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A relative humidity processing method for the sampling of aerosol particles with low growth-ability

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ABSTRACT

A method for the fractionation of aerosol particles with respect to size and ability to grow with an increased relative humidity has been developed. The system consists of cascade impactors, diffusion driers, a humidifier and a temperature stabiliser. Diffusion driers were designed and the vapour penetration was modelled below 20%. A humidifier which can be operated with an output relative humidity above 95% was developed. Flow-rates up to 5 l/min can be used and the relative humidity can be controlled within approximately 1%. The ability of the system to fractionate aerosol particles with respect to growth with relative humidity was investigated. The equivalent aerodynamic diameter growth factor for sodium chloride was determined to 2 at a relative humidity of 98%, in good agreement with theory. The growth is used to collect particles with no, or limited growth with increased relative humidity in separate fractions for chemical characterisation. This is obtained with an impactor stage operated at high relative humidity followed by a diffusion drier and an impactor stage with a factor of 1.4 lower cut-off diameter operated at low relative humidity, where the particles with low growth-ability are collected. The system was in operation during the EUROTRAC sub-project Ground-based Cloud Experiment (GCE) at Po Valley, supplying important information on the particle size related scavenging and the elemental composition of particles with a low growth-ability.

1. Introduction

The ever present aerosol particles in the atmosphere play an important role for the formation of fog and cloud droplets, acting as condensation nuclei. As the particles grow their chemical composition are changed by the dilution. The process affects the relation of the particles to gaseous compounds, leading to a dissolution of compounds such as HCl, HNO_3 and NH_3, which significantly can alter the acidity of the droplets. The dissolution and oxidation of SO_2 is controlled by the pH, which means that the process is dependent on the balance of the three above mentioned compounds (Hough, 1987). An initial diffusional growth of cloud droplets causes the smallest droplets, nucleated at the smallest particles activated, to be the most diluted (Jensen and Charlson, 1984). A droplet size-dependent solute concentration was experimentally observed by Ogren et al. (1989). When evaluating a model aerosol consisting of fine mode ammonium bisulphate and coarse mode sea-salt, Thowy et al. (1989) found that the major dissolution of SO_2 takes place in the sea-salt and in the smallest ammonium bisulphate droplets.

When clouds appear in the atmosphere, always interstitial aerosol particles, i.e., particles that have not grown to form cloud droplets, are found to co-exist with the droplets. The cause of their lack of ability to grow may be related to size as well as to chemical composition. The fractionation leads to that other chemical processes, such as metal catalysed reactions may be the most important for the sulphur oxidation in the interstitial aerosol. The fractionation is also important in view of deposition and hence life-time in the atmosphere. From these points of view, it is important to understand the processes governing the partition

of aerosol particles between acting as cloud condensation nuclei and appearing as interstitial aerosol particles.

This work is aimed at finding a method to fractionate particles with respect to hygroscopic properties and to collect them in different fractions for chemical analysis. The method is based on the use of cascade impactors and a combination of diffusion driers and a humidifier to obtain a particle size distribution for the total incoming aerosol and sized fractions of "hydrophobic" particles. It is possible to use the system for different kinds of aerosols. In the EUROTRAC project Ground-based Cloud Experiment (GCE) at Po Valley (Italy) the system was used to study the interstitial aerosol. Example of the results obtained are given. A more comprehensive evaluation and interpretation of the results are presented by Martinsson et al. (1992).

The method of creating an artificial high relative humidity for the characterisation of atmospheric aerosols has been used before. Hänel (1976) and Winkler (1988) presents average data of the growth of different kinds of atmospheric aerosols as a function of relative humidity for size-fractionated samples. The method was gravimetrical weighing of the sample where the relative humidity was varied. The measurements were undertaken after the samples were collected. Ahlberg et al. (1978) used two cascade impactors in parallel, one at high relative humidity and one at low. The samples collected were analysed for elemental composition and the growth was observed as shifts of the size distribution for the different elements. Covert and Heintzenberg (1984) used a cascade impactor at low humidity in parallel with a single stage impactor at high humidity to study the issue of external/internal mixture in different kinds of air-masses. The ammonium to sulphate ratio for the H_2SO_4–$(NH_4)_2SO_4$ system was studied by Larson et al. (1982) with an in situ technique which works after a humidification, heating and cooling scheme, and McMurry and Stolzenburg (1989) and Svenningsson et al. (1992) used a tandem differential mobility analyser technique to determine growth factors for individual aerosol particles. The technique described here allow the use of higher relative humidities during sampling than the other methods, thereby allowing the collection of samples for chemical analysis which are fractionated with respect to growth-ability.

2. System description

The system for the fractionation of aerosol particles with respect to size and "hygroscopic" growth is presented in Fig. 1a. After taking the aerosol sample with a suitable inlet, the aerosol is passed through a high-flow-rate diffusion drier, where the relative humidity is reduced to below 15%. The reduction of the relative humidity

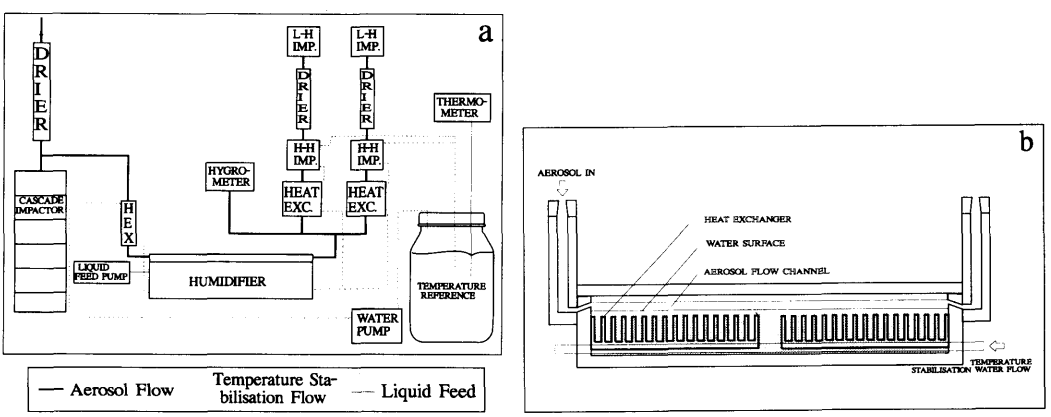


Fig. 1. (a) Block diagram of the relative humidity processing system for fractionation of particles with respect to ability to grow with increased relative humidity. "H-H IMP." denotes impactor operated at high relative humidity, "L-H IMP." impactor operated at low relative humidity and "HEAT EXC." heat exchanger. (b) Principle sketch of the humidifier.

defines the conditions downstream in the system. It cannot be ruled out that the drying process induces losses of certain water soluble compounds, although the situation is not comparable with the conditions during sampling by filtration where the sampling time is long. The residence time in the first drier is typically 15 s. An experiment by Martinsson and Hansson (1988) where a droplet aerosol, consisting of an aqueous solution with a mixture of equal amounts by mass of NH_4NO_3 and $(NH_4)_2SO_4$, was dried in a similar way as in the present system showed losses of below 5% for NH_4NO_3 at room temperature. The behaviour is dependent on the mixture (Bassett and Seinfeld, 1983). Other, probably less significant constituents of the atmospheric aerosol, such as NH_4Cl, may be affected by the drying process (Pio and Harrison, 1987).

After the initial drying of the aerosol, the flow is divided into two lines. One line contains a cascade impactor, where the incoming aerosol is sized and collected. The other line is used to collect "hydrophobic" particles in sized fractions by passing the aerosol through a humidifier (Fig. 1b), divide the flow in different lines, one for each size fraction, where the aerosol is size-fractionated at high relative humidity. After the high-humidity impactors, the aerosol is dried (residence time typically 5 s) and a sample of "hydrophobic" particles is taken in each line with an impactor cut-off diameter slightly lower than that of the high-humidity impactor. In order to obtain strong separation between particles with respect to their growth at high humidities, it is necessary to operate the system at as high relative humidity as possible. That, in turn, induces temperature stability problems. The present system is operated at a relative humidity of 97%. At temperatures of 0–30°C a temperature difference in the system of approximately 0.5°C, where the humidifier is at the higher temperature, will cause supersaturation and condensation problems. In order to avoid the problem, water is circulated by a water pump through heat exchangers in the system from a 25 l container which is used as the temperature reference. The system is passive, i.e., no relative humidity regulation is used. The relative humidity is observed using a dew point hygrometer at the

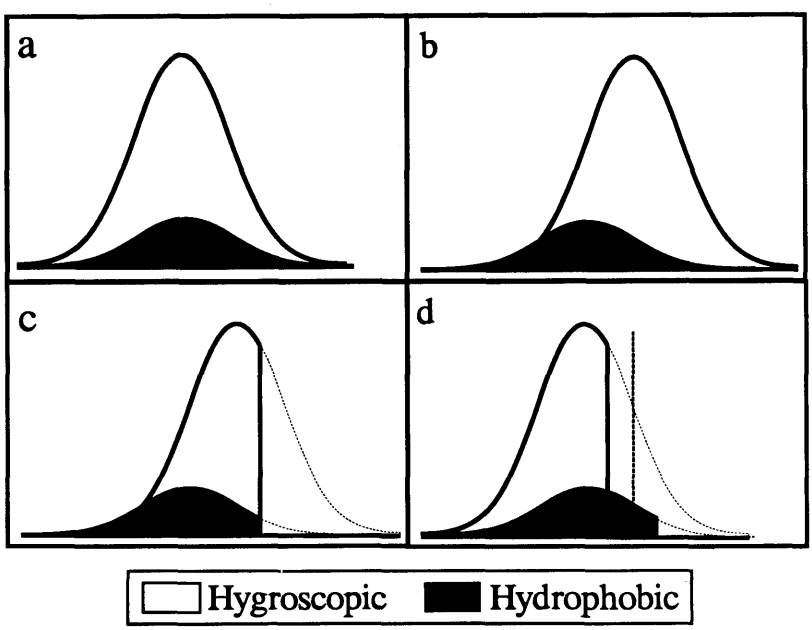


Fig. 2. The principle used to obtain a fraction consisting of "hydrophobic" particles. The matter is illustrated with a hypothetical aerosol composed of 2 different kinds of particles. The hydrophobic fraction collected is found in (d) at particle sizes above the broken, vertical line.

humidifier exit and a thermometer in the temperature reference tank. A liquid feed pump compensates for the water lost to the vapour phase in the humidifier. The water flow for temperature stabilisation passes a heat exchanger in the humidifier, but is not directly connected to the water used to humidify the aerosol.

The principle of operation of the system is demonstrated in Fig. 2 with a hypothetical aerosol consisting of two kinds of particles: those who grow with an increased humidity and those who do not. The aerosol at the humidifier entrance is dry and the size distributions of the two components are shown in Fig. 2a. The aerosol passes the humidifier and the "hygroscopic" fraction grows, while the "hydrophobic" remains unchanged, see Fig. 2b. The impactor at high relative humidity separates particles over a certain size from the aerosol (Fig. 2c), and the diffusion drier causes evaporation of the water content of the hygroscopic particles. These particles are reduced in size, while the hydrophobic particles are not affected by the drier, thus leaving a size fraction which consists of hydrophobic particles, see Fig. 2d. The broken line indicates the cut-off of the last impactor in the line, which is the impactor operated at low relative humidity where the hydrophobic fraction is collected. The choice of cut-off is strongly related to the relative humidity in the high-humidity impactor. In this system a factor of 1.4 between the high-humidity impactor cut-off diameter and the dry impactor is used, i.e., a 0.5 μm cut-off diameter in the high-humidity impactor is followed by a 0.35 μm cut-off in the low-humidity impactor. This matter will be discussed further in Subsection 4.3.

3. Materials and experimental methods

3.1. Materials

In order to obtain a high relative humidity in the system, a humidifier was designed. It is based on a passive technique, which means that there is no active regulation to control the humidity. This mainly because of the difficulty of finding a sensor which is fast enough when operated at relative humidities above 95%. The humidifier, see Fig. 1b, consists of a 26 cm long and 9 cm wide container. Deionized water fills the container to a certain level. The aerosol is entered close to the top of one of the short sides and flows in a slit with a height which is determined by the water surface and the container top. A heat exchanger is placed in the water. The heat exchanger is connected to tubes where water from the temperature stabilisation system flows, in order to keep the water evaporation rate controlled. The humidifier contained water, which is kept separated from the temperature stabilisation flow, completely covers the heat exchanger, leaving an open water surface facing the aerosol. The water content of the humidifier is reduced during operation due to the evaporation. This is compensated for by an infusion pump (Harvard), which supplies water continuously.

Diffusion driers (1 high-capacity and several low-capacity) were constructed and evaluated with respect to water vapour penetration as a function aerosol flow-rate and mass adsorbed. A low-capacity drier consists of a 40 cm long circular flow channel surrounded by a stainless steel net with a diameter of 12 mm. Aluminium oxide is used as the drying agent and it is placed between the stainless steel net and the 32 mm inner diameter stainless steel housing. The high-capacity drier consists of 30 stainless steel net tubes with a diameter of 12 mm and a length of 60 cm for the passage of aerosol. The net tubes are contained in a 130 mm diameter stainless steel tube, placed in a hexagonal pattern with a center distance of 20 mm, leaving the center of the tube without a net tube. The net tubes are mounted in 2 stainless steel plates, one at each side, and stretched out by 6 rods running between the plates, thus forming a cassette which is placed in the container. As for the low-capacity driers, the drying agent is aluminium oxide, which fill up the space between the net tubes.

3.2. Experimental methods

The humidifier capacity was investigated by entering dry, particle-free air. The exit dew-point was measured using a hygrometer (General Eastern mod. Hygro-M1) with a two-stage optical dew-point sensor (General Eastern mod. 1211H). Water was flowed through the heat exchanger of the humidifier, and the temperature was measured (Tegam mod. 872) in the temperature reference tank, see Fig. 1a. The initial water surface to top distance, i.e., the slit height for aerosol passage, was measured with a sliding calliper. The water

level was varied by adding or taking out a certain water volume with graded syringes, together with keeping a record over aerosol flow-rate, dew-point and time of operation in order to compensate for the amount of evaporated water. Particle losses in the humidifier was investigated by measuring the aerosol concentration before and after the humidifier. For particles larger than 1 μm, an Aerodynamic Particle Sizer (APS; TSI mod. 3310) was used for a polydisperse aerosol. For particles smaller than 1 μm, a polydisperse aerosol was generated and passed through a Differential Mobility Analyser (DMA; TSI mod. 3071). The particles were neutralised and counted with a Condensation Particle Counter (CPC; TSI mod. 3760). The stability during operation of the humidifier was investigated in a 24 hour run in basically the same manner as the capacity, but with an infusion pump to supply water to compensate for evaporation losses.

The capacity of the low-flow diffusion driers were investigated by passing dry, particle-free air through the humidifier and enter the air, with a relative humidity of 97%, to one or more driers. The temperature during the different experiments was between 20 and 25°C. The penetration was determined by comparing the dew-point before and after the drier. Six driers were used in the investigation, and they contained between 188–190 g of aluminium oxide. The high-flow diffusion drier was investigated with respect to capacity in a similar way, but high humidity at the inlet was obtained by running a triple Constant Output Atomiser (TSI mod. 3075) with Milli-Q water. The drying agent was regenerated by vacuum pumping using a two-stage rotary vane pump with a nominal pumping speed of 35 m^3/h and an ultimate vacuum of 10^{-4} hPa (Alcatel, model 2033) for the laboratory experiments.

The ability of the system to fractionate aerosol particles with respect to hygroscopic growth was investigated by comparing the performance for sodium chloride (NaCl) and dioctyl phtalate (DOP). A polydisperse aerosol was generated with a constant output atomiser and mixed with clean particle-free air. The aerosol was taken through the humidifier and through an impactor stage operated at high humidity. The aerosol was dried with a diffusion drier and entered to a differential mobility particle sizer (TSI; DMPS/C 3932). The cut-off characteristics when using the two substances was determined by comparing the penetration as a function of particle size with and without the impaction plate inserted in the impactor. The relative humidity was determined in the same way as described above.

During the field experiments, the system was placed in a container at room temperature. The aerosol inlet was placed outside the container approximately 6 m above the ground. The outdoor temperature varied between 0 and 15°C during the campaign. The system was operated as described above, except for the regeneration of the diffusion driers, where a Rietschle model VGB 20 pump with a nominal pumping speed of 20 m^3/h and an ultimate vacuum of 2 hPa was used.

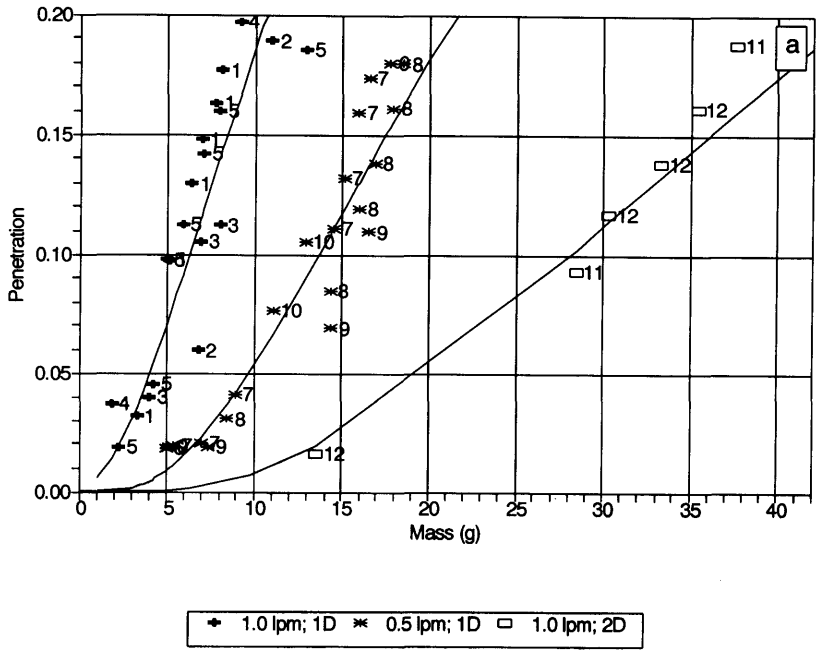
4. Results and discussion

4.1. Diffusion driers

The performance of the low-capacity diffusion driers was investigated at 2 different flow-rates, 1.0 and 0.5 l/min, with a single drier and at a flow-rate of 1.0 l/min with 2 driers in series. The results are presented in Fig. 3a as the water vapour penetration as a function of water mass adsorbed by the drying agent. The mass adsorbed was calculated from flow-rate and dew-point data at the entrance and the exit of the drier for each series and compared with weighing before and after each run. In most cases the results agreed within 5%, the largest deviation being 11%. It is difficult to reach the point where the drying agent is absolutely free from water. Hence the amount of water adsorbed can only be given at a relative basis. The lowest weight of the drying agent obtained after regeneration was taken as the zero point. When a regeneration resulted in a higher value, that mass difference was added to the mass adsorbed as presented in Fig. 3a. A water vapour penetration of 10% for the three conditions investigated is reached for adsorbed water masses of 6, 14 and 28 g, respectively. At a temperature of 20°C that corresponds to running times of approximately 7, 28 and 28 h.

The high flow-rate diffusion drier capacity was investigated at a flow-rate of 9 l/min. At a penetration of 10%, the adsorbed water mass was 280 g. This corresponds to a running time of 31 h at a temperature of 20°C.

The main interest with this study of diffusion



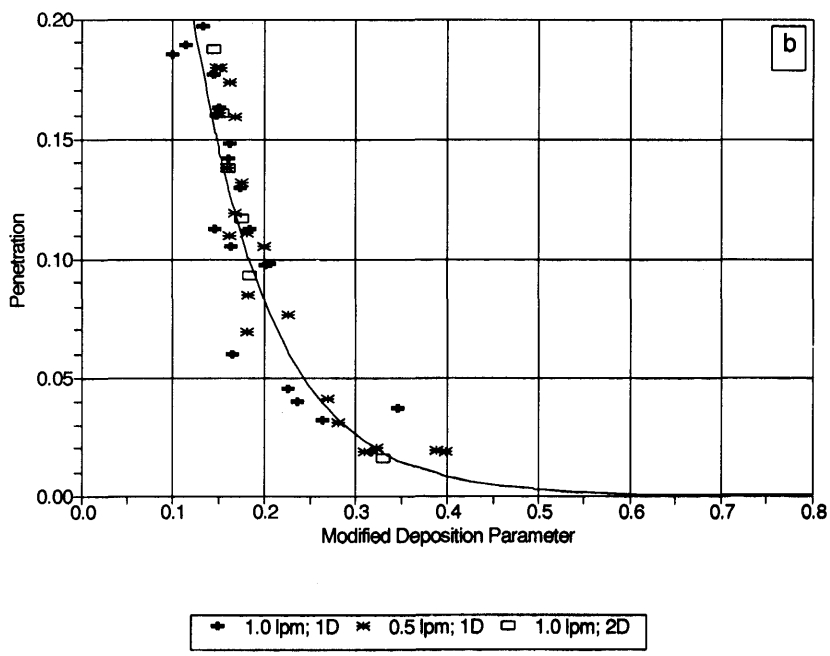


Fig. 3. The penetration of water vapour through the low-capacity diffusion driers for different flow-rates and number of driers placed in series. "1D" denotes 1 drier and "2D" denotes 2 driers in series. (a) As a function mass of water adsorbed. (b) As a function of the modified deposition parameter according to equation (3).

drying is to be able to produce a relative humidity that is lower than approximately 20 % at the outlet of the drying unit. In this section an approximate model for reaching that goal is presented. The drying of an aerosol as described above is basically a diffusion process. The deposition of particles by diffusion in a circular tube may be described by:

$$P = 0.819e^{-11.5\mu} + 0.0975e^{-70.1\mu} + 0.0325e^{-179\mu}, \qquad \mu > 0.007, \tag{1}$$

where the deposition parameter is defind by

$$\mu = \frac{DL}{Q}, \tag{2}$$

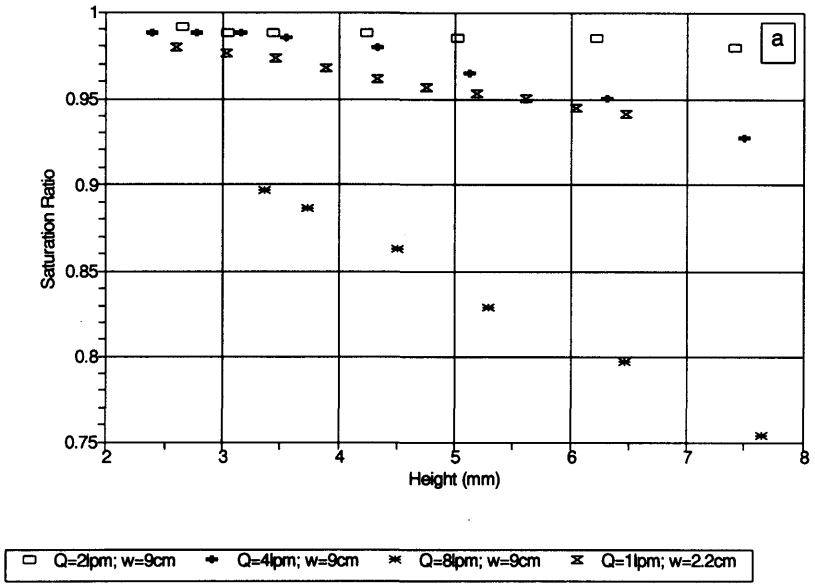
where D is the diffusion coefficient, L the length of the tube and Q the aerosol flow-rate. Expression (1) is valid under the assumption that the sticking efficiency is equal to 1 when particles hit the wall, which is true for diffusing particles. The situation is more complicated for water vapour diffusing to a drying agent, and the basic problem is that of the sticking efficiency which decreases with the amount of water deposited. When a humid aerosol passes through a regenerated diffusion drier, 50 % of the vapour will be deposited after 1.5 and 3 cm for flow-rates of 0.5 and 1 l/min according to eq. (1). Thus, the deposition rate is highest close the the entrance and decreases rapidly along the drier provided that the aerosol flow-rate is not very high. To simplify the behaviour of the drier, it is assumed that a drier that has been operated for a while consists of one part that has a sticking probability of zero and one part that has a sticking probability of one, i.e., it is assumed that the length of the drier is reduced as it becomes more loaded with water. To further complicate the situation, the vapour is primarily deposited close to the aerosol flow channel which results in a secondary diffusion from the part of the drying agent that is close to the flow channel to outer parts. In order to include these effects in the description of the diffusion drier performance, the deposition parameter is modified by the following approximation:

$$\mu' = \frac{D}{Q} L \left(1 - \frac{m}{cm_d + m}\right), \tag{3}$$

where m is the water mass adsorbed, m_d the mass of the drying agent and the product $c \cdot m_d$ can be interpreted as the capacity of water vapour adsorption for a freshly regenerated drying unit. The ratio $m/(cm_d + m)$ expresses the reduction of the drier length, while the denominator expresses the capacity of the drier. The increasing capacity with mass absorbed expresses the secondary diffusion which appear in the drying agent in a radial direction. The simple model with a modified deposition parameter in eq. (1) was applied to the experimental data and the value of the constant c was fitted. The operation resulted in values of the constant of 0.014, 0.013 and 0.013 g of water adsorption per g of drying agent for 1.0, 0.5 l/min with 1 drier and 1.0 l/min with 2 driers in series. The results of the fits are presented in Fig. 3a. The mean value, $c = 0.0136$, is used in Fig. 3b where the penetration as a function of the modified deposition parameter is shown. It can be seen that the experimental data fairly well follow the calculated curve. Eq. (3) predicts a linear dependence of the initial capacity on the amount of drying agent. An increased length of the drier and an increased diameter of the flow channel both increases the amount of drying agent facing the aerosol flow linearly. Hence the expression should be stable in that respect. The influence from the thickness of the drying agent layer is more difficult to predict since a much more elaborate expression for the secondary diffusion probably has to be used as the layer becomes significantly thicker. The value of the constant c was obtained with aluminium oxide as the drying agent and must be regarded as material dependent. The assumption that the water vapour deposition can be expressed as a reduced length of the drier can be justified only for low penetrations. This means that the model does not describe the behaviour of a diffusion drier at penetrations outside the range presented here.

4.2. The humidifier

The performance of the humidifier was investigated as a function of the height (h) of the slit between the water surface and the humidifier top for different aerosol flow-rates (Q) and an widths (w) of the slit. The results are presented in Fig. 4a. It can be seen that an increased flow-rate, a decreased slit width and an increased slit height decreases the output relative humidity. For the sake of bringing some order in the data, a scaling was attempted. Similar to the drying process, the humidification of the aerosol is a diffusion process,



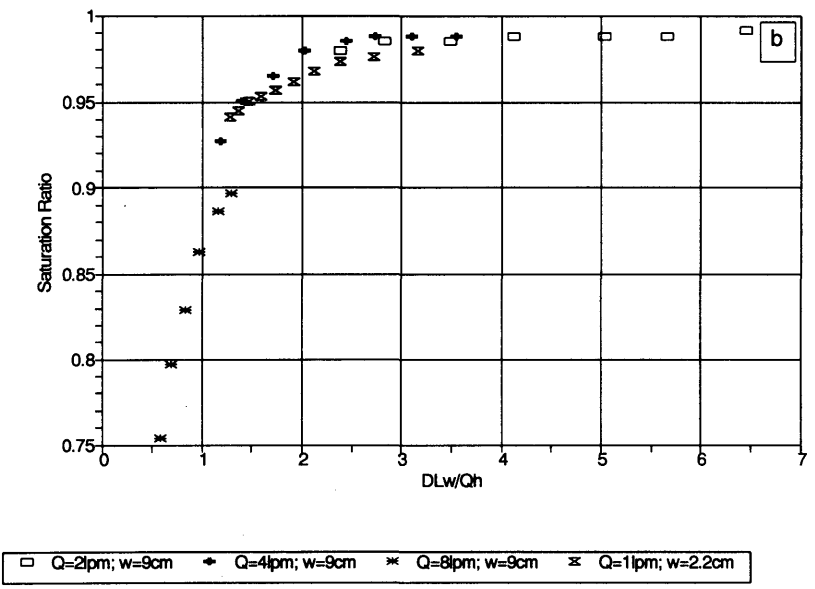


Fig. 4. The output water vapour pressure saturation ratio of the humidifier for different aerosol flow-rates (Q) and widths (w) of the slit for aerosol passage. (a) As a function of the height of the slit for the aerosol flow. (b) As a function of the scaling parameter (see the text) where D = the diffusion coefficient of water, L = the length of the humidifier and h = the slit height.

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but with the difference that the vapour diffuses into the aerosol and only from one direction. Nevertheless, a scaling by the diffusion deposition parameter for particles flowing in a slit was applied, i.e.,

$$S = \frac{DLw}{Qh}, \tag{4}$$

where S is the scaling parameter. The result of the operation is shown in Fig. 4b. It can be seen that the scaling results in a fairly high degree of organisation of the data around a single curve, which can be used to estimate the parameters for the construction of a passive humidifier. It should, however, be pointed out that the present experimental data only deals with three of the five parameters, height, width and flow-rate, while the humidifier length (L) and diffusion coefficient (i.e., evaporating substance) were not varied in the experiment.

The humidifier was investigated with respect to particle losses at a flow-rate of 4 l/min. At this flow-rate and a relative humidity output of 97%, i.e., with a slit height over the water surface of slightly below 5 mm, the mean air velocity is 15 cm/s which means that the residence time is 1.7 s. The investigation was made with a substance (DOP) that does not grow with an increased humidity, because the particles collected after the humidifier are of that nature. It was found that the penetration was between 94% and 98% in the particle size range 0.025 to 0.1 μm, 95% at 1 μm, 93% at 2 μm and 70% at 5 μm. The drop of the penetration for large particles can be attributed to sedimentation. For simplicity a "plug" flow is assumed, although a laminar profile eventually develops in the humidifier (Reynolds number is approximately 100). The fraction lost due to sedimentation is expressed by:

$$G = \frac{LwV_{TS}}{Q}, \tag{5}$$

where V_{TS} is the terminal settling velocity of the particle in the gravitational field. For the presented experiment the fraction lost according to eq. (5) would be 5% and 30% for 2 and 5 μm particles, respectively. The sedimentation of large particles is an inherent problem of this kind of humidifier, which has to be operated horizontally. When designing such a humidifier, the desired output relative humidity corresponds to a certain value of the scaling parameter S according to Fig. 4b. The ratio of the sedimentation loss factor to the scaling parameter is given by:

$$\frac{G}{S} = \frac{2V_{TS}}{D}h. \tag{6}$$

It can be seen that the slit height is the only parameter that can be used to minimise the losses due to gravitational settling for a certain relative humidity output.

The predictability of the output relative humidity of the humidifier was investigated in a 24-h continuous run with a flow-rate of 4 l/min. The results are presented in Fig. 5. The calculated values are based on the experimental data on the humidifier capacity (presented in Fig. 4), initial measurement of the slit height, the liquid feed rate from the infusion pump and the evaporation rate as obtained frow dew-point data and aerosol flow-rate. It can be seen that measured and calculated data agree well. The change of slope after about 10 h was caused by a change of the liquid feed rate. The importance of compensating for the water evaporated is demonstrated by the dotted line, which was calculated under the assumption that no water was fed to the humidifier. The temperature was between 21 and 22°C during the experiment.

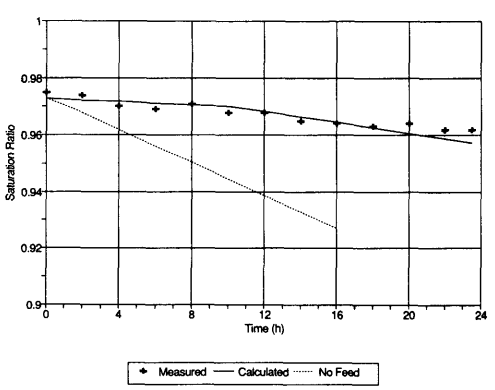

Fig. 5. The output water vapour pressure saturation ratio of the humidifier during a 24-h run. The symbol shows the values measured, the solid line shows the values calculated from the experimental parameters, while the dotted line shows the saturation ratio which would be obtained if the evaporated water was not replaced.

4.3. System performance

The system performance with respect to hygroscopic growth was investigated by passing aerosol particles of two different compositions, DOP and NaCl, through the humidifier, a high-humidity impactor and a diffusion drier to find the cut-off characteristics under these conditions for the two compounds. It can be expected that the particle size remains unchanged when DOP aerosol passes the drying unit, while the size of the NaCl particles is expected to be significantly reduced due to evaporation of the water content of the particles. The results are presented in Fig. 6. It can be seen that 50% penetration, i.e., the cut-off diameter, as determined with a DMA, occurs at 0.44 μm for DOP particles. The cut-off diameter for NaCl is significantly lower. With a relative humidity of 96 and 98% the cut-off diameters are 0.15 and 0.14 μm.

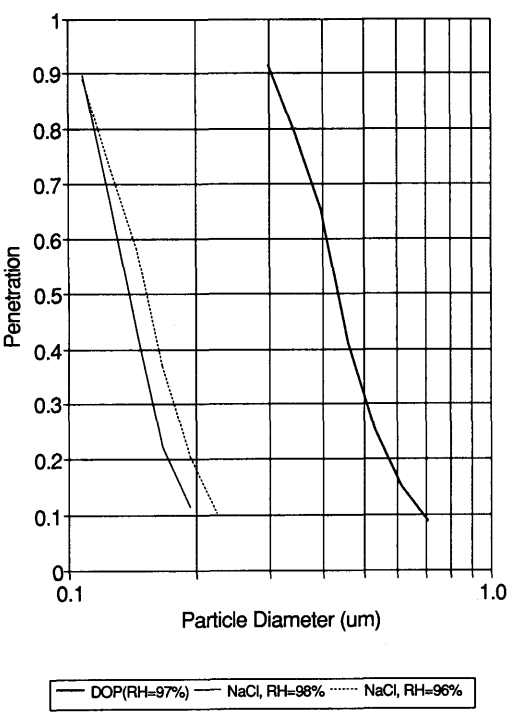

Fig. 6. The penetration of aerosol particles as a function of particle size as determined with a DMA. DOP and NaCl aerosol was passed through an impactor operated at high relative humidity (the values are given under the figure). The particle size was determined after a diffusion drier, i.e., the dry particle diameter was determined.

In order to evaluate the data it is necessary to use three different diameters: the diameter determined with the DMA (D_m), the volume equivalent diameter (D_e) and the equivalent aerodynamic diameter (D_a). The volume equivalent diameter can be determined by utilising the definition of the dynamic shape factor (χ)

$$D_e = \frac{C_c(D_e)}{C_c(D_m)} \times \frac{D_m}{\chi}, \tag{7}$$

where C_c is the Cunningham slip correction factor. The equivalent aerodynamic diameter is determined by

$$\rho_0 C_c(D_a)\, D_a^2 = \rho_p C_c(D_e) \frac{D_e^2}{\chi}, \tag{8}$$

where ρ_p is the particle density and $\rho_0 = 1$ g/cm^3. The DOP aerosol particles do not grow with an increased humidity, they are spherical and their density is close ρ_0 (0.983 g/cm^3). Thus the aerodynamic cut-off diameter of the impactor is 0.44 μm. The growth of particles with humidity is governed by the Kelvin effect and the water activity (a_w) by the expression

$$s = a_w e^{-4\sigma\rho_w/R_w T D_e}, \tag{9}$$

where s is the water vapour pressure saturation ratio, σ the surface tension, ρ_w the density of water, R_w the specific gas constant for water and T the absolute temperature. The water activity may be determined from the expression

$$a_w = e^{-\eta_s m_s/m_w}, \tag{10}$$

where η_s is the exponential mass increase coefficient, m_s mass of the solute and m_w mass of water.

Hänel (1976) presents an expression for the calculation of the exponential mass increase coefficient for NaCl which is valid for $m_s/m_w < 0.35$:

$$\eta_s = 0.616 - 5.40\left(\frac{m_s}{m_w}\right)^{0.5} + 5.88\left(\frac{m_s}{m_w}\right)^{0.539}. \tag{11}$$

The volume equivalent cut-off diameters for NaCl, with a dynamic shape factor of 1.08, at the 2 relative humidities are 0.15 and 0.13 μm. According to eqs. (9–11) they should grow a factor of 3.1 and 3.8 in terms of volume equivalent

diameter. At these dilution states the density of the humidified particles are 1.051 and 1.026 (Wolf et al., 1980), which means that the volume equivalent diameter of the dissolved NaCl particles at the impactor is 0.43 μm for both 96 and 98% relative humidity. The experimentally determined growth factors thus are 2.9 and 3.3 which is in fairly good agreement with the theoretical values. The resolution of the system, however, is determined by the aerodynamic diameters. The aerodynamic diameter ratios of NaCl at 96 and 98% relative humidity compared with substances that do not grow are 1.8 and 2.0 ($\rho_{NaCl} = 2.165$ g/cm^3). These figures should be compared with the cut-off difference of 1.4 between the high-humidity and the dry impactors of the system. It is instructive to compare NaCl with another substance that is important in the atmosphere, ammonium sulphate ($(NH_4)_2\,SO_4$). Using the expression (Hänel, 1976)

$$\eta_s = 0.409 - 7.10\left(\frac{m_s}{m_w}\right)^{0.5} + 7.50\left(\frac{m_s}{m_w}\right)^{0.540} - 0.590\,\frac{m_s}{m_w} \qquad (12)$$

to determine the linear mass increase coefficient for $(NH_4)_2\,SO_4$ (valid for $m_s/m_w < 0.40$), the volume equivalent diameter growth factors are 2.2 and 2.8 at relative humidities of 96 and 98%. The density of the substance is 1.769 g/cm^3, and the dynamic shape factor is estimated to be in the range of 1.1–1.2, wherefore $\chi = 1.15$ was used. Converting the diameters, the equivalent aerodynamic growth factors obtained are 1.8 and 2.1.

4.4. *Field measurements*

The presented system was operated in fog studies in the GCE campaign at Po Valley (Italy). The system was used to investigate the cloud interstitial aerosol, using an aerosol inlet which is penetrated by particles with an aerodynamic diameter of less than 5 μm. The aerosol particles were collected on paraffin-coated, thin polystyrene foils. The samples were analysed for elemental composition using Particle Induced X-ray Emission (Johansson and Campbell, 1988). The elemental composition of the hydrophobic fractions relative to the total interstitial aerosol

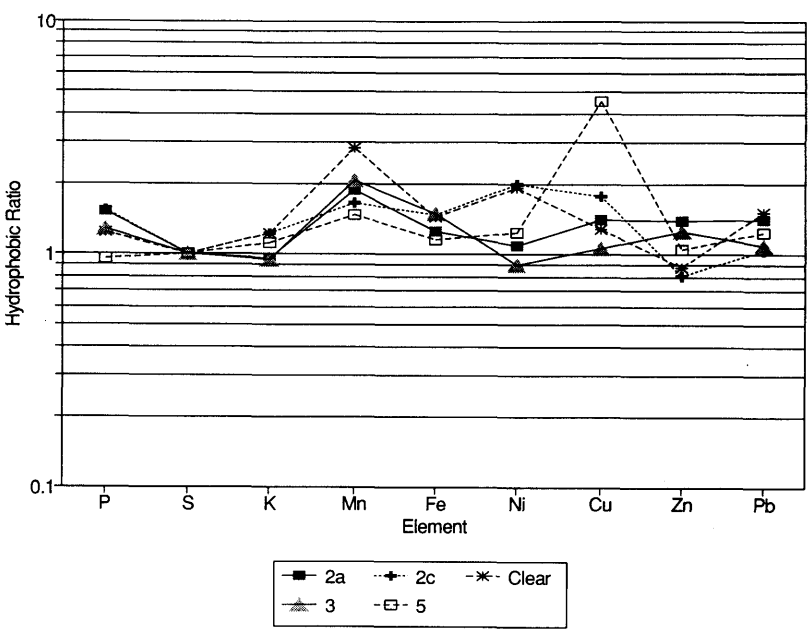

Fig. 7. The hydrophobic ratios (according to expression 13) for different elements. The measurement campaign covered five fog events. The figures of the legend refer to these events in chronological order. One sample was taken during clear weather conditions, and is denoted "Clear".

composition in similar sizes, as obtained from the cascade impactor, was evaluated by the expression ("the hydrophobic ratio"):

$$R_i = \frac{\left(\frac{m(E_i)}{m(S)}\right)_H}{\left(\frac{m(E_i)}{m(S)}\right)_T} , \qquad (13)$$

where m is the amount of the element as obtained in the analysis, E_i the element, S the sulphur and subscripts H and T are hydrophobic fraction and total interstitial aerosol in a similar size fraction. Sulphur was chosen to be the indicator element for particles with a high growth-ability. Thus, a value of R_i larger than 1 means that the element is contained in hydrophobic particles to a higher degree than sulphur. The hydrophobic ratio, where low growth-ability-particles with an aerodynamic diameter of between 0.35 and 0.5 μm are compared with the total interstitial aerosol in the size interval 0.25–0.5 μm, is presented in Fig. 7. It can be seen that no element systematically has a hydrophobic ratio of less than 1, i.e., no element is a stronger indicator of particles with a high growth-ability than sulphur. It can also be seen that manganese (Mn) and, to somewhat lesser extent, iron (Fe) systematically have a hydrophobic ratio larger than 1. This means that sulphur is associated with particles with a high growth-ability, while Mn and also Fe are enriched in particles with a low growth-ability. Sulphur is a major component of the aerosol. It is normally associated with water soluble sulphates in the atmosphere. The elements frequently appearing in low growth-ability particles, Mn and Fe, are present in a factor of 10–20 lower concentration than S. Thus they probably cannot affect the hygroscopic properties of the particles, but rather be the tracers of other particle constituents. However, these findings can be used to infer the importance of the particle hygroscopic properties for the scavenging due to the cloud nucleation process. A more detailed evaluation of the whole data set can be found in Martinsson et al. (1992).

5. Conclusions

A method for aerosol processing at a relative humidity above 95% has been developed. The temperature of the critical parts of the system is stabilised by flowing water from a reference temperature container in heat exchangers.

Diffusion driers have been designed and evaluated. A simple model for the penetration as a function of aerosol flow-rate, geometrical dimensions and mass adsorbed was developed. It was found that water vapour penetrations below 20% can be predicted from the model.

An aerosol humidifier based on a passive technique was constructed, and it was found that it was possible to produce the desired relative humidity of above 95% for aerosol flow-rates up to approximately 5 l/min. The predictability of the relative humidity output was found to be of the order of 1%.

The ability of the whole system to fractionate particles in respect of growth with increasing relative humidity was investigated by comparing the behaviour of DOP and NaCl aerosols in the system. The growth factor obtained for NaCl agreed well with theory. The aerodynamic diameter growth factor for NaCl was found to be approximately 2, and calculations show a similar figure for $(NH_4)_2 SO_4$. The growth is used to separate hygroscopic particles from the aerosol stream in a size-interval determined by the growth factor. Using an impactor resolution of a factor of 1.4, it can be concluded that the system can be used to collect particles that show no, or only a limited growth with an increased relative humidity in separate fractions for chemical analysis.

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