamination and sample degradation. Internal standard addition was found to be very convenient for calibration purposes with inherent high precision and accuracy obtained while no time is wasted for analyzing analyte standard solutions.

These combined factors makes the instrumentation very suitable to be used in field experiments.

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