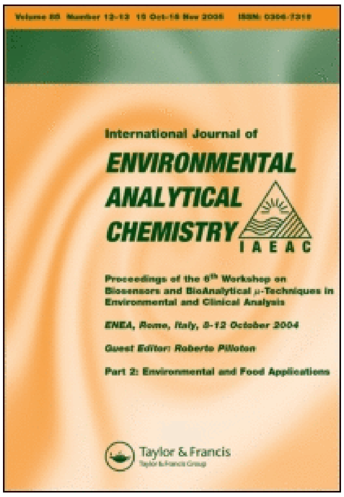

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A Thermoanalytical Approach to Speciation of Atmospheric Strong Acids

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A thermoanalytic device for the selective determination of atmospheric sulfuric acid, called a thermo-denuder, is described. The acid droplets are thermally decomposed in a heated glass tube and the small fragments formed are collected at the walls of the tube by diffusion-controlled deposition. High sampling efficiency is achieved when the inner wall of the glass tube is coated with sodium chloride as a trapping agent. Sulfate and bisulfate salt particles pass through the tube unaffected and can be collected on a back-up filter.

After the sampling the tube is rinsed with water and the dissolved coating analyzed for sulfate using isotope dilution analysis. Applying a nitrate-specific method to the analysis of the extract, the sum of nitric acid and ammonium nitrate can also be determined by the thermo-denuder technique.

Using labelled sodium chloride ($Na^{36}Cl$) as a wall coating, a direct signal for total air-borne strong acidity can be obtained. This is possible because a stoichiometric amount of $H^{36}Cl$ is evolved in the reaction between $Na^{36}Cl$ and a strong acid and can easily be collected and measured.

KEY WORDS: Aerosol sampling, sulfuric acid, nitric acid, thermoanalysis, diffusion separation.

INTRODUCTION

It is well known that the filter material used in the sampling of atmospheric aerosol may have a significant influence on the analytical result obtained.[1–16] In addition sampling artifacts due to gas-to-particle or particle-to-particle interaction have to be considered.[1,6,14–26] With respect to this serious problems arise in the collection of sulfuric acid and acidic sulfates on filters.[6,15,17,19,21–23] In order to avoid such unwanted effects, it is necessary to separate the reactive material (e.g. H_2SO_4) from other constituents of the aerosol under study during the sampling step, either by employing physical principles only[27–32] or by including an additional protecting reaction.[19,27,32,33]

A most promising approach to the determination of sulfuric acid in aerosols containing neutral and acidic sulfates is based on the different thermal behaviour of the sulfate species.[29–32] Thermal pre-treatment of the aerosol under study at suitable temperatures results in an evaporation of sulfuric acid droplets and in a practically complete loss of the acid at the wall of a diffusion separator (denuder). Hydrogen sulfate and other sulfate particles, however, pass through the denuder tube unaffected. The combination of thermal decomposition and diffusion separation with a flame photometric sulfur detector has led to different types of sulfuric acid monitors.[29–32]

We have modified the thermo-denuder conception in such a way that the sulfuric acid vapor, formed during thermal treatment of the aerosol in a heated denuder tube and trapped at the wall of this tube, is quantitatively determined. By this means it is also possible to obtain quantitative results from other acids (e.g. HNO_3).

EXPERIMENTAL

Submicrometer sulfuric acid aerosols ($<0.1\,\mu$m) were produced using a low output condensation type generator.[34] Polydisperse sulfate salt aerosols with a mean geometric diameter below $0.3\,\mu$m were generated with the aid of an atomizer[35] and dried with a diffusion dryer (r.h. $<30\,\%$). Aerosols produced by both the condensation type generator and the atomizer were diluted with dry nitrogen.

The design of the thermo-denuder can be taken from Fig. 1. A borosilicate glass denuder tube (length 90 cm, i.d. 0.6 cm) was attached to the aerosol generator by a ground glass joint. The other end of the tube was connected to a filter holder (37 mm diameter) with PTFE inlet. A resistor heating tape wound around a glass tube of 2.0 cm outer diameter was used to heat a section of 30 cm in length of the denuder tube to temperatures between 300 and 520 K. Different temperatures could be properly adjusted by using a variable transformer and a Ni/Ni-Cr thermocouple as a sensor.

For aerosol sampling behind the denuder tube polycarbonate filters of 37 mm diameter (Nuclepore®, 0.2 and $0.4\,\mu$m, respectively) were employed. Critical orifices, rated at 40 l/h and 21 l/h, respectively, were used in combination with a membrane vacuum pump to keep constant the sampling flow rate in the denuder tube.

The material deposited at the wall of the denuder and collected on the

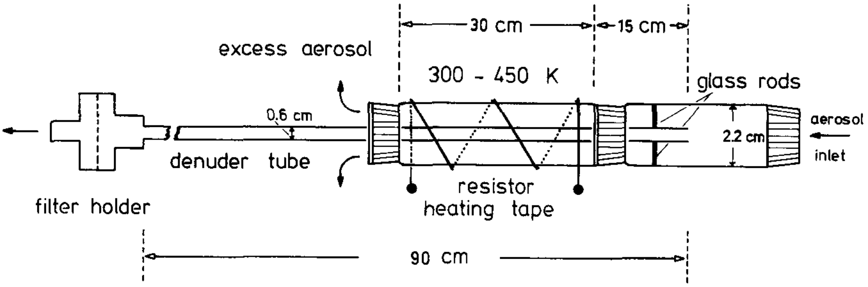

FIGURE 1 Thermo-denuder with filter holder.

back-up filter was analyzed by wet-chemical methods. Sulfate ions were determined by Isotope Dilution Analysis (IDA)[36,37] and protons by a Radio Thermo Diffusion technique (RTD).[15,38,39]

RESULTS AND DISCUSSION

1. Deposition of sulfuric acid and other sulfates in an empty denuder tube

The thermal decomposition of sulfuric acid and sulfate aerosols and the deposition of the corresponding fragments at the wall of the heated denuder tube was investigated at different temperatures. As a figure of merit the collection efficiency

$$E=\frac{m_{\text{tube}}}{m_{\text{filter}}+m_{\text{tube}}}\cdot 100[\%]$$

where

$m_{\text{tube}}=\mu g\ SO_4^{2-}$ and ng H^+, respectively, found at the wall of the tube, and

$m_{\text{filter}}=\mu g\ SO_4^{2-}$ and ng H^+, respectively, found on the back-up filter

of the denuder tube was used.

In Figs. 2a and b the collection efficiency E is plotted as a function of the temperature applied. As can be seen, there is a distinct difference in thermal behaviour of sulfuric acid on the one side and ammonium and sodium sulfates on the other side. Sulfuric acid is retained by the thermo-denuder to more than 90% already at 410 K, whereas $(NH_4)_2SO_4$ and $(NH_4)HSO_4$ start to decompose and to be trapped at the wall of the tube to a larger extent not below 470 K. These findings are very important for the applicability of the thermo-denuder to practical aerosol analysis and qualitatively compare with results obtained by other authors.[29]

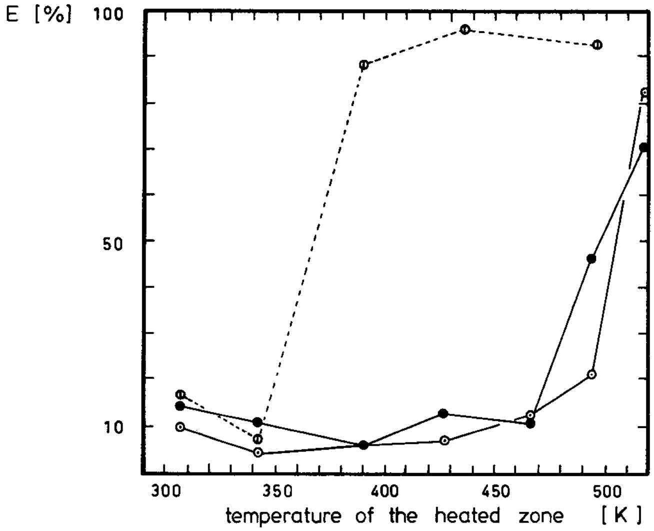

FIGURE 2a Deposition of H_2SO_4 (--⦶--), $(NH_4)HSO_4$ (—⊙—) and $(NH_4)_2SO_4$ (—●—) in an empty denuder tube as a function of the temperature applied. Flow rate 21 l/h. (Definition of E see text).

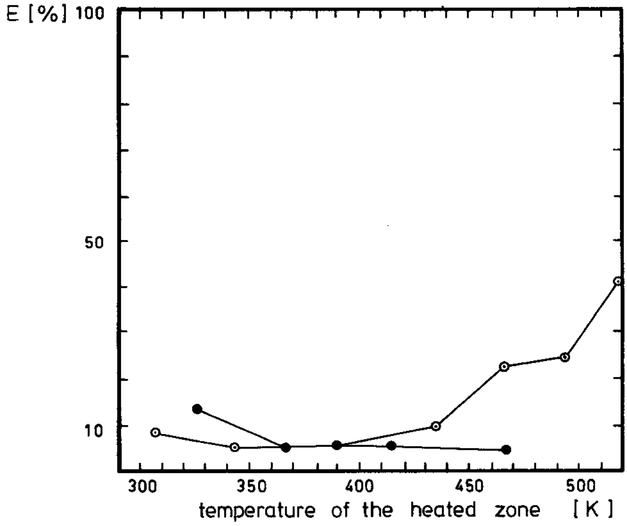

FIGURE 2b Deposition of $NaHSO_4$ (—⊙—) and Na_2SO_4 (—●—) in an empty denuder tube as a function of the temperature applied. Flow rate 21 l/h. (Definition of E see text).

In order to investigate the distribution of the sulfuric acid along the wall of the heated denuder tube, the latter was cut into pieces of 10 cm in length after sampling of sulfuric acid aerosol and each piece analyzed for the amount of acid adsorbed by using RTD. The results obtained at a temperature of 413 K and flow rates of 21 l/h and 40 l/h, respectively, are shown in Figs. 3a and b. It can be seen that the acid droplets rapidly

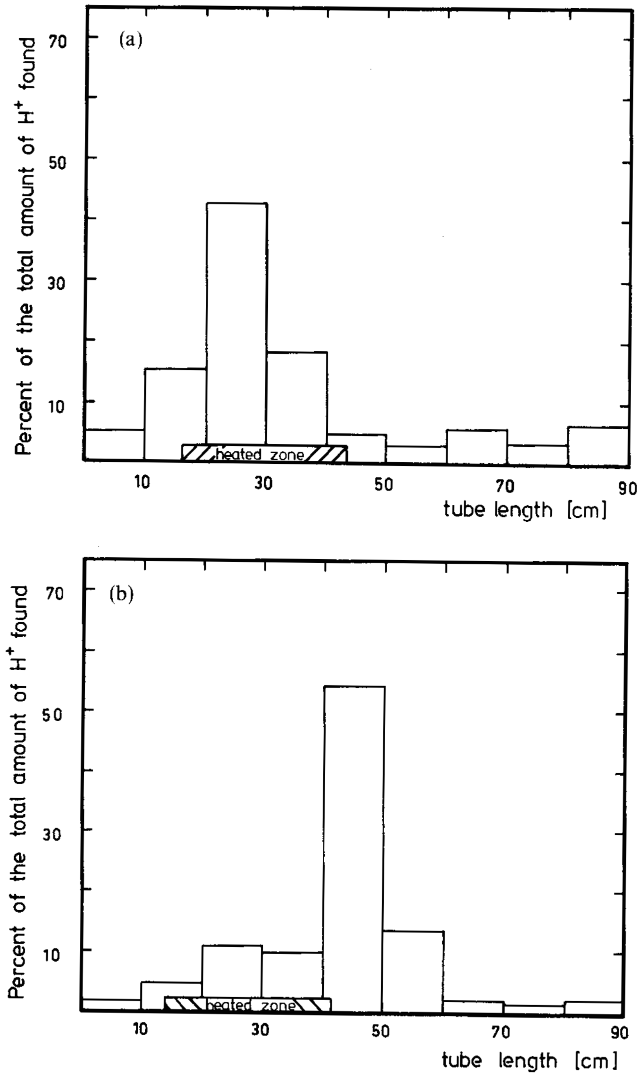

FIGURE 3 Distribution of H_2SO_4 along the wall of the denuder tube at a temperature of 413 K of the heated zone and at a flow rate of (a) 21 l/h and (b) 40 l/h.

evaporate and that the predominant portion of the vapor formed is deposited at the wall of the tube by diffusion either within the heated zone (Fig. 3a) or just behind it (Fig. 3b).

The results of the measurements described clearly indicate that the thermo-denuder can be operated at temperatures at which sulfuric acid is almost completely trapped, whereas sulfate salts retain their particulate form and do not diffuse to the wall within the time of residence in the denuder tube. With the experimental parameters given above (tube length 90 cm, i.d. 0.6 cm, flow rate 40 l/h, mean flow velocity 39 cm/sec, Reynolds number 156) and using diffusion coefficients as listed in ref. 40 it could be calculated,[26,41,42] that significant losses by diffusion will not occur at particle diameters above 0.01 μm.

2. Experiments using denuder tubes with coated walls

a) *Radioreagent technique.* In order to establish an irreversible sink for the sulfuric acid vapor and to convert the acid into a detectable product, the inner wall of the denuder tube was coated with labelled $Na^{36}Cl$. In this case a topochemical reaction takes place at the wall yielding radioactive hydrochloric acid:

$$H_2SO_4 + Na^{36}Cl \rightarrow NaHSO_4 + H^{36}Cl\uparrow$$

The $H^{36}Cl$ formed can easily be absorbed on an impregnated back-up filter and be determined by activity measurement. This procedure corresponds to a very large extent to the RTD technique[15,38,39] mentioned above.

Coated denuder tubes were prepared as follows: A mixture of 100 μl of a $Na^{36}Cl$ solution (190 μg Cl^-; spec. activity ca. 50 Bq/μg Cl^-) and 500 μl of isopropanole was pipetted into the tube and spread over the wall by slightly rotating it, so that mainly the section effective for sulfuric acid deposition (see Fig. 3b) was wetted. After having evaporated the solvent by passing a weak flow of clean dry nitrogen through the tube, the wall along the deposition zone was covered by a uniform thin layer of $Na^{36}Cl$.

The temperature of the thermo-denuder (with a coated tube) was adjusted to 413 K and the aerosol sampling flow rate to 40 l/h. A dual filter-pack system containing two cellulose filters (Schleicher & Schüll 589^2L, 37 mm diameter), each impregnated with 50 μl of 0.1 M NaOH, was used to absorb the $H^{36}Cl$ evolved. The activity of the filters was measured with a liquid scintillation counter. An increasing humidity of the aerosol under study will cause an increasing portion of the $H^{36}Cl$ formed to remain absorbed at the wall of the non-heated section of the denuder tube (downstream of the heated section). As a consequence this part of the tube was also heated for about 15 min after each sampling period in order to achieve a quantitative transfer of the $H^{36}Cl$ to the impregnated filters.

Using the condensation type generator as a sulfuric acid aerosol source, a linear relationship between sampling time and the amount of $H^{36}Cl$ absorbed on the back-up filters was obtained (see Fig. 4). In order to transform "sampling time" into "μg H_2SO_4" a separate calibration of the aerosol generator is necessary.[34] Under the experimental conditions employed the working range of the radio thermo-denuder was from 0.5 to 10 μg H_2SO_4. A denuder tube coated in the described manner could be used up to three times without significant change in $H^{36}Cl$ output.

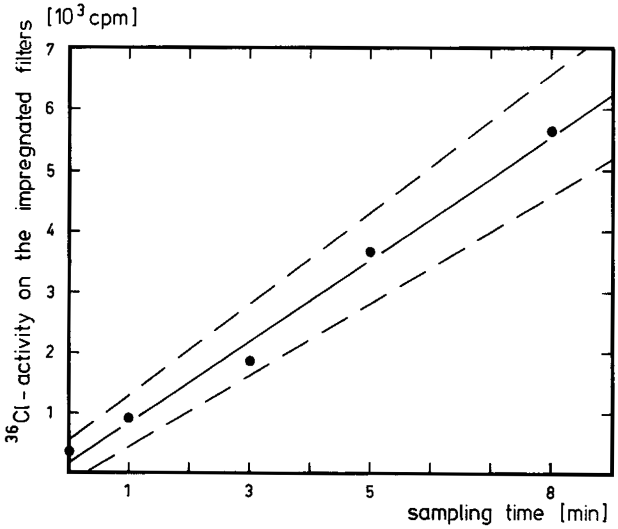

FIGURE 4 Performance of the radio thermo-denuder. Chlorine-36 activity collected on the impregnated back-up filters as a function of the sampling time. Temperature of the heated zone 413 K, flow rate 40 l/h. Regression line and its 95% confidence limits (dotted lines) obtained from 15 values.

Because the conversion of $Na^{36}Cl$ into $H^{36}Cl$ is an acid-base reaction, all acidic compounds reaching the wall of the coated denuder tube must be regarded as potential interferents. Therefore the following substances were investigated with respect to their behaviour in the radio thermo-denuder: $FeSO_4$, $Fe(NO_3)_3$, $Al_2(SO_4)_3$, $AlCl_3$, $Na_3H(SO_4)_2$, $NaHSO_4$, $NaH_3(SO_4)_2$, $Na(NH_4)HPO_4$, $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$, $(NH_4)HSO_4$, $(NH_4)H_3(SO_4)_2$, NH_4NO_3 and HNO_3. With properly diluted solutions of these compounds aerosols were generated by using the Collison atomizer[35] and passed through the $Na^{36}Cl$ coated denuder tube (413 K). The $H^{36}Cl$ formed was measured as described above.

The following results were obtained: Negligible or tolerable effects were observed for $FeSO_4$, $Al_2(SO_4)_3$, $Na_3H(SO_4)_2$, $NaHSO_4$, $NaH_3(SO_4)_2$, $Na(NH_4)HPO_4$, $(NH_4)_2SO_4$, $(NH_4)_3H(SO_4)_2$ and $(NH_4)HSO_4$ (compare Figures 2a and b). $(NH_4)H_3(SO_4)_2$ released an amount of $H^{36}Cl$ which corresponded to about 53% of the activity expected for a quantitative decomposition of the mixed salt into $(NH_4)HSO_4$ and H_2SO_4. The signals produced by $Fe(NO_3)_3$ and $AlCl_3$ were remarkably high. Because $FeSO_4$ and $Al_2(SO_4)_3$ had no influence, the observed effects were created most probably by hydrolytic decomposition of the salt particles in the humid aerosol, yielding HNO_3 and HCl, respectively. Both HNO_3 and NH_4NO_3 quantitatively reacted with the wall coating. This completely corresponds to the findings of other authors that sodium chloride is an effective absorbent for HNO_3[43,44] and that NH_4NO_3 easily disintegrates into NH_3 and HNO_3 at elevated temperatures.[45,46]

b) *Selective analysis of the wall coating.* With the radioreagent technique just described a summation signal for several strongly acidic compounds will be obtained. In order to determine only sulfuric acid a different way had to be tried, that is to say the specific determination of the sulfate deposited at the wall of the coated denuder tube.

At first the collection of labelled $H_2^{35}SO_4$ aerosol in denuder tubes coated with NaCl was investigated. The tubes were prepared as described above, using 500 μl of an isopropanolic NaCl solution (2 g NaCl in a mixture of 10 ml of deionized-distilled water and 10 ml of isopropanole). The radioactive test aerosol (up to 67 μg $H_2^{35}SO_4$) was produced with a condensation type generator as described in ref. 47, moved through the thermo-denuder and then collected on an impregnated back-up filter (see above). After each sampling the denuder tube and the filter were extracted with 2 ml and 1 ml, respectively, of deionized-distilled water. The extracts were measured for ^{35}S activity and the results used to calculate the collection efficiency E (see above). In Fig. 5 E is plotted as a function of the temperature of the thermo-denuder. It can be seen that the deposition curve obtained was nearly the same as the one shown in Fig. 2a, and that 99% of the sulfuric acid was collected in the denuder tube at about 410 K.

In the experiments just described, sampling times of only a few minutes were employed. In practical air pollution studies, however, sampling times of several hours or even days are frequently required. For that reason the long term stability of sulfuric acid trapped by the NaCl coating was investigated. An amount of 17.1 μg of labelled $H_2^{35}SO_4$ was collected in a coated denuder tube at 413 K. A stream of clean dry nitrogen (40 l/h) was then pulled through the heated tube and the impregnated back-up filter for 24 h. At different times in between the filter was changed, extracted and the extract measured for ^{35}S activity. The result was that only 2.7%

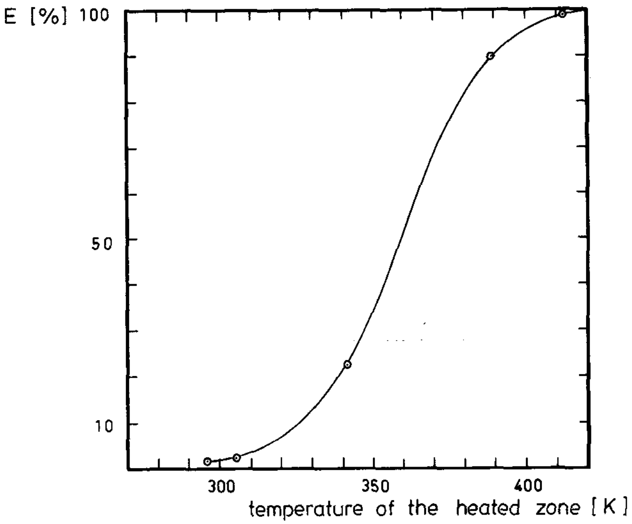

FIGURE 5 Deposition of labelled $H_2^{35}SO_4$ in a coated denuder tube as a function of the temperature applied. Flow rate 40 l/h. (Definition of *E* see text).

of the activity was lost from the thermo-denuder within the whole period of 24 h.

The behaviour of several sulfate salt aerosols in the NaCl coated denuder tube was investigated in the following manner: The same amount of a test aerosol (Collison atomizer, see above) was moved through a heated (413 K) as well as through a non-heated denuder tube and collected on Nuclepore® filters placed behind each tube. For each aerosol the experiment was repeated several times. The filters were then extracted with 1 ml of deionized-distilled water and the extracts analysed for sulfate by employing IDA.[36,37] The results listed in Table I clearly indicate that there is no significant difference in the amount of sulfate found behind a heated and a non-heated tube, except for $(NH_4)H_3(SO_4)_2$ and $NaH_3(SO_4)_2$. Consequently these mixed compounds[48] seem to be the only potential interferents in the proposed technique for the selective determination of sulfuric acid, which consists in a thermo-denuder sampling of the aerosol under study and in a subsequent analysis of the wall coating for sulfate (see below). A possible influence of SO_2, due to conversion to sulfate at the NaCl coating, was investigated at a SO_2 concentration of 68 ppb[49] and at 40% r.h. No measurable effect could be observed.

The results of the experimental studies just described have led to the following procedure for the selective determination of sulfuric acid in

TABLE I

Behaviour of different test aerosols in a heated and a non-heated denuder tube coated with NaCl. Flow rate 40 l/h. Each result is the mean of four measurements.

Test aerosol	Amount of sulfate [μg S] found on the back-up filter Heated denuder tube (413 K)	 Non-heated denuder tube
Na_2SO_4	3.88±0.49	3.91±0.09
$Na_3H(SO_4)_2$	3.42±0.14	3.22±0.14
$NaHSO_4$	3.35±0.25	3.43±0.04
$NaH_3(SO_4)_2$	1.90±0.09	3.02±0.05
$(NH_4)_2SO_4$	2.43±0.16	2.42±0.34
$(NH_4)_3H(SO_4)_2$	3.49±0.34	3.49±0.30
$(NH_4)HSO_4$	2.53±0.16	2.42±0.34
$(NH_4)H_3(SO_4)_2$	0.83±0.09	1.54±0.02

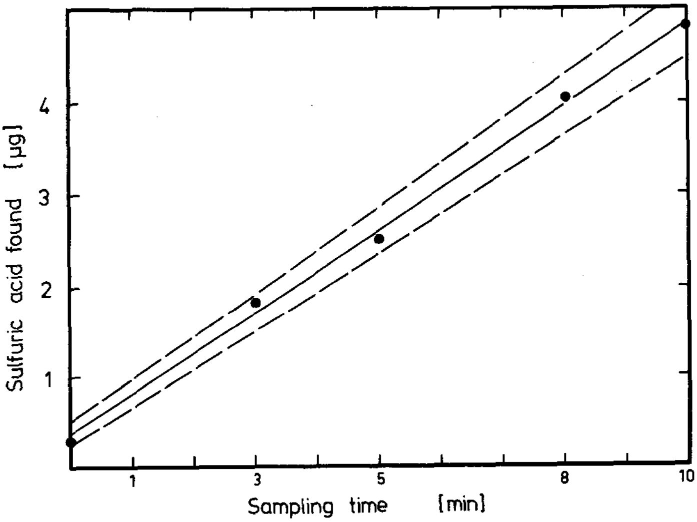

FIGURE 6 Thermo-denuder in combination with isotope dilution analysis for sulfate. Temperature of the heated zone 413 K, flow rate 40 l/h. Regression line and its 95% confidence limits (dotted lines) obtained from 20 values.

sulfate containing aerosols: A definite volume of a test aerosol or of ambient air is passed with about 401/h through the heated thermo-denuder (ca. 410 K) employing a NaCl coated denuder tube (see above). After having finished the aerosol collection the denuder is removed from the sampling train and 2 ml of deionized-distilled water are pipetted into the tube. The tube is closed at both ends, using a non-wettable plastic foil (e.g. Parafilm®), and shaken for a few seconds in order to dissolve the NaCl coating together with the sulfuric acid absorbed. Aliquots of the extract are then analysed for sulfate by using IDA,[36,37] taking into account the NaCl matrix in preparing the IDA calibration curve.

Employing the condensation type generator[34] as a sulfuric acid aerosol source and following the procedure just given, the relationship shown in Fig. 6 between sampling time and sulfate found in the NaCl coating could be established. From Fig. 6 a reproducibility of ±12% (rel. S.D.) can be derived for 2 μg of H_2SO_4. The detection limit of the method in its present form was calculated to be 0.7 μg of H_2SO_4. A further improvement, however, should be possible.

In a few experiments it was tried to analyze the NaCl coating for nitrate[50] after having passed a HNO_3 and NH_4NO_3 containing aerosol through the thermo-denuder. From the preliminary results it could be seen that it is possible to determine HNO_3 and NH_4NO_3 besides H_2SO_4 when nitrate and sulfate specific methods, respectively, are applied to the analysis of the NaCl absorbent. For this purpose ion chromatography[51,52] should be a powerful tool. At present a sequential analyzer based on the thermo-denuder principle and being able to detect nitric acid and sulfuric acid in ambient air besides the corresponding ammonium salts is tested.[53]

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