

CHROM. 21 833

PRECISION AND ACCURACY OF ION CHROMATOGRAPHY IN DRY DEPOSITION MEASUREMENTS

J. SLANINA*, M. P. KEUKEN and P. A. C. JONGEJAN

Netherlands Energy Research Foundation (ECN), P.O. Box 1, 1755 ZG Petten (The Netherlands)

SUMMARY

A combination of ion chromatography (IC) and a so-called wet denuder system for the measurement of the deposition velocities of components such as HCl, HNO₃ and SO₂ was tested. For this type of measurement, a precision of better than 5% is required when analysing the absorption solutions of the wet denuder systems. The accuracy and precision of an IC system constructed from commercially available components was tested in the concentration range 10–5000 $\mu\text{g l}^{-1}$ for chloride, nitrate and sulphate. The output of conductivity, UV and ion-selective electrode detectors was linearized. Setting the calibration accuracy at 5%, a precision of 5% was obtained for sulphate and nitrate at a concentration of 30 $\mu\text{g l}^{-1}$, and for chloride at 50 $\mu\text{g l}^{-1}$. A precision of 1% was attained at concentrations of 60 and 400 $\mu\text{g l}^{-1}$ for sulphate and nitrate, respectively. Accuracies of 5% and 2% were achieved at concentrations of 100 and 200 $\mu\text{g l}^{-1}$ for sulphate, nitrate and chloride, respectively. Setting the calibration accuracy at 2%, a precision of 5% was achieved at a concentration of 20 $\mu\text{g l}^{-1}$ for sulphate, nitrate and chloride and a precision of 1% at concentrations of 60, 400 and 500 $\mu\text{g l}^{-1}$ for sulphate, nitrate and chloride, respectively. An accuracy of 5% was obtained at concentrations of 30, 100 and 100 $\mu\text{g l}^{-1}$ for sulphate, nitrate and chloride, respectively. At a concentration of 200 $\mu\text{g l}^{-1}$ of these components the accuracy was 2% or better.

INTRODUCTION

In general, the requirements regarding precision and accuracy for environmental measurements are modest. In view of other uncertainties, an accuracy and precision of the order of 5–10% relative are generally considered to be acceptable for measurements of trace components in the range 10–2000 $\mu\text{g l}^{-1}$. Problems regarding sampling and sample integrity will generally cause errors of at least the same order of magnitude.

A notable exception exists in the field of acid deposition research. Both wet and dry deposition are responsible for the effects of air pollutants. The measurement of wet deposition presents surmountable problems in the view of the available knowledge and methodology. However, the situation for dry deposition measurements is very different and either very fast or very precise methods are required to measure dry deposition fluxes.

For many components, gradient measurements are used to derive dry deposition fluxes. Gradients of the air concentrations of compounds, temperature, wind speed and humidity are measured over an altitude of, *e.g.*, 10 m. From these gradients the turbulence of the atmosphere is derived and the deposition velocities and fluxes can be calculated. The concentration gradients are dependent on atmospheric conditions and the deposition velocities of the components. Generally, differences of the order of 5% (for compounds such as submicron aerosols with a deposition velocity of the order of $0.1\text{--}0.5\text{ cm s}^{-1}$) to 25% (for compounds such as HNO_3 or NH_3 with deposition velocities of $1\text{--}3\text{ cm s}^{-1}$) are measured between altitudes of 1 and $10\text{ m}^{1,2}$. Consequently, these gradient measurements must have a precision of at least 5% relative, but preferably 1%, to be useful. As differences in air concentrations are measured, accuracy is less important than precision.

Denuder techniques offer the best possibilities for measuring dry deposition velocities of important acid-deposition-related compounds such as HNO_3 , NH_3 and HCl . A denuder is a tube coated with a reagent. Gases, owing to their large diffusion velocities compared with aerosols, can reach the walls of the tube and be absorbed by the coating. Aerosols that pass the denuder can be collected by a filter pack mounted in series with the denuder. If the denuder has an annular form and air is passed through the narrow section between two concentric tubes, larger sampling flows can be applied. Consequently, the sampling time of annular denuders is of the order of 10–30 min whereas simple denuders generally have sampling times of the order of hours.

ECN has developed a so-called wet denuder system (Fig. 1)³. The denuder is rotated along its axis and about 15 ml of a solution are pumped into the annulus and cover the walls. Gases are absorbed in this solution, depending on the properties of the gases and the absorbing solution. After a sampling time of typically 40 min, the solution is pumped out of the denuder and analysed in the laboratory. Ambient concentrations of compounds such as HNO_3 , HNO_2 , NH_3 , SO_2 , HCl and H_2O_2 can be measured selectively. The precision of the method is illustrated by parallel measurements of HNO_3 concentrations in ambient air by two wet denuder systems (Fig. 2). The standard deviation, calculated from 45 pairs of measurements, is 5.5% relative. The same order of precision was observed in parallel measurements of NH_3 and SO_2 . The precision of the analytical method is 5% relative and could contribute the major part of the 5% standard deviation observed in measurements with wet denuder systems.

In view of the concentrations of important pollutants in the atmosphere, gradient measurements by means of a wet denuder system require precise measurements of Cl^- , NO_3^- , NO_2^- and SO_4^{2-} in the absorption solution of the wet denuder systems at concentrations of $50\text{--}2000\text{ }\mu\text{g l}^{-1}$. The ion chromatographic system must be capable of handling a large number of analyses, as 1 week of gradient measurements at three heights results in at least 500 samples.

A computerized ion chromatographic system has been developed at ECN, that is able to carry out the required number of analyses with a precision of at least 5% relative⁴. It was decided to optimize this system for precision and accuracy, in order to minimize the analytical errors with the aim of extending the possibilities for application of the wet denuder systems to the measurement of deposition fluxes of components such as HNO_3 , SO_2 , HCl , NH_3 and HNO_2 .

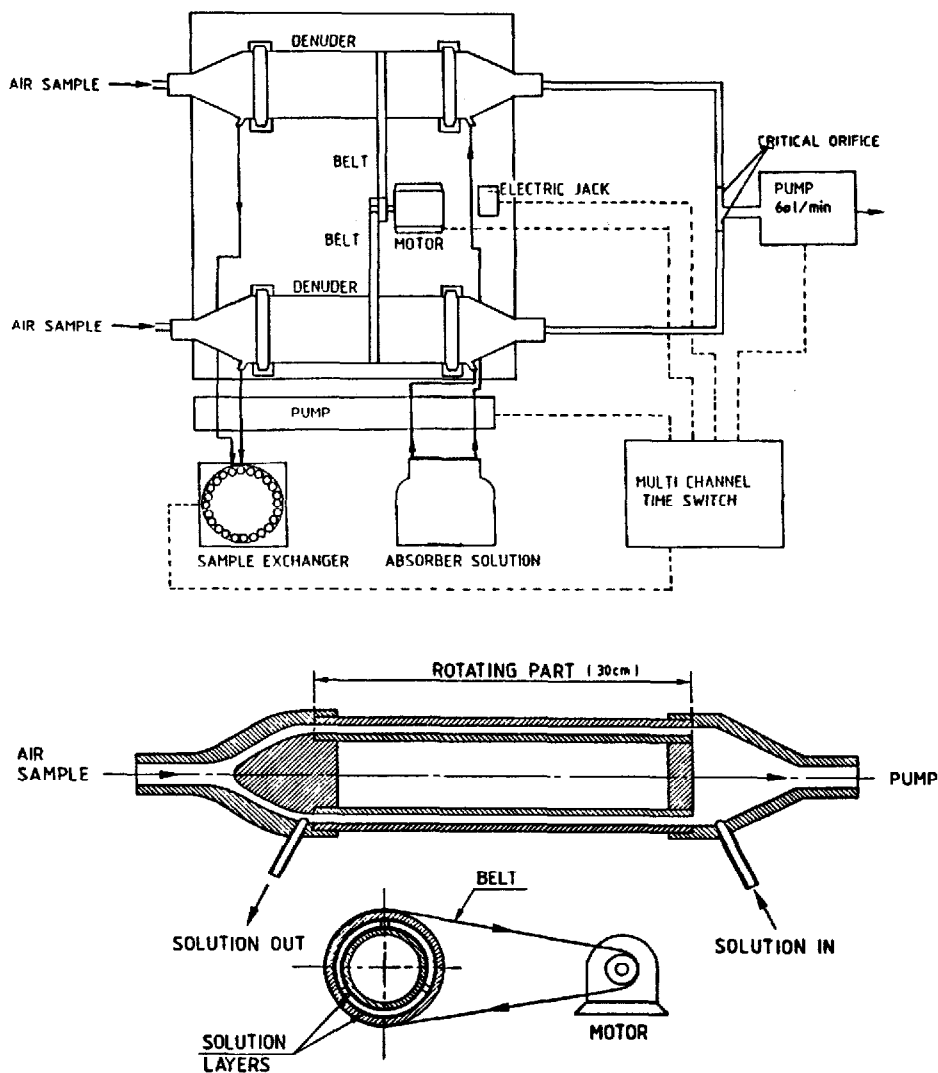


Fig. 1. Wet annular denuder system.

ION CHROMATOGRAPHIC SYSTEM

The IC system originally consisted of a Gilson sample changer, Dionex injection valves and columns, a Dionex membrane suppressor, a Waters Assoc. conductivity detector, a Shimadzu UV detector and a chloride ion-selective electrode detection system⁴. The detectors, sample changer and valves were interfaced to a Tulip microcomputer by means of a Keithley interface (Fig. 3). This was originally equipped with 12-bit analog-digital converters, which provided insufficient resolution in view of the very high signal-to-noise ratio of the Waters Assoc. conductivity detec-

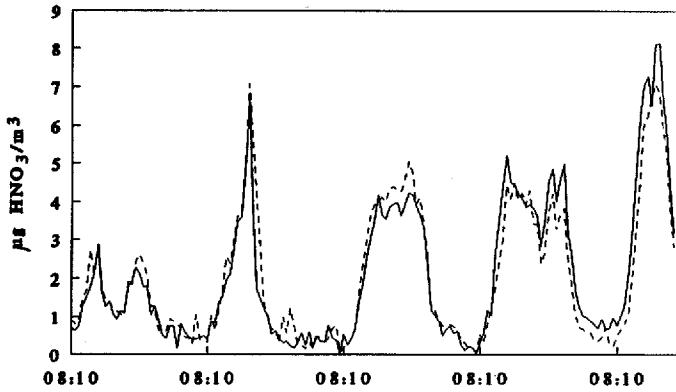


Fig. 2. Results for HNO₃ air concentrations sampled by two wet denuder systems in Rome during the period September 19th–23nd, 1988. Solid line, HNO₃ denuder 1; broken line, denuder 2.

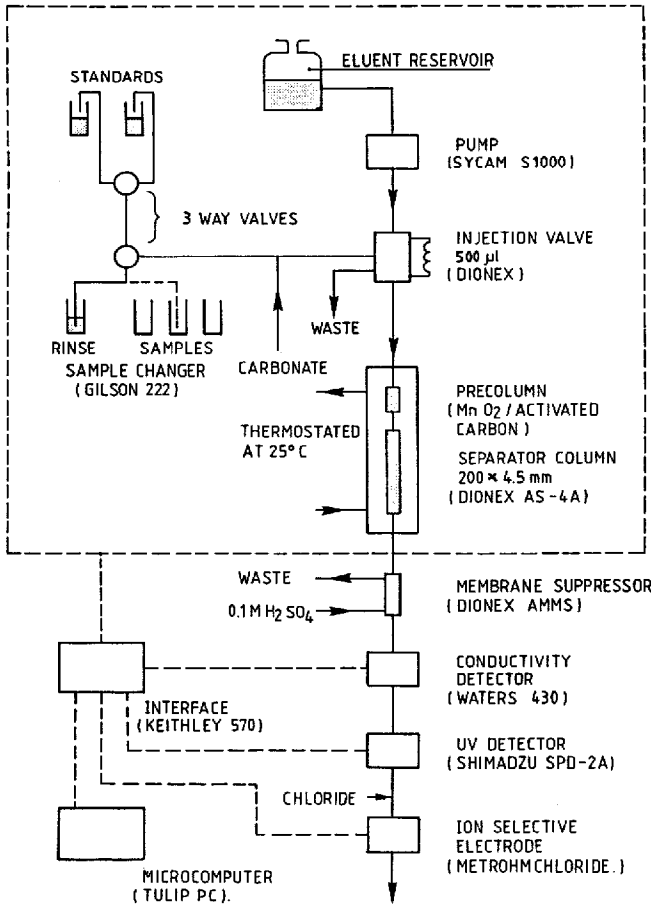


Fig. 3. Ion chromatographic system.

tor, and was replaced with a scanning digital voltmeter (Keithley) with a resolution of 5.5 digits. Enlargement of the sample loop from $100 \mu\text{l}^4$ to $500 \mu\text{l}$ resulted in detection limits of $10 \mu\text{g l}^{-1}$ or less for sulphate, nitrate and chloride.

Linearization of the signals of the conductivity detector, UV detector and ion-selective electrodes was performed as described previously⁴. Calibration was carried out by measuring two standard solutions containing 500 and 3000 $\mu\text{g l}^{-1}$ of sulphate, nitrate and chloride followed by linear regression of the results. Calibration was performed twice and accepted if a preset accuracy was attained. If this was not the case, the calibration procedure was repeated. After ten samples a standard was measured and the system was automatically recalibrated if the results of the standard exceeded preset boundaries.

RESULTS

Initially, precision and accuracy were investigated under "worst possible conditions". Calibration accuracy was set at a standard value of 5%. Samples in the concentration range 10–5000 $\mu\text{g l}^{-1}$ were analysed in random sequence. Ten samples were measured of each concentration in such a way that the results were obtained by means of different calibrations.

In Figs. 4–6, precision and accuracy are given for sulphate, nitrate and chloride as obtained from ten-fold analysis of standards in the range 10–5000 $\mu\text{g l}^{-1}$. The results are plotted double logarithmically. The 5 and 1% limits are indicated by straight lines. A second-order curve fit is shown to give a better indication of the overall results. Accuracy is of the order of 5% at concentrations of about 100 $\mu\text{g l}^{-1}$ for all components. An accuracy of 2% is possible for concentrations of more than 200 $\mu\text{g l}^{-1}$ of sulphate, nitrate and chloride.

A precision level of 5% is reached for sulphate and nitrate at a concentration of 30 $\mu\text{g l}^{-1}$ and for chloride at 50 $\mu\text{g l}^{-1}$. At this level, analytical errors will result in a sizable contribution to the overall error, as pointed out above. A precision of 1% for sulphate and nitrate measurements can be reached at levels of 60 and 400 $\mu\text{g l}^{-1}$,

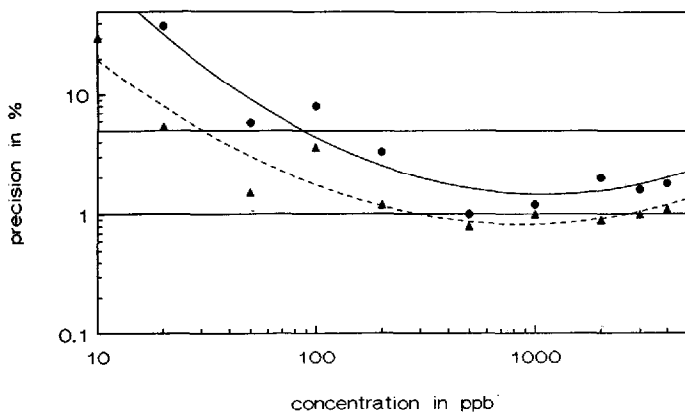


Fig. 4. (▲) Precision and (●) accuracy in percentages as a function of the sulphate concentration measured by the ion chromatographic system set at a calibration accuracy of 5%; straight lines indicate 1% and 5% precision limits.

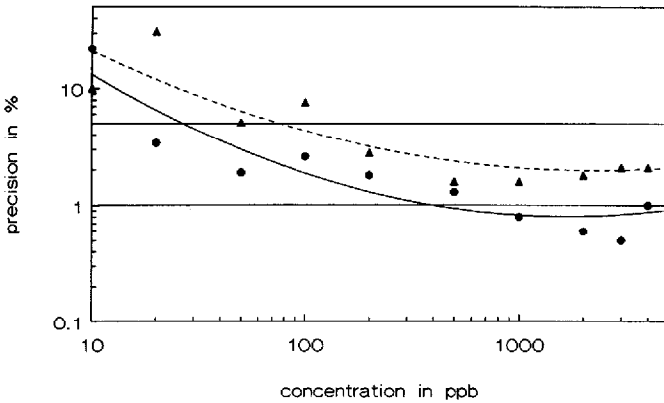


Fig. 5. (●) Precision and (▲) accuracy as a function of the nitrate concentration measured by the ion chromatographic system set at a calibration accuracy of 5%; straight lines indicate 1% and 5% precision limits.

respectively. The precision of chloride measurements is typically 2% or worse. It is expected that these precision levels will not contribute significantly to the overall error.

Generally, a sampling time of 1 h or less is employed in gradient measurements. The volume of the absorption solution of the wet denuder systems is typically 15 ml. The sampling flow of the wet denuder system is 30 l min^{-1} . The air concentrations of SO_2 , HNO_3 and HCl , corresponding to the concentrations in the absorption solution where the levels of 1 and 5% precision are obtained, are given in Table I.

HNO_3 and HCl have very high deposition velocities (of the order of $2\text{--}3 \text{ cm s}^{-1}$) so steep gradients are generally observed and measurements are possible at the 5% precision level, corresponding to ambient levels of about $0.2 \mu\text{g m}^{-3}$. This means that gradient measurements of the deposition of HNO_3 and to a lesser extent of HCl can be carried out under most circumstances, as the mean concentrations of these

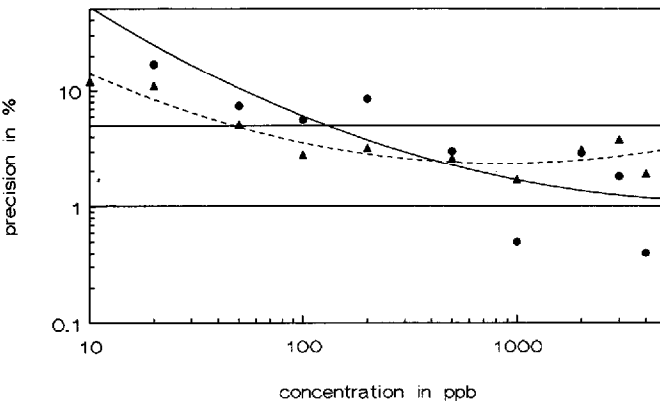


Fig. 6. (▲) Precision and (●) accuracy as a function of the chloride concentration measured by the ion chromatographic system set at a calibration accuracy of 5%; straight lines indicate 1% and 5% precision limits.

TABLE I

CONCENTRATIONS IN THE ABSORPTION SOLUTIONS OF THE WET DENUDER WITH 5% AND 1% PRECISION LIMITS AND THE CORRESPONDING AIR CONCENTRATIONS

Ion chromatographic system set at a calibration accuracy of 5%.

Species	5% limit ($\mu\text{g l}^{-1}$)	Air concentration ($\mu\text{g m}^{-3}$)	1% limit ($\mu\text{g l}^{-1}$)	Air concentration ($\mu\text{g m}^{-3}$)
SO ₂	30	0.2	400	2
HNO ₃	30	0.2	400	2
HCl	50	0.5	—	—

components in The Netherlands are 1.1 and 1 $\mu\text{g m}^{-3}$, respectively. Precise measurements at the 1% level are possible for SO₂ and HNO₃ at a level of 2 $\mu\text{g m}^{-3}$. This is not often observed for HNO₃ in The Netherlands, but the deposition flux of SO₂ can be measured precisely as the yearly average concentration of SO₂ in The Netherlands is of the order of 15 $\mu\text{g m}^{-3}$.

Accuracy and precision were also characterized for the following circumstances: limits for calibration and recalibration were set at 2%; calibration and recalibration take about twice as long as calibrations at the 5% level (eight standards are generally analysed instead of four); samples were grouped together for each concentration, which is a realistic situation as about the same concentration will be measured in gradient measurements at different altitudes; and samples of each concentration were analysed with the same calibration, a condition that in practice can be easily arranged for this type of measurements.

In Figs. 7–9, precision and accuracy are plotted for sulphate, nitrate and chloride as achieved by the analysis of six standards for each concentration in the range 10–5000 $\mu\text{g l}^{-1}$ under the above conditions. The 5% accuracy limit was reached at concentrations of 30, 100 and 100 $\mu\text{g l}^{-1}$ for sulphate, nitrate and chloride. At concentrations of 200–300 $\mu\text{g l}^{-1}$, an accuracy of 2% relative or better was obtainable.

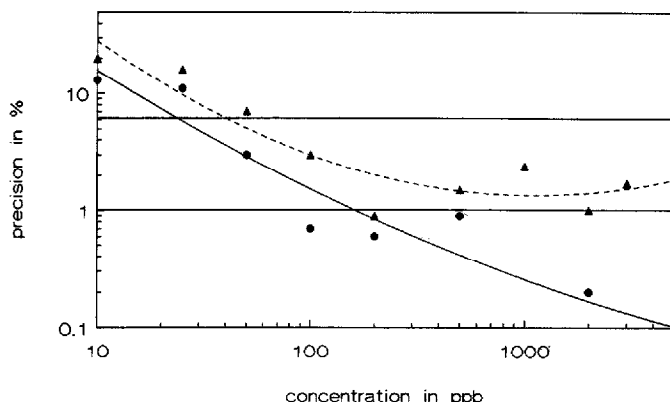


Fig. 7. (●) Precision and (▲) accuracy as a function of the sulphate concentration measured by the ion chromatographic system set at a calibration accuracy of 2%; straight lines indicate 1% and 5% precision limits.

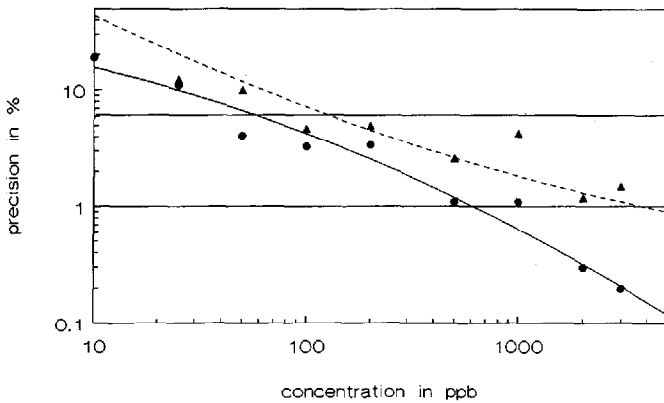


Fig. 8. (●) Precision and (▲) accuracy as a function of the nitrate concentration measured by the ion chromatographic system set at a calibration accuracy of 2%; straight lines indicate 1% and 5% precision limits.

The precision level of 5% was reached at a concentration of about $20 \mu\text{g l}^{-1}$ for all three components. The 1% level was reached at 60, 400 and $500 \mu\text{g l}^{-1}$ for sulphate, nitrate and chloride, respectively. The ambient concentrations, which correspond to the concentrations in the absorption solutions for which a precision of 5 and 1% can be claimed, were calculated as indicated before and given in Table II.

Deposition measurements are possible for HNO_3 and HCl , in view of their high deposition velocity, at ambient concentrations of $0.1 \mu\text{g m}^{-3}$, which means that these measurements can be performed under nearly all ambient conditions. Precise measurements are possible for SO_2 at a level of $0.3 \mu\text{g m}^{-3}$, a concentration that can be found in absolute background areas only. Precise deposition flux measurements for HCl and HNO_3 will only occasionally be feasible.

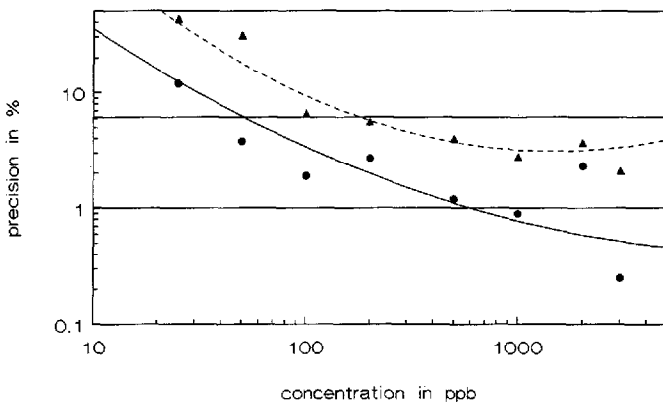


Fig. 9. (●) Precision and (▲) accuracy as a function of the chloride concentration measured by the ion chromatographic system set at a calibration accuracy of 2%; straight lines indicate 1% and 5% precision limits.

TABLE II

CONCENTRATIONS IN THE ABSORPTION SOLUTIONS OF THE WET DENUDER WITH 5% AND 1% PRECISION LIMITS AND THE CORRESPONDING AIR CONCENTRATIONS

Ion chromatographic system set at a calibration accuracy of 2%.

<i>Species</i>	<i>5% limit</i> ($\mu\text{g l}^{-1}$)	<i>Air concentration</i> ($\mu\text{g m}^{-3}$)	<i>1% limit</i> ($\mu\text{g l}^{-1}$)	<i>Air concentration</i> ($\mu\text{g m}^{-3}$)
SO ₂	20	0.1	60	0.3
HNO ₃	20	0.1	400	2
HCl	20	0.1	500	2.5

CONCLUSIONS

It is possible to optimize an ion chromatographic system in such a way that sufficient precision is obtained for this method to be applied to the measurements of gradients by means of wet denuder systems. The application to the measurement of the deposition fluxes of components such as HNO₃, HCl and SO₂ will hopefully result in more precise estimates of the deposition fluxes of acid-deposition-related components, as the present uncertainty is of the order of 40% or more.

REFERENCES

- 1 M. L. Wesely, D. R. Cook, R. L. Hart and R. E. Speer, *J. Geophys. Res.*, 90 (1985) 2131–2143.
- 2 H. J. Huebert and C. H. Robert, *J. Geophys. Res.*, 90 (1985) 2085–2090.
- 3 M. P. Keuken, C. A. M. Schoonebeek, A. van Wensveen-Louter and J. Slanina, *Atmos. Environ.*, 22 (1988) 2541–2548.
- 4 M. P. Keuken, J. Slanina, P. A. C. Jongejan and F. P. Bakker, *J. Chromatogr.*, 439 (1988) 13–21.