NBSIR 88-3721

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Annual Report
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U.S. DEPARTMENT OF COMMERCE, C. William Verity, *Secretary*
NATIONAL BUREAU OF STANDARDS, Ernest Ambler, *Director*

Abstract

An apparatus for the measurement of flux of small molecules through whole condoms has been developed. It is shown that the experiment can measure diffusion constants as low as 10^{-13} cm^2/s or a single pinhole as small as .4 micrometers in the condom. For pinhole measurements this is shown to be a factor of 10 better than current ASTM testing methods on the basis of flow considerations only. Analysis of the experimental data show the difficulties in making unambiguous determinations on the mechanisms of flow. Further experiments are necessary to distinguish between large holes and small holes and fluxes due to diffusion and those due to pinholes. These results suggest a more careful study of fluxes through condoms is necessary to assure that a particle about .1 micrometers cannot pass through the condom.

I. Introduction

The use of condoms as a barrier to the spread of the AIDS virus has been the topic of a number of recent discussions. One recent study has considered whether a herpes virus, a virus similiar in size to the AIDS virus, can get through a condom[1].

For a condom which does not suffer catastrophic failure, two mechanisms are available for molecules to flow through the latex membrane.

1. Flow through pores or pinholes in the condom membrane.
2. Diffusion of the molecules through the condom membrane.

This project was under taken to model and measure the flow through latex condoms and to relate this flow to either flow through pinholes in the condom or diffusive flow through the condom membrane.

II. Modeling of Flow Through Condoms

In the discussion that follows we shall compute and discuss the flux through a condom arising from capillary or pinhole flow and the flux from diffusion as extremes of possible flow mechanisms though the membranes.

A. Capillary or Pinhole Flow.

If one has a pinhole in the membrane then a particle can pass through this pinhole. We shall first consider what are the important mechanisms and parameters affecting transport of particles through pinholes before we make model calculations of flow through pinholes.

1. Pinhole Description

For modeling purposes to be presented later in this report we shall consider flow through pinholes as described by flow through a single capillary or a distribution of capillaries of uniform cross section throughout their length. It is clear that a realistic pinhole may have varying non-circular cross section along its length. This fact complicates the interpretation of the measurements of flow through the condom.

2. Particle Size Effects

Generally, flow through pinholes will be independent of the particle size for particles smaller than the smallest radius in the pinhole. As the particle size approaches that of the smallest radius in the pinhole, we expect to obtain increased flow velocity of the particle[3] until the particle reaches the size of the pinhole's smallest radius. For particles larger than the smallest radius of the pinhole we get no particle flow at all.

3. Pressure Effects

Increasing the pressure head increases the flow through a pinhole in an elastic material since 1) The pressure head is proportional to flow in a rigid capillary and 2) the pressure head extends the rubber. The latter effect increases the pinhole size and decreases the thickness of the rubber, both of which lead to increased flow.

4. Medium Effects

The viscosity of the medium will of course affect the flow of fluid through pinholes. Increasing viscosity will decrease the flow rate and thus reduce the number of molecules of interest passing through the pinhole in a given time. If the medium swells the rubber then the pore size would be expected to decrease slightly, decreasing flow. Otherwise, the chemical constitution of the medium is expected to have little or no effect on flow through pinholes.

5. Capillary Action or Wetting of Rubber

One could transport a fluid through a pinhole, and thus the particle in the fluid, by capillary action. If one side of the condom is wetted by the solution, the solution will be drawn by capillary action into and through the rubber thereby wetting the other side of the condom. This mechanism will certainly transport particles of a size smaller than the smallest pinhole in the rubber. Often the condom comes packaged in lubricating oils or carrier fluid. The properties of this additive will change the wetting characteristics of the rubber membrane and thus effect the mechanism of capillary action transport through the condom. We shall not model or discuss these mechanisms further in this report.

6. Modeling of Flow Through a Pinhole as Capillary Flow

For lack of a better model on which to compute, we shall use the model of flow in capillaries to describe the flow across membranes due to pinholes. The flow through one capillary J_i,[4] is given by

$$J_i = \pi R_i^4 \Delta p/(8 \eta L_i) \qquad (1)$$

where J_i is the flux in capillary i, Δp is the applied pressure, L_i the length of the capillary, R_i its radius, and η is the viscosity of the medium. Besides assuming each pinhole is a capillary of cylindrical cross section, the above equation assumes $L_i > R_i$ so that entrance effects are unimportant.

If we have a distribution of pinholes in a condom of uniform cross-section, L, then the total flow, J_T, is given by

$$J_T = \pi \Delta p/(8L\eta) \sum_i R_i^4 \qquad (2)$$

where J_T is the total flow and the sum is over all pinholes in a condom. We have assumed all lengths of capillaries are the same, L. A flux of J_T for a time t leads to a volume V_F flowing through the membrane of

$$V_F = J_T \ t \qquad (3)$$

The above equations estimate steady state capillary flow. We have a substance with concentration C_o in the solution which is on the side of the membrane on which a pressure head has been applied. The solution on the other side of the membrane, called the accepting solution, has a volume V_A. The concentration of the substance in the accepting solution, C_A, after a volume flow of V_F is

$$C_A = V_F \ C_o/(V_A+V_F) \qquad (4)$$

Since in all cases we will consider here $V_A >> V_F$, we have

$$C_A = C_o \ V_F / V_A \qquad (5)$$

From equation 3, 4 and 5 we have for the concentration in the accepting solution as a function of time after some initial delay (called the breakthrough time)

$$C_A = \pi \ C_o \ \Delta p \ t \ /(8 \ \eta \ L V_A) \sum_i R_i^4 \qquad (6)$$

From equation 4 we can estimate the volume flow V_F from concentration measurements on the accepting solution. If there is a single pinhole in the membrane we can estimate the pinhole radius from this steady state flow .

$$R_m^4 = 8 C_A \ \eta \ V_A \ L/(\pi \ C_o \ \Delta p \ t) \qquad (7)$$

where R_m is the radius of the lone pinhole. If we have more than one pinhole in the membrane, then all pinholes must have smaller radii than that estimated from R_m.

Although the volume flow does not tell us pore size it allows us to estimate the range of allowable pores. Equations 6 and 7 will be used later in our interpretation of the data.

We expect that there is an initial transient as the pinhole fills with flowing solution. This transient is not easily estimated since it involves wetting properties of the rubber, surface tension of the solution and entrance effects in the capillary. Part of that transient will be the time to fill the capillary by simply steady state flow. For a capillary i the time t_{bi} can be estimated as the time to fill the capillary by steady state flow. Since the

volume of capillary i is $\pi R_i^2 L$ we have

$$\pi R_i^2 L = \pi \Delta p R_i^4 t_{bi}/(8 \eta L) \qquad (8)$$

Solving for the estimated breakthrough time we have

$$t_{bi} = 8 \eta /\Delta p (L/R_i)^2 \qquad (9)$$

Thus, the total volume V_t, including the initial transient to fill the capillary at the time t in steady state flow is given by

$$V_t = V_F - \pi \sum_i R_i^2 L \qquad (10)$$

Generally, for times over a few minutes the second term on the rhs of equation 10 is small. To estimate the order of magnitude of flows expected from our experiment and from other tests for pinholes, we use the set of parameters given in table 1.

We have estimated the values in table 1 in the following way: L is the smallest value for thickness of condoms allowed by ASTM D3492[5]; η is the viscosity of water at room temperature; C_o is the concentration of uranine inside the condom in our experimental set up (see discussion below and in appendix B); V_A is the volume of buffer solution outside the condom (see discussion of experiment setup below and in appendix A); Δp is the estimated

pressure head on the condom membrane, A is the approximate surface area of the condom and is obtained assuming the condom is 180 mm long and 52 mm wide.[5]

From the parameters in table 1 we compute the transient time we estimated in equation 9. Table 2 gives the estimated breakthrough times for these parameters for pinholes of various radii. From this table the breakthrough times estimated from just the steady state flow to fill up the capillary are insignificant compared to any time to be considered in this measurement. Thus they may be disregarded. Furthermore, it is likely that this estimation of the breakthrough time is only a minor component of the total breakthrough time for pinhole flow through a capillary.

Let us assume that the condom has a single pinhole. We can estimate the size of a single pore that can be measured by our method. If the flux through the membrane of a small molecule like a fluorescence probe dissolved in water is a result of pinhole flow then the equations above tell us of the concentration change. On the other hand, if we can measure a given concentration change then we can estimate the minimum detectible flow. Equation 7 immediately tells us the radius of the pinhole that could cause that flow if there is one pinhole and it is cylindrical.

We note below and in appendix B that we can detect as little as $1.\times10^{-9}$ molar in uranine concentration in the accepting solution. We have by rearranging equation 5

$$V_F = C_A \ V_A / C_o \qquad (11)$$

where as before V_F is the volume that flowed, C_A is the concentration measured in the accepting solution, V_A is the volume in the accepting solution and C_o is

the concentration in the flowing solution. Since we use a concentration of 10^{-3} molar in the flowing solution of the condom in our experimental setup and the volume in the accepting solution inside the condom is about 250 mL we estimate from eq. 11 that a V_F as small as 2.5×10^{-4} mL can be measured.

We estimate the radius of the smallest single pinhole we can see by using equation 1 and 3

$$R^4 = 8\ V_F\ \eta\ L_1/(\pi\ \Delta p\ t_0) \qquad (12)$$

where all terms have been defined before except t_0 which is the time in seconds of the measurement.

Assuming the constants in table 1 we have for the radius of a single capillary in the condom

$$R^4 = 10^{-12}\ /t_0 \qquad (13)$$

where t_0 is the flow time in seconds. Our flow times can easily exceed 40 hours (t_0 of 1.4×10^5 seconds) which corresponds to detecting a single pinhole of $.5 \times 10^{-4}$ cm (or .5 μm) radius. Of course, this flow could just as well have come from 10,000 pinholes of .05 μm.

Finally, we ask what size pinhole can be detected by a method like that described in the section on leakage in ASTM Method D3492[5]. The following calculation is made on flow considerations only. Surface tension effects at the air-water interface for a liquid passing through a small hole may be a more significant factor in determining the minimum hole radius measurable by a technique like the leak test described in ASTM Method D3492. Thus the

following calculation may be viewed as a lower bound to the minimum radius which can be measured by the ASTM method.

We shall assume the values of Δp, η and L given in table 1. We assume we can detect a droplet of 1.0 mm^3 ($V_F=10^{-3}$ mL) and that there is no evaporation of the droplet which would decrease its size. In a correct treatment we would have to balance evaporation rate and spreading or wetting rate with the flux through the pinhole to get a good estimate of the overall rate. As these effects are difficult to treat we select a short flow time to minimize their importance. A time of 30 seconds for the droplet to form (t_0=30 s) was selected. We find that the ASTM method can detect a pinhole of radius 6 micrometers. From the point view of flow considerations only our method is about ten times more sensitive than the ASTM method.

B. Flow by Diffusion through the Membrane.

Even if there are no pinholes in the rubber, particles could pass through the membrane by diffusion. This is a much slower process than pinhole flow, however, since the whole membrane is available to diffusion, the total flux from diffusion can be high. We shall discuss the properties of the rubber and the flowing medium and how they affect diffusion before we consider modeling the diffusion process.

1. Particle Size

In general, the larger the diffusing particle the smaller the flux from diffusion. The Stokes-Einstein[6] relation suggests that the diffusion constant and thus the flux of a diffusing particle is inversely proportional to the radius of the molecule.

2. Medium Effects

The diffusion depends strongly on the state of the rubber, its thickness and density variation. For example, the diffusion is faster in low density regions. Medium effects on diffusion can be significant as well. For example, the medium may swell the rubber causing an order of magnitude increase in the diffusion coefficient of the diffusing particle.

3. Modeling of Flow through a Membrane Arising from Diffusion

Modeling of diffusion for this system is described by the diffusion through a plane sheet. Although the condom is not a plane sheet the radius of curvature of it is so large that the difference between a more correct representation and a plane sheet insignificant. The mathematics and models have been described in detail by Crank[7]. His equation 4.24a best describes our situation. This equation is

$$Q_t/LC_1 = Dt/L^2 - 1/6 - 2/\pi^2 \sum_n (-1)^n/n^2 \exp(-Dn^2\pi^2 t/L^2) \qquad (14)$$

where Q_t is the total mass of diffusing species per unit area from the membrane and, D is the diffusion constant of the species through the membrane in cm^2 per second. All other quantities have been defined previously except C_1 which is the concentration of diffusant in the membrane on the side of the membrane facing C_o which is in equilibrium with C_o. In general, the relation between C_1 and C_o is

$$C_1 = KC_o \qquad (15)$$

where K is the partition coefficient. Equations 14 and 15 lead to figure 1. The dashed line in figure 1 is the asymptotic line given by

$$Q_t = DKC_o\, t/L - LKC_o/6 \qquad (16)$$

while the intercept on the time axis is given by

$$t_{in} = L^2/(6D) \qquad (17)$$

t_{in} is called the breakthrough time since it estimates the time for some small amount of material to appear on the other side of the membrane.

The total mass of uranine out of the condom in time t is $Q_t A$ where A is the area of the condom. Thus, the concentration increase in the accepting solution is

$$C_A = Q_t A/V_A \qquad (18)$$

where again we have assumed the volume of the accepting solution is essentially unchanged by the mass diffusing into it. For times much longer than the breakthrough time we have from equation 16 and 18

$$C_A/C_o = DtKA/(V_A L) \qquad (19)$$

For comparison purposes we need an estimate of the diffusion constants and partition coefficients of molecules in rubber. In table 3 we list some literature values of diffusion constants of small molecules in rubbers. These range from 10^{-6} to 10^{-9} cm^2/s.

From the above equations and table 1 we can estimate what diffusion and partition coefficients can be measured using our experimental setup. Breakthrough times, t_{in}, of 1/2 hour to 40 hours can easily be measured by our technique. Thus, diffusion constants greater than $1.0 \times 10^{-11} cm^2/s$ can be observed. We expect to be able to measure changes as small as C_A/C_o of 2×10^{-5} in uranine concentration in 40 hours and products of KD greater than $.5 \times 10^{-13}$ cm^2/s.

C. Interpretation of Models of Flow

From the above discussion, it is clear that one cannot distinguish between flow of small molecules across a membrane arising from pinholes in the membrane or by diffusion of the molecules through the membrane. In both cases we expect an initial delay time followed by a period during which the flux is linear in time.

III Experimental

Since any measure of the number of molecules through a membrane depends on the sensitivity of the method used to detect the species, we have chosen a fluorescence method since (1) it is extremely sensitive (for example, the fluorescence compound we have chosen for our preliminary experiments, uranine, may be detected in concentrations as low as one part per billion) and (2)

biological molecules with protein-like outer surfaces similar to the outer surfaces of viruses can be labeled with fluorescent molecules.

Apparatus development and the preliminary experiments have been done using uranine, the water soluble form of fluorescein, as the diffusing molecule. This molecule is relatively small. It has a high fluorescence intensity and is easily attached to a number of biological molecules. If uranine is used as a tag of biological molecules it is important to have the diffusion properties of the free molecules through the condom as baseline data. The present measurements of the flux of uranine through a condom could act as preliminary data to that end. Otherwise, it serves as a measure of the volume flow through pinholes or as a way to estimate the diffusion constants of larger molecules.

A sodium phosphate buffer solution of pH 7 was chosen as the medium for the experiment.

A test apparatus was constructed with the following considerations: 1) The condom should be expanded to around 300 mL. This constraint is in concert with the filling volume used in the ASTM Method[5]. 2) The apparatus should exert no excessive stresses on the condom. 3) As much of the surface of the condom should be tested as possible. 4) The volume of the outer solution should be as low as can conveniently be stirred. (This allows us to achieve high sensitivity. 5) Test conditions should be maintained for at least 20 hours. A detailed description of the apparatus is given in appendix A.

Large pinholes, those which do not allow us to keep a head of water in the condom for even a few minutes, were a source of problems during the apparatus development. Most large pinholes have been found near the rim of the opened

condom. Large pinholes near the rim of the condom are allowed by the ASTM Method D3492[5]. A method has been designed to pretest the condoms for large pinholes before they are put on the test apparatus since large pinholes in the body of the condom or close to the rim did not allow the apparatus to obtain a steady head of water.

Three different brands of condoms were tested. Measurments were made on four or five condoms of each brand. One of the three brands showed significant differences from the other two. We shall discuss the data on all three brands.

A. Data on Brand B2

Experiments were made on condoms of type B2. Condoms designated B2B, B2D and B2E allowed little or no uranine to pass through the condoms in 20 hours although we did see a fluorescence background increase. The fluorescence spectra of the outer solutions of condom B2E is shown in figure 2. The reader should notice the spectra is different from the spectrum of uranine of 10^{-9} molar shown on the same plot. Blank experiments with buffer alone indicated almost no background increase in the fluorescence.

In one condom, B2C, we found a significant increase in the fluorescence spectrum in the outer solution well above the background measured in any of the other samples or in the blank. The outer solution had a concentration of uranine of more than 2×10^{-9} molar after 20 hours. Since the fluorescence spectrum of this outer solution is very close to that of uranine, we conclude that the concentration of uranine is greater than 1 ppb in the outer solution. Since the first two hours of the run showed no fluorescence increase we are confident that the fluorescence observed in the outer solution is not due to

contamination . The spectra of the outer solution at various times up to 20 hours for condom B2C is given in figure 3. The plot of the concentration (in the outer solution) versus time is given in figure 4. The data roughly showed the expected breakthrough curve for molecules passing membranes with a breakthrough time for this data at about 3 or 4 hours.

B. Data on Brand B1

In experiments on condoms of type B1 we found that little or no uranine passed through the condoms in the first 6 hours although we did see a fluorescence background increase. Measurements at 60 and 96 hours showed uranine breakthrough the membrane. Blank experiments with buffer alone indicated almost no background increase in the fluorescence.

Since the fluorescence spectrum of this outer solution is very close to that of uranine for the 60 and 96 hour measurements, we conclude that the concentrations of uranine are greater than 1 ppb in the outer solution. Since the first six hours of the run showed no fluorescence increase we are confident that the fluorescence is due to neither contamination nor a large pinhole. Figure 5 shows the spectra of each condom of the B1 type at 96 hours. Intensity data for the peak at 514 nm up to 96 hours for all condoms of this type given in figure 6. The data roughly showed the expected breakthrough curve for molecules passing through membranes with a breakthrough time of about 48 hours for all four condoms. The slope on the linear portion differ by a factor of two for this set of condoms. The highest slope B1B has a value of 2.2 I/s where I is the fluorescence intensity in arbitrary units at 515 nm resulting from 490 nm excitation.

C. Data on B3

Experiments on condoms of type B3 showed this condom to be qualitativly different from the other two brands tested. Within 1 hour of the start of the experiment uranine in concentrations greater the $1.0x10^{-8}$ molar had passed through the condoms. Measurements were taken up to 20 hours. Blank experiments with buffer alone indicated as shown in figure 7 almost no background increase in the fluorescence. This figure should be compared with the extremes of performance given in figure 8 of B3D which showed the lowest concentration after 20 hours and figure 9 of B3B which shows the greatest concentration in the outer solution after 20 hours. Plots of these data are given in figure 10 which show normal breakthrough curves with breakthrough times of less then 1 hour. Slopes for the linear portion of the curves range from S=140 I/s for B3B to S=2.4 I/s for B3D. Although the slopes are very different if we rescale all the data so they are all normalized against their concentration at 20 hours, the functional dependence of all four condoms look remarkably similar (see figure 11). This suggests that the condoms are experiencing similar breakthrough times.

D. Comments on experiments

These preliminary experiments indicate that a valid method has been developed which can be used to measure the rate at which molecules pass through the condoms. The method should be useful on other condoms and may be useful for determining the rates of passage of larger biological molecules.

IV Data Analysis

From the above preliminary data on the condoms we draw some conclusions about the nature of the flow through the condoms that we have tested. As discussed in earlier sections the concentration of uranine in the outer solution can be estimated for both diffusion and flow through a capillary mechanism of mass transport through the condom membrane. From the description above both pinhole and diffusive flow will show essentially the same concentration versus time behavior. Equation 6 describes the concentration increase in the accepting solution (or outer solution) in the case of a flow through pinholes and equations 16-19 describe the concentration increase in the accepting solution (or outer solution) in the case of diffusive flow of the uranine through the membrane. In table 4, we collect together the data from the three runs described above for estimated breakthrough times and slopes on the linear portion of the concentration versus time plot. For diffusion there is a known relation between the breakthrough time and the slope of the long time portion of the curve through the diffusion constant and the partition coefficient. In table 5, we give the estimated diffusion constants and partition coefficients using all method with our numbers. The data seem inconsistent. For example, B3B and B3D have very different partition coefficients. However, considering the experimental errors and the assumptions made in analyzing the data the data are surprisingly consistent.

The diffusion constants obtained in table 5 are small when compared with those of organics in rubber. However, uranine maybe charged in this highly polar medium. We have noticed that the condoms are translucent when first put into the buffer and become white after about 1 hour in the buffer solution. This suggests that the condoms are taking up water. The diffusion constant of

water in rubber decreases with increasing water concentration[8]. Perhaps this water also reduces the diffusion rate of uranine in rubber. This low diffusion constant and the clouding of the condom indicates more studies on the effect of the medium on the state of the condom are needed.

We may also estimate the flux of solution for pinhole flow through the condom. Assuming the condom has only one pinhole, we may also estimate the pinhole size. For this we use equation 7. The maximum pinhole that the condom can have with this flux is given in table 6 for the data given in table 4.

The data suggest flows from pinholes of about 1 micrometer. As we pointed out before, these results may result from many more and much smaller holes. These measurements have no way to distinguish between the two cases.

V Conclusions

An apparatus for the measurement of flux of molecules through whole condoms has been developed. It is shown that the experiment can measure diffusion constants as low as 10^{-13} cm^2/s or a single pinhole as small as .4 micrometer in the condom. On the basis of flow considerations only, the size of pinholes measured by this technique is a factor of 10 smaller than that detectible by current ASTM testing methods. Three different brands of condoms were tested with the apparatus. Preliminary experiments suggest at least one brand had significant flux through the condom. Other brands had smaller but measurable fluxes. Effects of the character of the medium have been noted. Further experiments are necessary to distinguish between large holes and small holes and fluxes due to diffusion and those due to pinholes. These results

suggest a more careful study of fluxes through condoms is necessary to assure that a particle of diameter .1 micrometer cannot pass through the condom.

Table 1

$L = 0.03$ mm

$\eta = 0.001$ Pa · s

C_o=.001 molar=.3 g/L=.0003 g/mL

V_A=250 mL

$\Delta p = 2 \times 10^3$ Pa

A=18500 mm^2

Table 2

Estimate Breakthrough Times from Solution Flow Only for Different Radius of the Capillary

Radius capillary(cm)	Time(s)
$3x10^{-5}$	$4.0x10^{-2}$
$3x10^{-4}$	$4.0x10^{-4}$
$3x10^{-3}$	$4.0x10^{-6}$

Table 3

Diffusion Constants and Partition Coefficients of Some Small Molecules in Latex Rubbers+

	D cm^2/s
	10^6
O_2	1.7
C_2H_2	.6
n-C_4H_{10}	.14
n-C_5H_{12}	.17

+ G. J. Van Amergon, Rubber Reviews, 37, 1063, (1961).

Table 4

Data for Various Condoms

Condom	Approximate Breakthrough time		Approximate slope
	s	I/s	C/s 10^{13} (molar/s)
B1B	1.6×10^5	2.2	1.8
B1D	1.7×10^5	1.1	.91
B3B	> 1800	140	97
B3D	> 3600	1.9	1.3
B2C	7.2×10^3	.58	.44

Table 5

Estimated Diffusion Constants (D) and Partition Constants (K)

Condom	Approximate D from Breakthrough time cm^2/s $x10^{10}$	Approximate KD from slope cm^2/s $x10^{10}$	Approximate K
B1B	.09	6.8	.05
B1D	.09	3.2	.02
B3B	>8.3	430	.02
B3D	>74.1	7.7	.001
B2C	2	1.2	.001

Table 6

Estimated Maximum Possible Pinhole Size in Condom[+]

Condom	Estimated Pinhole size in micrometers
B1B	1.1
B1D	.96
B3B	3.11
B3D	.11
B2C	.81

[+]Notice the results in this table are very model dependent. The model assumes that flow comes from a single pinhole showing Pouisille flow throughout the thickness of the condom. No diffusive flow is allowed. All modifications of the model are expected to predict smaller pinholes.

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CAPTION

Figure 1. Plot of mass of material, Q_1, as a function of time for diffusion flow. A plot of similar functional form is expected from flow through a pinhole.

Figure 2 Fluorescence emission spectra from condom B2E. Each solid line is at a later time the lowest solid line being at 2 hours, the next three at 1 hour intervals. The last line is the emission spectra at 20 hours.Dashed line is $1.0x10^{-9}$ M uranine. Notice even the 20 hour spectra does not look like uranine.

Figure 3. Fluorescence emission spectra from condom B2C. Each solid line is at a later time, the lowest solid line being at 2 hours, the next three at 1 hour intervals. The last emission spectra is at 20 hours. Dashed line is $1.0x10^{-9}$ M uranine. Notice all the later spectra look like uranine.

Figure 4. Intensity of uranine that has flowed through a condom designated as B2C. For the conditions stated (excitation and emission wavelengths) an intensity of about $1.4x10^{+5}$ counts per second is equivalent to a concentration of uranine of $1.0x10^{-8}$ M. The curve has normal breakthrough behavior with a breakthrough time of about 2 to 4 hours. The estimated slope for the linear portion S=.58 in units of I/s.

Figure 5. Fluorescence emission spectra B1A to B1E at 96 hours. Each solid line is at a different condom. The lowest solid line is the blank B1A and is at

the baseline. Dashed line is 1.0×10^{-8} M uranine. Notice all the spectra except the blank look like uranine.

Figure 6. Intensity of uranine that has flowed through a condoms designated as B1. B1A is the blank, no uranine solution in the condom. All the rest have uranine of concentration in the condom as explained in text. For the conditions stated (excitation and emission wavelengths) an intensity of about 1.4×10^{5} counts per second is equivalent to a concentration of uranine of 1.0×10^{-8} molar. All the condoms here show similar breakthrough times of 48 hours and slope differences of about a factor of 2 on the linear portions. The slopes range from 2.2 I/s for B1B to 1.0. I/s for B1D.

Figure 7. Fluorescence emission spectra from condom B3A, the blank run for the B3 series. Each solid line is at a later time, the lowest solid line being at 1 hours, the next three at 1 hour intervals. Dashed line is 1.0×10^{-9} M uranine.

Figure 8. Fluorescence emission spectra from condom B3D. Each solid line is at a later time, the lowest solid line being at 1 hours, the next three at 1 hour intervals. Dashed line is 1.0×10^{-9} M uranine. Notice all the spectra from the condom solutions look like the urnaine spectra.

Figure 9. Fluorescence emission spectra from condom B3B. Each solid line is at a later time, the lowest solid line being at 1 hours, the next three at 1 hour intervals. Dashed line is 1.0×10^{-9} M uranine. Notice all the later spectra look like urnaine.

Figure 10. Intensity of uranine that has flowed through condoms designated as B3. B3A is the blank,no uranine solution in the condom. All the rest have uranine of concentration in the condom as explained in text. For the conditions stated (excitation and emission wavelengths) an intensity of about 1.4×10^5 is equivalent to a concentration of uranine of 1.0×10^{-8}M. These condoms were very different than the rest. On this plot all of the condoms show similar breakthrough times but have large slope differences.

Figure 11. Same data as in figure 10 but all data is rescaled so all concentrations after 6 hours are the same. In this plot the data from the flow through all the condoms of type B3 indicate similar breakthrough times of 2 hours or less.

Appendix A

Detailed description of the test apparatus.

In constructing a test apparatus, the following items were considered:

1. The condom should be expanded to around 250 mL.
2. Fluorophore used to detect breakthrough time should be soluble in pH 7 sodium phosphate buffer.
3. The volume of the outer solution should be as low as can conveniently be stirred.
4. Test conditions should be maintained for at least 20 hours.

A single brand (B1) was selected for trials until a reliable test procedure was worked out.

The sample was suspended by stretching the open end over the lip of an inverted 35/20 borosilicate glass socket. A 59 mm ID round-bottom borosilicate glass tube served as immersion container. Prior to immersion and filling of the condom with fluorescent (dye) solution, the container held a 4 mm OD borosilicate glass sampling tube, a Teflon spinbar and 250-270 mL. buffer. In initial experiments, expansion pressure was achieved by adding excess dye solution to a height at 12 cm above the outer liquid level. Dye leakage at the line of attachment was observed. Therefore, a pneumatic expansion of the rubber was adopted, allowing excess dye solution to rise in an open-ended vertical tube. Pressure was maintained by means of an adjustable bubbler manostat with a flow rate just sufficient to make up for any gas leakage. By adjusting dye solution volume and manostat, the liquid levels of inner and outer solutions were equalized. This facilitated calculation of the inner volume by displacement. Volumes of 250-260 mL at 12 cm H_2O pressure were

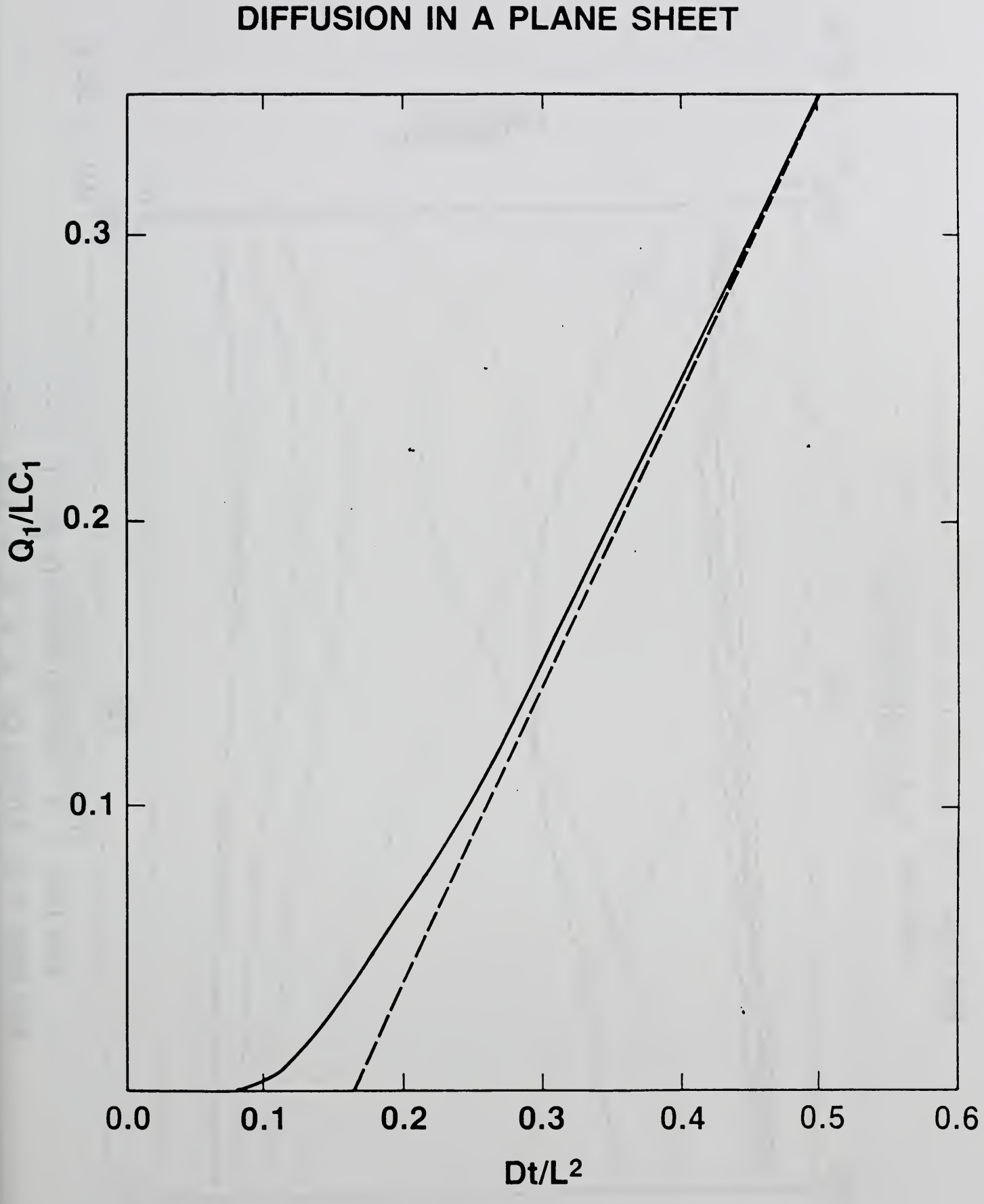
typical. At constant flow rate and fixed manostat setting, a subsequent rise in the outer volume level was found to be caused by large pinholes. This was verified by forcing dye solution through the condom until droplets emerged.

The current design of the apparatus allows five tests be run simultaneously on the same manostat.

In some instances we found that after 8 hours or so the volume of the condom changed. As a result, we adjust the pressure head slightly to return the volume of the condom to its original value.

It should be noted that upon immersion in the buffer or solution, all the condoms appeared translucent. Within an hour or so all of them were opaque (white). This may indicate that the condoms absorbed water.

Figure 1


DIFFUSION IN A PLANE SHEET
0.3
0.2
0.1
Q_1/LC_1
0.0
0.1
0.2
0.3
0.4
0.5
0.6
Dt/L^2

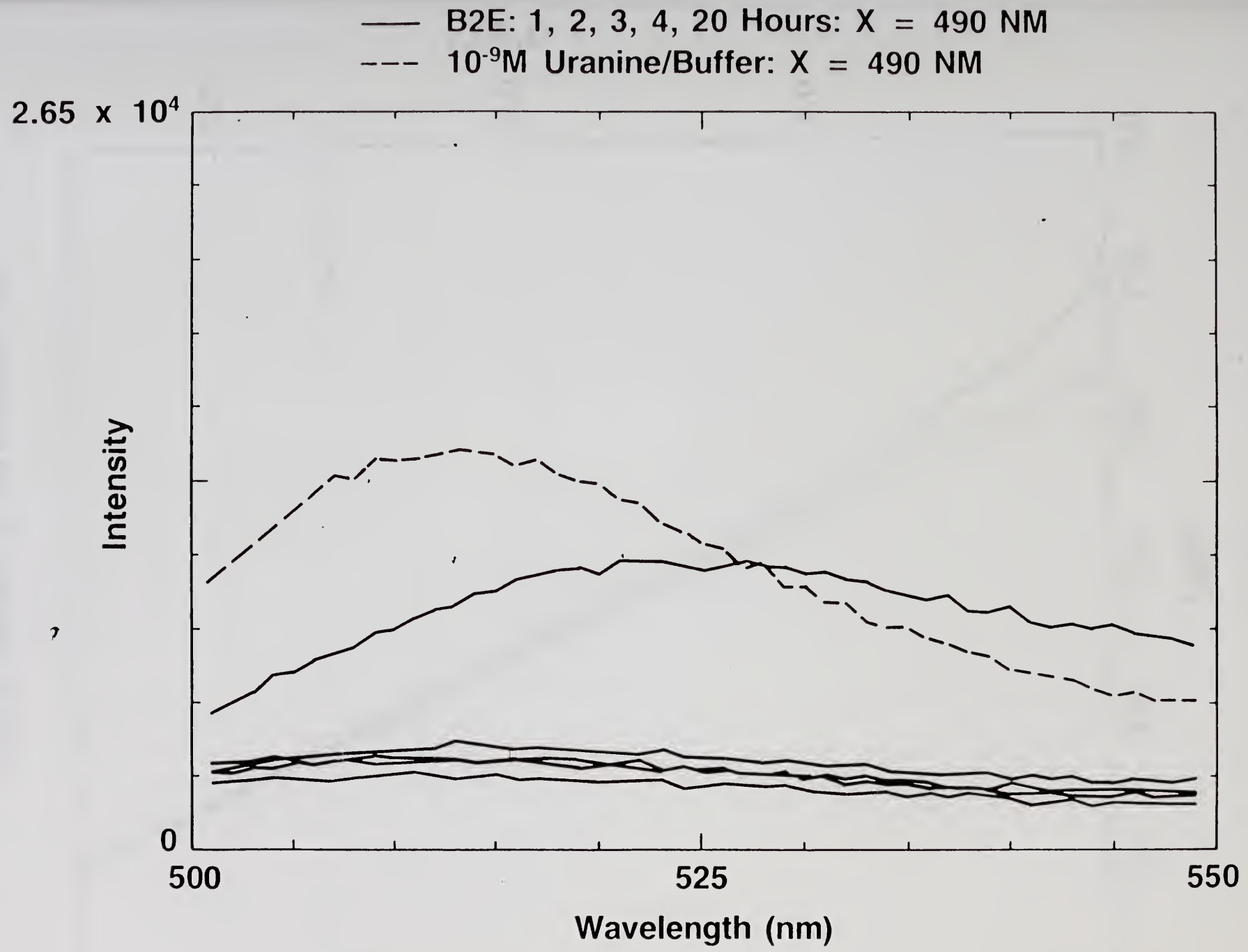
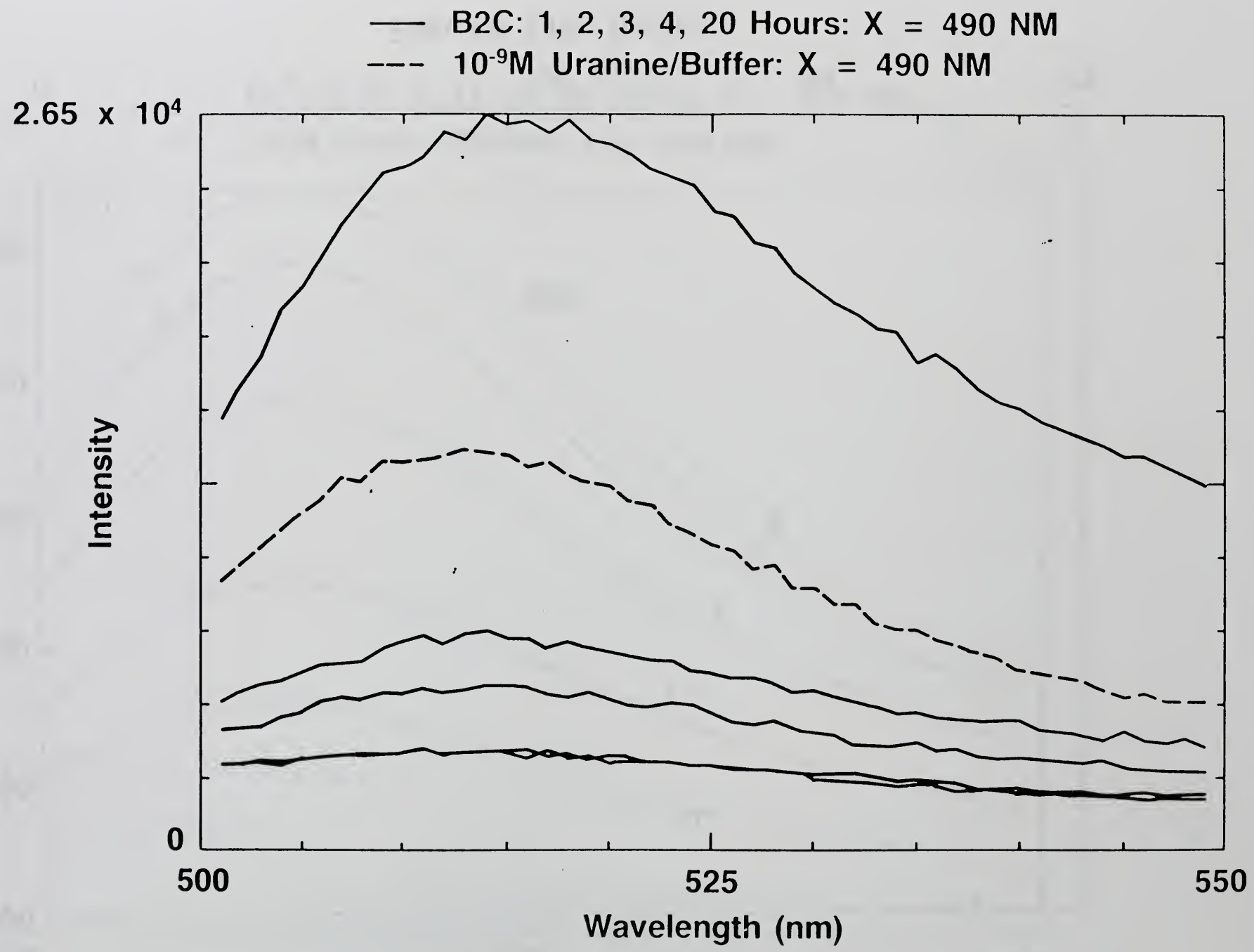
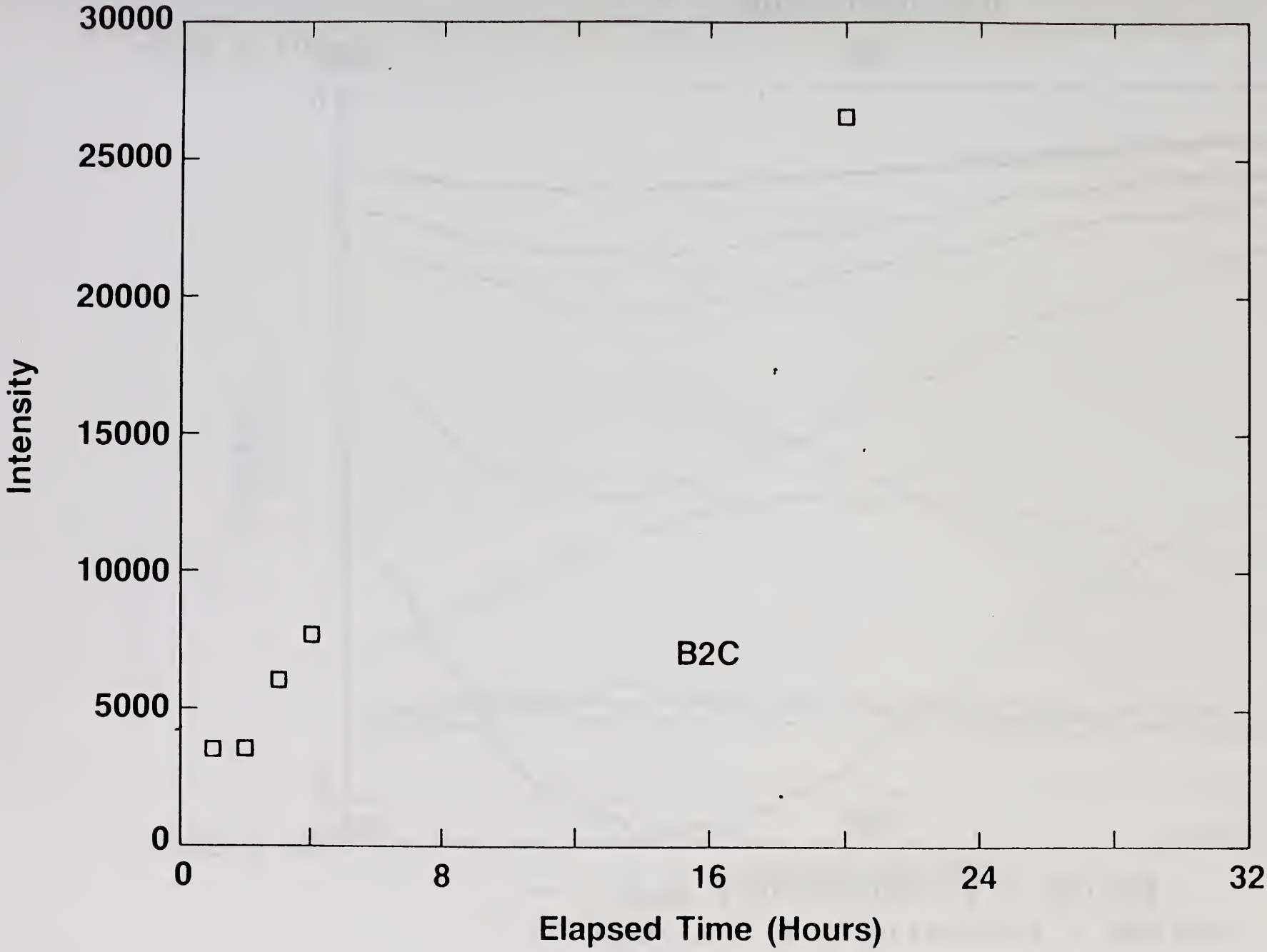
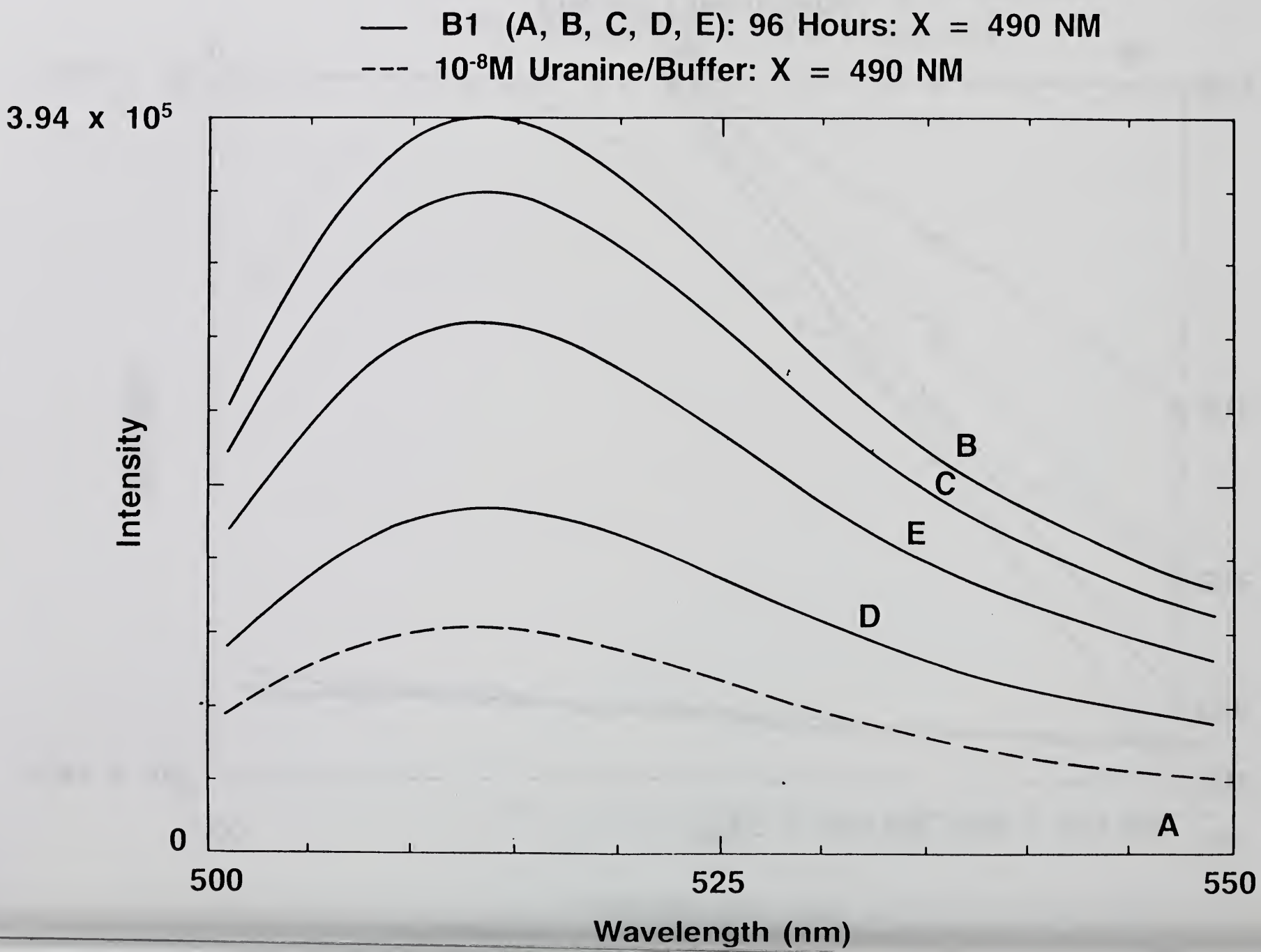

B2E: 1, 2, 3, 4, 20 Hours: X = 490 NM
10-9M Uranine/Buffer: X = 490 NM
2.65 x 10^4
Intensity
0
500
525
550
Wavelength (nm)

Figure 3


B2C: 1, 2, 3, 4, 20 Hours: X = 490 NM
10-9M Uranine/Buffer: X = 490 NM
2.65 x 10^4
Intensity
0
500
525
550
Wavelength (nm)


30000
25000
20000
15000
10000
5000
0
Intensity
B2C
0
8
16
24
32
Elapsed Time (Hours)


—— B1 (A, B, C, D, E): 96 Hours: X = 490 NM
--- 10-8M Uranine/Buffer: X = 490 NM
3.94 x 10^5
Intensity
0
500
525
550
Wavelength (nm)
A
B
C
D
E

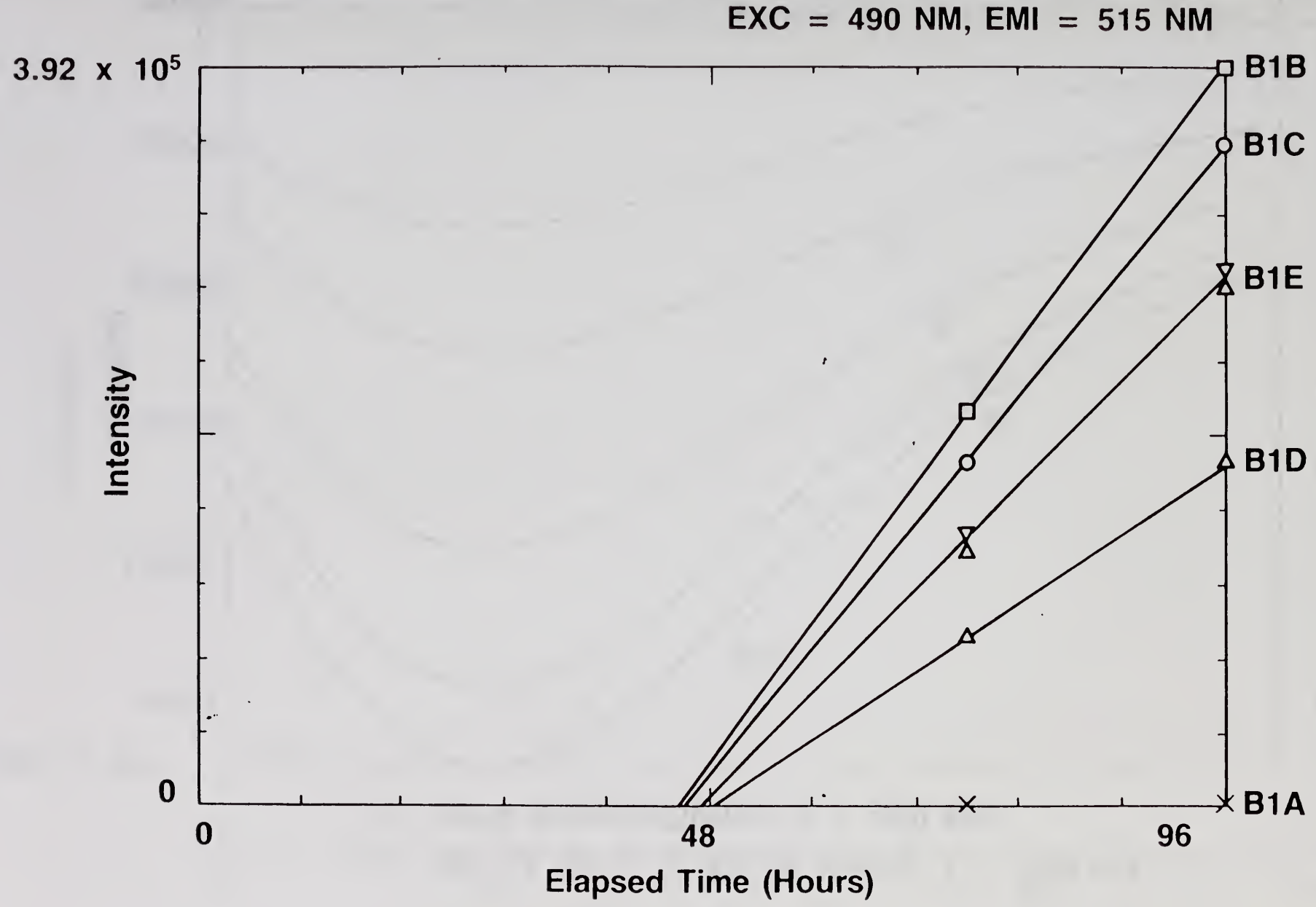
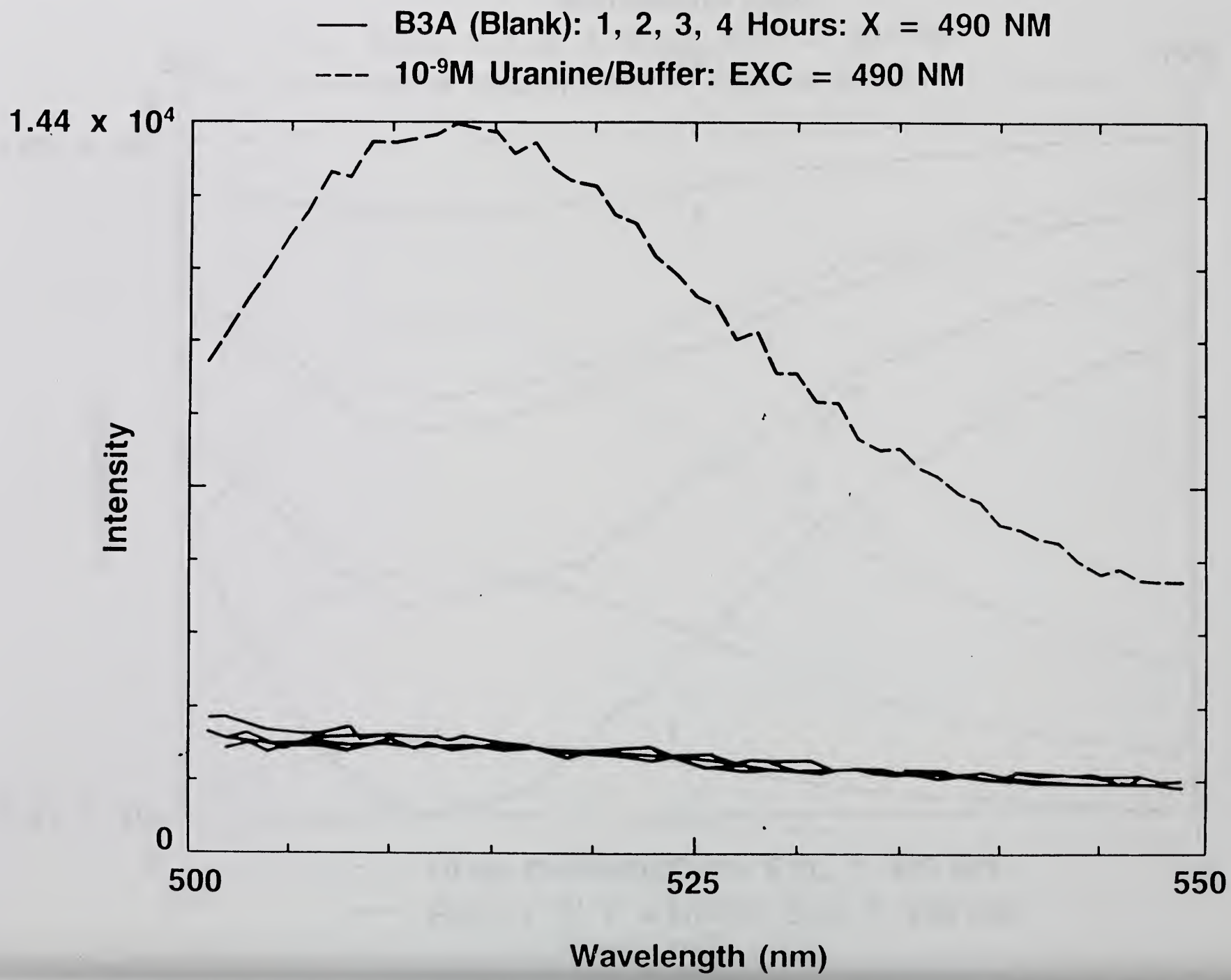
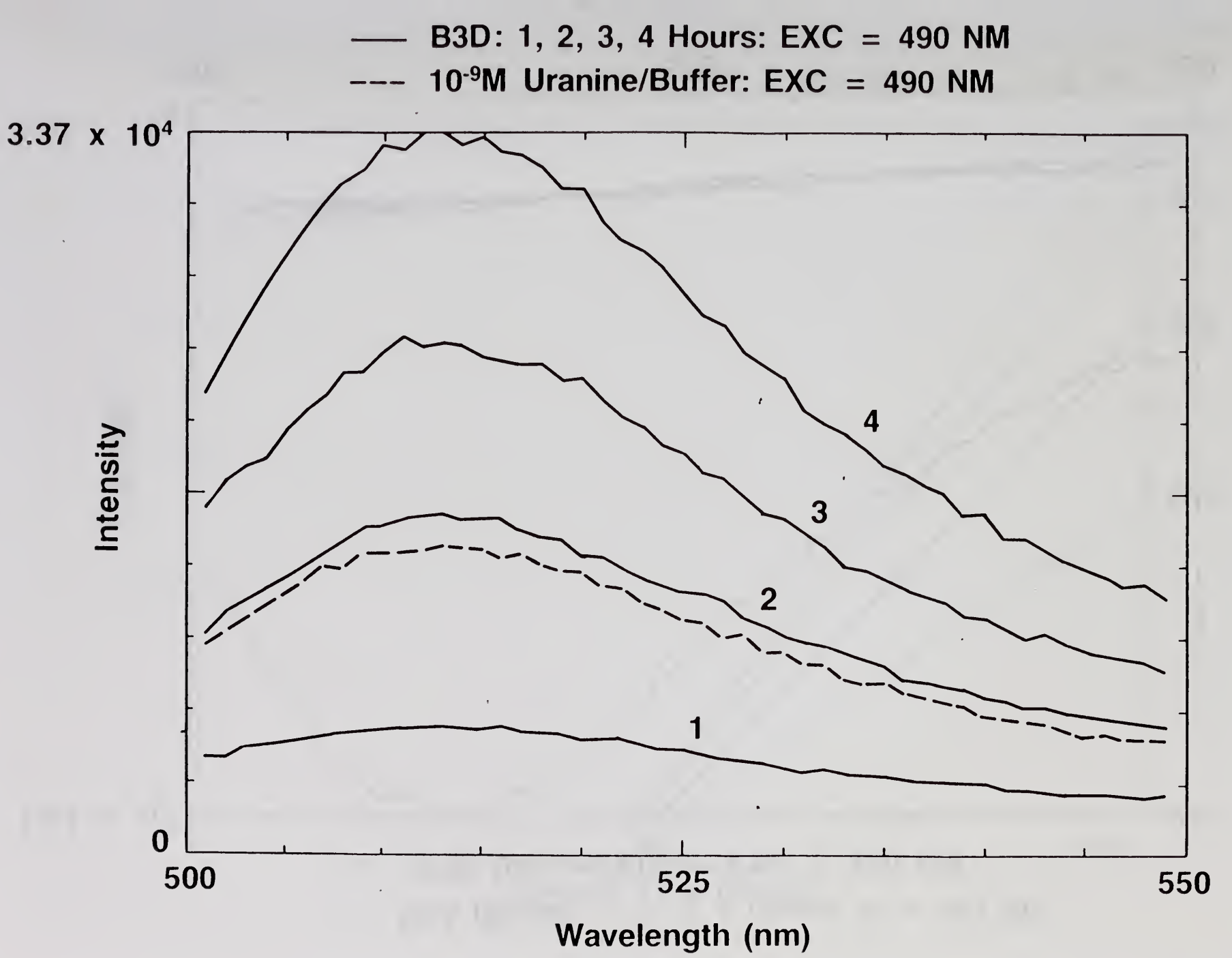
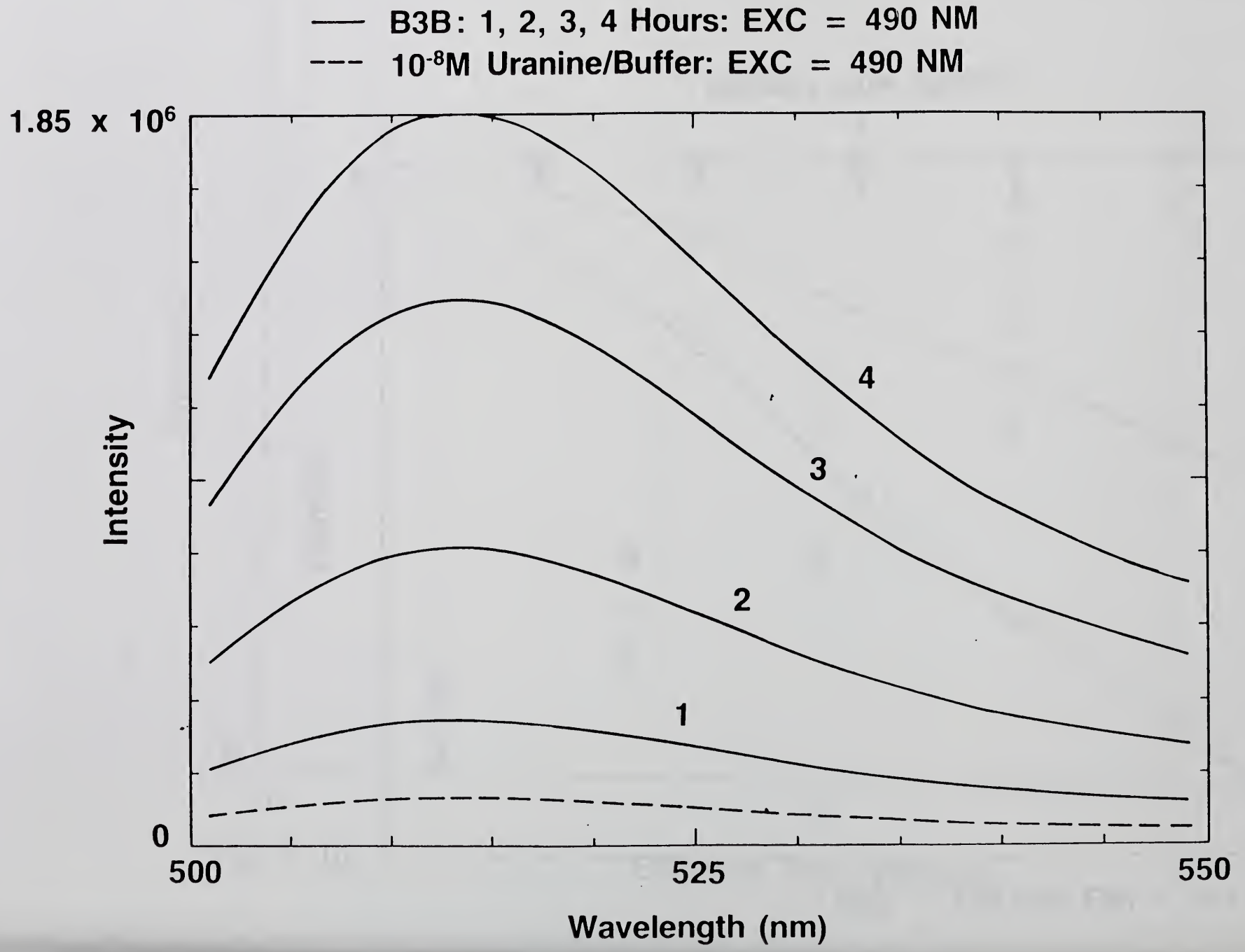

EXC = 490 NM, EMI = 515 NM
3.92 x 10^5
0
Intensity
0
48
96
Elapsed Time (Hours)
B1B
B1C
B1E
B1D
B1A

Figure 7.


B3A (Blank): 1, 2, 3, 4 Hours: X = 490 NM
10-9M Uranine/Buffer: EXC = 490 NM
1.44 x 10^4
Intensity
0
500
525
550
Wavelength (nm)


B3D: 1, 2, 3, 4 Hours: EXC = 490 NM
10-9M Uranine/Buffer: EXC = 490 NM
3.37 x 10^4
Intensity
0
500
525
550
Wavelength (nm)
1
2
3
4


B3B: 1, 2, 3, 4 Hours: EXC = 490 NM
10-8M Uranine/Buffer: EXC = 490 NM
1.85 x 10^6
Intensity
0
500
525
550
Wavelength (nm)
1
2
3
4

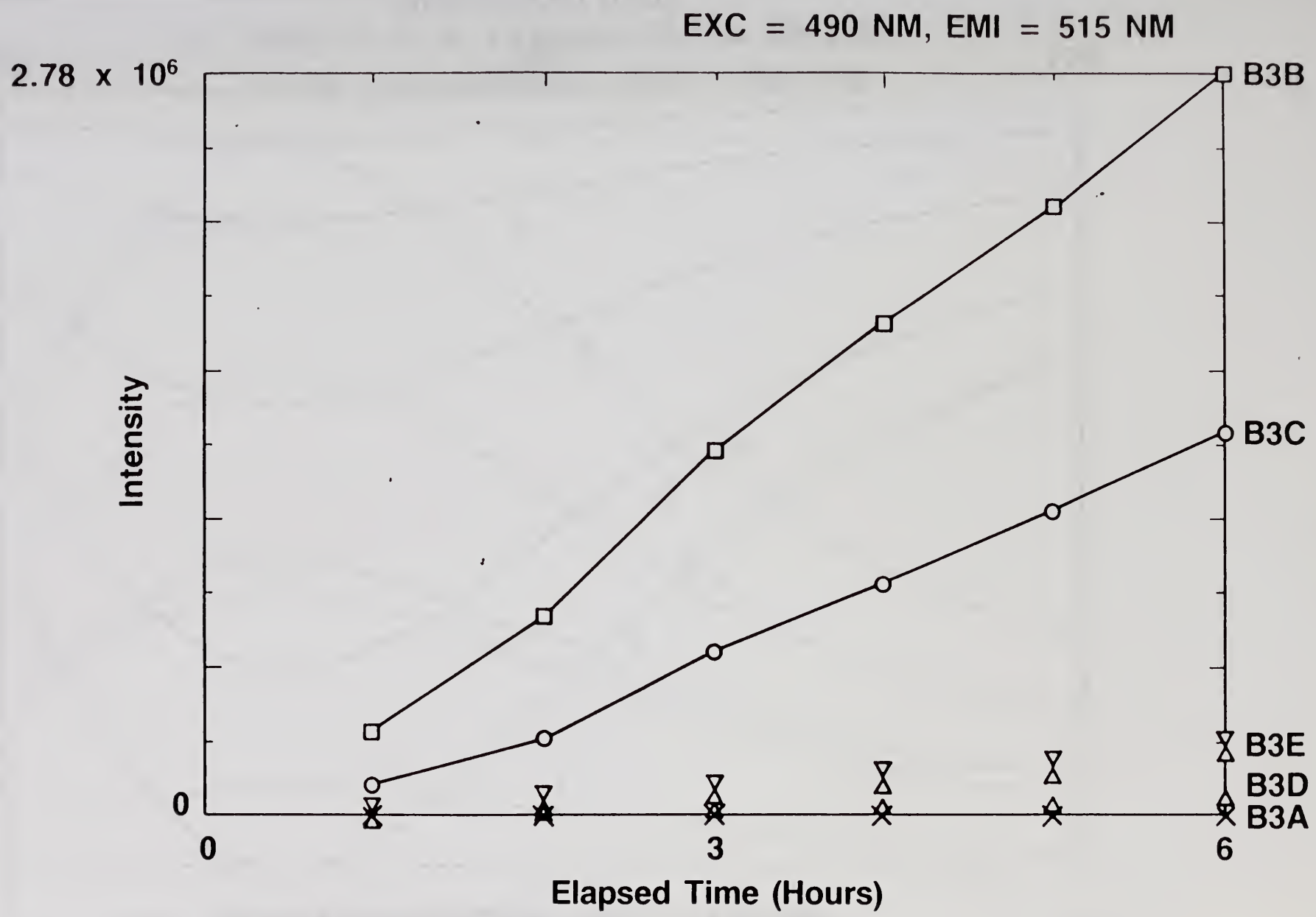
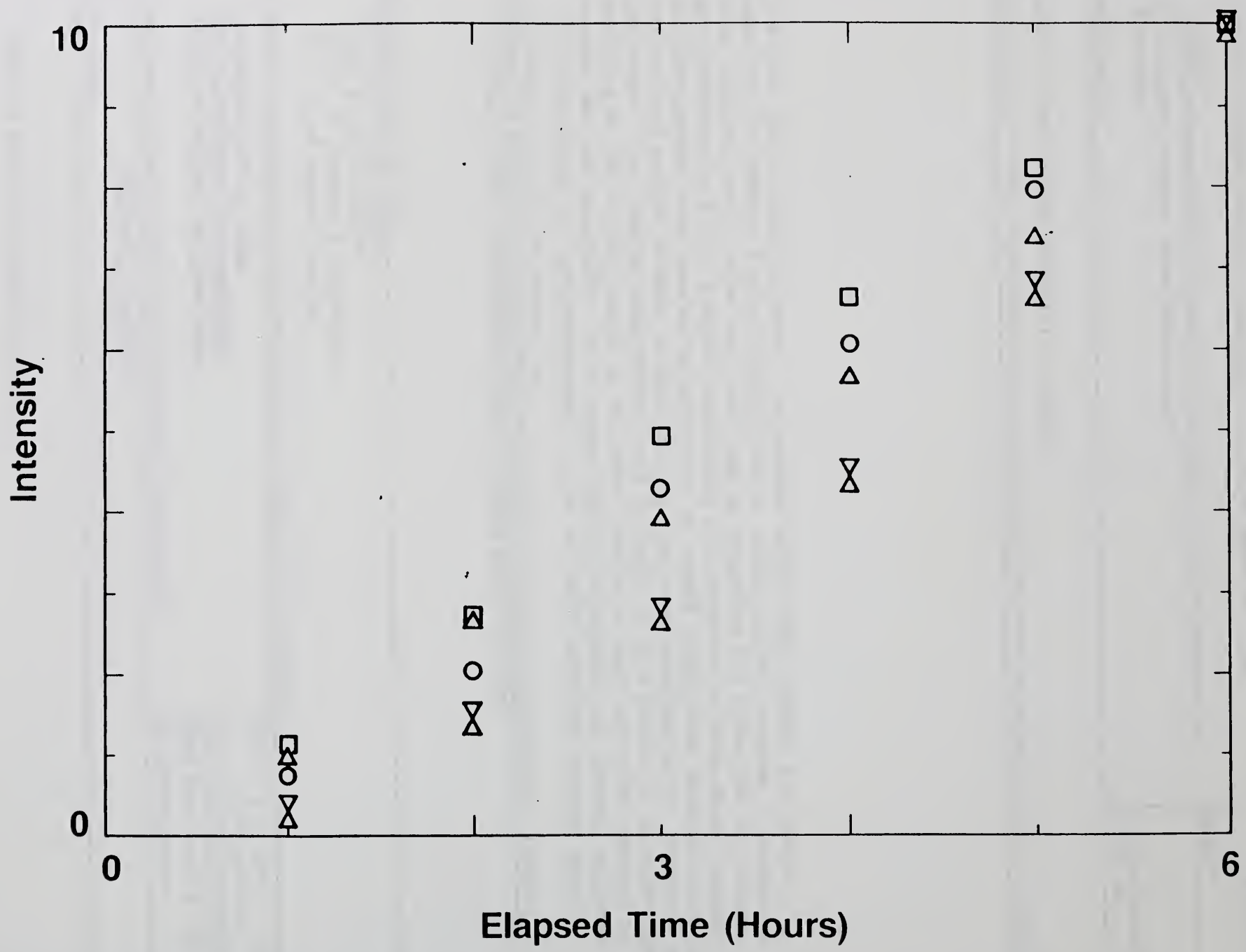

EXC = 490 NM, EMI = 515 NM
2.78 x 10^6
Intensity
0
0
3
6
Elapsed Time (Hours)
B3B
B3C
B3E
B3D
B3A

Figure 11



NBS-114A (REV. 2-8C)

U.S. DEPT. OF COMM. BIBLIOGRAPHIC DATA SHEET (See instructions)	1. PUBLICATION OR REPORT NO. NBSIR 88-3721	2. Performing Organ. Report No.	3. Publication Date APRIL 1988

4. TITLE AND SUBTITLE

"Flow of Molecules Through Condoms"

5. AUTHOR(S)

Charles M. Guttman

6. PERFORMING ORGANIZATION (If joint or other than NBS, see instructions)

NATIONAL BUREAU OF STANDARDS
U.S. DEPARTMENT OF COMMERCE
GAITHERSBURG, MD 20899

7. Contract/Grant No.

FDA 224-79-5023, Mod 16

8. Type of Report & Period Covered

Final Report
March 1 to May 1, 1987

9. SPONSORING ORGANIZATION NAME AND COMPLETE ADDRESS (Street, City, State, ZIP)

Food & Drug Adminsitration
Office of Science & Technology
12000 Wilkins Avenue
Rockville, MD 20852

10. SUPPLEMENTARY NOTES

☐ Document describes a computer program; SF-185, FIPS Software Summary, is attached.

11. ABSTRACT (A 200-word or less factual summary of most significant information. If document includes a significant bibliography or literature survey, mention it here)

An apparatus for the measurement of flux of small molecules through whole condoms has been developed. It is shown that the experiment can measure diffusion constants as low as 10^{-13} cm^2/s or a single pinhole as small as .4 micrometers in the condom. For pinhole measurements this is shown to be a factor of 10 better than current ASTM testing methods on the basis of flow considerations only. Analysis of the experimental data show the difficulties in making unambiguous determinations on the mechanisms of flow. Further experiments are necessary to distinguish between large holes and small holes and fluxes due to diffusion and those due to pinholes. These results suggest a more careful study of fluxes through condoms is necessary to assure that a particle about .1 micrometer cannot pass through the condom.

12. KEY WORDS (Six to twelve entries; alphabetical order; capitalize only proper names; and separate key words by semicolons)

condom; latex condom; pinhole; diffusion

13. AVAILABILITY

☒ Unlimited
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☐ Order From Superintendent of Documents, U.S. Government Printing Office, Washington, D.C. 20402.
☒ Order From National Technical Information Service (NTIS), Springfield, VA. 22161

14. NO. OF PRINTED PAGES

46

15. Price

$11.95

USCOMM-DC 6043-P80