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A MODEL FOR PREDICTING PERFORMANCE OF AN ANNULAR DENUDER SYSTEM

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Abstract—A mathematical model for simultaneous gas diffusion, aerosol diffusion and evaporation is presented to predict performance of the annular denuder system. Approximating the aerosol size distribution by a lognormal function and using the statistical method of moment, the evolution of the three aerosol moments and the mass balance equations for the two associated gases in the annular denuder system are obtained. The governing equations were cast into dimensionless form and the performance of the model was validated by the existing data available in the literature. The effects of governing dimensionless groups on the model performance were evaluated in the sensitivity analysis. The model was then applied for sampling nitric acid gas using a typical range of atmospheric aerosol and gas properties to derive the performance equation of the annular denuder system. The methodologies presented herein are helpful in providing design and operational criteria of the annular denuder system for a real sampling of atmospheric reactive gases that minimizes measurement artifacts.

NOTATION

- A_1 dimensionless parameter, $U_a r_0^2 / D_1 L$
 A_2 dimensionless parameter, $n_s / C_{11} N_{av}$
 A_3 dimensionless parameter, D_2 / D_1
 B_1 particle diffusivity constant, $k_B T / (162\pi^2)^{1/3} \mu$
 B_2 slip correction constant for diffusion, $3.314\lambda(\pi/6)^{1/3}$
 B_3 evaporation constant (free molecule), $(36\pi)^{1/3} v_1 n_s (k_B T / 2\pi m_1)^{1/2}$
 B_4 evaporation constant (continuum), $(48\pi^2)^{1/3} / 3 \lambda v_1 n_s (8k_B T / \pi m_1)^{1/2}$
 B_5 constant ($= r_0^2 / D_1 \tau$)
 B_6 constant ($= k_B T / 6\pi \mu r_1 D_1$)
 B_7 constant ($= 1.657 \text{ Kn}$)
 C_j concentration of gas j
 D_j diffusivity of gas j
 D_p diffusivity of particle
 E_1 constant $\{ = B_6 v_g^{*-1/3} \exp(1/2 \ln^2 \sigma_g) [1 + B_7 v_g^{*-1/3} \exp(3/2 \ln^2 \sigma_g)] \}$
 E_2 constant $\{ = B_6 v_g^{*2/3} \exp(2 \ln^2 \sigma_g) [1 + B_7 v_g^{*-1/3} \exp(-3/2 \ln^2 \sigma_g)] \}$
 E_3 constant $\{ = B_6 v_g^{*5/3} \exp(25/2 \ln^2 \sigma_g) [1 + B_7 v_g^{*-1/3} \exp(-9/2 \ln^2 \sigma_g)] \}$
 $f(k, r)$ flow parameter term
 G evaporation rate
 Kn Knudsen number for monomer, λ / r_1
 k ratio of inner to outer radius of the denuder
 k_B Boltzmann constant
 K_p equilibrium constant
 L denuder length
 M_q q th aerosol moment with respect to particle volume
 m_1 monomer mass
 m_f mass fraction of evaporating species contained in the aerosol particles
 n_s monomer concentration at saturation
 N_{av} Avogadro's number
 p_1 vapour pressure of monomer
 p_d vapour pressure of monomer in equilibrium with the surface
 Q sampling flow rate
 r radial distance
 r_0 denuder outer radius
 r_1 monomer radius
 S_1 monomer surface area

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S	saturation ratio
T	ambient temperature in K
U_{av}	average gas velocity
v	particle volume
v_1	monomer volume
v_g	geometric mean particle volume
v_M	molar volume of evaporating species
V_{dj}	deposition rate of gas j
z	axial distance

Greek letters

α	accommodation coefficient
γ, β	coefficients for performance equation of the annular denuder system
Δ	dimensionless parameter for calculating the sampling efficiency of the annular denuder system, $\pi D_1 L(1+k)/4Q(1-k)$
ε	evaporation coefficient for second moment, $1/\varepsilon = 1/\varepsilon_{FM} + 1/\varepsilon_C$, $\varepsilon_{FM} = B_3 v_g^{2/3} \exp(8 \ln^2 \sigma_g)$, $\varepsilon_C = B_4 v_g^{1/3} \exp(7/2 \ln^2 \sigma_g)$
ε^*	dimensionless evaporation coefficient for second moment, $1/\varepsilon^* = 1/\varepsilon_{FM}^* + 1/\varepsilon_C^*$, $\varepsilon_{FM}^* = B_3 v_g^{2/3} \exp(8 \ln^2 \sigma_g)$, $\varepsilon_C^* = 4/3 Kn B_4 v_g^{1/3} \exp(7/2 \ln^2 \sigma_g)$
η	evaporation coefficient for first moment, $1/\eta = 1/\eta_{FM} + 1/\eta_C$, $\eta_{FM} = B_3 v_g^{2/3} \exp(2 \ln^2 \sigma_g)$, $\eta_C = B_4 v_g^{1/3} \exp(1/2 \ln^2 \sigma_g)$
η^*	dimensionless evaporation coefficient for first moment, $1/\eta^* = 1/\eta_{FM}^* + 1/\eta_C^*$, $\eta_{FM}^* = B_3 v_g^{2/3} \exp(2 \ln^2 \sigma_g)$, $\eta_C^* = 4/3 Kn B_4 v_g^{1/3} \exp(1/2 \ln^2 \sigma_g)$
λ	mean free path of gas molecules
μ	viscosity
σ_g	geometric standard deviation
τ	characteristic time for particle growth, $1/n_s s_1 (k_B T / 2\pi m_1)^{1/2}$

Subscripts

i	inlet condition
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Superscripts

*	dimensionless quantity
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INTRODUCTION

In recent years, annular denuders have become the most widely employed instruments for sampling and collecting reactive gases such as SO_2 , NH_3 , HNO_3 and organic vapors in the atmosphere (Koutrakis *et al.*, 1988; Coutant *et al.*, 1989; Benner *et al.*, 1991; Lee *et al.*, 1993). They have advantages of allowing higher sampling velocities as well as having larger sampling capacities as compared to hollow tube denuders and parallel plate denuders.

Possanzini *et al.* (1983) proposed design equations for gas collection in annular denuders by fitting experimental data to a modified form of the Gormley–Kennedy equation (Gormley and Kennedy, 1949). Koutrakis *et al.* (1988) used this equation to evaluate performance of the Harvard-EPA annular denuder system for sampling pollutant gases and associated aerosols. The differences between measured and calculated collection efficiencies were small in their studies. Winiwarter (1989) derived a mathematical expression for describing the sampling efficiency in an annular denuder and indicated a general agreement of calculated and measured sampling efficiencies.

However, as the pollutant gases are adsorbed at the denuder walls, the state of equilibrium between gas and particle phases is disturbed, which results in evaporation of aerosols and release of additional pollutant gases. Therefore it is possible that excessive amounts of pollutant gases are being sampled. This phenomenon may particularly be true for volatile aerosols such as NH_4NO_3 and NH_4Cl containing aerosols and their associated gases (Durham *et al.*, 1987; Harrison *et al.*, 1990). In addition, the diffusional deposition of particles which contain compounds similar to the sampling gases may also introduce measurement artifacts (Durham *et al.*, 1987). Clearly, these important mechanisms which may significantly influence performance of the annular denuder system cannot be described by the equations of Possanzini *et al.* (1983) and Winiwarter (1989).

The performance of annular denuders for sampling reactive gases in the presence of evaporating particles has been theoretically studied by Pratsinis *et al.* (1989) and Biswas *et al.* (1990). As a result of their studies, significant measurement artifacts from evaporating aerosols may occur during gas sampling in the denuder system. However, in their theoret-

ical studies, the gas stream was assumed to contain monodisperse aerosols. As indicated by Bai *et al.* (1995), particle polydispersity plays an important role in the evaporation of dry NH_4NO_3 and NH_4Cl aerosols in the annular denuder system. An increase in the particle polydispersity leads to a significant reduction in the evaporation rate for particles with a mass median diameter of about $0.5 \mu\text{m}$.

Therefore the goal of this study is to develop a mathematical model that modifies the theory of Pratsinis *et al.* (1989) and Biswas *et al.* (1990) to include the effects of evaporation and diffusion of polydisperse particles. The shape of the particle size distribution is approximated by a lognormal function and the statistic method of moment is employed to obtain the evolution of the three aerosol moments and the mass balance equations for the two associated gases. The performance of the model is validated by comparing its predictions with the analytical and experimental data available in the literature. The effects of governing dimensionless groups on the model performance are evaluated and the derivations of performance equations using a typical range of the atmospheric aerosol and gas properties are demonstrated. The optimal operating conditions of the annular denuder system for sampling reactive gases and aerosols can be achieved from the performance equations.

THEORY

When particles in equilibrium with two associated gases 1 and 2, $C_{1(g)} + C_{2(g)} \rightleftharpoons C_{3(s)}$, enter an annular denuder system, gas 1 is removed by diffusional absorption at the denuder wall with which equilibrium is distorted. At the same time the aerosol stream may undergo simultaneous diffusion and evaporation processes. The physical concept of this phenomenon that occurs in the annular denuder system is shown schematically in Fig. 1.

Basic assumptions

The following major assumptions are made in developing a mathematical model to predict the performance of an annular denuder system:

- (1) The system is in a steady-state operating condition.
- (2) The flow field in the system is a fully developed laminar flow.
- (3) No production or reaction of the gas or aerosol occurs in the system.
- (4) The sticking efficiency of aerosols is 100% on the collector wall surface.
- (5) A gas-particle equilibrium is assumed at the interfaces of solid particles and their surrounding gases, which is independent of the denuder residence time.

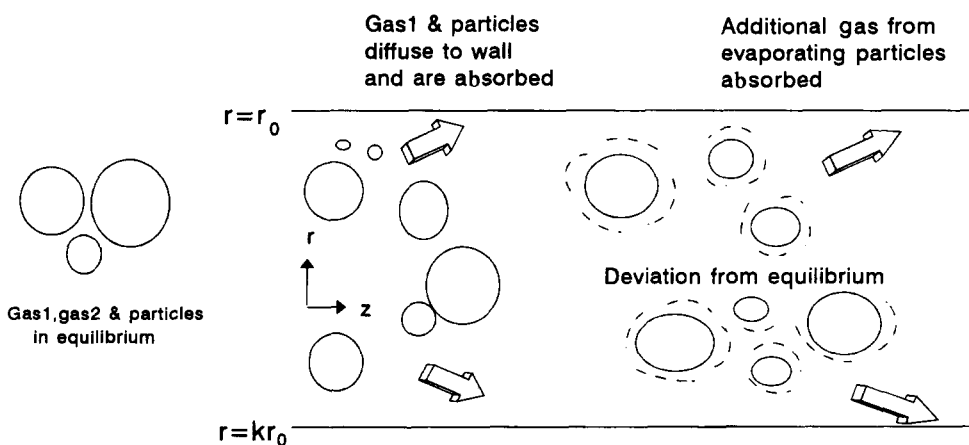


Fig. 1. A schematic diagram of the annular denuder system showing simultaneous gas diffusion, aerosol diffusion and evaporation.

(6) The size distribution is approximated by a lognormal function. This is because an impactor with a cutoff diameter of around $2.5 \mu\text{m}$ is usually installed before aerosols entering the annular denuder system. It removes the coarse mode of the usually appearing atmospheric log-bimodal aerosol size distribution.

(7) The effect of diffusion in the direction of flow is neglected as compared to convection. This is a valid assumption since the Peclet number of the annular denuder system is much greater than unity in all tests.

(8) The lognormal size distribution should be preserved throughout the annular denuder system since the residence time is very short.

(9) Only dry aerosols are considered in this study, that is, the relative humidity of the annular denuder system is below the deliquescent humidity.

(10) A mole of gas 1 and a mole of gas 2 are formed when a mole of particle is evaporated.

Model development

For aerosols undergoing simultaneous diffusion and evaporation processes in an annular denuder, the steady-state general dynamic equation is expressed as (Friedlander, 1977)

$$U_{\text{av}} f(k, r) \frac{\partial n}{\partial z} = \frac{1}{r} \frac{\partial}{\partial r} \left[r \frac{\partial (D_p n)}{\partial r} \right] + \frac{\partial (Gn)}{\partial v}, \quad (1)$$

where U_{av} is the average gas velocity through the denuder, $f(k, r)$ is the flow parameter, k is the ratio of inner to outer radius of the denuder, r is the radial distance, n is the aerosol size distribution function, z is the axial distance, D_p is the particle diffusivity, G is the evaporation rate, and v is the volume of a particle. The left-hand-side (LHS) term accounts for convection of particles. The first and second terms on the right-hand-side (RHS) account for particle losses by Brownian diffusion and evaporation, respectively. The fully developed flow parameter in the annular denuder is written as (Bird *et al.*, 1960)

$$f(k, r) = \frac{2[(1 - k^2) \ln(r/r_0) + \ln(1/k)(1 - r^2/r_0^2)]}{(1 + k^2) \ln(1/k) - (1 - k^2)}, \quad (2)$$

where r_0 is the outer radius of the annular denuder.

The evaporation of aerosols leads to the release of two gases, C_1 and C_2 . The mass balance equation of the gaseous species j under consideration is expressed as

$$U_{\text{av}} f(k, r) \frac{\partial C_j}{\partial z} = \frac{D_j}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_j}{\partial r} \right) - \frac{1}{v_M} \int_0^\infty Gn \, dv, \quad (3)$$

where C_j is the concentration of gaseous species j ($j = 1$ or 2), D_j is the diffusivity of gaseous species j , and v_M is the molar volume of the evaporating species. The LHS term accounts for convection of gaseous species j . The first RHS term accounts for the diffusional loss of gaseous species j onto the denuder wall while the second RHS term accounts for the gain of gaseous species j by aerosol evaporation at rate G .

Since the aerosol size distribution is approximated by a lognormal function, combining the method of moments with the lognormal distribution has the advantage of simplicity while evaluating the evolution of polydisperse aerosols (Pratsinis, 1988). The q th moment of an aerosol size distribution is given by (Friedlander, 1977)

$$M_q = \int_0^\infty v^q n(v) \, dv, \quad (4)$$

while the size distribution function, $n(v)$, for lognormally distributed aerosols is defined as

$$n(v) = \frac{N}{3\sqrt{2\pi v \ln \sigma_g}} \exp \left[-\frac{\ln^2(v/v_g)}{18 \ln^2 \sigma_g} \right]. \quad (5)$$

Three parameters that completely describe a lognormal size distribution are the total number concentration, N , the geometric mean particle volume, v_g , and the geometric

standard deviation based on particle radius, σ_g . The values of v_g and σ_g can be expressed in terms of the first three moments as (Lee *et al.*, 1984)

$$v_g = \frac{M_1^2}{M_0^{3/2} M_2^{1/2}}, \quad (6)$$

$$\ln^2 \sigma_g = \frac{1}{9} \ln \left(\frac{M_0 M_2}{M_1^2} \right), \quad (7)$$

where M_0 is the zeroth moment which represents the total particle number concentration ($=N$), M_1 is the first volume moment which denotes the total particle volume, and M_2 is the second volume moment which indicates the amount of light scattered due to the particles. Thus, M_0 , M_1 and M_2 are sufficient to describe the behavior of lognormally preserving particles and the q th moment of the distribution can be written in terms of M_0 , v_g , and σ_g as

$$M_q = M_0 v_g^q \exp(4.5q^2 \ln^2 \sigma_g). \quad (8)$$

Multiplying equation (1) by $v^q dv$ on both sides, integrating over all particle sizes, and using the lognormal function as an approximation of the entire size spectrum, the evolution of the three aerosol moments and the mass balance equations for the two associated gases inside the annular denuder are written as

$$U_{avf}(k, r) \frac{\partial M_0}{\partial z} = \frac{B_1}{r} \frac{\partial}{\partial r} \left[r \frac{\partial}{\partial r} (M_{-1/3} + B_2 M_{-2/3}) \right], \quad (9)$$

$$U_{avf}(k, r) \frac{\partial M_1}{\partial z} = \frac{B_1}{r} \frac{\partial}{\partial r} \left[r \frac{\partial}{\partial r} (M_{2/3} + B_2 M_{1/3}) \right] + \eta(S-1)M_0, \quad (10)$$

$$U_{avf}(k, r) \frac{\partial M_2}{\partial z} = \frac{B_1}{r} \frac{\partial}{\partial r} \left[r \frac{\partial}{\partial r} (M_{5/3} + B_2 M_{4/3}) \right] + 2\varepsilon(S-1)M_1, \quad (11)$$

$$U_{avf}(k, r) \frac{\partial C_1}{\partial z} = \frac{D_1}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_1}{\partial r} \right) - \frac{\eta}{v_M} (S-1)M_0, \quad (12)$$

$$U_{avf}(k, r) \frac{\partial C_2}{\partial z} = \frac{D_2}{r} \frac{\partial}{\partial r} \left(r \frac{\partial C_2}{\partial r} \right) - \frac{\eta}{v_M} (S-1)M_0, \quad (13)$$

where B_1 and B_2 are the particle diffusivity constant and the slip correlation constant for diffusion, η and ε are the evaporation coefficients for the first and second moments, and S is the system saturation ratio. The parameters of η and ε were derived for particles in the free molecular and continuum regimes, respectively. A harmonic average of the two regimes is then employed for the entire particle size range. The detailed derivations of B_1 , B_2 , η , and ε can be seen in Kim and Pratsinis (1988) and Pratsinis (1988), and their definitions are listed in the Notation.

The initial conditions for equations (9)–(13) are:

$$\begin{aligned} \text{at } z = 0, \quad M_0 &= N_i, \quad M_1 = N_i v_{gi} \exp(4.5 \ln^2 \sigma_{gi}), \\ M_2 &= N_i v_{gi}^2 \exp(18 \ln^2 \sigma_{gi}), \\ C_1 &= C_{1i}, \quad C_2 = K_p / C_{1i}, \end{aligned} \quad (14)$$

where subscript i represents the inlet condition, and K_p is the equilibrium constant of particles with the two associated gases. The boundary conditions at both inner and outer denuder walls for three aerosol moments and gases 1 and 2 are:

$$\text{at } r = kr_0 \text{ and } r = r_0, \quad M_0 = M_1 = M_2 = 0, \quad (15)$$

$$D_1 \partial C_1 / \partial r = -V_{d1} C_1, \quad D_2 \partial C_2 / \partial r = -V_{d2} C_2,$$

where V_{d1} and V_{d2} are the deposition rates of gases 1 and 2, which are proportional to the degree of absorptivity of the denuder surface (Seinfeld, 1986). Three different wall conditions

may be used depending on the wall characteristics: (a) total absorption ($V_d \rightarrow \infty$ or $C = 0$); (b) total reflection ($V_d = 0$ or $\partial C/\partial r = 0$); (c) partial absorption (V_d is some finite value).

For mathematical simplicity and to combine model parameters into a smaller set of governing dimensionless groups, equations (9)–(13) are nondimensionalized as

$$A_1 f(k, r^*) \frac{\partial M_0^*}{\partial z^*} = \frac{E_1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial M_0^*}{\partial r^*} \right), \quad (16)$$

$$A_1 f(k, r^*) \frac{\partial M_1^*}{\partial z^*} = \frac{E_2}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial M_0^*}{\partial r^*} \right) + \eta^*(S - 1)M_0^*, \quad (17)$$

$$A_1 f(k, r^*) \frac{\partial M_2^*}{\partial z^*} = \frac{E_3}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial M_0^*}{\partial r^*} \right) + 2\varepsilon^*(S - 1)M_1^*, \quad (18)$$

$$A_1 f(k, r^*) \frac{\partial C_1^*}{\partial z^*} = \frac{1}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial C_1^*}{\partial r^*} \right) - A_2 \eta^*(S - 1)M_0^*, \quad (19)$$

$$A_1 f(k, r^*) \frac{\partial C_2^*}{\partial z^*} = \frac{A_3}{r^*} \frac{\partial}{\partial r^*} \left(r^* \frac{\partial C_2^*}{\partial r^*} \right) - A_2 \eta^*(S - 1)M_0^*, \quad (20)$$

where $r^* = r/r_o$, $z^* = z/L$, $C_1^* = C_1/C_{1i}$, $C_2^* = C_2/C_{1i}$, L is the denuder length, M_0^* , M_1^* and M_2^* are the dimensionless zero, first and second moments, E_1 , E_2 and E_3 are the dimensionless particle diffusivities for zero, first and second moments, η^* and ε^* are the dimensionless evaporation coefficients for first and second moments, and A_1 , A_2 and A_3 are the dimensionless parameters that govern the performance of the model. A_1 is the parameter that determines what fraction of the gas or particle is absorbed in the annular denuder system. If particle evaporation is neglected, the primary design parameter is A_1 . A_2 is the parameter that appears in the source term of equations (19) and (20), and is inversely proportional to the inlet concentration of the absorbed gaseous species, C_{1i} . If the particle evaporation is taken into account then A_2 is an effective design parameter. A_3 is the ratio of the diffusivities of gas 2 to gas 1. The definitions of the above dimensionless parameters are also listed in the Notation.

The initial conditions for equations (16)–(18) are $M_0^* = N_i/n_s$, $M_1^* = N_i v_{gi} \exp(4.5 \ln^2 \sigma_{gi})/n_s/v_1$, $M_2^* = N_i v_{gi}^2 \exp(18 \ln^2 \sigma_{gi})/n_s/v_1^2$ at the inlet of the annular denuder system, where n_s is the saturated monomer concentration, and v_1 is the molecular volume of monomer. The boundary conditions at both inner and outer denuder walls are $M_0^* = M_1^* = M_2^* = 0$. The initial conditions for equations (19) and (20) are $C_1^* = 1$, $C_2^* = K_p/C_{1i}^2$, while the boundary conditions at both inner and outer denuder walls are $\partial C_1^*/\partial r^* = -V_{d1}^* C_1^*$ and $\partial C_2^*/\partial r^* = -V_{d2}^* C_2^*$, where $V_{d1}^* = V_{d1} r_o/D_1$, $V_{d2}^* = V_{d2} r_o/D_2$.

Equations (16)–(18) describe simultaneous aerosol diffusion and evaporation while equations (19) and (20) describe diffusion of gases 1 and 2 and the source term from aerosol evaporation in the annular denuder system. These equations along with the appropriate boundary conditions constitute a set of coupled partial differential equations (PDEs). Using an explicit-finite difference scheme at P radial points across the denuder, the five PDEs are transformed to ordinary differential equations (ODEs). These ODEs are then solved by a stiff ordinary differential equation solver, DIVPAG (IMSL, 1987). The cup-mixing average (X_{av}^*) is used to evaluate effects of process parameters on the evolution of the three aerosol moments and the gaseous concentrations and is calculated by

$$X_{av}^* = \frac{\int_k^1 X^*(r^*, z^*) f(k, r^*) r^* dr^*}{\int_k^1 f(k, r^*) r^* dr^*}, \quad (21)$$

where $X^* = M_0^*$, M_1^* , M_2^* , C_1^* , or C_2^* .

RESULTS AND DISCUSSION

Model verification

Prior to analysis of the performance of an annular denuder system, the numerical scheme of the present model is systematically validated. The present model for gas sampling in the

absence of evaporating particles was first examined by comparing its numerical solutions with those predicted by the Gormley–Kennedy equation (Gormley and Kennedy, 1949) which is based on the assumption of zero concentration ($V_d \rightarrow \infty$) of the diffusing species at the tube wall. Equation (19) is solved to determine the cup-mixing average concentration of C_1^* as a function of z^* by removing the source term, that is setting $A_2 = 0$. The fully developed flow parameter for a tubular pipe is expressed as $f(k, r) = 2(1 - r^2/r_0^2)$. The results are plotted in Fig. 2. It is seen that excellent agreement between the two models was obtained.

The numerical solutions of the present model in the absence of evaporating particles were also compared with the experimental data of sampling SO_2 gas by an annular denuder system documented by Possanzini *et al.* (1983). The experimental conditions of Possanzini *et al.* (1983) are summarized as: the annular denuder was 20 cm long with an inner diameter of 1.0 cm and an outer diameter of 1.32 cm which provided a value of the inner-to-outer radius ratio (k) equal to 0.76. The sampling flow rates were between 4 and 40 lpm. The diffusivity of SO_2 in air was assumed to be $0.136 \text{ cm}^2 \text{ s}^{-1}$. Assuming that the flow profile is fully developed, Possanzini *et al.* (1983) introduced a correlation equation for predicting the performance of their annular denuder system as

$$C_{1e}^* = \gamma \exp(-\beta\Delta), \quad (22)$$

where C_{1e}^* is the ratio of the concentration of the absorbed gas at the exit to that at the entrance, $\Delta = \pi D_1 L(1+k)/4Q(1-k)$, Q is the sampling flow rate, and γ and β are the coefficients of the correlation equation which can be determined either from the experimental measurements or from the theoretical calculations.

Possanzini *et al.* (1983) applied this correlation equation to their experimental data at different denuder geometries and different sampling flow rates. However, a fully developed laminar flow is not reached in some of the experimental conditions of Possanzini *et al.* (1983). Therefore only the experimental results of the fully developed laminar flow were employed as a comparison basis.

A regression of 200 points of numerical data obtained from the present model was performed and the correlation equation is

$$C_{1e}^* = (0.923 \pm 0.002) \times \exp[(-30.478 \pm 0.086)\Delta]. \quad (23)$$

The dimensionless SO_2 concentration profiles at the exit of the annular denuder system as a function of Δ obtained from Possanzini *et al.* (1983) and calculated from equation (23) are

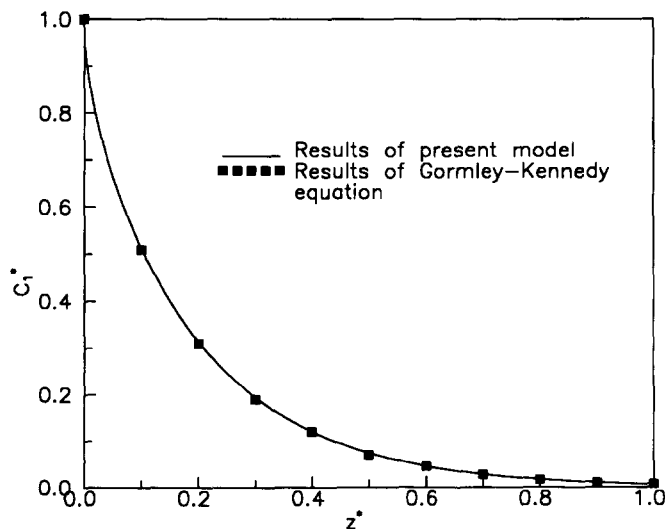


Fig. 2. Comparison of the numerical results predicted by the present model with the Gormley–Kennedy equation in a tubular denuder ($A_1 = 0.122$).

shown in Fig. 3. As can be seen, close agreement was obtained between the measured and predicted results. The slight discrepancies may be attributed to experimental inaccuracies which have been encountered, especially when measuring low gas concentrations (Possanzini *et al.*, 1983). In addition, the assumptions of perfect sink ($V_d \rightarrow \infty$) of diffusing species at the denuder wall may also lead to the overprediction of the outlet concentrations.

The performance of the present model considering evaporating particles was validated by simultaneously solving equations (16)–(20). The numerical solutions were compared well with known solutions at certain limiting cases for pure particle diffusion and pure particle evaporation by both monodisperse and polydisperse aerosols (Gormley and Kennedy, 1949; Friedlander, 1977; Pratsinis, 1988).

The present model was then applied to simulate experimental data documented by Harrison *et al.* (1990) for the change of particle radii of dry NH_4Cl aerosols due to their evaporation in the annular denuder system. The experimental conditions are summarized as: the denuder was 100 cm long with an inner diameter of 3.7 cm and an outside diameter of 4 cm. The inner tube was coated with a 5% methanolic solution of citric acid or phosphorous acid for collecting NH_3 , whilst the outside tube was coated with 5% NaOH in methanol for HCl collection. The coating length was 88 cm; the first 12 cm of the denuder was left uncoated to establish a laminar fully developed air flow. Since the flow rate through the denuder was less than 0.1 lpm, the Reynolds number is well within the laminar flow regime. The experimental system was operated at $20 \pm 2^\circ\text{C}$. The initial geometric mean particle radius and geometric standard deviation were equal to $0.53 \mu\text{m}$ and 1.67, respectively. The initial particle number concentration was selected as 10^5 cm^{-3} (Bai *et al.*, 1995) and the accommodation coefficient (α) was set to unity (Raes *et al.*, 1990). The diffusivities of NH_3 and HCl were chosen as 0.227 (Winiwarter, 1989) and $0.117 \text{ cm}^2 \text{ s}^{-1}$ (Reid *et al.*, 1988).

The equilibrium constant of dry NH_4Cl particles with the two associated gases, NH_3 and HCl, is taken from Pio and Harrison (1987):

$$\ln K_p = 2.2358 \ln T - \frac{2.13204 \times 10^4}{T} + 65.4375 - 8.167 \times 10^{-3} T + 4.644 \times 10^{-7} T^2 - 1.105 \times 10^{-10} T^3. \quad (24)$$

The vapor pressure of NH_4Cl monomer in the bulk phase (p_1) can be written as $p_1 = S \times p_d$, where p_d is the vapor pressure of NH_4Cl monomer in equilibrium with particle surface and is commonly expressed as $p_d = p_{\text{NH}_3}^e + p_{\text{HCl}}^e = 2K_p^{1/2}$ (Harrison and MacKenzie, 1990), where superscript e denotes the state of equilibrium. The system saturation ratio S is defined

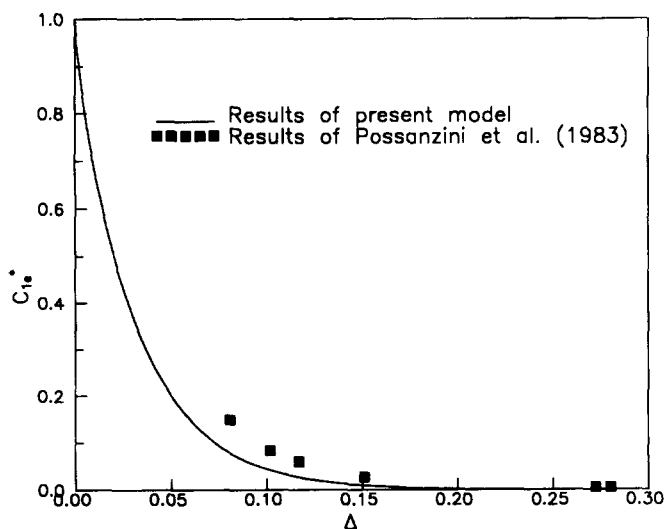


Fig. 3. Comparison of the measured and predicted results on C^* as a function of Δ .

as (Kodas *et al.*, 1986)

$$S = \frac{C_{\text{NH}_3} C_{\text{HCl}}}{K_p} \quad (25)$$

When the value of saturation ratio is unity, the system is in an external state of equilibrium. The driving force of the evaporation process of NH_4Cl aerosols is determined by $(1 - S)$. The walls are considered perfect sinks ($V_d \rightarrow \infty$) in the simulation.

Figure 4 shows the measured and simulated results on the change of particle radius of dry NH_4Cl aerosols as a function of residence time in the annular denuder system. As can be seen, good agreement between the simulated results using a polydisperse distribution and the experimental data is obtained. The simulated results using a monodisperse distribution is also shown in Fig. 4. The calculations were based on a harmonic average of evaporation rates of monodisperse aerosols in the continuum and free molecular regimes [Friedlander, 1977, equations (9.23) and (9.24)]. It is seen that significant departures from experimental data are observed using a monodisperse distribution. This indicates that particle polydispersity plays a very important role in the overall evaporation rate.

It must be noted that the experimental conditions of Harrison *et al.* (1990) were used for studying the evaporation of ammonium-containing aerosols; therefore, they were taken at an extremely low flow rate not typical of that for the annular denuder system employed in the field.

Sensitivity study

Having established the accuracy and consistency of the present model, a sensitivity analysis was carried out to investigate the effects of the three governing parameters (A_1 , A_2 , A_3) on the performance of an annular denuder system. A_1 and A_2 were identified to strongly influence the model performance and the effect of A_3 can be neglected.

Figure 5a and b shows plots of C_{1e}^* and mass median diameter of evaporating particles at the exit of the denuder for different values of A_2 as a function of design parameter, $\Delta (= 1/4A_1(1 - k)^2)$, respectively. The values of A_2 and Δ examined herein are the typical range for the annular denuder system used in the field. The variations of C_{1e}^* and mass median diameter in the absence of evaporating particles ($A_2 = 0$) are also shown in Fig. 5. As can be seen, an increase of Δ produces an increase of the collection efficiency of the annular denuder and a reduction of the mass median diameter of evaporating particles. This

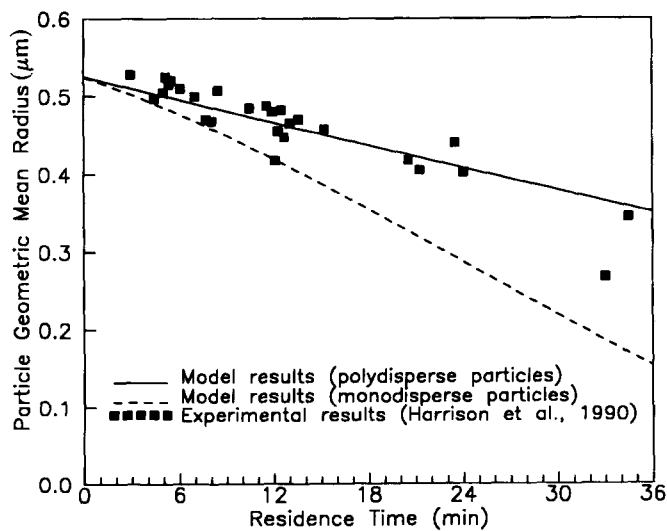


Fig. 4. Comparison of the measured and simulated results on the change of particle radius of dry ammonium chloride aerosols in the annular denuder system.

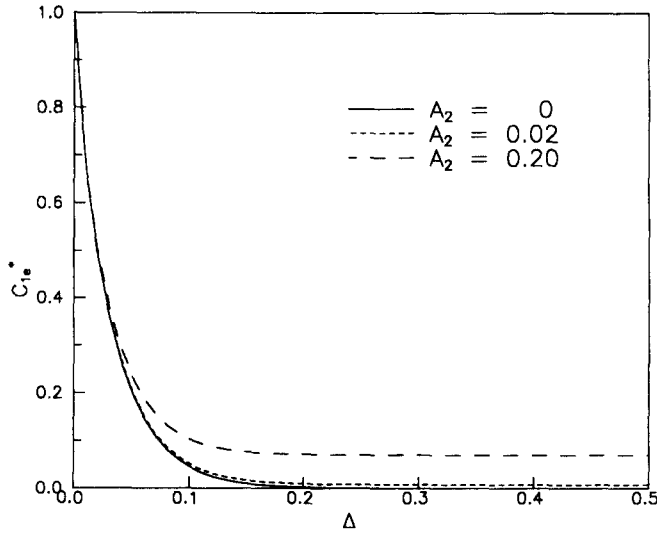


Fig. 5(a). Plots of C_1^* at the exit of the annular denuder for different values of A_2 as a function of Δ .

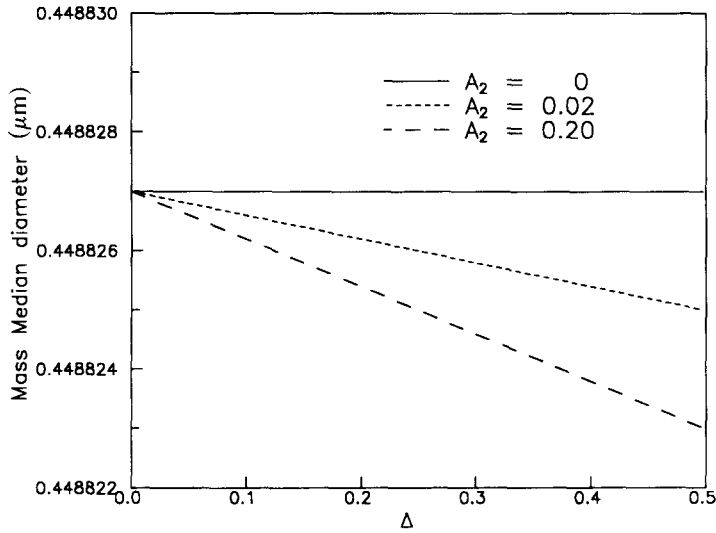


Fig. 5(b). Plots of mass median diameter of evaporating particles at the exit of the annular denuder for different values of A_2 as a function of Δ .

can be attributed to a long residence time or a large ratio of inner to outer radius. It is also seen that due to particle evaporation, additional gases are released in the denuder; hence the value of C_{1e}^* is higher for a larger value of A_2 . This can be explained by the fact that for a larger value A_2 implies that the inlet concentration of gas 1 is smaller and the driving force for evaporation of particles and release of additional gases is higher. A similar reasoning can be used to explain the increase of change of mass median diameter of evaporating particles for a larger value of A_2 due to a higher particle evaporation rate.

Practical application

From a design or operational perspective, one would like to reach a relatively high gas sampling efficiency and minimize the particle evaporation effects in the annular denuder system. Therefore, the performance equation is necessary for selecting an optimal operating

condition. A performance equation for sampling HNO_3 gas using a typical range of the atmospheric aerosol and gas properties is derived as follows.

The employed denuder is the Harvard-EPA annular denuder system (HEADS) (Vossler *et al.*, 1987). The system is composed of an impactor followed by two annular denuders, a filter pack, a pump and a flow controller. The flow rate through the system is operated at 10 lpm, and the cutoff diameter for the impactor is $2.5 \mu\text{m}$. The denuder was 20 cm long with an outer diameter of 1.2 cm. The inner diameter was determined by a given value of k . Both outer and inner denuder walls were coated with a suspension of MgO powder in methanol for collecting HNO_3 gas (Harrison *et al.*, 1990). The walls can be considered perfect sinks ($V_d \rightarrow \infty$) in the following predictions (Bai *et al.*, 1995). The diffusivity of HNO_3 gas is selected as $0.118 \text{ cm}^2 \text{ s}^{-1}$ (Winiwarter, 1989).

The equilibrium constant of dry NH_4NO_3 particles with the associated gases, HNO_3 and NH_3 , is taken from Mozurkewich (1993):

$$\ln K_p = 118.87 - \frac{24084}{T} - 6.025 \ln T. \quad (26)$$

It must be noted that the above relationship would only be valid for the ambient relative humidity below the deliquescent point of NH_4NO_3 aerosols. For the ambient relative humidity above the deliquescent point, the equilibrium constant is affected by the relative humidity over a wide range (Seinfeld, 1986). Furthermore, the presence of other species in the particle could also affect the equilibrium.

The atmospheric aerosol and gas properties are adopted from a typical value available in the literature (Benner *et al.*, 1991; Lin *et al.*, 1993; Lee *et al.*, 1993). The inlet total particle number concentration, the mass median diameter of aerosols and the HNO_3 gas concentration were selected as 10^5 cm^{-3} , $0.45 \mu\text{m}$ and $0.77 \mu\text{g m}^{-3}$, respectively. The inlet geometric standard deviation of aerosols (σ_g) and the mass fraction of NH_4NO_3 contained in the aerosol particles (m_f) are evaluated within a typical range.

Equation (22) was employed to obtain the performance equations which contain a range of σ_g from 2 to 3 and k from 0.76 to 0.92. Tables 1–3 list the performance equations of m_f of 1%, 2% and 4%, respectively, under different ambient temperatures (T). It is seen that the coefficients of γ and β are relatively small for higher values of T and m_f . This implies that the collection efficiencies of HNO_3 gas by the annular denuder system are lower and sampling artifacts may be significant under these conditions.

The comprehensive performance equation which includes a range of T from 15 to 45°C and m_f from 1 to 4% is derived from Tables 1–3 as

$$C_{1e}^* = (0.9076 \pm 0.0008) \times \exp[-(29.3305 \pm 0.0327)\Delta]. \quad (27)$$

Applications of equation (27) are demonstrated as follows: for 98% HNO_3 gas removal, Δ must be greater than or equal to 0.13 (determined by substituting $C_{1e}^* = 0.02$ in equation (27), and calculating Δ). Thus $(Q/L)_{\text{design}}$ should be less than or equal to $6.038D_1(1+k)/(1-k)$. If the denuder length is 40 cm, $D_1 = 0.118 \text{ cm}^2 \text{ s}^{-1}$ and $k = 0.76$, then the optimal operating value of Q must be less than or equal to 12.54 lpm. If $k = 0.84$

Table 1. Performance equations of the Harvard-EPA annular denuder system for a 1% mass fraction of NH_4NO_3 contained in the aerosol particles at different ambient temperatures

Temperature ($^\circ\text{C}$)	$C_{1e}^*(2 \leq \sigma_g \leq 3; 0.76 \leq k \leq 0.92)$
15	$(0.9178 \pm 0.0004) \exp[-(30.1943 \pm 0.0177)\Delta]$
20	$(0.9175 \pm 0.0004) \exp[-(30.1644 \pm 0.0190)\Delta]$
25	$(0.9168 \pm 0.0005) \exp[-(30.1089 \pm 0.0222)\Delta]$
30	$(0.9156 \pm 0.0007) \exp[-(30.0096 \pm 0.0295)\Delta]$
35	$(0.9136 \pm 0.0010) \exp[-(29.8350 \pm 0.0443)\Delta]$
40	$(0.9074 \pm 0.0028) \exp[-(29.7322 \pm 0.1120)\Delta]$
45	$(0.9040 \pm 0.0027) \exp[-(29.0287 \pm 0.0150)\Delta]$

Table 2. Performance equations of the Harvard-EPA annular denuder system for a 2% mass fraction of NH_4NO_3 contained in the aerosol particles at different ambient temperatures

Temperature ($^{\circ}\text{C}$)	C_{Te}^* ($2 \leq \sigma_g \leq 3$; $0.76 \leq k \leq 0.92$)
15	$(0.9174 \pm 0.0004) \exp[-(30.1606 \pm 0.0190)\Delta]$
20	$(0.9167 \pm 0.0005) \exp[-(30.1009 \pm 0.0226)\Delta]$
25	$(0.9154 \pm 0.0007) \exp[-(29.9897 \pm 0.0310)\Delta]$
30	$(0.9131 \pm 0.0011) \exp[-(29.7906 \pm 0.0481)\Delta]$
35	$(0.9090 \pm 0.0019) \exp[-(29.4422 \pm 0.0791)\Delta]$
40	$(0.9019 \pm 0.0031) \exp[-(28.8436 \pm 0.1305)\Delta]$
45	$(0.8896 \pm 0.0051) \exp[-(27.8344 \pm 0.2092)\Delta]$

Table 3. Performance equations of the Harvard-EPA annular denuder system for a 4% mass fraction of NH_4NO_3 contained in the aerosol particles at different ambient temperatures

Temperature ($^{\circ}\text{C}$)	C_{Te}^* ($2 \leq \sigma_g \leq 3$; $0.76 \leq k \leq 0.92$)
15	$(0.9166 \pm 0.0005) \exp[-(30.0955 \pm 0.0230)\Delta]$
20	$(0.9152 \pm 0.0008) \exp[-(29.9751 \pm 0.0323)\Delta]$
25	$(0.9126 \pm 0.0012) \exp[-(29.7528 \pm 0.0515)\Delta]$
30	$(0.9079 \pm 0.0020) \exp[-(29.3557 \pm 0.0868)\Delta]$
35	$(0.8996 \pm 0.0035) \exp[-(28.6589 \pm 0.1456)\Delta]$
40	$(0.8851 \pm 0.0057) \exp[-(27.4653 \pm 0.2354)\Delta]$
45	$(0.8600 \pm 0.0090) \exp[-(25.4708 \pm 0.3558)\Delta]$

and 0.92, the optimal operating values of Q must be less than or equal to 19.66 and 39.0 lpm, respectively.

CONCLUSIONS

A model that accounts for simultaneous gas diffusion, aerosol diffusion and evaporation has been developed to predict performance of the annular denuder system. The governing equations were cast into dimensionless form and the performance of the model was validated by the analytical and experimental data available in the literature. The effects of governing dimensionless groups on the performance of the model were evaluated in the sensitivity analysis. The parameters that account for what fraction of the gas or particle is absorbed (A_1) and particle evaporation (A_2) are identified to strongly influence model performance.

Practical application of the present model was demonstrated for sampling atmospheric HNO_3 gas. A performance equation of the annular denuder system was derived for a typical range of ambient temperature, ratio of inner to outer annular radius, and atmospheric aerosol and gas properties. It was then applied to obtain the optimal operating condition which maximizes the collection efficiency of HNO_3 gas and minimizes the sampling artifact at the same time. Using similar approaches to those presented in this study, analogous performance equations for sampling other gas species can also be derived.

Ultimately, it must be recognized that the model predictions are valid for the inlet section when laminar flow is fully developed. In addition, the information of gas deposition rate at the denuder wall for each coating and each absorbate would also require extensive empirical support in an effective modelling.

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