Denuder Tubes for Sampling of Gaseous Species

A Review

Zulfiqur Ali, C. L. Paul Thomas and John F. Alder
Department of Instrumentation and Analytical Science, UMIST, P.O. Box 88, Manchester M60 1QD, UK

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Introduction

Denuder tubes were first considered on a theoretical basis in the 1890s during a study on the diffusion of ions into gases.[1] Later, in the 1930s, studies of atmospheric condensation nuclei revealed significant particulate losses from gas flows in sample pipelines and, consequently, the diffusional removal of particulates in both cylindrical and rectangular section pipelines was considered.[2] Subsequent measurements of the diffusional properties of micro-particulates were made with multi-tubular assemblies and diffusion batteries, consisting of several flat plates with narrow gaps between them.[3] In an appendix to this work, a mathematical treatment was presented of the diffusion from a stream flowing through a thin rectangular tube.

Diffusion measurements based on these methods continued, and in 1949 Gormley and Kennedy[4] derived a solution describing diffusion from a stream flowing through a cylindrical tube, originally proposed by Townsend.[1] Diffusion coefficients for sulphur trioxide and ammonia were determined by trapping these gases chemically in a glass tube lined with oleic acid or copper sulphate impregnated paper, respectively.[5] Laminar flow subduction zones were incorporated at the inlet to these devices, and the diffusion coefficients of sulphur trioxide and ammonia were measured by determining the mixing ratios of these gases within the tubing.

A study undertaken in the early 1960s was concerned with the effects of fluorides in the atmosphere.[6] An annular unit was used to separate gaseous fluoride species from their particulate counterparts. The unit consisted of three concentric cylinders coated with sodium hydrogen carbonate or aluminium. No theoretical basis was given for this design, and annular systems were not studied again until the early 1980s. Following on from this, an analytical technique using an "aerosol-passing gas adsorber" was described.[7] Fabricated from a series of glass tubes lined with potassium hydroxide and magnesium perchlorate, it was employed to remove water vapour from an aerosol sampling system for a hydrogen flame chemiluminescence detector used for aqueous sulphate ion determination. The removal of sulphur dioxide from a laminar flow gas stream by a diffusion denuder coated with lead(IV) oxide was shown to conform to the Gormley - Kennedy equation.[8] Sulphur dioxide at a concentration of 1.5 p.p.m. in air was passed through the tube, which was then cut into 0.5-in sections and analysed radiochemically. The diffusion coefficients for sulphur dioxide at 1 atm were found to be 0.117, 0.132 and 0.146 cm^2 s^{-1} at 0, 20 and 37 °C, respectively. Lead-based sulphur dioxide denuders were then used to remove sulphur-containing gaseous interferences quantitatively for measurements of the sulphate ion content in airborne aerosols.[9–12] The use of a heated sample tube to effect thermochemical changes in incoming sampled ammonium sulphates was first reported in 1978.[12] Other gases, notably ammonia, were removed from environmental gas samples by arrays of denuder systems,[13] which allowed the use of higher gas flow-rates than previously encountered. However, it was not until 1979 that the role of the denuder tube was reversed and it was used as a gas collection device rather than an instrument to denude a sample of certain gaseous components.[14] In this work, Ferm achieved a detection limit of 0.4 nmol m^{-3} of ammonia in air (0.01 p.p.b.) after a 24-h sample period. Interference from particulate ammonium salts at "extremely high" (400 nmol m^{-3}) concentrations was of the same order as the detection limit.

Description of Operation

For a denuder tube to function, a series of criteria must be met.

The removal of the analyte must have no global effect on the sample, the gas flow must be stable and laminar and the viscosity and temperature distribution within the gas flow must be homogeneous. Any axial diffusion of the sampled gas must be insignificant in comparison to the sample flow, and the collection surfaces should behave as infinitely large and perfect sinks towards the analyte. Adsorbate species should be neither created nor destroyed in the gas phase within the denuder tube. Schematic diagrams of the two types of denuder unit in common use are shown in Fig. 1.

Air is drawn through either the centre of the tube, or the annulus, at a rate such that its flow is laminar [Reynold's number (Re) < 2100].[15] Laminar flow is achieved a short distance from the inlet. In a tube of diameter d, the length of this subduction zone can be calculated as follows:

$$l = 0.07dRe \qquad \qquad \ldots \quad \ldots \quad \ldots \quad (1)$$

where l is the length of the laminar flow subduction zone.

The establishment of laminar flow is important as this ensures that radial mixing can only take place via diffusion-based processes. It is essential that areas of collection surfaces where turbulent flow exists, and particulates therefore impinge on, do not contribute towards the analysis. Often a PTFE former or inlet is used to establish laminar flow prior to the collection surfaces. Molecular species diffuse through the laminar flow to the active collection surfaces, where they undergo irreversible adsorption or chemical bonding and are removed from the gas stream. Particulates with their much lower diffusion velocities cannot migrate to the walls during their residence time within the unit and hence, provided the above conditions are met, do not contribute to the final measurement. The deposition of particulates as a result of gravitational sedimentation would disrupt the performance of the unit. This problem is negated by using the tube in a vertical orientation, and employing cyclones and virtual impactors to remove large pieces of airborne detritus from the sample also ensures the effectiveness of this method.

Theory

Cylindrical Systems

The behaviour of trace amounts of gases in a denuder system can be described in terms of Fickian diffusion. The expression in common usage was derived by Gormley and Kennedy.[4] For a cylindrical denuder, their solution can be summarised as follows.

For a laminar flow, the velocity of the gas at any point in the denuder tube (Fig. 1) is given by

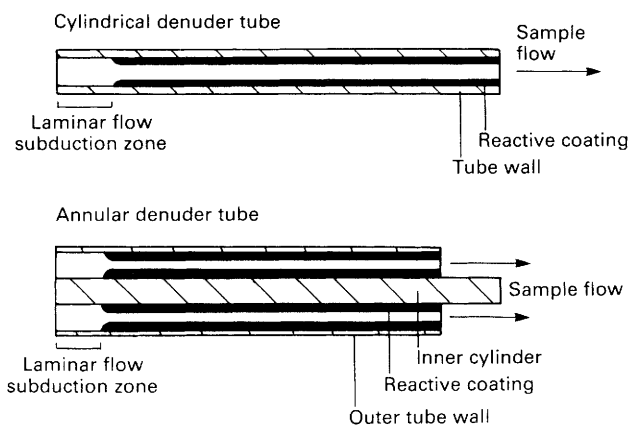$$V = F(R^2 - r^2)/2\pi R^4 \quad \ldots \quad \ldots \quad \ldots \quad (2)$$

Fig. 1. Schematic diagrams of the cylindrical and annular denuder tubes

where V is the velocity of the gas flow at a radial displacement r from the axis, F is the sampled gas flow-rate and R is the radius of the tube.

The diffusive motion of the gaseous analyte within the unit is resolved into its cartesian components. The equations of motion that describe the transport of analyte parallel to the laminar flow and the denuder axis contain the appropriate correction:

$$dP_aD/dx = -P_au \quad \ldots \quad \ldots \quad \ldots \quad (3)$$
$$dP_aD/dy = -P_av \quad \ldots \quad \ldots \quad \ldots \quad (4)$$
$$dP_aD/dz = -P_a(w - V) \quad \ldots \quad \ldots \quad (5)$$

where D is the diffusion coefficient of the analyte, P_a is the partial pressure of the analyte and u, v and w are the diffusive velocities of the analyte with respect to the x, y and z axes, respectively.

The parameters u, v and w are then substituted into the continuity equation

$$\frac{d}{dx}(P_au) + \frac{d}{dy}(P_av) + \frac{d}{dz}(P_aw) = 0 \quad \ldots \quad \ldots \quad (6)$$

giving

$$\nabla P_a - \frac{1}{D} \cdot \frac{d}{dz}(P_aV) = 0 \quad \ldots \quad \ldots \quad \ldots \quad (7)$$

where

$$\nabla = \frac{du}{dx} + \frac{dv}{dy} + \frac{dw}{dz}$$

A transfer from cartesian to cylindrical co-ordinates provides the following expression:

$$\frac{1}{r} \cdot \frac{d}{dr}\left(r\frac{dP_a}{dr}\right) + \frac{1}{r^2} \cdot \frac{d^2P_a}{d\theta^2} + \frac{d^2P_a}{dz^2} - \frac{1}{D} \cdot \frac{d}{dz}(P_aV) = 0 \quad \ldots \quad (8)$$

where θ is the angle of displacement from the x axis in the x - y plane.

It is then assumed that $dP_a/d\theta = 0$ for reasons of symmetry and $d^2P_a/dz^2 = 0$ for $V \gg w$. The resulting equation forms the basis of the Gormley - Kennedy solution

$$\frac{d^2P_a}{dr^2} + \frac{1}{r} \cdot \frac{dP_a}{dr} - \frac{2F}{\pi R^4D} \cdot (R^2 - r^2) \cdot \frac{dP_a}{dz} = 0 \quad \ldots \quad (9)$$

for which the boundary condition is set such that

$$P_{a|R} = 0 \quad \ldots \quad \ldots \quad \ldots \quad \ldots \quad (10)$$

The mean radial concentration $\bar{c}$ at a length Z along the tube axis is proportional to

$$_0\!\int^R P_a2\pi Vr.dr \quad \ldots \quad \ldots \quad \ldots \quad (11)$$

The mixing ratio of the analyte at length Z can be expressed as

$$\bar{c}/c_0 = [4/(R^4P_{a0})] \, _0\!\int^R P_a(R^2-r^2)r.dr \quad \ldots \quad (12)$$

where P_a is the solution to equation (9), P_{a0} the ambient vapour pressure of the analyte, c_0 the ambient concentration of the analyte and $\bar{c}$ the mean radial concentration of the analyte. Gormley and Kennedy provided the solution to equation (12) as a series:

$$\bar{c}/c_0 = 0.819\exp(-7.314\Delta_c) + 0.0975\exp(-44.6\Delta_c) + 0.0325\exp(-212\Delta_c) \quad \ldots \quad \ldots \quad \ldots \quad (13)$$

where, at standard temperature and pressure,

$$\Delta_c = \pi D_0Z/2F \quad \ldots \quad \ldots \quad \ldots \quad (14)$$

(subscript c refers to the cylindrical system). For most sampling applications, where $\Delta_c \leqslant 0.05$, only the first term of this series will be significant and equation (13) can be approximated to

$$\bar{c}/c_0 = 0.82\exp(-7.3\Delta_c) \quad \ldots \quad \ldots \quad (15)$$

From these expressions it can be seen that the collection efficiency of a denuder tube increases with length, and also

with increasing values for the diffusion coefficient of the analyte. The collection efficiency is enhanced further by decreasing the radius of the tube and reducing the mean axial velocity of the sampled gas. Davies[16] has indicated that low values for the kinematic viscosity of the sample also lead to increased sampling efficiency; this is underlined further by Ferm's[14] treatment of the Gormley - Kennedy solution. The performance of a denuder tube can be seen to be affected by variables such as pressure, temperature and relative humidity. Such detail is often not reported in experimental studies, and no mention has been made of procedures that enable data obtained under different environmental conditions to be corrected. In some situations (*i.e.*, at high altitude) these factors will become significant.

Diffusion Coefficients

A number of studies involved analysis of the contents of segmented denuder tubes to determine the diffusion coefficient of the analyte, see Fig. 2. The sampling efficiency of each segment is defined by

$$E = \text{number of moles adsorbed/} \\ \text{number of moles sampled} \quad \quad (16)$$

For the first segment

$$E = a/c \quad \quad \quad \quad (17)$$

and for the second segment

$$E = b/(c - a) \quad \quad \quad (18)$$

where c is the number of moles sampled, a the number of moles adsorbed in the first segment and b the number of moles adsorbed in the second segment. Combining equations (17) and (18) gives

$$E = (a - b)/a \quad \quad \quad (19)$$

hence

$$c/c_0 = b/a \quad \quad \quad (20)$$

Repeating this analysis for further segments yields a series of values for Δ_c with increasing values of Z. Then a plot of Δ_c against Z is a straight line of slope $\pi D_0/2F$. Hence the diffusion coefficient D_0 can be determined. The values obtained for the diffusion coefficient then allow elucidation of the analyte form in the sampled gas. Hence the diffusive mechanism of the sampling process can be verified, and information about any hydration or other molecular aggregation of the analyte obtained.

Annular Systems

The Gormley - Kennedy solution discussed here [equation (13)] does not apply to annular systems. Possanzini *et al.*[17] proposed an empirically modified form:

$$c/c_0 = A\exp(-\alpha\Delta_a) \quad \quad (21)$$

where A and α are experimentally determined constants.
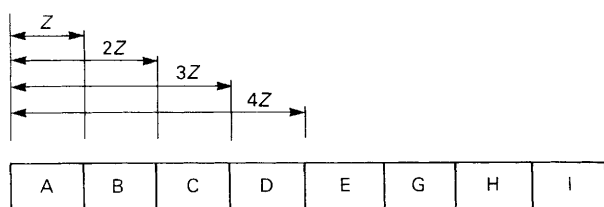
Fig. 2. Schematic diagram showing the denuder divided into a series of equal sections for the measurement of diffusion coefficients. $\bar{c}/c_0 = b/a = c/b = \ldots = i/h$, where a = number of moles in section A, b = number of moles in section B, etc. Finally, $\bar{c}/c_0 = (i + h + g + e)/(a + b + c + d)$ and $\bar{c}/c_0 = 0.82\exp(-7.3\Delta_c)$, $\Delta_c = D_0\pi Z/2F$

The form of Δ_a (subscript a refers to the annular system) was also modified to incorporate the equivalent diameter of the annular channel. This was defined as four times the hydraulic radius, which in its turn was defined as the ratio of the cross-sectional area of the annular channel to its perimeter. The final form of Δ_a was given as

$$\Delta_a = \frac{\pi D_0 Z}{2F}\left(\frac{d_1 + d_2}{d_1 - d_2}\right) \quad \quad (22)$$

where d_1 is the internal diameter of the external cylinder and d_2 the external diameter of the internal cylinder.

Values for A and α were calculated by determining Δ_a and the mixing ratio for three denuder tubes of different sizes, hence giving the following expression:

$$\bar{c}/c_0 = 0.82 \pm 0.1\exp[(-11.27 \pm 0.61)\Delta_a] \quad (23)$$

The parameters A and α were determined with test atmospheres in the range 0.29–1.45 mg m^{-3} of sulphur dioxide in air and the relative humidity between 60 and 80%. The sampling rate ranged from 0.072 to 2.4 m^3 h^{-1}; the temperature at which these experiments were run was not given. The determination of A and α could have been accomplished by sectional analysis of the denuder units, but no indication was given as to why such an approach was not adopted, despite its inherent precision. It should be noted that the reliability of the results obtained by this method is dependent on the accuracy of the value assigned to the diffusion coefficient of the analyte under study.

As the hydraulic radius of the annular system increased, the velocity profile of the sampled gas tended towards that obtained between two infinite parallel sheets, *i.e.*, A and α tended towards the limiting values of a parallel-plate system as the hydraulic radius increased. No reference was made to previous work, which investigated diffusional deposition in rectangular channels.[3] A comparison between equations (15) and (23) revealed the advantages of the annular design over its cylindrical counterpart. For an equivalent sampling efficiency the annular system could be shorter and more compact, operate at higher sample flow-rates and have a larger sampling capacity, or a combination of any of these factors. These claims were subsequently verified in a comparative study,[18] which concluded that annular units were a substantial improvement over all other denuder tube designs.

Development of the Gormley - Kennedy Solution

Some of the assumptions underlying the Gormley - Kennedy solution have been challenged, and, subsequently, alterations to equation (13) have been proposed.

Braman *et al.*[19] pointed out that the surfaces of a denuder tube would be depleted with increasing sample volume. The corollary to this was that the effective length of the denuder tube decreased with increasing sample volume. If the denuder was being operated at a constant sampling rate, then the collection efficiency would decrease with increasing sampling time. By assuming pseudo-first-order adsorption kinetics, it was proposed that the effective length of a denuder tube at any time after the commencement of sampling could be described by

$$Z_t = Z_0\exp(-kt) \quad \quad \quad (24)$$

where Z_t is the effective length of the denuder at time t, Z_0 the length of the denuder at $t = 0$, k the depletion constant (feed rate/tube capacity) and t the sample time. The sample size dependency of the length of the denuder was incorporated in the original expression, equation (15), which was modified to

$$\bar{c}/c_0 = 0.82\exp\left[-7.31 \cdot \frac{\pi D_0}{2F} \cdot Z_0\exp(-kt)\right] \quad (25)$$

The significance of the increased precision obtained by this approach is dependent on the experimental conditions. Large depletion rate constants, due to high analyte concentrations or low surface capacities, would result in measurable reductions in the effective length of the denuder. High analyte concentrations do not require long sampling times however, and an appropriate choice of reagent for the tube coating ensures an adequate surface capacity. For the analysis of sulphur dioxide in air using a denuder tube,[20] the prediction given by equation (25) for the concentration of sulphur dioxide in the tube exhaust, after sampling for 17 h (a sample volume of 0.683 m³) is 0.32 μg m⁻³. This can be compared to the value of 0.29 μg m⁻³ obtained from equation (15). The measured analyte concentration was 30.5 μg m⁻³ and the difference between the two predictions is not significant. Measurements of the diffusion coefficients of gaseous species obtained by the denuder tube method would be more accurate if equation (25) were applied, but the practical advantages that could be carried over to the trace analysis of gas are limited.

Other modifications to the Gormley - Kennedy equation have been suggested by Murphy and Fahey.[21] The perfect sink criterion was challenged and the boundary condition that arises from it [equation (10)] was shown to be an approximation. Instead, a constant reaction probability γ was proposed. This alternative treatment, based in part on previous work concerning haemodialysis,[22] resulted in a new equation for the mixing ratio:

$$\bar{c}/c_0 = \sum_{n=1}^{n=\infty} B_n \exp(-\Lambda_n^2 Z^*) \quad .. \quad .. \quad (26)$$

where Z^* is a function of Z [see equation (30)]. As for its predecessors, equation (26) can be approximated to the first term:

$$\bar{c}/c_0 = B_1 \exp(-\Lambda_1^2 Z^*) \quad .. \quad .. \quad (27)$$

The constants B_n and Λ_n are eigenvalues that arise out of the solution to the revised differential equation, which incorporates the new boundary condition. These two constants are also functions of a new dimensionless parameter the Sherwood number (N_{shw}), which can be likened to the Nusselt number used in heat-transfer theory. It is approximated by the following equation:

$$N_{shw} \approx 36 \left(\frac{T}{m}\right)^{\frac{1}{2}} \left(\frac{T_0}{T}\right)^{\beta} \frac{RP}{D_0} \cdot \frac{\gamma}{1 - (\gamma/2)} \quad .. \quad (28)$$

where T is the temperature (K), m the relative molecular mass of the analyte, T_0 the standard temperature (K), R the radius of the tube (cm) and P the pressure (kPa). The exponent β is derived from the expression describing the variation of the diffusional coefficient with temperature and pressure:

$$D = D_0 \left(\frac{T}{T_0}\right)^{\beta} \left(\frac{P_0}{P}\right) \quad .. \quad .. \quad .. \quad (29)$$

where P_0 is the standard pressure. The term Z^* is given by the expression

$$Z^* = Z \cdot \frac{\pi}{2} \cdot \frac{D_0}{F} \left(\frac{T}{T_0}\right)^{\beta-1} \quad .. \quad .. \quad .. \quad (30)$$

Murphy and Fahey[21] produced a table with values of B and Λ for a range of Sherwood numbers.

This treatment models the physical processes that take place in a denuder tube more exactly than the Gormley - Kennedy approach, and hence can be seen as an improvement. The introduction of the Sherwood number enables parameters such as temperature and pressure to be incorporated in the denuder unit design. Murphy and Fahey demonstrated that at low pressures, where the Gormley - Kennedy solution fails, this new approach yielded data that fitted the experimental results with significantly greater precision. This method demands a priori knowledge of the reaction probability factor and the diffusional behaviour of the analyte. To obtain such information may require extensive experimental work. The assumption of a constant reaction probability over the entire collection surface is not necessarily valid. The point made by Braman et al.,[19] that the effective length decreases with increasing sample volume, is not included in this treatment. Such an approach would require that the reaction probability factor be expressed as a sample size dependent variable. As the Sherwood number approaches infinity, equation (27) tends towards a limiting value, that given by the Gormley - Kennedy solution. Under normal sampling conditions the differences between this approach and the Gormley - Kennedy expression are not significant and the usefulness of this method in the analysis of trace amounts of gas has yet to be established.

Assessment of the Empirically Derived Annular Equations

Based on previous work,[4,14] Possanzini et al.[17] derived an expression describing diffusion in an annular system. The exponent term Δ was redefined in terms of the Reynolds number (Re) and the equivalent diameter of the system:

$$\Delta = \frac{2D_0 Z}{\gamma Re\delta} \quad .. \quad .. \quad .. \quad .. \quad (31)$$

where γ is the kinematic viscosity, δ the equivalent diameter (defined under Annular Systems) and $Re = \bar{V}\delta/\gamma$, where $\bar{V}$ is the mean axial velocity of the gas. For a cylindrical system

$$\delta = 4(\pi R^2/2\pi R) = d$$

and

$$\bar{V} = 4F/\pi d^2$$

therefore

$$Re = 4F/\pi d\gamma$$

and hence

$$\Delta = \pi D_0 Z/2F = \Delta_c$$

from equation (14).

For an annular system the equivalent diameter changes:

$$\delta_a = 4\left[\frac{\pi}{4} \cdot (d_1^2 - d_2^2) \cdot \frac{1}{\pi(d_1 + d_2)}\right] = d_1 - d_2 \quad .. \quad (32)$$

and

$$\bar{V}_a = \frac{4F}{\pi(d_1^2 - d_2^2)^{-2}} \quad .. \quad .. \quad .. \quad (33)$$

therefore

$$\Delta = \frac{\pi D_0 Z}{2F} \cdot \frac{(d_1 + d_2)}{(d_1 - d_2)} = \Delta_a \quad .. \quad .. \quad (22)$$

Gormley produced an expression describing diffusion through a laminar flow in a rectangular section pipeline (i.e., between infinite parallel planes[3]). The rectangular section had a width of $2a$ and a height of $2b$, where $b >> a$. A treatment similar to that for the cylindrical system yielded the expression

$$\bar{c}/c_0 \approx 0.91 \exp\left(-3.77 \cdot \frac{b}{a} \cdot \frac{D_0 Z}{F}\right) .. \quad .. \quad (34)$$

Equations (34) and (23) may be compared, for an annulus can be considered to be a distorted rectangle (see Fig. 3). To a first approximation the two sections are equivalent with respect to gas flow behaviour within them. The centroid of the annulus is assigned to the height of the rectangle $(2b)$ and the annulus gap to its width $(2a)$.

$$b_a = \pi(d_1 + d_2)/4 \quad .. \quad .. \quad .. \quad (35)$$

$$a_a = (d_1 - d_2)/4 \quad .. \quad .. \quad .. \quad (36)$$

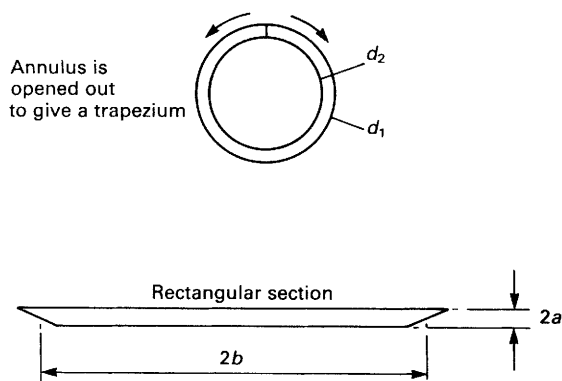where subscript a refers to the annular system.

Fig. 3. Schematic diagram of a section of the annulus and its corresponding rectangular section

Substitution of equations (35) and (36) into equation (34) gives

$$\bar{c}/c_0 \approx 0.91 \exp\left[\frac{-3.77\pi D_0 Z}{F}\left(\frac{d_1 + d_2}{d_1 - d_2}\right)\right] \quad \cdot \cdot \ (37)$$

Equation (37) only differs from equation (23) in the values of the numerical coefficients used.

The data obtained by Possanzini et al.[17] have been used to generate graphs of collection efficiency versus length using equations (23) and (37), Fig. 4. In a later study by the same group, nitrogen dioxide was removed from a gas sample by an annular denuder coated with potassium iodide in a Carbowax matrix.[23] The procedure for deriving the empirical constants A and α was repeated and another expression for the mixing ratio resulted:

$$\bar{c}/c_0 \approx 0.82 \exp\left[\frac{-1.125\pi D_0 Z}{F}\left(\frac{d_1 + d_2}{d_1 - d_2}\right)\right] \quad \cdot \cdot \ (38)$$

Graphs are also shown in Fig. 4(b) comparing the efficiencies predicted from equations (38) and (37) and based on the data supplied by Possanzini et al.[23] The large difference betweeen the two empirically derived expressions [equations (38) and (23)] emphasises the drawbacks to such an approach. The explanation given by Possanzini et al. for this difference was the occurrence of non-quantitative adsorption of nitrogen dioxide on the potassium iodide impregnated Carbowax. This is a feasible explanation when the nature of the adsorbing surface is considered, but no other experimental evidence was offered.

The distorted-rectangle approach produces an expression with an apparently large disparity between it and that derived empirically. The numerical constants in the exponent terms are −3.77 and −5.633 for equations (37) and (23), respectively. The difference between the two solutions is illustrated in Fig. 4. The divergence between the predicted collection efficiencies after a length of 20 cm is not significant, and is generally less than the experimental errors associated with the measurement of low gas concentrations. No work has been published that reproduces the result of Possanzini et al.,[17] however, it would appear that their result is valid, provided quantitative or near quantitative adsorption takes place. An expression based on a solution to equation (9) for an annular system would provide an interesting result. However, in the context of gas sampling the derivation of such an expression would make little material difference.

Applications to Analysis

Organic Atmospheric Species

Comparatively few results have been published on the collection of volatile organic compounds with denuder systems. Most of the work in this area has been concerned with species originating in automobile exhaust emissions. Annular denuders have been used to collect formaldehyde[24] and, using
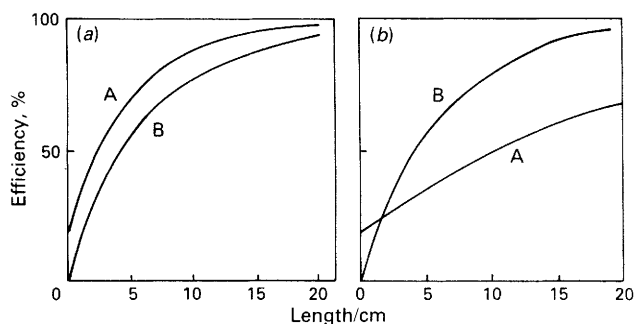

Fig. 4. Graphs of predicted collection efficiency versus denuder length. A, Possanzini equation; B, Gormley equation. (a) Sulphur dioxide; (b) nitrogen dioxide

a sodium hydrogen sulphate - triethanolamine coating, test atmospheres of 0.4 mg m⁻³ of formaldehyde in air were determined. A detection limit of 0.3 μg m⁻³ of formaldehyde in air was calculated for a sample time of 24 h and a flow-rate of 0.15 m³ h⁻¹, although no supporting data were given to validate this claim. The analysis involved leaching the collection surfaces with water and using the chromotropic acid spectrophotometric technique[24] to determine the formaldehyde content of the washings. Phenol was found to interfere with the analysis. A 10–20% loss in apparent formaldehyde was reported for a phenol to formaldehyde ratio of 1 : 2. The effects of humidity and temperature on the analysis were not reported. A study of ageing indicated that coated exposed and unexposed units underwent no significant change after being sealed for 4 weeks. The conditions under which they were stored were not described.

This work was subsequently extended to include other low boiling-point aldehydes, using high-performance liquid chromatographic (HPLC) techniques.[25] Annular denuders were coated with 1% 2,4-dinitrophenylhydrazine and phosphoric acid in acetonitrile. Sampled aldehydes underwent derivatisation on adsorption yielding the appropriate 2,4-dinitrophenylhydrazone derivative. The products were eluted with acetonitrile, separated using HPLC and detected by UV - visible absorbance measurements or voltammetry. Test atmospheres of 1.2 mg m⁻³ of propionaldehyde in air and 1.6 mg m⁻³ of acetaldehyde in air were determined from sample volumes in the range 0.015–0.095 m³. Collection efficiencies observed for this system were significantly lower than predicted. Variations in solubility were advanced as an explanation, but no experimental evidence was given in support of such a mechanism. Variations in the stability and the kinetics of the derivatisation products and processes were not discussed, and the possibility of non-quantitative adsorption was not considered either. The effect of humidity on the system was investigated and relative humidity levels of 50–90% were found to have no effect on the collection efficiency. Lower humidity levels were not reported. Samples taken from cigarette smoke, diesel exhaust and rural air were presented, showing that a number of aldehydes had been collected including acrolein and propionaldehyde. No data were given as to the stability of the unit with time, nor to the effects of chemical interference.

Further studies with annular denuders resulted in gaseous organolead compounds being determined.[26] Tetraalkyllead compounds were trapped on an iodine monochloride coating, stabilised in a polyethylene glycol - Carbowax 600 matrix. Elution was performed manually by washing with acidified hydrogen peroxide and the resulting washings were analysed using atomic absorption spectrometry at the 283.3-nm lead absorption line. The initial characterisation of this system was based on tetraethyllead atmospheres. However, the experimental details reported were sparse, with few details of concentration, calibration, sample volume or sensitivity being supplied. Interference from chemical or physical sources was not considered, but a study of ageing revealed that exposed

tubes could be stored for 3 d prior to analysis without any significant effect on the final result. The storage conditions were not given. In initial field trials of this system, samples taken from underground garages were found to have concentrations of organic lead as high as 1.5 µg m^{-3} in air, which was claimed to comprise 27% of the total lead content of the atmosphere. The technique could not distinguish between different organic moieties and the determination of a specific organolead compound was not possible.

A glass tube coated to a depth of 0.1 µm with the soot from a benzene or toluene flame has been employed as a general purpose gas adsorber.[27] The system was interfaced directly to a gas chromatograph and sample transfer was effected by thermal desorption. A temperature of 270 °C was maintained for 2.5 min to ensure quantitative desorption of all the trapped compounds. No other information was given as to the construction or operation of the thermal desorption unit. Diffusion coefficients calculated on the basis of the Gormley - Kennedy equation[3] were presented. As non-quantitative adsorption was reported, the validity of this method is questionable, for the perfect sink criterion of the Gormley - Kennedy solution was not fulfilled. Vapour profiles arising from the headspace analysis of foodstuffs, and from shipboard atmospheres were presented. Distinct vapour patterns were clearly obtained, but neither high-volatility compounds, nor low-volatility compounds normally associated with the particulate phase, were retained. No calibration or sample volume data were presented and no claims were made as to the sensitivity of this technique.

Ammonia Species

Ammonia occurs at low concentrations in the atmosphere and is thought to control atmospheric acidity owing to the formation of ammonium salts, which results in acid removal.[28,29] The equilibrium between ammonia and its salts is complicated due to the large number of precursors and reaction products involved. The model may be simplified by considering ammonia in the vapour phase to be in equilibrium only with ammonium nitrate.[30] Sampling using filtration techniques has led to the introduction of artifacts in the measurement of this equilibrium. The analyte might be overestimated by the release of ammonia from ammonium nitrate; alternatively, particle - particle reactions of ammonium salts with alkaline particles may result in the release of gaseous ammonia. The ammonia concentration might be underestimated as a result of the reaction of gaseous ammonia with acids deposited on the filter. It is important, therefore, to employ a sampling strategy that separates gaseous and particulate species.

Ferm[14] first reported the use of a denuder system for the measurement of ambient ammonia. The separation of gaseous ammonia from its particulate phase was achieved by employing a cylindrical denuder tube (l = 50 cm, i.d. = 3 mm) coated with oxalic acid. The analysis was achieved by dissolution of the sorption layer with 2 cm^3 of 0.1 M NaOH solution and the ammonium ions were determined by an ion-selective electrode with a detection limit of 8.5 mg m^{-3} of ammonia in air.

Collection efficiency studies[14] were carried out for ammonia in air in the concentration range 8.5–51 µg m^{-3}, with a sampling time of 24 h and a flow-rate of 2.9 l min^{-1}; collection efficiencies of 90.6% were achieved. An experimental value of 2.47 × 10^{-5} m^2 s^{-1} was obtained for the diffusion coefficient of ammonia, in agreement with a value of 2.36 × 10^{-5} m^2 s^{-1} obtained by Coulson and Richardson[15] at 1 atm and 25 °C. Ferm[14] also investigated particle deposition by sampling the ambient atmosphere with 1 m long uncoated tubes for a period of 2 weeks. The interference due to the particle phase was claimed to be of the same magnitude as the detection limit. The possibility of vaporisation of the ammonium ion, which may be significant with a sampling time of 2 weeks, was not considered.

Further studies of particulate deposition have been carried out by Dimmock and Marshall[31] using the technique described by Ferm. Ammonium nitrate aerosols were generated by an ultrasonic nebuliser and characterised by light scattering. Their results showed that 2.84 µg m^{-3} of ammonium nitrate in air contributed 0.2 µg m^{-3} to a measured free ammonia concentration of 22.45 µg m^{-3}. It was also reported that the concentration of ammonia recorded by this technique was dependent on the timing of the analytical procedure. Coated denuder units left to stand unsealed for 2.5 h prior to their analysis gave blank values ten times greater than normal. Similar units that were sealed before being left to stand showed no significant uptake of ammonia, even after 4 d. Further, exposed units that were sealed and stored before analysis gave elevated values for the ammonia concentration. The maximum increase in concentration reported was 20% relative to units analysed immediately after sampling. A 10-min period was sufficient to produce a measurable difference. The authors emphasised the importance of prompt analysis of exposed denuder samplers, although an explanation for these effects was not offered. The collection of ammonia by the unexposed tubes left open to the atmosphere can be explained by a passive diffusive process. Ammonia present in the air within the denuder tube is removed rapidly by the collection surfaces. The concentration gradient that results between the ammonia-free atmosphere in the denuder and the ambient air causes continuous transport of ammonia to the surface of the denuder. The diffusional pumping continues until the collection surfaces are saturated.

The reported increase of trapped ammonia in the sealed and exposed units can be attributed to the dissociation of trapped particulates within the sealed assembly. Particulate impaction occurs in the laminar flow subduction zone during sampling. Normally this region is excluded from the subsequent analysis; in a sealed denuder unit the natural equilibrium between these solids and free ammonia is disrupted, causing dissociation of the solids. The liberated ammonia is promptly trapped by the collection surfaces. These observations are important and any measurement technique for ammonia should take effects such as these into account.

Annular denuder tubes (l = 25 cm, annulus i.d. = 0.16 cm) coated with 1% oxalic acid in methanol have been used for sampling ammonia and ammonium ion species.[30] A flow-rate of 20 l min^{-1} and a sampling time of 30 min were used. Sampling artifacts were analysed by employing two denuders placed in series and separated by a filter and the concentration of gaseous ammonia was determined by analysing the contents of the first denuder. The ammonium ion concentration was determined as the sum of the ammonium in the filter and the ammonia released by the filter into the second denuder. The data showed that there was a significant release of free ammonia from the filter. In one instance 6.98 µg m^{-3} of free ammonia were measured in the second denuder. A second corresponding concentration of 7.9 µg m^{-3} of ammonium particulates was determined on a Gelman GA-4 type filter. The artifact appeared to vary not only with different types of filter but also with the same filter.

Dasgupta[32] has described a denuder tube with a thin cation-exchange membrane as the collecting element. Gaseous ammonia was collected on the perfluorosulphonate membrane as the ammonium ion, which diffused through the membrane and was carried off in a dilute acid stream for analysis by ion chromatography. The acidic solution also served to maintain the exchange sites in the H$^+$ form. Collection efficiencies of greater than 99% were obtained for ammonia concentrations from 15 ng m^{-3} to 1.2 µg m^{-3}, with flow-rates from 0.44 to 1.54 l min^{-1}. The cation-exchange membrane will allow a number of species to diffuse through; however, no interference studies were carried out. The gas phase limit of detection was predicted to be 45 ng m^{-3} of ammonia in air.

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The use of two denuders in series separated by a filter, illustrates the extent of ammonia release associated with filters[30] and the importance of denuder tubes as sampling devices. The accurate determination of low levels of free ammonia in the atmosphere is made possible by the use of oxalic acid coated denuder tubes. However, immediate analysis of the oxalic acid coated denuder is required to avoid dissociation of ammonium particulates in the subduction zone. Particulate dissociation may be significant where long sampling times are required and, in addition, long sampling times do not permit diurnal studies. Annular denuder tubes, however, may be used to overcome many of these problems. The oxalic acid technique, although low-cost, is labour intensive and difficult to automate. The problem of ammonia adsorbing on to the uncoated glass sections of a denuder system has been neglected, despite the work of Dasgupta.[32] Until the results of such a study are known, the error associated with such processes is difficult to estimate.

Dasgupta's design of the denuder tube[32] is an important development in the technique. A variety of gaseous atmospheric species may be sampled by using the appropriate membrane material and scrubber solution. If the scrubber solution is used as part of a continuous flow analysis system, then spectrophotometric methods of detection can be employed, although in this mode the concentrating ability of the device is largely lost.

Nitrate Species

Nitric acid is an important acidic atmospheric species. Its measurement and that of its salts in the particulate phase enable the role of nitrogen oxide species in atmospheric chemistry to be elucidated.

Nitric acid and nitrate salts have been sampled using dual-filter techniques in which particulate nitrate was collected on the first filter and nitric acid on the second.[33,34] This method gives rise to positive and negative interferences arising from sampling artifacts. Nitric acid will be converted to the solid nitrate in the presence of sodium chloride or basic particulate species.[35] Conversely, the dissociation of ammonium nitrate, or its reaction with sulphuric acid, gives rise to elevated nitric acid levels within the sampling assembly, with an accompanying reduction in the nitrate-containing species.[36,37] Shaw et al.[38] overcame these problems with a denuder difference experiment. This method employs two sampling assemblies, both consisting of a nylon filter that collects both gaseous HNO_3 and particulate nitrate; in one of the assemblies the filter was preceded by a denuder tube coated with magnesium oxide. The difference between the amounts of nitrate collected in the two assemblies was due to the removal of gaseous nitric acid from the sample. Experiments run for 23 h at a flow-rate of 3.4 l min^{-1} showed that nitric acid concentrations exceeded those of particulate nitrates. Diurnal studies revealed that particulate nitrate concentrations remained fairly constant, whereas nitric acid levels increased during the day.

In a comparative study, particulate nitrate and nitric acid were measured by the penetration, denuder difference and dual-filter methods.[39] The sampler for the penetration method consisted of two nylon-lined denuder tubes (l = 80 and 18 cm) separated by a Teflon filter. Sampling was carried out at a flow-rate of 1.5 l min^{-1} with a sampling time of 24 h. Nitric acid and volatile particulate nitrates were analysed from the long upstream denuder. The short downstream denuder was used to collect the volatile particulate nitrate only. The denuder tube assembly used in the denuder difference technique allowed shorter sampling times. The assembly consisted of nine denuder tubes (l = 50 cm, i.d. = 3 mm) coated with sodium hydrogen carbonate.

The results of the two denuder methods and the dual-filter method for total inorganic nitrate agreed.[39] However, the dual-filter method gave a very high value (4.52 μg m^{-3}) for

nitric acid in air; this could be due to the dissociation of particulate ammonium nitrate. A nitric acid concentration of 3.75 μg m^{-3} was obtained by the penetration method compared with an average of 3.11 μg m^{-3} for the denuder difference method. This overestimation is thought to be due to turbulent flow caused by the intersection of the flow stream with the leading edge of the nylon filter. Alternatively, it has also been suggested that the collection efficiencies of the two methods are incorrect. The penetration method has a relatively poor sensitivity and requires time-consuming sample preparation and it appears to have no advantage over the denuder difference method, which has been shown to give precise experimental data.

The denuder tube methods described assume that the evaporation of particulate nitrates as they pass through the denuder tube is negligible. Larsen and Taylor[40] examined the artifacts that may arise from the sampling of ammonium nitrate aerosols. Gaseous ammonia and nitric acid were removed from the ammonium nitrate aerosol by means of a diffusion stripper employing sodium hydroxide and sulphuric acid chemical sinks. The rate of evaporation was measured by following the changes in size distribution of the aerosol with time.

Resistance to the transport of molecules across the vapour-liquid interface was small and sampling errors due to the evaporation of ammonium nitrate were calculated to be 2.5 and 1.8% for gaseous nitric acid and particulate ammonium nitrate, respectively. A number of factors will, however, cause these errors to decrease. Steady-state gas profiles in the denuder are not achieved instantaneously, hence in the time required to form steady-state profiles, the evaporation of particles would be less as a result of the higher concentration. Calculations performed by Stelson and Sienfeld[41] suggest that in the presence of ionic mixtures such as ammonium sulphate and ammonium nitrate the vapour pressures of ammonia and nitric acid would be lowered, and hence the sampling error would be lower.

Ferm and Sjodin[42] used a cylindrical denuder tube coated with sodium carbonate to sample nitrous acid. A flow-rate of 2 l min^{-1} yielded a collection efficiency of 95%. The sodium carbonate denuder was leached in water and the nitrite concentration was determined spectrophotometrically. A number of sampling artifacts exist including the formation of nitrous acid in the presence of nitrogen monoxide, nitrogen dioxide, water and peroxyacetylnitrate (PAN), the last of which is also partly adsorbed and hydrolysed to the nitrite. Corrections for interferences may be made by placing two denuder tubes in series. Assuming a 96% collection efficiency the ambient nitrous acid concentration may be calculated from the following equations:

$$I = 0.96[HNO_2] + \sigma_1 \qquad \cdots \quad \cdots \quad (39)$$

$$J = 0.0384[HNO_2] + \sigma_2 \qquad \cdots \quad \cdots \quad (40)$$

where I and J are the average nitrite contents in the denuders and σ_n denotes the fraction of nitrite not originating from ambient nitrous acid. As σ_1 and σ_2 are equal, solving equations (39) and (40) gives $[HNO_2] = 1.085(I - J)$. The applied corrections are not applicable where the concentrations of PAN are greater than those of nitrous acid. The method is therefore only useful in air close to NO_x sources, such as polluted urban air. It cannot be used to measure natural background levels of nitrous acid.

Automated monitoring of nitric acid and ammonia has been achieved by multi-stage selective thermal desorption from a tungsten(VI) oxide coated cylindrical denuder tube.[19,43] The analysis took 40 min with a sensitivity of sub-p.p.b. The adsorption of ammonia on tungstic acid is thought to be an acid-base reaction that is reversible at 350 °C

$$NH_3 + H_2WO_4 \xrightleftharpoons[]{350\,°C} NH_4HWO_4$$
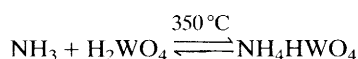
The mechanism for nitric acid adsorption is unclear, although it has been suggested that irreversible adsorption is involved. Nitric acid desorbs as nitrogen dioxide. The denuder tubes are coated by the vacuum deposition of tungsten wire. Blue tungsten(IV) oxide is oxidised to yellow tungsten(VI) oxide by heating at 500 °C. Alkylamines, nitrogen dioxide and PAN were all shown to interfere. The amount of ammonia adsorbed decreased in the presence of 100 p.p.b. of ozone. Diurnal studies of nitric acid and ammonia showed that in most instances higher nitric acid concentration maxima correlated with lower ammonia concentration maxima. Diffusion coefficients obtained by section analysis agreed with those reported by Wilke and Lee.[44] Braman et al.[19] concluded that, although the nitric acid may be associated with water or other compounds, hence decreasing the diffusion coefficient, ammonia existed in the non-associated form. These findings contradict those of a parallel study,[45] which showed that ammonia existed in its associated form. The tungstic acid denuder used in this study was prepared by coating six sections of tubing ($l = 15$ cm, i.d. = 0.56 cm) with a thin film of sodium hydroxide (0.5 M) - sodium tungstate [0.05 M in water - propan-2-ol (50 + 50 V/V)]. By rolling the tubes on a horizontal roller the coating was air dried. Sodium tungstate was converted to tungstic acid by passing hydrogen chloride through the tubes, which were then washed with water to remove sodium chloride and then heated at 500 °C in a furnace for 8 h. The sample capacity was shown to be much greater than that of the tube coated by vacuum deposition of tungsten wire although the vacuum deposition method did produce blank values that were 20 times lower. Both nitrate and ammonia were extracted quantitatively with three successive 3-cm³ portions of 1.0 mM LiOH solution at 90 °C and then the nitrate and ammonium ions in the extract solution were determined by ion chromatography.

The measurement of atmospheric nitric acid[46] was carried out in a comparative study of the tunable diode laser absorption, tungstic acid denuder tube and Teflon - nylon filter-pack methods. The laser method gave higher nitric acid concentrations than the other methods and quantitative agreement between these techniques was not obtained, although general trends in the variation of the nitric acid concentration could be identified. The tungstic acid method measured higher nitric acid concentrations than those using the filter pack, the difference being 5% for daytime measurements and a factor of two lower during the night. The difference could be due to the retention of nitric acid on the particulate matter of the filter.[47,48] The tungstic acid method also showed higher particulate nitrate concentrations than the filter-pack method and this may be due to the dissociation of particulates on the filter. Nitric acid concentrations were investigated in a further comparative study of the tungstic acid and filter-pack methods.[49] The former gave nitric acid concentrations three times higher than the latter and this difference was attributed to interference from organic nitrates in the denuder tube; however, no data were produced to confirm this. Interferences from nitrogen dioxide, PAN and propyl nitrate in the denuder tube were shown not to be significant.

A number of denuder tube techniques have been developed for the measurement of nitric acid with the tungstic acid denuder tube being the most widely reported for this purpose. Since its introduction, a number of studies have compared the tungstic acid method with measurements performed using other techniques, the result being a great deal of scatter in the inter-comparison. However, it was shown that the tungstic acid denuder tube produced larger apparent nitric acid mixing ratios than the filter-pack technique and the source of this difference has not yet been identified. The dissociation of particulate nitrates in the subduction zone of the denuder tube, which is particularly likely if the subduction zone is heated during the thermal desorption cycle, has not been

considered. In a recent study Roberts et al.[50] concluded that tungstic acid coatings were subject to "slow evolutionary and occasionally catastrophic failure," indicating that tungstic acid coatings are not viable for long-term unattended use. There is a need for properly characterised adsorbing surfaces with high thermal stabilities and in this respect transition metal oxide surfaces may prove useful.

Hydrogen Chloride

Natural sources of hydrogen chloride include the reaction of marine-salt aerosols with atmospheric sulphuric and nitric acids, or volcanic emissions. The gas can also be released from refuse incineration plants and result from the combustion of certain types of coal.

Dimmock and Marshall[51] described a manual method for the determination of hydrogen chloride using a cylindrical denuder tube coated with sodium fluoride. The extraction was carried out using distilled water with detection by a chloride ion-selective electrode. Adsorption efficiencies >90% were obtained and the room air sampled was found to contain hydrogen chloride concentrations in the range 0.16–0.55 µg m⁻³. Interferences from particulate chloride, sulphur dioxide and nitrogen dioxide were found to be negligible.

Sulphur Species

Sulphur dioxide has been sampled with a cylindrical denuder tube coated with a mixture of sodium tetrachloromercurate(II) and malein buffer [the malein buffer was used to neutralise the hydrogen chloride produced during the reaction between tetrachloromercurate(II) and sulphur dioxide].[20] The cylindrical denuder tube was coated by injecting 0.4 cm³ of 0.1 M sodium tetrachloromercurate(II) - 0.1 M malein buffer in 1 + 1 methanol - water. The extraction was carried out using distilled water and the analysis by isotope dilution.

Sampling was performed in a polluted industrial atmosphere with a sampling time varying from 3 to 24 h with the relative humidity in all instances being >50%. Collection efficiencies of 90% were achieved except where the relative humidity approached 100% and the results obtained for the collection of sulphur dioxide in denuders and on potassium hydroxide filters agreed.

Gas-phase concentrations of dimethyl sulphate and monomethyl hydrogen sulphate have been determined by collecting the species on cylindrical denuder tubes.[52] A paper-lined denuder tube was used for the collection of monomethyl hydrogen sulphate and a nylon denuder was used for sampling total gas-phase alkyl sulphates. Dimethyl sulphate was first collected on an XAD-2 resin bed and then determined by ion chromatography. The aqueous-extractable dimethyl sulphate hydrolyses to the monomethyl hydrogen sulphate and the increase in the monomethyl hydrogen sulphate concentration between the paper and the nylon denuder tubes was used as a measure of the dimethyl sulphate concentration.

Agreement between the expected and calculated diffusion coefficients supported the identification of dimethyl sulphate and monomethyl hydrogen sulphate as the species adsorbed on the denuder tubes. Laboratory studies did, however, show that up to 10% of the sulphur dioxide passing through the nylon denuder may be adsorbed on the walls, and a correction procedure was developed to overcome this interference effect. In field trials, this denuder approach did not yield results that agreed with those obtained from filter-based techniques. The authors[52] stated that the agreement was not good and they were unable to indicate which technique was the most reliable.

Ambient sulphuric acid aerosols have been sampled by means of a heated denuder tube coated with manganese and palladium oxides[53] with interferents being selectively removed from the sample by a series of pre-denuders. On completion of

sampling the denuder was placed in an oven and desorbed thermally at 800 °C into a convertor, which reduced any sulphur liberated to hydrogen sulphide, before being passed into a silver wool chemical pre-concentrator. Flash heating of the silver wool resulted in a concentrated injection of hydrogen sulphide into the gas chromatograph. A detection limit of 0.1 μg m^{-3} of sulphuric acid in air was obtained using this technique. A study of particulate dissociation at various denuder temperatures was undertaken and this underlined the possible dissociation of particulates in the subduction zone during thermal desorption. The results of this study indicated that dissociation of particulates trapped on the walls of the laminar flow subduction zone could occur during thermal desorption. Such findings[53] have important ramifications for the design criteria of automated denuder systems.

Multi-component Sampling

The criterion of laminar flow limits the sample flow-rate; therefore, in order to collect a measurable amount of analyte, long sampling times are required. To overcome this problem Stevens *et al.*[13] utilised 16 parallel tubes arranged in a circle to separate ammonia from ammonium salt particulates. No data relating to the amount of ammonia trapped were given in this report, and the problems of ensuring the reproducible handling of 16 tubes were not discussed. Forrest *et al.*[47] employed 48 sodium carbonate coated cylindrical tubes for sampling nitric acid, which allowed sampling flow-rates of 10–30 l min^{-1}. In this study, the unit was heated such that the relative humidity of the sample was lowered below the deliquescence point of sodium carbonate. The authors claimed that this did not significantly influence the results obtained, but the supporting data were not comprehensive. The results of a detailed study into such a procedure would establish whether heating the sample to permit better instrument operation is an acceptable practice in this area of application. Lewin and Hansen[54] described a diffusion denuder assembly, which, by means of a vacuum and a pressurised air system, allows the individual coating and extraction of 15 quartz glass tubes. This semi-automated method enabled denuder tube assemblies to be coated with a number of selective absorbents, decreasing the risk of contamination compared with manual methods.

Ammonia was sampled using tubes coated with 1.5% oxalic acid in ethanol[54] and acidic gases were sampled using tubes coated with 1 M potassium hydroxide in methanol. Automatic spectrophotometric methods were employed for sulphate, nitrate and chloride determinations and the indophenol method for the determination of ammonia. The data supplied for this system were sparse and few details on sensitivity, reproducibility and calibration procedures were given. However, the advantages of using the device described for batch-processing denuder tubes are self evident.

Liberti *et al.*[55] employed three annular denuders in series for the determination of sulphur dioxide, ammonia, nitric acid and hydrogen chloride. Sulphur dioxide was sampled using a sodium tetrachloromercurate(II) coated tube. Collection efficiencies >90% were obtained for sulphur dioxide with a sampling flow-rate of 20 l min^{-1}. Ammonia was sampled with an oxalic acid coated tube, and hydrogen chloride and nitric acid on a sodium fluoride coated tube. Little experimental detail was reported, but data obtained from the denuder assembly over a 7-month period indicated that ammonia and sulphur dioxide could be monitored with such a system. Nitric acid and hydrogen chloride were detected only intermittently by the unit. No explanation was given for this behaviour, and complementary data from other techniques would be required to support any conclusions drawn from their results regarding the presence, or lack of it, of hydrogen chloride and nitric acid in the sample.

A series of coated cylindrical denuder tubes operated at different temperatures was used to collect free ammonia and to distinguish nitric acid from ammonium nitrate and sulphuric acid from ammonium sulphate by their different thermal behaviour.[56] The tubes were extracted with doubly de-ionised water. Ammonium ions were detected by means of a gas-sensing membrane and nitrate and sulphate species were determined by ion chromatography.

The tubes were coated for collecting nitric acid, free ammonia and sulphur dioxide.[56] A tube operated between 390 and 410 K and coated with sodium fluoride was used for the collection of sulphuric acid and a sodium fluoride coated tube operated at 490–510 K was used to retain the sulphuric acid produced from the dissociation of ammonium sulphate and a further tube collected the liberated ammonia.

This last technique appears to be a simple and low-cost method for carrying out multi-component analysis. However, the dissociation of ammonium nitrate and sulphate before they reach their target tubes causes a degree of uncertainty and it was noted that at ammonium nitrate concentrations of 20 μg m^{-3}, half of the liberated nitric acid was found in the first tube.

The selective collection and determination of airborne sulphuric acid and ammonium sulphate has also been achieved using two copper(II) oxide coated denuder tubes at temperatures of 120 and 240 °C, respectively.[57] This method relies on the adsorption of sulphuric acid on copper - copper(II) oxide and the decomposition of ammonium sulphate at temperatures above 220 °C. The resulting copper sulphate was converted to sulphur dioxide by heating at 800 °C and then measured using a flame photometric detector. Interferences due to inorganic and organic sulphur species were avoided by passing the sample stream through potassium carbonate and active carbon-coated denuders.

The copper - copper(II) oxide was prepared by filling the tube with 3% m/V hydrated copper(II) nitrate in ethanol. The tube was emptied, dried first at room temperature and then at 200 °C to remove water of crystallisation. Nitrogen was passed through the tube at 400 °C for 5 min. Both ends of the tube were cleaned by inserting the tube in 1 M nitric acid and a black copper - copper(II) oxide coating was obtained after flushing with nitrogen and heating at 900 °C for 5 min. The technique employed two parallel copper - copper(II) oxide denuders. After completion of the sampling period in the first set of denuders, the sample flow was switched to the second set of denuders and the first set was analysed individually.

The data presented showed that very little ammonium sulphate was found in the first tube at the selected temperatures and at ammonium sulphate concentrations above 30 μg m^{-3}. No data were presented for possible dissociation artifacts at ammonium sulphate concentrations below 30 μg m^{-3}. This may be significant as the measured ambient ammonium sulphate concentrations were less than this value. Earlier work with the sodium fluoride manual method showed that dissociation of ammonium sulphate becomes significant at lower concentrations.[56] The copper - copper(II) oxide denuder tube has also been employed for the measurement of sulphur dioxide.[58] The effect of humidity on collection efficiencies and an investigation of sulphur-based interferents were carried out in the same study. A significant decrease in the collection efficiency with decreasing humidity was reported, but no explanations for the reasons were given. The interference from organic sources was stated as "not important" and data were presented that demonstrated agreement between results obtained from denuder systems and those produced through filter techniques insensitive to the presence of organic sulphur species. The reproducibility of the technique was claimed to be 3% and the available data showed the relative standard deviation to vary between 1.5 and 5%.

Slanina[59] have developed a "wet denuder" system for the sampling of ammonia, nitric acid, hydrochloric acid, sulphur dioxide and hydrogen peroxide. The wet denuder consisted of

an annular denuder coated with an aqueous layer, which was rotated about its axis to keep the surfaces wet. Two parallel wet denuders were employed. In one denuder the absorption solution contained formaldehyde and p-hydroxyphenylacetic acid to collect and stabilise sulphur dioxide and hydrogen peroxide. The absorption solution in the second denuder contained a formic acid buffer of pH 4 for the collection of ammonia, nitric acid and hydrochloric acid. After sampling, the absorption solutions were pumped out of the denuders into two sampling tubes. Hydrogen peroxide and sulphate were determined using fluorimetric and photometric detectors, ammonium ions by spectrophotometric measurement and nitrate and chloride ions by ion chromatography. A cyclone was used to reduce interferences from particulates. The effects of rotation of the collection surfaces and moving liquids within the denuder unit on laminar flow and particulate transmission efficiency were investigated; no significant perturbation of the system was reported. Clearly, the device described has other atmospheric monitoring applications and this approach may be expected to be extended to other areas of atmospheric analysis.

Conclusions

The determination of atmospheric species is fraught with problems; the dynamic equilibria between the various species make their determination particularly difficult. Separation of the gas and particulate phases by denuder tubes avoids the artifacts that may otherwise occur with filter-based methods. The denuder tube has the additional advantage of pre-concentrating the gaseous analyte, which is not possible using conventional filters. Denuder tubes have proved to be an important development in atmospheric sampling, allowing the daily patterns and long-term trends of atmospheric species to be discerned.

The use of simple, cylindrical denuder tubes has several disadvantages. Their use is labour intensive, as both a coating procedure and extraction of the collected gases are involved and the low sampling flow-rates require long sampling times, hence causing a number of other artifacts. The introduction of the annular denuder tube allows much higher sampling flow-rates and hence shorter sampling times and the use of thermal desorption denuders eliminates the need for washing or re-coating. However, in this last method, the interference due to vaporisation of particulates in the subduction zone has not been clearly established. The wet denuder system has placed a much older sampling device, the bubbler, into a denuder tube context and may have wide application for the monitoring of thermally unstable species.

A degree of complexity has been introduced by the development of multi-component denuder tube systems. However, further fundamental work has to be carried out to realise the full potential of the technique. In particular, considerations have to be made about the nature and influence of non-adsorbing surfaces within the denuder tube. Considerations also have to be made about the employment of various sampling strategies such as the incorporation of iso-kinetic sampling from laminar gas flows.

The use of a wide range of denuder tube systems has been demonstrated, although they have been employed mainly for the measurement of species involved in atmospheric pollution and acid rain studies. Few applications have been reported for organic vapours in the atmosphere. It is most likely that the applications to which denuder tubes are employed will increase in the future, as they are attractive by virtue of their simplicity, ruggedness and ability to undergo long-term exposure to particle-laden atmospheres with minimal interference from the aerosol and particle content.

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