

CAPILLARIES AS CONTROLLED RELEASE DEVICES FOR INSECT PHEROMONES AND OTHER VOLATILE SUBSTANCES—A REEVALUATION

Part I. Kinetics and Development of Predictive Model for Glass Capillaries¹

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Abstract—Controlled release formulations are required for the dissemination of behavior-modifying chemicals in insect control strategies. Among the types of formulations that have been used for some time are glass and plastic capillaries. Erratic release rates on field use of such capillaries prompted us to reexamine the release of volatile materials with regard to (1) kinetics of the release, (2) the effect of the vapor-air column above the liquid, and (3) developing a predictive model. Results indicate that the release is not zero order, and that the length of the vapor-air column is a critical factor of the system; a predictive model has been developed that will allow better design of capillary controlled-release formulations.

Key Words—Controlled release, capillaries, volatile substances, pheromones, release rates, kinetics, predictive model.

INTRODUCTION

The use of behavior-modifying chemicals in insect control strategies requires that they be disseminated from controlled-release formulations. Capillaries made of glass, polyester terephthalate, and Celcon[®] have been employed for some time as controlled-release vehicles for insect pheromones (Roelofs, 1979, and references therein). Such pheromone-containing capillaries have been used as trap baits in both monitoring (e.g., Haworth et al., 1982) and mass trapping programs (Pitman, 1971) as well as in control programs employing aerially applied

pheromone to disrupt mating communication (Brooks et al., 1977; Doane et al., 1982; Golub et al., 1983).

The ideal controlled-release device utilizes all of the active material in a given time period, releasing it at a constant rate (zero-order kinetics). In the practical application of insect pheromones, it is unlikely that the ideal device will be achieved. As reported by Brooks (1980), after an initial burst, the release from capillaries remains relatively constant (pseudo zero-order kinetics); hence they would appear to be superior to impregnated plastic and rubber matrices, plastic laminates, microcapsules etc., all of which have first-order kinetics.

Richardson (1959), investigated the evaporation of liquids from tubes, of 4, 6, and 8 mm in diameter, into a gas stream and applied Stefan's law relating the rate of evaporation to the height of the vapor-air column above the surface of the liquid. He suggested that in tubes of too small a diameter the velocity profile of the diffusing vapor would be affected and the relationship would not hold. This statement, together with problems of erratic release rates during the field use of Albany International hollow fibers, both normal Celcon (white) and black Celcon used in disruption formulations (Weatherston, unpublished), and polyester terephthalate used in trapping studies (J. Sharpe, personal communication), prompted us to reexamine the release of volatile materials from capillaries with regard to (1) kinetics of the release, (2) the effect of the vapor-air column above the liquid, and (3) developing a predictive model for the release of volatile materials.

METHODS AND MATERIALS

The compounds used in this study were obtained as follows: hexane, ethyl acetate, methanol, and *n*-butanol, distilled in glass, from Burdick and Jackson Laboratories Inc., Muskegon, Michigan; isopropyl alcohol and 1,2-dichloroethane from Fisher Scientific Co., Fairlawn, New Jersey; benzene from J.T. Baker Chemical Co., Phillipsburg, New Jersey; butyl acetate (gold star) and hexyl acetate from Aldrich Chemical Co. Inc., Milwaukee, Wisconsin. All compounds were used without further purification.

The 0.0475-cm-radius glass capillaries were Kimax-51 capillary tubes purchased from Ace Glass Inc., Vineland, New Jersey. The 0.0244-cm-radius glass capillaries were Drummond Microcaps purchased from Drummond Scientific Company, Broomhall, Pennsylvania, and flame sealed at one end.

The wide-bore capillaries ($N = 5$ or 7) were filled from a 25- μ l Hamilton syringe to the desired level. The narrow-bore capillaries ($N = 7$) were filled from a 10- μ l syringe fitted with a fused silica needle of the type used for on-column injection in capillary gas chromatography. The tubes were put in a fume hood at 23–30°C with an average wind speed of 0.2 m/sec or in an environmental chamber at 15°C with an average wind velocity of 0.7 m/sec.

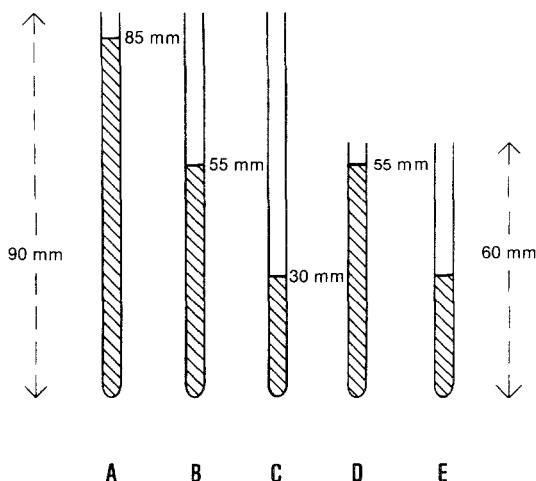


Fig. 1. Glass capillaries (0.0475 cm radius) used in the initial experiments

Weight-loss measurements were recorded on a Mettler M-S Microgramatic Balance (precision ± 0.002 mg). For meniscus regression measurements, the evaporation was followed by direct reading from the open end of the capillary against 10×10 to the centimeter graph paper, or with a light microscope fitted with a reticle.

RESULTS AND DISCUSSION

Initially, a series of five capillaries (0.0475 cm in radius) ($N = 5$), set up as in Figure 1, were charged with hexane and the release at 30°C followed by weight-loss measurements. By plotting the amount released from the capillaries against time (Figure 2), it can be seen that capillaries A and D give similar curves, B and E give similar curves but release at a slower rate, and C releases at the slowest rate; that the rate is not zero order; and that the initial length of the vapor-air column is a critical factor in controlling the release rate. This can also be seen from Table 1 where the mean release rates over the initial 17.5 hr between A and D, and B and E are in good agreement.

Figure 3 illustrates the data for *n*-butanol released from 0.0475-cm-radius capillaries at 30°C . The release rates for benzene, isopropanol, and dichloroethane were also determined; the data comparing their release with that of hexane and *n*-butanol from A capillaries are shown in Figure 4.

The shape of the curves in Figures 2–4 suggest that the amount of material evaporating from the capillaries varies directly with the square root of time. This is borne out by regression analyses which give high r^2 values, e.g., for the

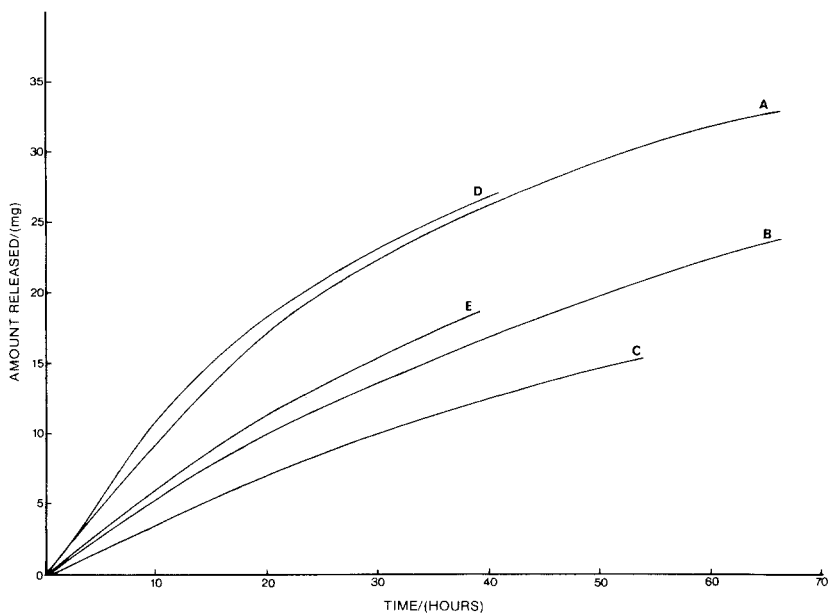


Fig. 2. Release of hexane from glass capillaries (0.0475 cm radius) as shown in Figure 1 at 30°C by the weight-loss method.

release of hexane (Figure 2): $r^2 = 0.9994, 0.9994, 0.9992, 0.9990,$ and $0.9986,$ respectively, for capillaries A to E.

$$x = Kt^{1/2} \quad (1)$$

were x = amount evaporated, t = time, and K = constant.

TABLE 1. MEAN RELEASE RATE ($\bar{X} \pm SD$) ($\mu\text{g/hr}$)/TIME PERIOD FOR HEXANE FROM GLASS CAPILLARIES (RADIUS = 0.0475 cm) AT 30°C BY WEIGHT LOSS

Capillary	Time (hr)						
	17.5	23.9	29.3	40.3	46.8	52.5	63.9
A	909 (± 33)	508 (± 59)	478 (± 40)	343 (± 13)	329 (± 15)	327 (± 15)	288 (± 9)
B	521 (± 13)	409 (± 11)	377 (± 7)	296 (± 6)	294 (± 6)	287 (± 5)	266 (± 6)
C	359 (± 12)	318 (± 11)	314 (± 6)	246 (± 8)	240 (± 5)	196 (± 6)	e
D	970 (± 27)	533 (± 11)	486 (± 11)	371 (± 12)	e ^a	e	e
E	578 (± 24)	437 (± 16)	435 (± 30)	e	e	e	e

^ae = capillaries empty.

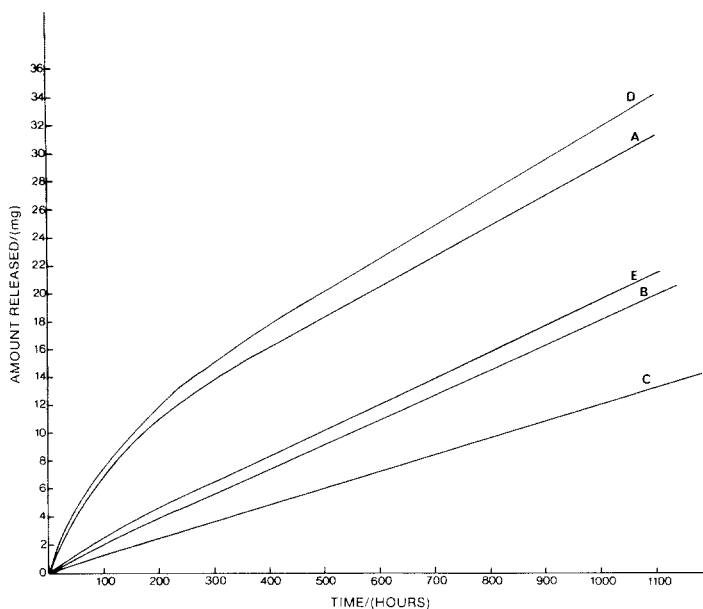


Fig. 3. Release of *n*-butanol from glass capillaries (0.0475 cm radius) as shown in Figure 1 at 25°C by the wight-loss method.

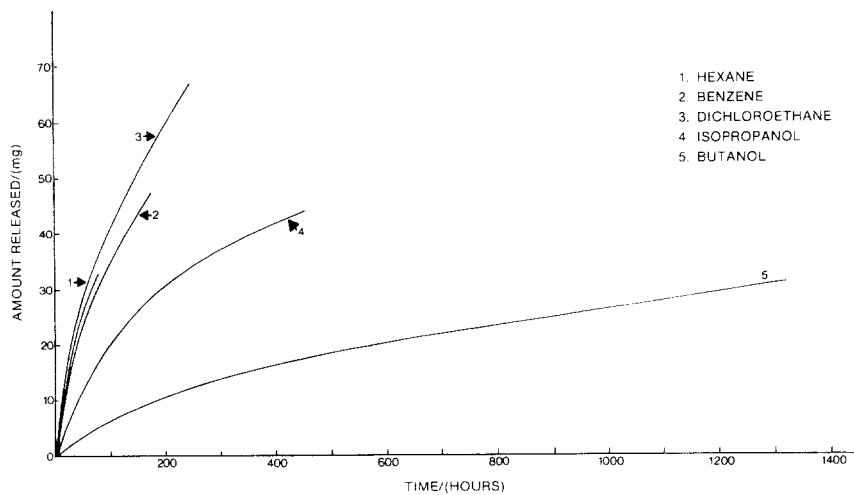


Fig. 4. Comparison of the release of five volatile compounds from A capillaries (0.0475 cm radius) at 25°C by meniscus-regression measurements.

From the volume of a cylinder, the amount evaporated can also be related to the length (l) of the vapor-air column within the capillary above the liquid surface

$$x = l \pi r^2 \rho \quad (2)$$

were r = inner radius of the capillary, ρ = density of the liquid charge.

Therefore,

$$\frac{dx}{dl} = \pi r^2 \rho \quad (3)$$

$$\frac{dx}{dt} = \frac{1}{2} K t^{-1/2} \quad (4)$$

Combining equations 3 and 4

$$\frac{dl}{dt} = \frac{K}{2 \pi r^2 \rho} \cdot t^{-1/2} \quad (5)$$

The mechanism of vapor release from capillaries, if transwall permeation is excluded, is, as reported by Ashare et al. (1975, 1976), Brooks et al., (1977) and Brooks (1980), a simple three-stage process: (1) evaporation at the liquid-vapor interface, (2) diffusion through the vapor-air column to the end of the capillary, and (3) convection away from the end of the capillary, with the diffusion step being the controlling factor. These authors developed an equation from a theoretical treatment of the release of volatile materials from capillaries relating rate with time

$$\frac{dl}{dt} = \left[\frac{-McD}{2\rho} \cdot \ln \left(1 - \frac{P_{\text{vap}}}{P} \right) \right]^{1/2} t^{-1/2} \quad (6)$$

where M = molecular weight of the liquid, c = molar density of the vapor-air column (Bird et al., 1960), D = diffusion coefficient, P_{vap} = vapor pressure of the liquid, P = atmospheric pressure, and ρ = density of the liquid.

Combining equations 5 and 6

$$K = \pi r^2 \left[-2 McD\rho \ln \left(1 - \frac{P_{\text{vap}}}{P} \right) \right]^{1/2} \quad (7)$$

Table 2 shows the comparison of the calculated and experimentally derived values for K for the five compounds studied and illustrates their agreement. This now permits us to calculate, instead of measuring experimentally, the rate of release for volatile compounds from glass capillaries

Substituting equation 2 into equation 1, and rearranging we obtain

$$t^{1/2} = \frac{l \pi r^2 \rho}{K} \quad (8)$$

TABLE 2. COMPARISON OF CALCULATED AND OBSERVED VALUES FOR K FOR VARIOUS COMPOUNDS

Compound	Amount ($\mu\text{g}/\text{hr}^{1/2}$)		$K_{\text{calc}}/K_{\text{obsv}}$
	K_{calc}	K_{obsv}	
Butanol	805	862	0.934
Isopropanol	2000	2093	0.956
Benzene	3530	3782	0.933
Hexane	3776	4033	0.936
1,2-Dichloroethane	4199	4479	0.937

Substituting equation 8 into equation 4 leads to

$$\frac{dx}{dt} = \frac{K^2}{2\pi r^2 \rho} \cdot \frac{1}{l}$$

which by substituting the value of K (7) is equivalent to

$$\frac{dx}{dt} = -McD\pi r^2 \ln\left(1 - \frac{P_{\text{vap}}}{P}\right) \cdot \frac{1}{l} \quad (9)$$

Equation 9 is the basis of the model for predicting the release rate of volatile materials from glass capillaries which may be used to design capillary formulations. For practical considerations an algorithm was developed which allows us to calculate the release rate from the capillaries with respect to “ l ” and time, given the various constants and parameters, for the volatile material indicated in equation 9. In this way the effects of such factors as capillary length and radius, temperature, materials of different volatilities, and atmospheric pressure on the release rate may be tested very rapidly.

To test the model, the rates of evaporation of various compounds from glass capillaries of various lengths and of two internal diameters were measured at two temperatures. The validity of the model is shown in Figures 5–9.

Considering a situation where there is a requirement to release *n*-butanol at 10 $\mu\text{g}/\text{hr}$ at 25° over 500 hr, it can be calculated from the results presented in Figure 3 with 0.0475-cm-radius capillaries that all five formulations would accomplish this. However, formulation C would be the most efficient of those illustrated. If the desired rate and longevity were 60 $\mu\text{g}/\text{hr}$ over 115 hr, then only formulations A and D would give the required activity, with D being the more efficient since it uses less active material. However, in a case requiring the release of 60 $\mu\text{g}/\text{hr}$ over 500 hr at 25°C, there are several choices, three of which are to use formulations A or D and reapply the treatment every 115 hr (i.e., 4.35 \div 5 applications) or use a source consisting of six C capillaries. Simple calculations reveal that formulation A would require 2.36, and D 1.53 times

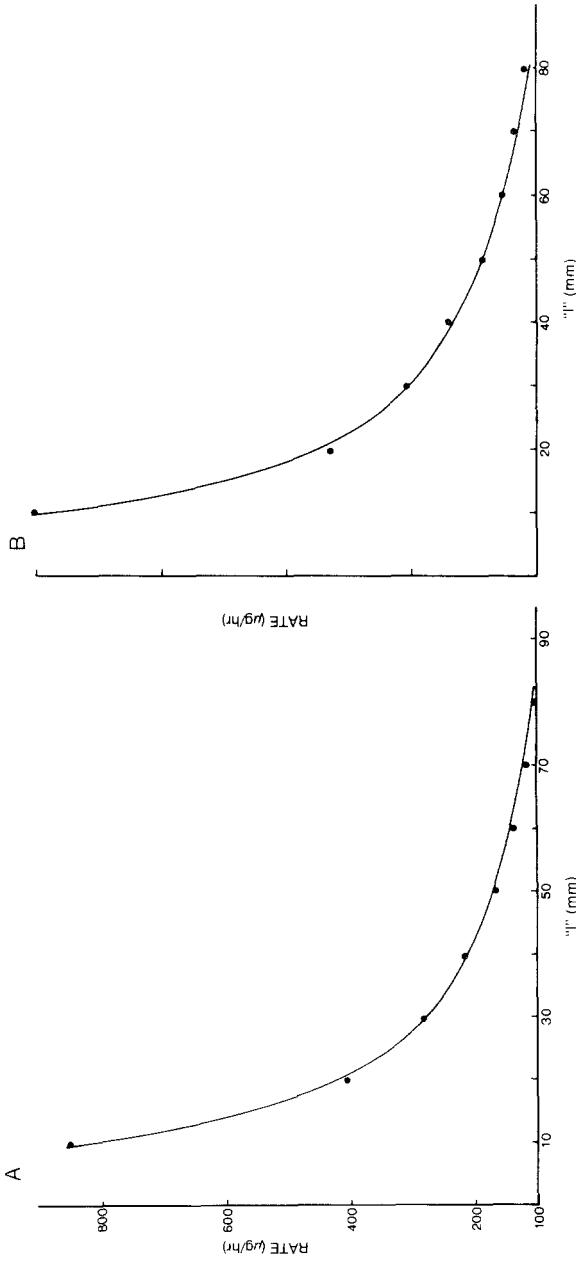


Fig. 5. Release of (A) methanol and (B) ethyl acetate from glass capillaries (0.0475 cm radius) at 24°C relative to *l*. (—) predicted rate, (●) observed rate.

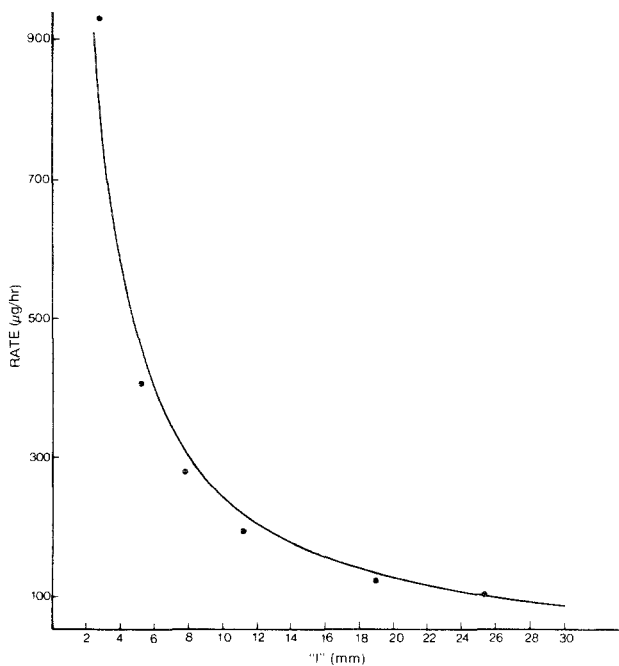


Fig. 6. Release of ethyl acetate from glass capillaries (0.0244 cm radius) at 23° relative to l . (—) predicted rate, (●) observed rate.

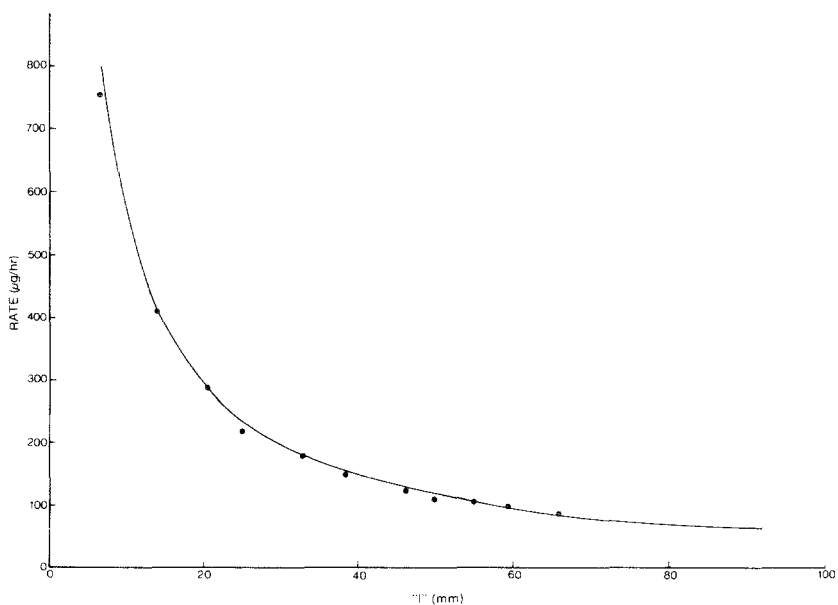


Fig. 7. Release of ethyl acetate from glass capillaries (0.0475 cm radius) at 15°C relative to l . (—) predicted rate, (●) observed rate.

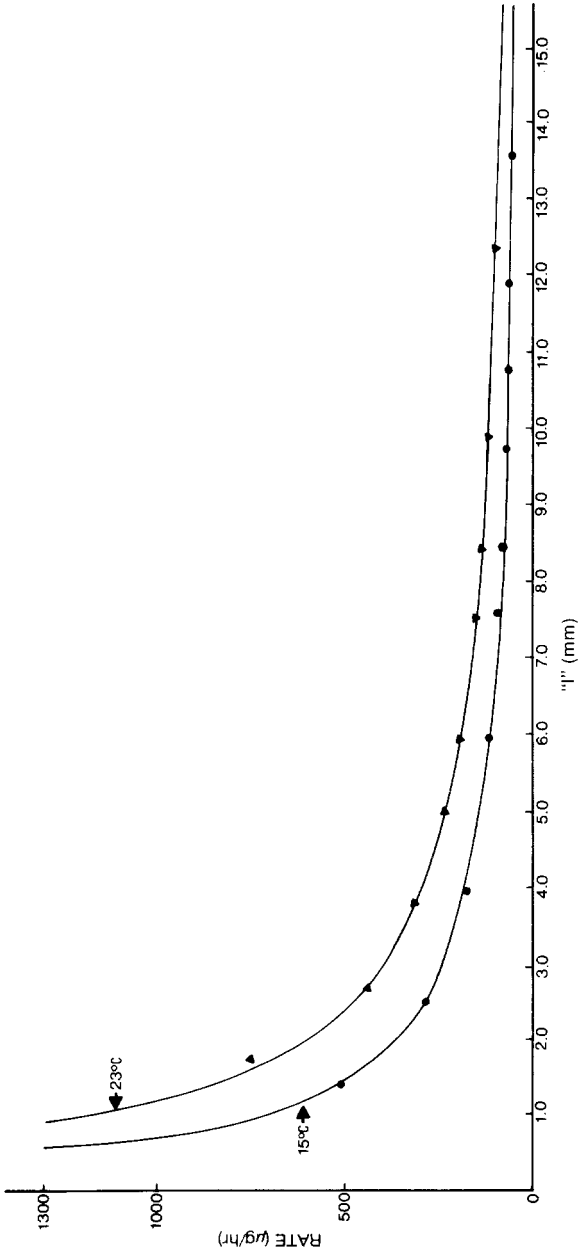


Fig. 8. Release of butyl acetate from glass capillaries (1.5 cm long and 0.0475 cm radius) at 15° and 23°C relative to *l*. (—) predicted rate, (● and ▼) observed rate.

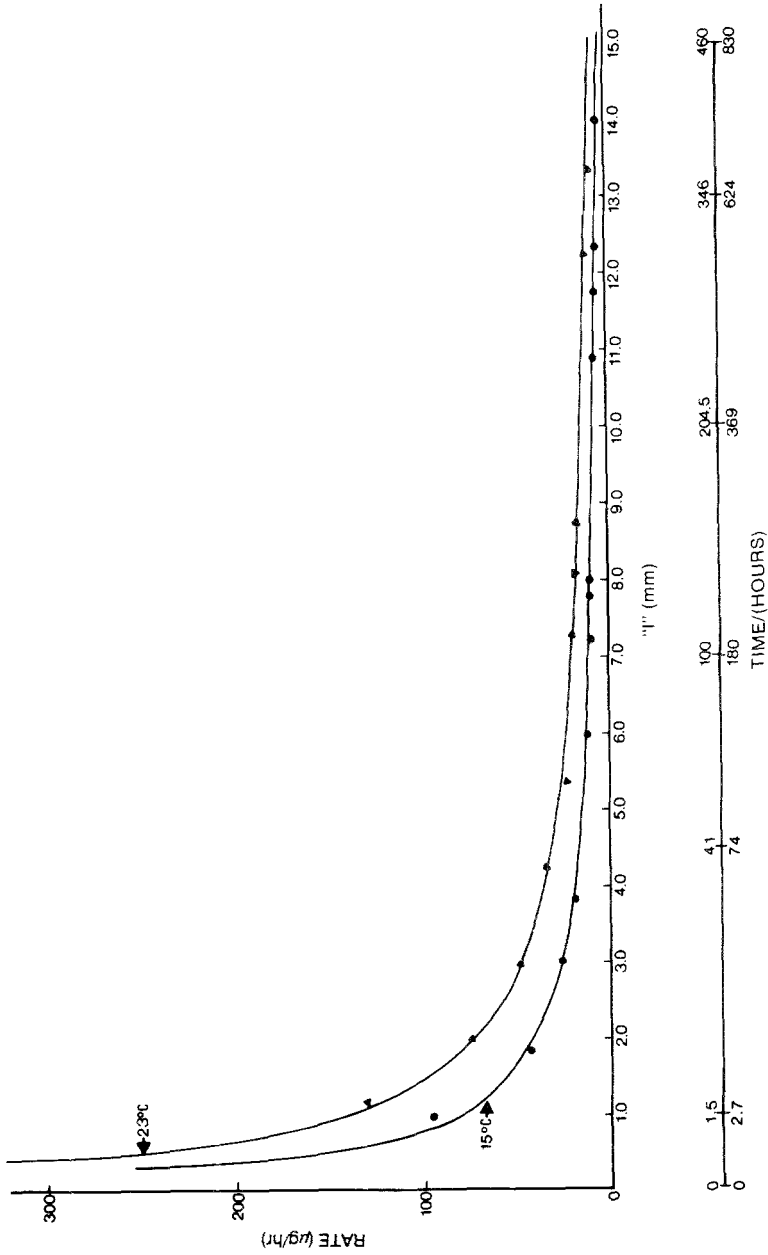


Fig. 9. Release of hexyl acetate from glass capillaries (1.5 cm long and 0.0475 cm radius) at 15° and 23°C relative to l and time. (—) predicted rate, (● and ▼) observed rate. Time scale upper numbers for 23°C, lower numbers for 15°C.

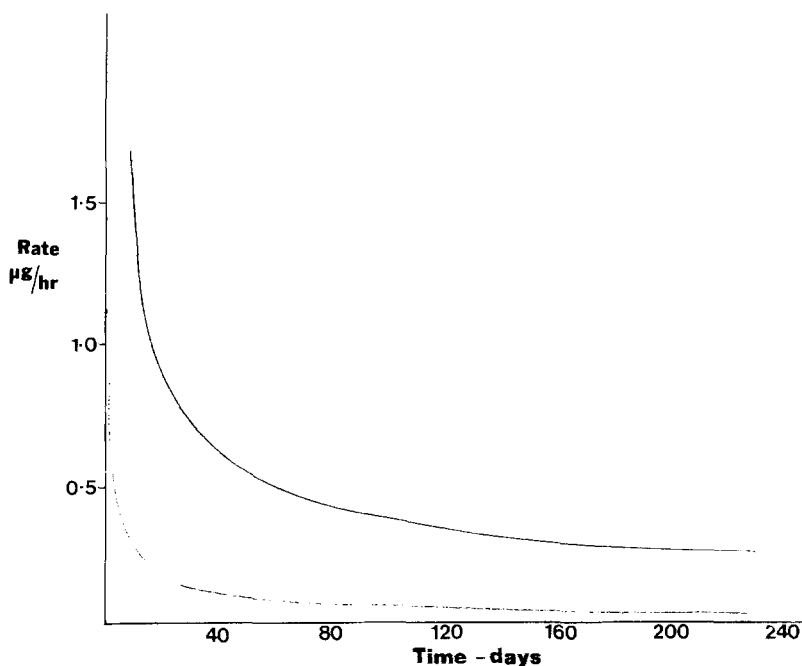


Fig. 10. Predicted release rate for (Z)-9-tetradecen-1-yl acetate from glass capillaries at 30°C. Upper curve, 1.5-cm-long \times 0.0254-cm-radius capillaries; lower curve, 1.5-cm-long \times 0.0102-cm-radius capillaries.

more active ingredient than the combination C formulation. Transferring this rationale to insect pheromones and their use for monitoring or control by aerial dissemination, when the current manufacturer-quoted price for bulk quantities of Z-9-tetradecen-1-yl acetate is (US) \$4000.00/kg and for gossypure is (US) \$2000.00/kg, it is clear there is an urgent need to design better formulations with respect to both their efficacy and economics. We believe the development of predictive models will partly satisfy this need.

Figure 10 is the graphical representation of the prediction for the release of (Z)-9-tetradecen-1-yl acetate from both 0.0254-cm and 0.0102-cm-radius glass capillaries 1.5 cm in length at 30°C. The graph represents the release characteristics when the initial column of liquid in the capillaries is 1.45 cm in length. The device will take 220 days to empty, with, after the first 40 days, a mean release rate of $57.3 (\pm 13.6)$ ng/hr for the smaller-diameter capillary. If, in a given field situation, the requirement was for the release of this pheromone at 50 ng/hr for 45 days at 30°C, the model indicates that this may be obtained by using a 0.0102-cm-radius capillary of total active length 1.35 cm with an initial vapor-air column of 1.1 cm; this will ensure that the device will release at the correct rate of 50 ± 3 ng/hr from day 1 in the field and function over the

required 45 days. With the same longevity and temperature parameters but a release rate of 300 ng/hr for the same pheromone, the model indicates that a 0.0254-cm-radius capillary with the same fill characteristics as above should be used.

Work is in progress to further develop the model for predicting the release rates of binary mixtures, and to take into account the variations in temperatures found in field situations.

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