

# On the design of capillary and effusive gas dosers for surface science

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We present a theoretical analysis of flux distributions and enhancement factors for dosers of two types: capillary arrays and arrays of effusive sources. Our analysis introduces an important distinction between the flux per solid angle and the flux per unit area of the sample, and encompasses array diameters both smaller and larger than the sample. We find, contrary to earlier assertions, that a single effusive source gives unacceptably large flux gradients unless it is located so far from the sample that its enhancement factor is negligible. Arrays of a small number of effusive sources located near the sample edge, however, are competitive with capillary arrays for doser-to-sample distances comparable to the sample radius, and are readily adapted to large or unusually shaped samples. Capillary arrays outperform effusive arrays at all doser-to-sample distances, and are particularly effective when placed very close to the sample. If flux uniformity is a concern, a capillary doser should generally be at least 20% larger than the sample. Additional effects due to trapping by cold surfaces in the chamber and multiple collisions of the emitted molecules are discussed qualitatively. © 1995 American Institute of Physics.

## I. INTRODUCTION

One of the most common needs in surface science is to expose a surface to a known and uniform flux of gas. In many cases this can be accomplished simply by filling the vacuum chamber to a uniform pressure. In other cases—highly reactive gases, gases that are not pumped effectively, gases that exchange rapidly on the chamber walls, very high flux levels—it is necessary to use a doser that provides a high flux at the sample while keeping the background pressure in the chamber low. The primary criteria in designing a doser are the uniformity of the flux on the sample and the enhancement factor. The enhancement factor is defined as the ratio of the flux at the sample to the flux on a surface elsewhere in the chamber, or equivalently the ratio of the “effective pressure” at the sample to the rise in the background pressure. The design of a doser inevitably involves a tradeoff between these two criteria.

We consider two common doser types: effusive, in which the aperture diameter is much larger than its length, and capillary, in which the diameter is much smaller than the length. Either type can be used singly or in an array. All dimensions are assumed to be much smaller than the mean free path of the gas molecules. Campbell and Valone<sup>1</sup> have published a theoretical analysis comparing capillary arrays with a single effusive source. They calculated flux distributions and enhancement factors for circular capillary arrays ranging from a single capillary to an array with a diameter equal to the sample diameter, for a range of sample-to-doser distances. Their results show that a single needle doser<sup>2</sup> gives a very large enhancement factor but an extremely nonuniform flux distribution. They also concluded that a single effusive source (“cosine emitter”) is in many cases as good as

a capillary array in both uniformity and enhancement factor. To obtain reasonable uniformity, a capillary array needs to be at least as large as the sample; no results were given, however, for arrays larger than the sample. Winkler and Yates<sup>3</sup> considered larger arrays but calculated only the enhancement factor, not the flux distribution.

In this paper, we extend Campbell and Valone’s calculations to larger capillary array sizes. We also show that a single effusive source is far *less* effective than their curves suggest, and indeed is usually inadequate unless a very large flux gradient across the sample is tolerable. We present flux calculations for effusive *arrays* consisting of a relatively small number of effusive sources situated near the perimeter of the sample, and show that such arrays can be competitive with capillary arrays if the doser is not too close to the sample.

## II. THEORETICAL BASIS

The starting point is the calculation of  $F(\theta)$ , the integral-normalized flow of molecules per unit solid angle from a single source, at an angle  $\theta$  to the source axis

$$F(\theta) = \frac{\pi I(\theta)}{N_{\text{tot}}}, \quad (1)$$

where  $I(\theta)$  is the flux in molecules  $\text{s}^{-1} \text{sr}^{-1}$ , and  $N_{\text{tot}}$  is the total flow out of the source in molecules  $\text{s}^{-1}$ . For an effusive source  $F(\theta)$  is

$$F(\theta) = \frac{\cos \theta}{\pi}, \quad (2)$$

and for a single straight capillary of length  $L$  and radius  $a$  it is<sup>4</sup>

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$$F(\theta) = \frac{1}{W}, \quad \theta = 0,$$

$$F(\theta) = \frac{2 \cos \theta}{\pi W} \left\{ \left( 1 - \frac{W}{2} \right) R(p) + \frac{2}{3p} (1 - W) \times [1 - (1 - p^2)^{3/2}] + \frac{\cos \theta}{2} \right\}, \quad 0 < \theta < \theta_c, \quad (3)$$

$$F(\theta) = \frac{\cos^2 \theta}{\pi \sin \theta} + \frac{\cos \theta}{2}, \quad \theta > \theta_c,$$

where  $p = L(\tan \theta)/2a$ ,  $R(p) = \cos^{-1}(p) - p(1 - p^2)^{1/2}$ ,  $\theta_c = \tan^{-1}(2a/L)$ , and  $W = (8a/3L)(1 + 8a/3L)^{-1}$ . As other authors have noted,<sup>4</sup> the flux from a capillary of large  $L/a$  is highly collimated; for  $L/a = 40$ , 97% of the molecules emerge within a cone of half-angle  $\theta_c = 2.9^\circ$ . Little is gained by using larger  $L/a$  ratios; the central peak becomes sharper, but the fraction of flux at larger angles does not change. For this reason, we will follow Campbell and Valone in using  $L/a = 40$  throughout this work.

The highly collimated flow from a single capillary has been cited<sup>1</sup> as demonstrating that a single needle doser is unsatisfactory. This conclusion is correct but probably overstated. The expressions for  $F(\theta)$  for  $\theta < \theta_c$  in Eq. (3) assume that some molecules can go directly through the capillary from the reservoir behind it, without hitting the walls.<sup>4</sup> This is generally correct for capillary arrays, but a needle doser more often consists of a tube with at least one bend between the open end and the gas reservoir. Such a geometry will lead to a flux distribution less strongly peaked in the forward direction than that given by Eq. (3). Nevertheless it will be more directional than a single effusive source, which we show below is already unacceptably nonuniform for most applications.

From a practical point of view the flux per unit solid angle is of less interest than the flux per unit area of the sample, which we denote  $G(\theta)$ . For a planar sample oriented perpendicular to the axis of the emitter, it is easy to show (see Fig. 1) that

$$G(\theta) = F(\theta) \cos^3 \theta. \quad (4)$$

The extra factor of  $\cos^3 \theta$  has a noticeable but modest effect on the directional flux from a capillary, but a severe effect on the flux from an effusive source. (The term "cosine emitter" is in this context somewhat misleading.) The flux uniformity plots shown by Campbell and Valone plotted  $G(\theta)$  for the capillary arrays, but  $F(\theta)$  for the effusive source. The result is a serious underestimate of the flux gradient for the effusive source. When the flux per unit area is considered, an effusive emitter placed 1/2 the sample diameter away has a flux at the edge of the sample that is only 25% of the flux at the center, not 71% as Ref. 1 suggests. Such nonuniformity is unacceptable for most surface science experiments, particularly those such as infrared reflectance and temperature-programmed desorption that average over the entire sample area.

The enhancement factor  $E$  is given by<sup>1</sup>

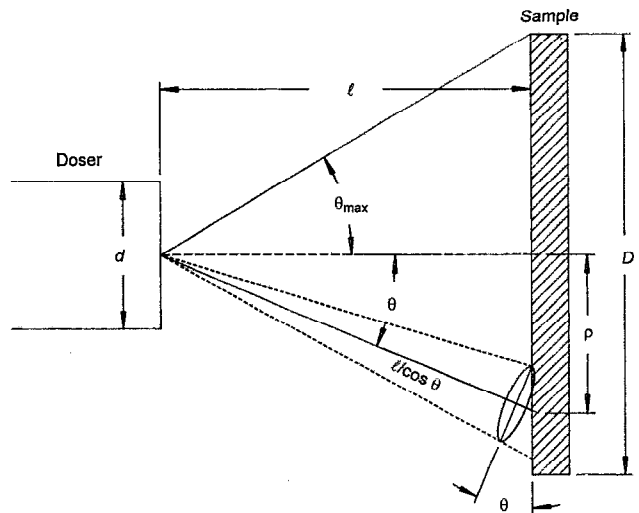


FIG. 1. Geometry of the doser calculation. The  $\cos^3 \theta$  term in the conversion from flux per solid angle to flux per unit sample area arises from the distance  $l/\cos \theta$  from the doser to a point on the sample, which reduces the flux by a factor of  $\cos^2 \theta$ , and from the area projection from the sample surface to a surface perpendicular to the flux, which contributes another factor of  $\cos \theta$ .

$$E \geq 1 + \frac{f_s S}{A(1 - f_s)} \sqrt{\frac{2\pi}{k_B T}}, \quad (5)$$

where  $A$  is the sample area,  $S$  is the pumping speed,  $k_B$  is the Boltzmann constant,  $T$  is the temperature,  $s$  is the sticking coefficient, and  $f_s$  is the fraction of molecules leaving the doser that directly impinge on the sample. The right-hand side of Eq. (5) gives the value of  $E$  if all molecules that do not immediately strike and stick to the surface are scattered into the vacuum chamber and subsequently pumped at speed  $S$ .  $E$  can be much larger if many of the molecules that miss the sample strike and are immediately trapped on other surfaces—cold surfaces of the sample mount or manipulator, for example. Since the expression for  $E$  involves quantities that are not properties of the doser, we characterize the effective enhancement of the doser with  $f_s$ , which is a property of the doser alone.

### III. CALCULATIONS

We assume a circular sample of diameter  $D$  parallel to a circular doser array of diameter  $d$  and a distance  $l$  away, as shown in Fig. 1. We characterize the doser-to-sample distance with the angle  $\theta_{\max}$  from the center of the doser to the edge of the sample;  $\tan \theta_{\max} = D/2l$ . The capillary arrays consist of 5096 capillaries with  $L/a = 40$ , on a square net. Tests with larger numbers of capillaries showed that this was a sufficiently dense grid to be effectively continuous. The flux is calculated along a line of 50 points from the center to the edge of the sample. The effusive arrays consist of a set of holes equally spaced on a circle of diameter  $d$ , with or without an additional hole in the center. More complex geometries, with multiple rings of holes, would probably improve the results when the doser and sample are very close together, but do not provide much improvement for  $\theta_{\max} < 60^\circ$ .

TABLE I. Comparison of circular effusive doser arrays with various numbers of holes. All designs except those with 8 holes comprise a single center hole surrounded by a ring of equally spaced holes at  $d/D=0.8$ . The 8-hole arrays have only the ring of holes, without a center hole. It can be seen that increasing the number of holes from 9 to 17 has little effect. The center hole improves the enhancement factor slightly; it improves the uniformity for  $\theta_{\max}=60^\circ$  and degrades it for  $\theta_{\max}=40^\circ$ , but in both cases the effects are small.

$\theta_{\max}$	Number of holes	$f_s$	$\sigma$
40°	5	0.32	0.15
	9	0.31	0.12
	17	0.30	0.11
	8	0.30	0.09
60°	5	0.56	0.25
	9	0.54	0.10
	17	0.53	0.08
	8	0.51	0.13

Since the effusive arrays we considered have fourfold, but not full rotational symmetry, we calculate the flux at 1254 points in a square net covering one quadrant of the sample.

At each point on the sample, the flux per unit area from the entire array,  $G_{\text{arr}}(\rho)$ , is calculated by summing the contributions from all the individual sources

$$G_{\text{arr}}(\rho) = \sum_i G(\theta_i), \quad (6)$$

where  $\theta_i$  is the angle from the  $i$ th source to the point  $\rho$  and the sum runs over all the sources. Each emitted molecule is given only one chance to stick so that no multiple collisions are included.

We characterize the uniformity of the flux distribution with the area-weighted fractional standard deviation in flux, which is given by

$$\sigma = \frac{\sqrt{\frac{1}{A} \int [G_{\text{arr}}(\rho) - G_{\text{ave}}]^2 dA}}{G_{\text{ave}}}, \quad (7)$$

where

$$G_{\text{ave}} = \frac{1}{A} \int G_{\text{arr}}(\rho) dA \quad (8)$$

is the average flux,  $A$  is the sample area, and the integrals are taken across the entire sample. Since the flux distribution functions are normalized to the total rate at which molecules are emitted, the fraction of gas directly hitting the sample is given by

$$f_s = \frac{G_{\text{ave}} A}{N}, \quad (9)$$

where  $N$  is the total number of sources. All calculations are accurate within  $\pm 1\%$ ; convergence was checked by performing calculations with larger numbers of data points.

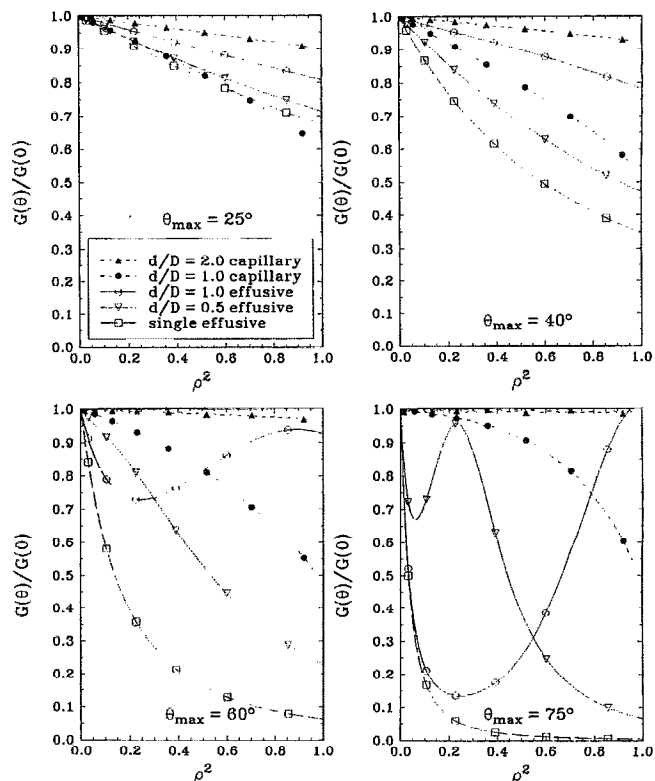


FIG. 2. Normalized flux per unit sample area plotted vs the square of the distance from the sample's center for various sample to doser distances, parametrized by  $\theta_{\max} = \tan^{-1}(D/2\ell)$ , and various values of  $d/D$ . Shown are plots for capillary arrays with  $d/D=2.0$  and  $1.0$ , centered circular 9-hole effusive arrays with  $d/D=1.0$  and  $0.5$ , and a single effusive doser.

#### IV. RESULTS AND DISCUSSION

In Table I we present the values of  $f_s$  and  $\sigma$  for several effusive array designs with  $d/D=0.8$  and  $\theta_{\max}=40^\circ$  and  $60^\circ$ . The 5-, 9-, and 17-hole arrays include a center hole; the 8-hole arrays lack the center hole. For  $\theta_{\max}=60^\circ$  the inclusion of the center hole improves both the uniformity and the enhancement modestly; for  $\theta_{\max}=40^\circ$  it slightly improves the enhancement at some cost in uniformity. Increasing the number of outer holes from 4 (5-hole array) to 8 (9-hole array) leads to significant improvement, but further doubling the number of outer holes to 16 (17-hole array) has little effect. Based on these observations, we confine our study of effusive arrays to 9-hole arrays comprising a ring of 8 holes around a central hole.

Figure 2 compares the flux uniformity across the sample for several choices of doser design at different doser-to-sample distances, parametrized by the angle  $\theta_{\max}$  (see Fig. 1). The plots show the flux per unit sample area  $G_{\text{arr}}(\rho)$ , normalized to the value in the center of the sample,  $G_{\text{arr}}(0)$ , along a radial line. For the effusive arrays the line passes directly in front of one of the perimeter holes. The data are plotted versus the *square* of the distance from the center of the sample,  $\rho^2$ , so that equal intervals along the  $x$  axis correspond to equal *areas* of the sample. This presentation provides a more accurate visual representation of the uniformity than a plot of the flux versus  $\rho$ , which underemphasizes the

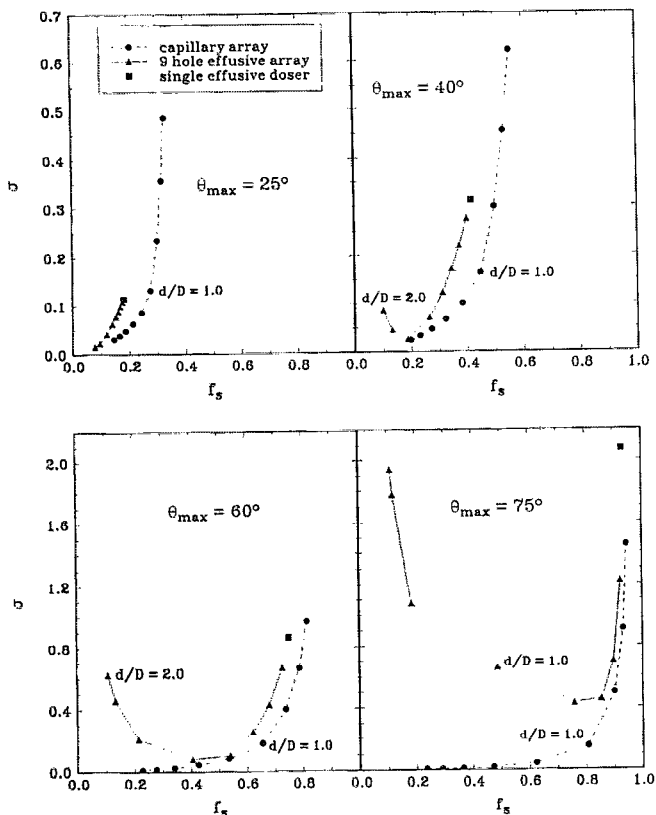


FIG. 3. Area-weighted fractional standard deviation  $\sigma$  plotted vs the fraction of emitted molecules directly impinging on the sample,  $f_s$ , for various sample to doser distances. The data shown are for capillary arrays with  $d/D=0.4, 0.6, 0.8, 1.0, 1.2, 1.4, 1.6, 1.8,$  and  $2.0$ ; centered circular 9-hole effusive arrays with  $d/D=0.3, 0.5, 0.65, 0.8, 1.0, 1.35, 1.7,$  and  $2.0$ ; and a single effusive emitter. In all cases the smaller  $d/D$  values give higher values of  $f_s$ .

significance of the region near the edge. For those capillary array geometries that were also considered in Ref. 1, the two calculations are in excellent agreement. For the single effusive doser, however, there is strong disagreement, since Ref. 1 plotted the flux per solid angle  $F(\theta)$  rather than the flux per sample area  $G(\theta)$ . Our results show that the single effusive doser provides reasonable uniformity only when the doser-to-sample distance is very large ( $\ell > D$ ).

Not surprisingly, the greatest uniformity is provided by a large diameter ( $d/D=2$ ) capillary array. Perhaps more surprising is the relatively poor uniformity given by a capillary array equal in size to the sample. Even for  $\theta_{\max}=75^\circ$ , with the doser very close to the sample ( $\ell=0.13D$ ), 20% of the sample area receives a flux that is smaller than that at the center by more than 20%. When the doser is farther away,  $\theta_{\max}<45^\circ$ , the 9-hole effusive array with  $d/D=1$  provides a more uniform distribution than the  $d/D=1$  capillary array. As the doser and sample are moved closer together the discrete nature of the effusive array becomes apparent in the strongly peaked flux distribution. It is likely that greater uniformity for short doser-to-sample distances could be achieved with more elaborate patterns of effusive emitters, but this is really the regime in which capillary arrays afford the greatest advantage.

A complete comparison of doser designs must of course consider enhancement as well as uniformity. Figure 3 plots  $\sigma$ , the area-weighted fractional standard deviation of the flux, versus  $f_s$ , the fraction of emitted gas that impinges directly on the sample, for effusive and capillary arrays of varying diameters and for different values of  $\theta_{\max}$ . (Our values of  $f_s$  for the  $d/D=1$  capillary array agree with those of Campbell and Valone<sup>1</sup> and Winkler and Yates.<sup>2</sup>) The single effusive doser represents the  $d/D=0$  limit of the effusive array. In the  $d/D \rightarrow \infty$  limit the value of  $\sigma$  must again approach the single source value, since the outer holes are too far away to contribute any flux; this is why the effusive array curves have a "U" shape.

An ideal doser would have a small value of  $\sigma$  and a large value of  $f_s$ , and would lie in the lower right-hand corner of the graph. Acceptable maximum values of  $\sigma$  and minimum values of  $f_s$  of course depend upon the application.

Several conclusions can be drawn from Fig. 3. (1) Single effusive dosers and small capillary arrays ( $d/D \ll 1$ ) are of little use unless very large flux variations ( $\sigma > 0.2$ ) are acceptable. (2) For any value of  $\theta_{\max}$  capillary arrays outperform effusive arrays. (3) For large doser-to-sample distances (small  $\theta_{\max}$ ) dosers of any design are of marginal usefulness, since it is virtually impossible to achieve  $f_s$  greater than 0.3. (4) For small doser-to-sample distances, capillary dosers with diameters 20%–40% larger than the sample perform extremely well. (5) Effusive arrays perform best when the holes are placed near the perimeter of the sample. (6) For intermediate doser-to-sample distances ( $\theta_{\max} \sim 60^\circ$ ), effusive arrays perform nearly as well as the best capillary arrays.

Under some experimental conditions these conclusions must be modified. One reason for using a doser arises when the dosed molecules are very rapidly pumped, for example by cold surfaces in the chamber, so that backfilling requires admitting an excessive amount of gas. In such cases a large enhancement  $E$  can be achieved even with a small value of  $f_s$ , and an effusive doser placed far enough from the sample to ensure good uniformity becomes a more attractive option.

A second situation in which dosers are often used is when the dosed molecules have a low sticking probability  $s$ . In this case the flux uniformity for capillary arrays placed close to the sample will not be as good as our calculations suggest. Molecules that do not stick to the sample are likely to scatter off the doser or its mount and reimpinge on the sample.<sup>1</sup> These multiple collisions, which are not included in our model, will tend to enhance the relative flux at the center of the sample at the expense of the edges, leading to a less uniform flux distribution. In such a case a larger doser-to-sample distance may be preferable, and an effusive array, because of its simplicity and smaller optimal diameter, becomes a more attractive option.

One virtue of effusive arrays is that they are easily made, and can be tailored to unusual shapes and sizes of samples. For example, surface infrared spectroscopy usually requires relatively larger oval or rectangular samples, and the doser must often be placed at some distance from the sample to allow optical access. Since the infrared beam usually probes the entire sample surface, good uniformity is essential. An effusive array with holes placed near the edges of the sample

can be an effective doser for such an application.

The model presented here can be readily implemented using commercial software on a personal computer, and calculations can be performed for any desired sample and doser geometry. It is then straightforward to optimize a doser design for the demands of any particular experimental situation.

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