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ARTICLE *in* ANALYTICAL CHEMISTRY · OCTOBER 1994

Impact Factor: 5.64 · DOI: 10.1021/ac00092a032

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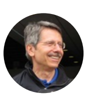

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Anal. Chem. **1994,** *66,* 3503–3504

Comment on Wet Effluent Denuder Coupled Liquid/Ion Chromatography Systems: Annular and Parallel Plate Denuders

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Simon and Dasgupta (Simon, P. K.; Dasgupta, P. K. *Anal. Chem.* 1993, *65*, 1134–1139) have reported on the design and characterization of high-efficiency wetted denuders of parallel plate and annular geometries. On the basis of laboratory results evaluated according to a theoretical treatment which refers to previous literature, they found that a "supertheoretical" collection efficiency was exhibited by the parallel plate denuder. It was found that a factor of 2 should be taken into account in the expression which describes the diffusion-based collection efficiency. By using the correct formula, the parallel plate denuder shows an excellent agreement to the theoretical efficiency curve. Discrepancies noted in the paper for the annular denuder and possible explanations for them have also been discussed.

In a recent paper in this journal, Simon and Dasgupta[1] described an interesting instrumental application of denuder technology. They reported on the design and characterization of high-efficiency wetted denuders of parallel plate (PPD) and annular (AD) geometries.

I feel that some reflections on this and earlier papers could be useful for defining better the issue of collection efficiency of denuders.

On the basis of the laboratory results evaluated according to a theoretical treatment reported by Ali et al.,[2] which refers to a paper of Gormley,[3] Simon and Dasgupta found that "... a supertheoretical collection efficiency was exhibited by the parallel plate denuder...". This anomalous behavior has a simple explanation. In their paper, they assume that the collection efficiency (f) for a PPD is expressed by

$$1 - f = 0.91 \exp(-3.77\alpha DL/Q) \tag{1}$$

where D is the diffusion coefficient of the gas, L is the length of the tube, and Q is the volumetric flow rate. For a PPD, the parameter α is given by

$$\alpha = b/a \tag{2}$$

where b is the long dimension of the denuder cross section.

The correct value for a, as deduced from the original paper of Gormley[3] or from Fuchs,[4] corresponds to the half-depth of the rectangular channel and not, as Simon and Dasgupta (following Ali et al.[2]) erroneously assume, to its depth. Therefore, a factor of 2 should be taken into account in the expression which describes the diffusion-based collection efficiency. Following Ali et al.,[2] Simon and Dasgupta also assume that this equation is valid for the annular denuder with the provision that α be defined as

$$\alpha = \pi(d_o + d_i)/(d_o - d_i) \tag{3}$$

where d_o and d_i are the outer and inner diameters defining the annulus, respectively. From the original paper of Gormley[3] it can be deduced that the equation for the annular denuder is the following:

$$1 - f = 0.91 \exp\left[-7.54\frac{\pi(d_o + d_i)}{(d_o - d_i)}\frac{DL}{Q}\right] \tag{4}$$

The correct formulas 1 and 4 have been applied to the evaluation of the PPD and AD denuders by using the data set obtained from Figure 6 of the Simon and Dasgupta paper. The results are shown in Figure 1. Now the PPD shows an excellent agreement to the theoretical efficiency curve, whereas the AD shows a systematic negative deviation, especially at higher flow rates.

Simon and Dasgupta advance some hyphotheses related to the practical aspects of the PPD geometry, such as formation of dry spots, or of "oscillating waves" in the liquid film, that can alter the theoretical performance of the denuder. These hyphotheses can also be considered viable in the case of the AD geometry.

In particular Simon and Dasgupta point out that the hydraulic cross section of the AD is substantially lower than that of the PPD. This results in a corresponding higher flow velocity which can cause the efficiency to be significantly underestimated because of channeling and dry spot formation.

It should be stressed that theoretical predictions simply establish an upper limit which can be reached or not, depending on the characteristics of the denuder (in particular on the reactivity of the coating).

In general, if we are interested in the behavior of a denuder, be it a cylindrical, annular, or parallel plate, the determination of the collection efficiency can be calculated by the Winiwarter equation,[5] a solution of Fick's diffusion equation which holds at any geometry of the denuder. Following this approach, the fractional penetration of a pollutant inside a denuder can be expressed as a function of the parameter $k = d_i/d_o$ by means

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(3) Gormley, P. G. *Proc. R. Ir. Acad. Sec. A* **1938**, *45*, 59–63.
(4) Fuchs, N. A. *The Mechanics of Aerosols*; Pergamon Press: Oxford, England, 1964; p 206.
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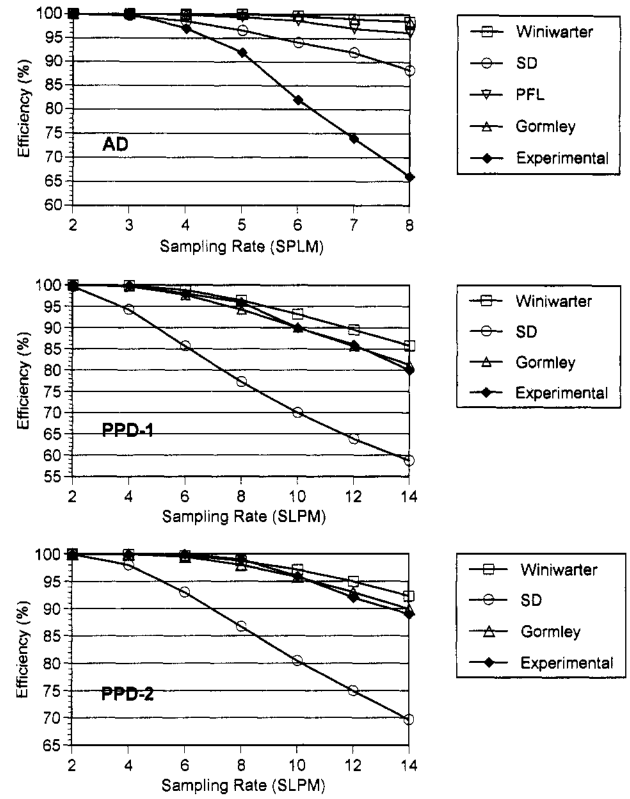

Figure 1. Collection efficiency of wet denuders for Simon and Dasgupta's data.

of the formula

$$C/C_o = B_{(k)} \exp(-\beta^2_{(k)}X) \tag{5}$$

with

$$X = (2LD)/d^2v_m$$

where d is the hydrodynamic equivalent diameter and v_m the mean flow velocity. The $B_{(k)}$ and $\beta_{(k)}$ values are obtained by numerical integration.

Parallel plate and cylindrical geometry represents an upper (k = 1) and lower (k = 0) limit, respectively, whereas the annular denuder employed in the Simon and Dasgupta paper is characterized by k = 0.7. The solutions in the case of the parallel plate ($(C/C_o)_{pp}$), and annular denuder ($(C/C_o)_{ad}$), derived from Table 1 and by graphical interpolation from Figure 2 of the Winiwarter paper, assuming laminar flow and that every collision to the wall results in uptake, are given by

$$(C/C_o)_{pp} = 0.91 \exp(-3.883^2X) \tag{6}$$

$$(C/C_o)_{ad} = 0.91 \exp(-3.874^2X) \tag{7}$$

In the units employed by Gormley these equations are (for the PPD denuder)

$$1 - f = 0.91 \exp\left[-15.08\frac{DL(2a + b)^2}{4Qab}\right] \tag{8}$$

(for the AD denuder)

$$1 - f = 0.91 \exp\left[-15.01\frac{\pi DL(d_o + d_i)}{2Q(d_o - d_i)}\right] \tag{9}$$

If we assume that $b \gg a$, eq 8 becomes the expression used by Gormley.[3] As an example of the application of the Winiwarter equation and of the limits imposed by the nature of the coating, we might consider a paper of Possanzini et al.[6] These authors adapted the well-known Gormley–Kennedy equation for cylindrical denuders[7] to annular geometry and suggested an empirical equation on the basis of the sampling efficiency of annular denuders coated with tetrachloromercurate for the collection of SO_2. In the same units as above their equation is

$$(C/C_o)_{ad} = 0.85 \exp(-3.36^2X) \tag{10}$$

The comparison with the Winiwarter theoretical solution ($B_{(k)}$ and $\beta_{(k)}$ values calculated for k = 0.75) shows that the theory values are significantly higher than the experimental values (B is 0.91 and β is 3.878). Winiwarter contended that a better agreement between the two expressions can be achieved by adaptation of one parameter and suggested an optimized diffusion coefficient $D = 0.107$ cm^2/s. This procedure has no physical meaning as in the expression 6 the values for $B_{(k)}$ and $\beta_{(k)}$ arise from the channel geometry and reactivity of the wall, respectively. A simple explanation for the observed discrepancy is that the theoretical equation assumes, as stated above, complete retention of the pollutant upon contact with the coated surface (the wall should be a "perfect sink"). Apparently, this is not verified in the case of tetrachloromercurate and SO_2. A better sink for SO_2 is sodium carbonate, a coating species which has subsequently been adopted by the same authors.[8] The Possanzini et al.[6] equation (PFL in the figure) and the Winiwarter equation have also been applied to the data of Simon and Dasgupta for the annular denuder. The experimental values are much lower than theoretical predictions.

In conclusion, if we compare the experimental behavior of the PPD and the AD denuders, we can state that the surface coating used by Simon and Dasgupta presents the characteristics of a perfect sink (i.e., the PPD follows exactly the theoretical prediction) whereas the poor performance of the AD seems likely to be due to its design. It may be theoretically interesting to know why the AD behaves as it does. For instance, this could be done by examining AD denuders of different cross sections.

(6) Possanzini, M.; Febo, A.; Liberti, A. *Atmos. Environ.* **1983**, *17*, 2605–2610.
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Received for review April 12, 1994. Accepted June 27, 1994.[⊗]

[⊗] Abstract published in *Advance ACS Abstracts*, August 1, 1994.