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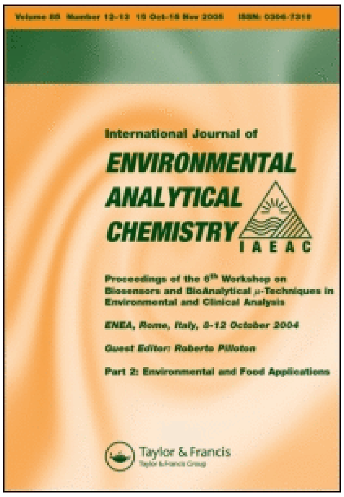

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# Application of a Thermo-Denuder Analyser to the Determination of $H_2SO_4$, $HNO_3$ and $NH_3$ in Air

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# Application of a Thermo-Denuder Analyser to the Determination of $H_2SO_4$, $HNO_3$ and $NH_3$ in Air

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*(Received August 14, 1980)*

The thermoanalytical method for speciation of atmospheric strong acids developed by Nießner and Klockow has been extended to the measurement of the $HNO_3/H_2SO_4/NH_3$ system in air.

A series of coated tubes operated at different temperatures are used to collect selectively nitrate- and sulphate-containing atmospheric trace compounds as well as free ammonia. $HNO_3$ and $NH_3$ are collected at room temperature by NaF- and $H_3PO_4$-coated tubes, respectively. $H_2SO_4$ and $HNO_3$ resulting from the dissociation of $NH_4NO_3$ are collected by the NaF coating of a denuder tube heated to 390–410 K. The liberated $NH_3$ (from $NH_4NO_3$) is deposited in a subsequent $H_3PO_4$-coated tube. At 490–510 K ammonium sulphates decompose forming $H_2SO_4$ and $NH_3$. The fragments are trapped in the same way using tubes with a NaF and a $H_3PO_4$ layer, respectively. All tubes are washed out with water. In the extracts $NO_3^-$ and $SO_4^{2-}$ are determined by ion-chromatography, $NH_4^+$ by means of an ion-selective electrode.

KEY WORDS: $HNO_3$, $H_2SO_4$, $NH_4NO_3$, $NH_4HSO_4$, $(NH_4)_2SO_4$; Aerosol sampling, thermoanalysis.

## INTRODUCTION

Filter methods for the determination of $H_2SO_4$ and $HNO_3$ are susceptible to interferences.[1,2] A possible solution for the $H_2SO_4$ problem was given by Cobourn *et al.*[3] applying a thermodiffusion denuder in connection to a flame emission sulphur analyser. For the determination of $HNO_3$ a denuder difference technique has been proposed.[4]

Recently Nießner and Klockow developed a thermoanalytical method for the determination of $H_2SO_4$ in air.[5] The acid droplets are thermally evaporated in a heated glass tube and the small fragments formed are collected on the walls of the tube by diffusion-controlled deposition. Sulphuric acid is bonded by means of a sodium chloride coating on the walls and is determined by analysing the coating for sulphate. Sulphate and bisulphate salt particles pass through the tube unaffected, dependent on the temperature of the tube and the flow rate.

The application of this method to the $HNO_3/H_2SO_4/NH_3$ system was investigated. An aerosol particle will not reach the wall of a tube as long as the flow is laminar, whereas gases will diffuse to the wall. Therefore a separation of gaseous $HNO_3$ and $NH_3$ from $H_2SO_4$ droplets or sulphate particles is possible. Furthermore $H_2SO_4$ and ammonium sulphates, $(NH_4)_xH_y(SO_4)_{1/2(x+y)}$, can be distinguished by their different thermal behaviour.

A characterization of the $H_2SO_4/HNO_3/NH_3$ system in air is in principle possible if a number of tubes which contain suitable wall coatings and which are operated at different temperatures is placed in series. Strong acids rapidly react with a NaF coating, whereas $NH_3$ is effectively absorbed by $H_3PO_4$.

## GENERAL SET-UP OF THE METHOD

$HNO_3$ is presumably present as a gas in the atmosphere and reacts at room temperature with the wall coating of a denuder tube. $NH_4NO_3$ is probably partly dissociated into $NH_3$ and $HNO_3$ at ambient temperature.[6,7] We measured a complete dissociation at 410 K at concentrations of about $4000\,\mu g \cdot m^{-3}$ $NH_4NO_3$. $H_2SO_4$ will reach the wall of the tube at 390–410 K because of evaporation. $(NH_4)_xH_y(SO_4)_{1/2(x+y)}$ decomposes sufficiently fast into $x$ $NH_3$ and $1/2(x+y)$ $H_2SO_4$ at 490–510 K to allow a complete reaction of the $H_2SO_4$ formed with the coating of a denuder tube.[5] $NH_3$ can be trapped separately.

We tested different coatings for $HNO_3$, $H_2SO_4$ and $NH_3$. $HNO_3$ and $H_2SO_4$ react rapidly with NaCl and NaF. As we use ion-chromatography to determine $NO_3^-$ and $SO_4^{2-}$ after having dissolved the coating we prefer NaF, which does not interfere even at high concentrations. $NH_3$ reacts very rapidly with a $H_3PO_4$ coating.

As a simultaneous detection of all $SO_4^{2-}$ and $NO_3^-$ species was desired, a set-up of 7 tubes, connected in series, was tested (see Figure 1):

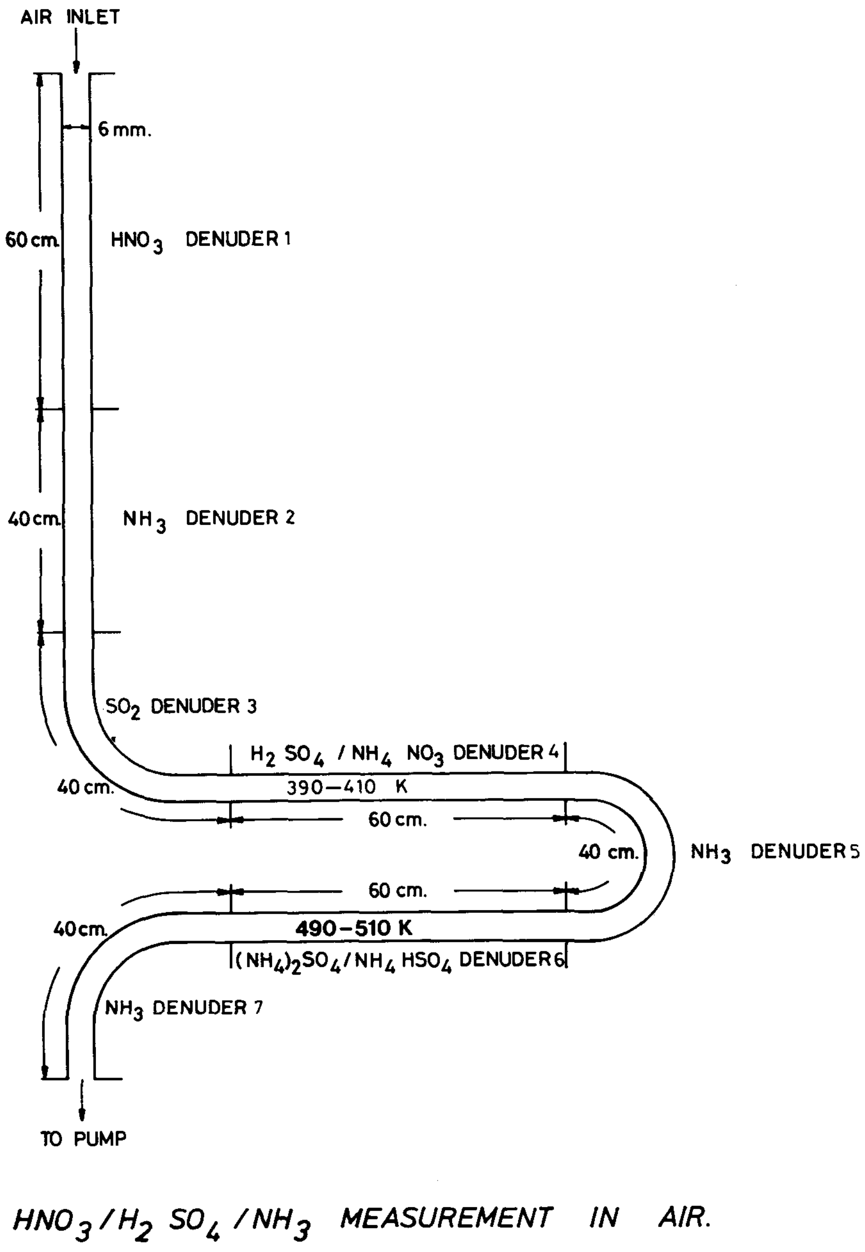

FIGURE 1 General set-up of the apparatus.

Tube 1: Ambient temperature, coated with NaF; $HNO_3$ is retained.
Tube 2: Ambient temperature, coated with $H_3PO_4$; free $NH_3$ is absorbed.
Tube 3: Ambient temperature, coated with NaOH; $SO_2$ (a possible interferent) is trapped.
Tube 4: Temperature is 390 to 410 K, coated with NaF; $H_2SO_4$ is retained; $NH_4NO_3$ (if any) dissociates and the resulting $HNO_3$ reacts with NaF.
Tube 5: Ambient temperature, coated with $H_3PO_4$; $NH_3$ (from $NH_4NO_3$ dissociation) is retained.
Tube 6: Temperature is 490–510 K, coated with NaF; $H_2SO_4$ resulting from $(NH_4)_xH_y(SO_4)_{1/2(x+y)}$ dissociation is retained.
Tube 7: Ambient temperature, coated with $H_3PO_4$; $NH_3$ resulting from the decomposition of ammonium sulphates is retained.

# EXPERIMENTAL

## Generation of test atmospheres

$H_2SO_4$ and $(NH_4)_2SO_4$ aerosols were generated by nebulizing aqueous solutions by means of a Wright nebulizer.[8] The droplets (*ca.* 2 $\mu$m diameter) were carried by the nebulizer gas flow (10 l $N_2$ min$^{-1}$) to a glass tube (diam. 20 cm, length 2.5 m) and mixed with dry gas (20 l $N_2$ min$^{-1}$) to evaporate the droplets (see Figure 2). Measurements indicated that the diameters of the final particles were in the range of 0.3–0.01 $\mu$, depending on the concentration of the nebulized solution.

$H_2SO_4$ aerosols were also generated by the method of Nießner and Klockow where gas is passed over heated concentrated $H_2SO_4$.[9] We employed this method because the particles are very small (0.03 $\mu$) and nearly monodisperse. In this way we were able to test whether the particle diameter influenced the results of the method. Ammonium sulphate particles with a comparable diameter can be generated by the reaction of $NH_3$ with the sulphuric acid aerosol.

$HNO_3$ test atmospheres can be obtained by evaporating a nebulized $HNO_3$ solution. At low concentrations of $HNO_3$, however, difficulties arise because of ad- and desorption processes at the glass wall of the generator tube. It will take at least 48 h before a stable test atmosphere, containing about 10 $\mu$g $HNO_3$ m$^{-3}$, is obtained. A better method to create low $HNO_3$ concentrations is given in Figure 3. Concentrated $HNO_3$ is thermostated in a glass vessel at 303.5 K. A capillary is connected to the vessel by a NS 14 groundjoint. The $HNO_3$ production can be regulated

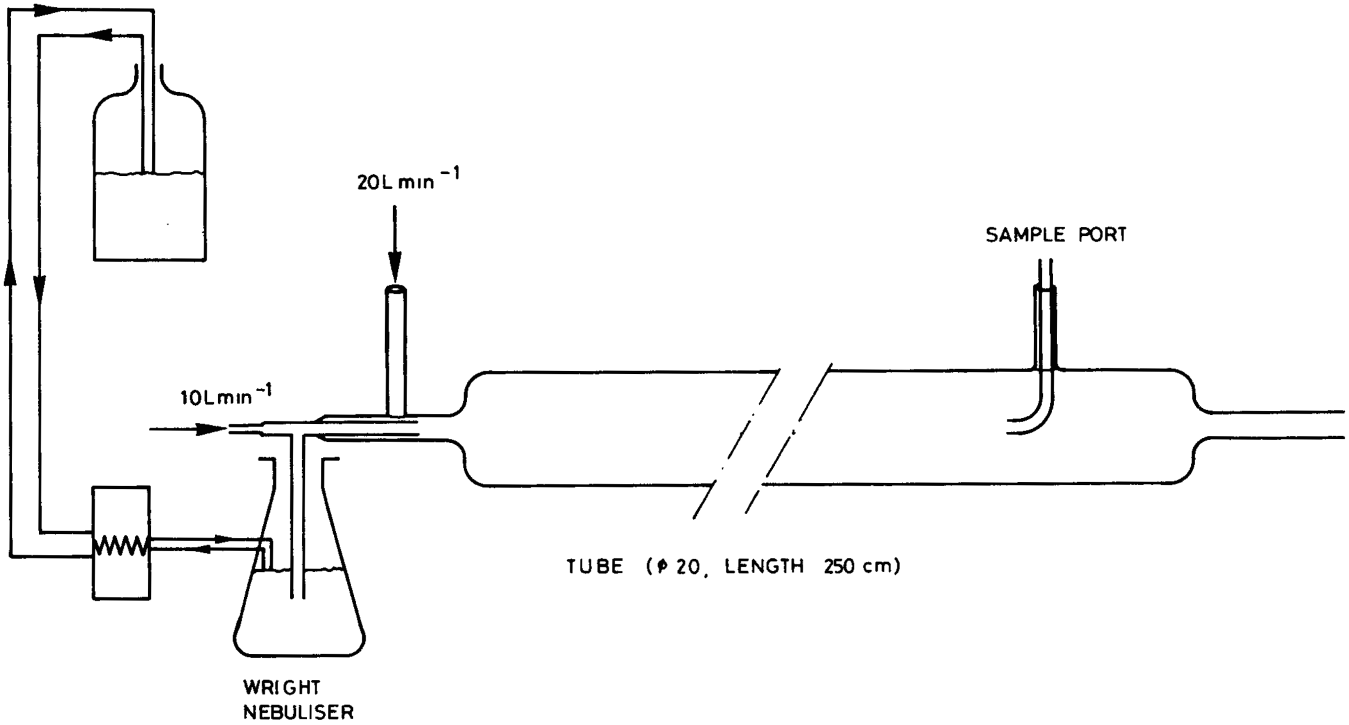

FIGURE 2 Apparatus for the generation of test aerosols.

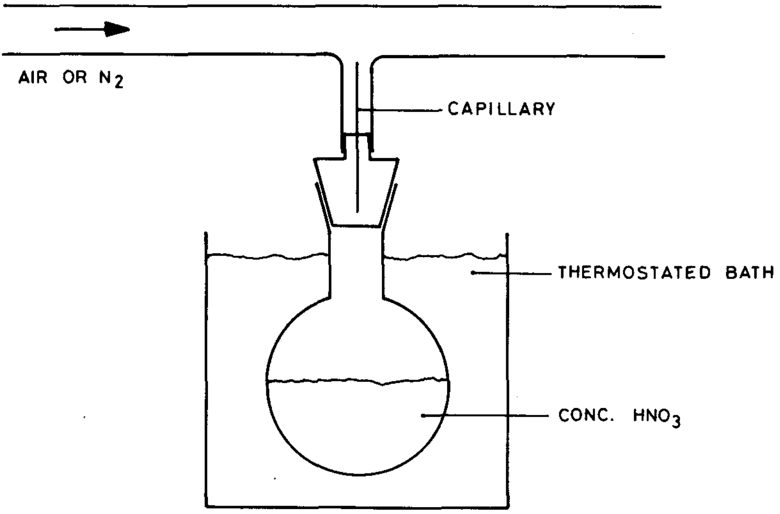

FIGURE 3 Apparatus for the generation of $HN_3$ containing test atmospheres.

by changing the diameter and length of the capillary and the temperature of the $HNO_3$.[10]

$NO_2$ and $SO_2$ were obtained from standard permeation tubes. NO was generated by a permeation tube consisting of a stainless steel body and a thick teflon membrane (the pressure is 20–30 bar).

Coatings were as follows. NaF: 0.5 ml of 0.05 M NaF in 1:1 water-methanol is brought into the tube. The walls are wetted with the reagent and the solvent is evaporated under vacuum. $H_3PO_3$: 0.5 ml of 0.015 M $H_3PO_4$ in methanol is used; procedure is the same as for NaF. NaOH: 0.5 ml of 0.1 M NaOH in methanol is employed in the same procedure as described for NaF.

## Determination of $SO_4^{2-}$, $NO_3^-$ and $NH_4^+$

The tubes are washed out with 5 ml (in case of NaF-coated tubes) or 2 ml ($H_3PO_4$-coated tubes) of doubly deionized water. $NH_4^+$ is measured by means of a gas-sensing membrane electrode, equipped with a 1-ml sample cell.[11] $NO_3^-$ and $SO_4^{2-}$ are determined by ion-chromatography. A 4-ml sample is pumped through a concentrator-column filled with Zipax-SAX ion-exchanger. The ion-chromatograph is adapted to obtain a high resolution and low detection limit (*ca.* 10 ppb).[12]

## RESULTS

### $H_2SO_4$ analysis

The efficiency of tube 4 (390–410 K) for $H_2SO_4$ was tested at high concentrations (400 $\mu g \cdot m^{-3}$) by comparison with filter measurements, and was found to be $\geq 98\%$, in agreement with the results obtained earlier by Nießner and Klockow[5] and Cobourn *et al.*[3] The precision of the method was tested by repeated analysis of a test aerosol containing about 10 $\mu g \cdot m^{-3}$ of $H_2SO_4$ (calculated from the $H_2SO_4$ concentration of the nebulized solution). A mean value of 8.7 $\mu g$ with a standard deviation of $\pm 1.0$ $\mu g \cdot m^{-3}$ of $H_2SO_4$ was found ($n = 5$). No $SO_4^{2-}$ was detected in the other tubes at sample flow rates of up to 2 $l \cdot min^{-1}$. At higher flow rates $SO_4^{2-}$ was found in tube 6 also (see Figure 4).

The detection limit (at a sample flow rate of 2 $l \cdot min^{-1}$ and a sampling time of 4 h) is 0.4 $\mu g \cdot m^{-3}$ of $H_2SO_4$.

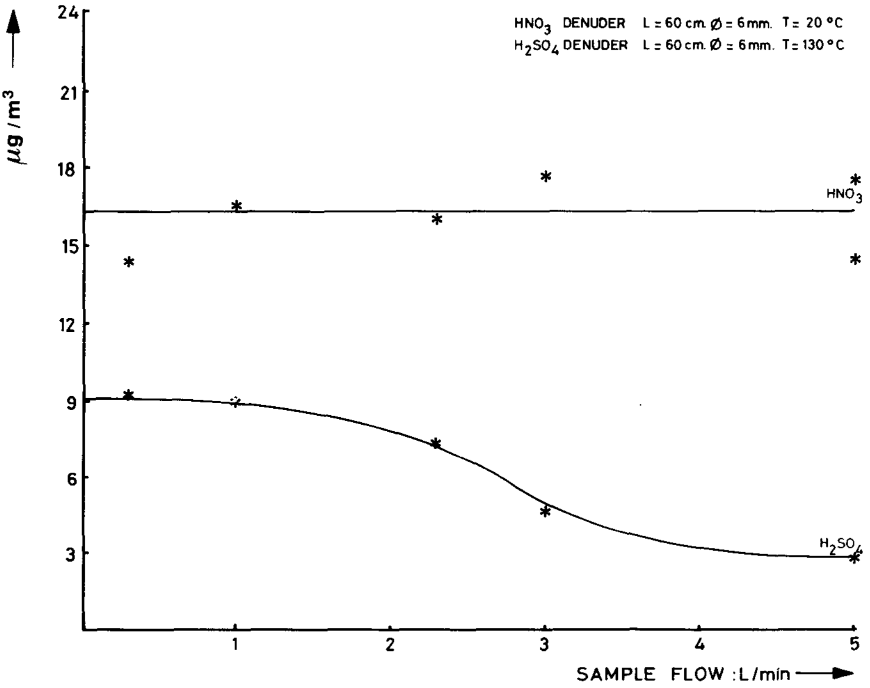

FIGURE 4 Concentration of $H_2SO_4$ and $HN_3$ found in air as a function of the sample flow.

## $HNO_3$ analysis

The collecting efficiency of NaF was tested between 290 and 430 K and was found to be 95% or higher independent of the temperature. Above 360 K HF was liberated by $HNO_3$. All $HNO_3$ was retained in tube 1, no $NO_3^-$ was detected in the other tubes at sample flow rates of up to $3\,l \cdot min^{-1}$ (see Figure 4). The precision was tested by repeated analysis of a $HNO_3$ test atmosphere, and a concentration of $15.8 \pm 1.5\,\mu g \cdot m^{-3}$ $HNO_3$ was found ($n=5$). Figure 5 gives the amount of $HNO_3$ found as a function of the sample volume. At a sample flow rate of $2\,l \cdot min^{-1}$ and a sampling time of 4 h the detection limit is $0.2\,\mu g \cdot m^{-3}$ $HNO_3$.

## $NH_3$ analysis

We employed the method of Ferm *et al.*,[13] but $H_3PO_4$ was used as a coating instead of oxalic acid. Because of its vapor pressure oxalic acid disappears from tubes 5 and 7 by sublimation (elevated temperature of the

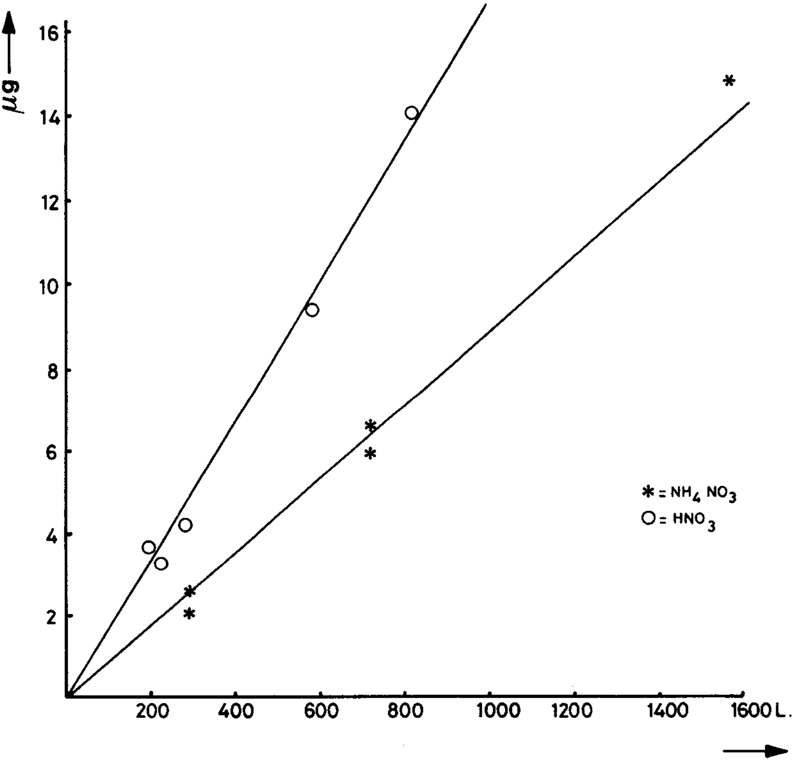

FIGURE 5 Amount of $HNO_3$ and $NH_4NO_3$ found (µg) as function of the sample volume.

carrier gas) during the sampling period. We encountered severe blank problems, which are currently investigated, but the sampling is no problem as one can conclude from Figure 6.

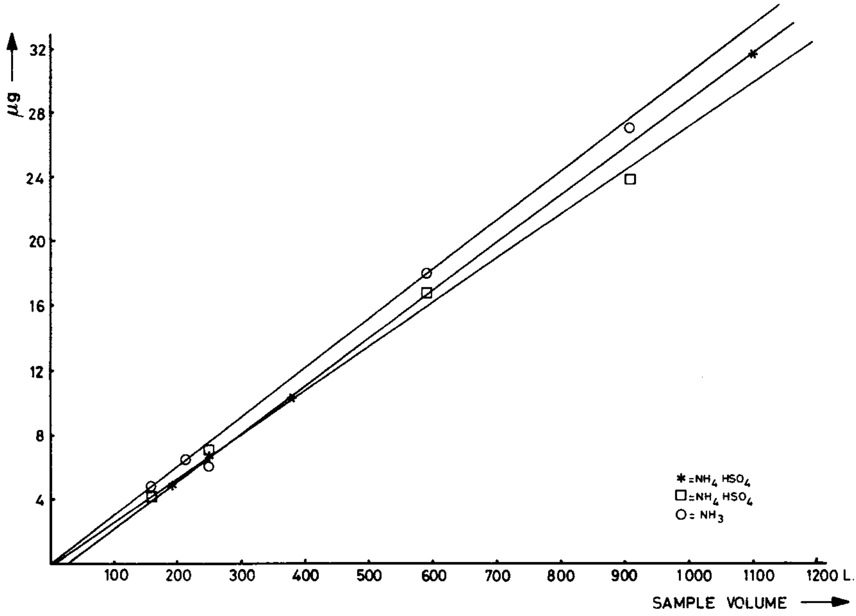

FIGURE 6 Amount of $NH_3$, $NH_4HSO_4$ and $(NH_4)_2SO_4$ found (μg) as function of the sample volume.

## $NH_4NO_3$ analysis

Experiments at Dortmund and E.C.N. indicated that no or very little dissociation of $NH_4NO_3$ takes place when test aerosols containing 4000 $\mu g \cdot m^{-3}$ of $NH_4NO_3$ are passed through a denuder tube at 290 K. Appreciable dissociation is found, however, at a temperature of 340 K. Also a test atmosphere with a concentration of 20 $\mu g \cdot m^{-3}$ of $NH_4NO_3$ was analysed (tube 1 at room temperature). At least half of the $NO_3^-$ was found in tube 1 and half of the $NH_3$ in tube 2 indicating that in this case $NH_3NO_3$ was dissociated partly into $NH_3$ and $HNO_3$.[6,7] If $NH_3$ was added to inhibit the dissociation all $NO_3^-$ was found in tube 4 (393 K) at sample flow rates of up to $2 l \cdot min^{-1}$.

The precision was checked by repeated analysis of a $NH_4NO_3$ test aerosol, which was stabilised by the addition of free $NH_3$. The result was $8.1 \pm 1.5$ μg $NH_3NO_3^-$ ($n = 5$). Figure 6 gives the amount of $NH_4NO_3$

found as a function of the sample volume. The $NH_4/NO_3$ ratio was calculated from the $NH_4^+$ content of tube 5 and the $NO_3^-$ content of tube 4 and was found to be 1.3, probably because of blank problems.

## $(NH_4)_xH_y(SO_4)_{1/2(x+y)}$ analysis

The efficiency of the capture of $H_2SO_4$ produced by dissociation of $(NH_4)_xH_y(SO_4)_{1/2(x+y)}$ in tube 6 at 490–510 K was tested at a concentration of $400\,\mu g \cdot m^{-3}$ of $NH_4HSO_4$ and $(NH_4)_2SO_4$ by comparison with filter measurements and was found to be $\geq 98\%$ at sample flow rates of up to $1\,l \cdot min^{-1}$ (see also Figure 7). At this concentration all $NH_3$ resulting from the dissociation of the sulphates was found in tube 7. The $NH_4^+/SO_4^{2-}$ ratio observed for $(NH_4)_2SO_4$ varied between 1.8 and 2.2.

At lower sulphate concentrations (below $30\,\mu g \cdot m^{-3}$) and at sample flow rates of up to $1\,l \cdot min^{-1}$ the situation was different. If $NH_4HSO_4$

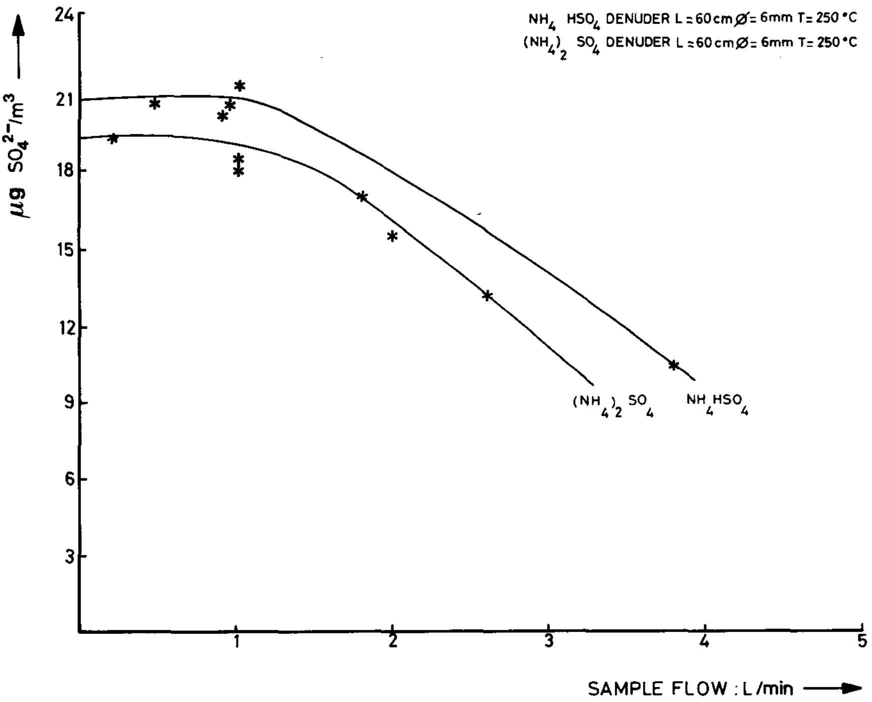

FIGURE 7 Concentration of $NH_4HSO_4$ and $(NH_4)_2SO_4$ found in air as a function of the sample flow.

was sampled, all $NH_4^+$ was found in tube 7, but in the case of $(NH_4)_2SO_4$ about equal amounts of $NH_4^+$ were measured in tube 5 and in tube 7. This indicates that at low concentrations $(NH_4)_2SO_4$ dissociates already in tube 4 at about 400 K according to $(NH_4)_2SO_4 \rightleftarrows NH_3 + NH_4HSO_4$.[14] This phenomenon could possibly be a help in the speciation of $(NH_4)_xH_y(SO_4)_{1/2(x+y)}$ and will be further investigated.

The precision of the measurements of ammonium sulphates was tested by repeated analysis of test aerosols containing *ca.* 25 $\mu g \cdot m^{-3}$ of $NH_4HSO_4$ and $(NH_4)_2SO_3$, respectively. Concentrations of 25.8 ± 1.5 $\mu g \cdot m^{-3}$ of $NH_4HSO_4$ with a $NH_4^+/SO_4^{2-}$ ratio of 1.1 and 24.9 ± 1.6 $\mu g$ $(NH_4)_2SO_4$ $m^{-3}$ with a $NH_4^+/SO_4^{2-}$ ratio of 2.2 were found. Again blank problems are responsible for the high $NH_4^+/SO_4^{2-}$ ratios. The detection limit for $NH_4HSO_4$ and $(NH_4)_2SO_4$ in tube 6 at a sample flow of 1 $l \cdot min^{-1}$ and a sampling time of 4 h is 0.4 $\mu g \cdot m^{-3}$.

## INTERFERENCES

A quite detailed report about possible interferences of the described method is given by Nießner and Klockow.[5] The possible influence of $SO_2$ was re-examined. In addition the effects of NO, $NO_2$ and $HNO_2$ (prepared from $NaNO_2$ and $H_2SO_4$) were investigated. Air containing up to 1000 $\mu g$ $SO_2$, 100 $\mu g$ NO, 400 $\mu g$ $NO_2$ and 200 $\mu g$ $HNO_2$ per $m^3$ was sampled several times, the sample period being varied between 5 min and 6 h. A very slight deposition of $SO_2$ was found in tube 4 (393 K). Obviously the NaOH coating of tube 3 effectively removes the $SO_2$. NO, $NO_2$ and $HNO_2$ did not interfere at all.

## INITIAL FIELD MEASUREMENTS

Some initial field measurements have been performed at E.C.N. The prototype sampler we used was not optimal because of an inaccurate temperature control of tubes 4 and 6 and because of an improper design of the sample inlet. Therefore impaction of aerosol particles at the entrance of the first tube may occur and generate erroneous information.

Though the results of these field measurements can be interpreted only with certain reservations, they indicate that $HNO_3$, $NH_3$, $H_2SO_4$, $NH_4NO_3$ and ammonium sulphates can be detected separately by using the sampling system described. The maximum concentrations measured were 5.0 $\mu g$ $HNO_3$, 2.3 $\mu g$ $NH_3$, 3.8 $\mu g$ $H_2SO_4$, 8.0 $\mu g$ $NH_4NO_3$ and 19.8 $\mu g$ $SO_4^{2-}$ (from $(NH_4)_xH_y(SO_4)_{1/2(x+y)}$) per $m^3$.

The dissociation of $(NH_4)_2SO_4$ into $NH_3$ and $NH_4HSO_4$ is not observed very clearly in these field measurements. Insufficient temperature control of tube 4 could be the reason. Besides, ternary sulphate mixtures which react in a different thermochemical way may have been present.

## CONCLUSIONS

Laboratory experiments and some initial field measurements indicate that the described method is a better approach to the characterization of the $HNO_3/H_2SO_4/NH_3$ system in air than are filter techniques.

Additional laboratory experiments and refinements in the field measurements are necessary to improve the method. Especially the determination of $NH_4NO_3$ and of $(NH_4)_xH_y(SO_4)_{1/2(x+y)}$ species is still a problem.

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