

VOLATILITIES OF NONAQUEOUS LIQUID SYSTEMS
BY THE FILTER PAPER AND DROPLET METHODS

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ABSTRACT

A simple gravimetric method was developed to determine the evaporation characteristics of spray diluents and pesticide formulations, and was compared with droplet evaporation characteristics. The method involves evaporation of a liquid film from a filter paper surface and is applicable only to oils and non-aqueous formulations. Results indicate that the method is quite suitable for providing information on the comparative evaporation characteristics of liquids, and in that respect, it is comparable to the droplet evaporation technique. In addition, it provided greater precision than the droplet method.

With either method, the percentage of mass or volume remaining at time 't' followed an exponential decay curve. Curvilinear regression analysis of the data indicated that with either method, the residual amounts of liquids at the final time of measurements was inversely related to the initial evaporation rates. This means that either the residual amounts at time 't' or the initial rates of evaporation would provide equally satisfactory information on the comparative volatility of pesticide formulations and spray diluents.

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INTRODUCTION

In aerial application of pesticides for spruce budworm control, spray droplets of volatile formulations undergo evaporation in transit and decrease in droplet size. With the high volume application techniques which utilize the emission of large droplets ($\sim 300 \mu\text{m}$) with high sedimentation rates, the droplets deposit on targets so quickly that in-flight evaporation is unlikely to be a problem. However, with the ultra-low-volume (ULV) spray practices very fine sprays are emitted, the droplets of which are carried to the target primarily by the prevailing wind and its accompanying eddies (Johnstone 1978). These small droplets take a considerably longer time to reach the target and are therefore highly susceptible to evaporation in transit and loss to the environment. Consequently, the evaporation characteristics of a spray formulation is of prime importance towards the success or failure of an aerial spray operation involving the ULV techniques. Since the major portion of a spray formulation is the spray vehicle or the diluent, the properties of a spray mix are dictated to a large extent by the properties of the diluent. It is therefore very necessary for a formulation scientist to investigate the evaporating nature of diluents and pesticide formulations, so that the optimum spray mixture can be selected for each spray situation.

Methods are published in the literature to determine spray droplet evaporation (Seymour 1969; Hopewell 1959; Picot 1981). These describe wind tunnel studies and/or microscopic measurements of droplets. These techniques are generally elaborate and therefore, there is a need to develop a simple, rapid and economical method for comparing the evaporation characteristics of pesticide formulations and diluents under laboratory conditions. The long-term objective is to use the method to prepare spray mixes with optimum evaporation characteristics which are essential for maximizing on-target deposition, and for minimizing spray loss to the environment. In the present study, a gravimetric method is developed involving the evaporation of a liquid film from a Whatman filter paper, and is compared with droplet evaporation characteristics since the filter paper is affected by the water present in water-based formulations, this method is applicable only to oil-based spray mixes.

MATERIALS AND METHODS

Diluent oils and pesticide formulations used in the study are listed in Table 1, along with the names of companies who supplied them. The percentage composition of the ingredients used in preparing the spray formulations are listed in Table 2.

Table 1. Diluent oils and pesticide formulations used in the study.

Name	Abbreviation used in the text	Source
Cyclosol [®] 63 ID 585	Cycl-63 ID-585	Shell (Toronto, Ontario)
Arotex [®] 3470	Aro-3470	Texaco (Toronto, Ontario)
Dowanol [®] TPM	Dow-TPM	Dow Chemical (Sarnia, Ontario)
Canola oil	Can-oil	Canada Packers (Toronto, Ontario)
Fenitrothion technical	Fe-tech	Sumitomo Chemical (Osaka, Japan)
Maticil [®] 180F Maticil [®] 180D	Mat-180F Mat-180D	Chemagro Ltd. (Mississauga, Ontario)
Zectran [®] technical Zectran [®] UCZF-19	Ze-tech Zect-UC-19	Union Carbide (North Carolina, USA)

Gravimetric method

A circular polyurethane sponge 'S' (Figure 1) of diameter 4.7 cm and thickness 1.5 cm was placed inside the lid of a plastic petri dish 'PT' of diameter 4.8 cm and height 0.8 cm, with four pins 'P' fixed on to the sponge to form the apices of a square (Figure 1). The pointed ends of the pins provided the base for mounting a Whatman No. 1 filter paper of diameter 4.25 cm and a thickness of 250 ± 25 μ m (Figure 1). This system was placed on the pan

Table 2. Composition of diluent oil mixtures and spray formulations used in the study.

Abbreviation	Composition (v/v %)
Oils and mixtures for making spray formulations	
C-CA-DOW ^a	Cycl-63 61/Can-oil 9.75/Dow-TPM 29.25
C-CA-ID-585 ^b	Cycl-63 16.67/Can-oil 33.33/ID-585 50
Zect-AJ ^c	Ze-tech 19.18 ^d g/C-CA-DOW 82.0
Spray Formulations	
FCID-585-1	Fe 11/Cycl-63 35/ID-585 54
FCID-585-2	Fe 11/Cycl-63 40/ID-585 49
FC-1	Fe 22/Cycl-63 78
FD-1	Fe 22/Dow-TPM 78
FD-2	Fe 30/Dow-TPM 70
AID-585-1	Mat-180F 26/ID-585 74
AID-585-2	Mat-180F 26/ID-585 74
ZE-UC-19-DIL	Zect-UC-19 22.1/C-CA-ID-585 77.9
ZE-AJ-DIL	Zect-AJ 25/C-CA-ID-585 75

^a Diluent for dissolving Ze-tech to prepare Zect-AJ.

^b Diluent for preparing ZE-UC-19-DIL and ZE-AJ-DIL.

^c Zect-AJ is used for preparing ZE-AJ-DIL.

^d When 19.18 g of Ze-tech solid is dissolved in 82.0 ml of C-CA-DOW solvent mixture, the total volume reaches 100 ml.

FIG. 1. FILTER PAPER SYSTEM FOR GRAVIMETRIC METHOD

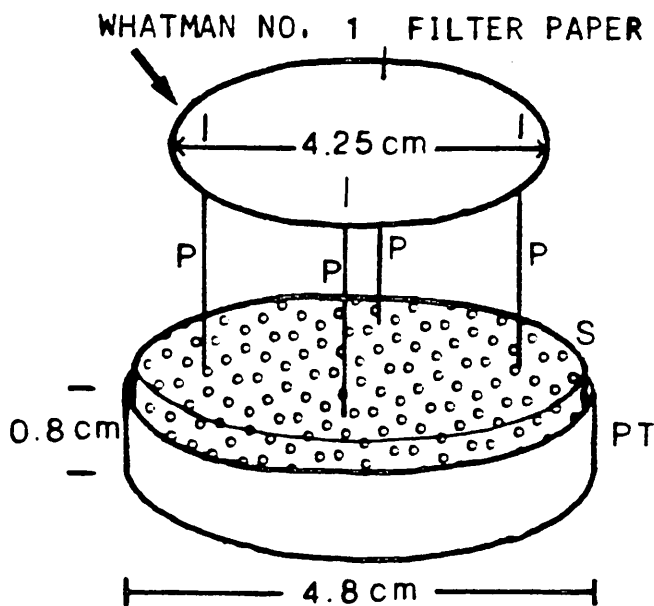
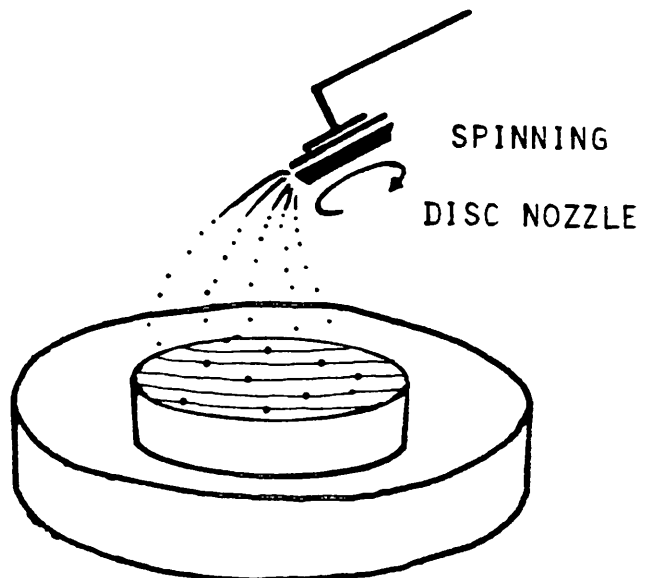


FIG. 2. EVAPORATION OF A DROPLET ON GLASS FIBRE FOR THE DROPLET METHOD



of a Mettler balance of sensitivity 0.0001 g and the empty weight was recorded. A 100 μ l aliquot of the oil to be studied was pipetted out on to the filter paper and the initial weight was recorded at once. As the liquid film continued to evaporate, the doors of the balance were left open to allow air circulation. Residual weights were recorded at 2, 4, 6, 10, 20, 30, 60, 120 and 180 minutes after the initial weighing. Results are presented in terms of the percentage of initial weight remaining at time 't'. The experiment was carried out in triplicate to obtain the mean and standard deviations (Table 3).

The study was carried out in an environmental chamber of dimensions 2.2m x 1.6 m x 2.4 m, maintained at $20^{\circ} \pm 1^{\circ}\text{C}$ and 70-75% relative humidity (RH). Although evaporation of oil-based films are generally unaffected by the RH of the ambient air, the filter paper weight and texture was somewhat influenced at RH's $> 85\%$. Therefore, this method is suitable only for RH values below 80%.

Droplet method

A spray cloud of a narrow droplet spectrum was produced by a battery-operated spinning disc nozzle (FlakTM, Micron Corporation, Wingham, Ontario), and droplets of 250 ± 30 μ m diameter were captured on a glass fibre of 5.6 ± 0.8 μ m thickness mounted on a plastic petri dish which was placed close (about 10 cm) to the nozzle (Fig. 2). This was done to minimize in-flight evaporation of the droplet, so that accurate value can be obtained for the initial droplet diameter on the glass fibre. Droplet diameters were measured under a dissecting microscope at 25x and 40x magnifications at time intervals of 0, 2, 5, 10, 15, 20, 25, 30, 40 and 60 minutes. During measurements, the temperature and humidity values of the environmental chamber were maintained at $20^{\circ} \pm 1^{\circ}\text{C}$ and 70-75% RH respectively. Results are presented in terms of the volume percentage of droplets remaining at time 't'. This was done so that the data can be compared to those of the gravimetric method. The experiment was carried out in triplicate to obtain the mean and standard deviations (Table 4).

Table 3. Residual weight percent of pesticide formulations and diluent oils at time 't' after evaporation. Temp. = 20°±1°C. RH = 70-75%. Gravimetric Method.

Time (min)	Cycl-63		Aro-3470		Dow-TPM		FCID-585-1		FCID-585-2		FC-1	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
0	100.0	0.00	100.0	0.00	100.0	0.00	100.0	0.00	100.0	0.00	100.0	0.00
2	93.9	1.31	97.7	0.17	95.7	0.31	93.9	0.32	91.8	1.24	95.2	0.55
4	87.0	0.67	95.1	0.55	93.8	0.36	88.7	0.47	86.9	1.69	89.9	0.23
6	80.1	1.04	92.8	0.92	92.4	0.29	84.3	1.23	82.9	1.17	84.4	0.59
10	67.5	1.39	87.7	1.31	89.7	0.36	77.9	1.27	77.3	1.38	76.1	0.69
20	41.6	1.52	78.0	1.95	86.9	0.47	62.5	0.74	64.0	1.55	59.3	1.40
30	22.2	1.87	69.8	2.87	84.6	0.87	55.2	1.18	54.3	1.18	46.4	1.80
60	1.07	0.08	53.7	1.97	81.7	1.03	39.7	1.18	40.7	1.04	32.6	0.47
120	0.88	0.07	41.7	1.38	78.7	1.52	27.2	1.37	28.2	1.19	25.5	0.56
180	0.69	0.11	34.6	1.30	77.1	2.06	23.0	1.49	20.4	1.02	22.2	0.47

	FD-1		FD-2		AID-585-1		AID-585-2		ZE-UC-19-DIL		ZE-AJ-DIL	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
0	100.0	0.00	100.0	0.00	100.0	0.00	100.0	0.00	100.0	0.00	100.0	0.00
2	100.4	0.31	100.5	0.31	97.1	0.15	95.1	0.26	94.9	1.18	94.7	0.87
4	99.9	0.50	100.7	0.26	94.0	0.46	91.9	0.10	92.7	1.30	91.3	1.33
6	99.7	0.50	100.6	0.25	91.9	0.55	87.6	0.36	89.5	1.72	87.7	0.06
10	99.3	0.50	100.4	0.26	88.1	0.95	83.8	0.46	82.9	1.78	81.3	1.06
20	98.3	0.78	100.1	0.32	79.7	1.55	77.0	0.31	74.3	1.57	72.6	1.00
30	97.6	0.35	98.9	0.57	75.7	1.65	71.8	1.01	67.1	1.40	67.0	0.21
60	95.3	1.10	97.3	0.36	68.4	1.95	62.0	1.75	59.8	1.10	56.5	1.16
120	91.5	1.25	94.7	0.49	60.4	1.60	52.9	1.59	51.7	0.44	52.2	1.40
180	88.4	1.06	92.4	0.30	55.9	1.07	48.6	1.79	44.6	0.87	44.4	0.50

1
5
1

Table 4. Residual weight percent of pesticide formulations and diluent oils at time 't' after evaporation. Temp. = 20°±1°C. RH = 70-75%. Droplet Method.

Time (min)	Cycl-63		Aro-3470		Dow-TPM		FCID-585-1		FCID-585-2		FC-1	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
0	100.0	0.00	100.0	0.00	100.0	0.00	100.0	0.00	100.0	0.00	100.0	0.00
2	32.7	2.45	87.8	3.93	92.5	1.66	77.5	4.54	77.9	3.91	75.0	5.05
5	8.0	2.10	77.5	1.90	86.3	0.80	64.5	5.74	64.9	4.91	58.1	2.25
10	2.4	0.64	61.3	3.00	72.1	2.72	48.8	7.51	49.4	6.81	48.9	0.74
15	1.0	0.10	52.1	3.45	66.7	3.15	40.1	5.14	40.7	4.10	38.6	1.97
20	1.0	0.10	43.5	3.46	59.4	5.45	36.2	3.52	36.6	3.21	30.3	4.03
25	1.0	0.10	36.8	3.66	54.8	4.74	33.0	3.99	33.5	3.48	23.1	2.76
30	1.0	0.10	30.9	3.81	50.3	4.38	29.8	3.90	30.4	3.19	23.1	2.76
40	1.0	0.10	26.3	3.25	45.0	2.93	25.4	4.39	26.0	3.86	23.1	2.76
60	1.0	0.10	22.9	3.50	39.8	2.42	24.0	3.19	23.8	3.94	23.1	2.76

	FD-1		FD-2		AID-585-1		AID-585-2		ZE-UC-19-DIL		ZE-AJ-DIL	
	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD	Mean	SD
0	100.0	0.00	100.0	0.00	100.0	0.00	100.0	0.00	100.0	0.00	100.0	0.00
2	92.6	1.69	94.7	1.29	88.1	0.58	90.0	1.60	73.3	0.66	73.3	0.66
5	86.4	0.72	88.1	2.03	82.2	1.14	79.1	0.69	69.2	0.40	65.3	1.04
10	75.2	0.89	76.6	1.90	66.6	3.10	63.0	1.15	60.4	0.61	58.8	2.53
15	66.2	0.85	71.0	2.12	58.6	3.11	52.8	1.67	54.7	0.69	52.7	2.55
20	60.7	0.78	63.6	4.52	51.1	3.61	45.8	0.98	49.3	0.76	46.5	1.46
25	55.6	1.51	58.6	3.78	43.9	3.46	39.7	0.97	45.8	0.85	42.8	1.37
30	51.7	1.86	55.4	3.47	38.7	3.01	35.0	0.90	42.8	1.37	39.5	1.32
40	47.1	2.64	50.0	1.75	36.1	3.40	31.1	1.31	37.0	1.33	37.1	1.33
60	42.7	3.31	44.9	1.88	34.8	2.29	30.0	1.95	34.3	1.35	34.3	1.35

When measuring droplet sizes, a tracer dye solution, Automate Red B, (Morton Williams Limited, Ajax, Ontario, Canada) was added to each test liquid at 2% v/v, to make the droplets more easily visible under the microscope. For the sake of uniformity, the same dyed liquids were also used in the gravimetric method.

To maintain the constant temperature and humidity conditions throughout the environmental chamber, a system of continuous air flow was provided. However, if fluctuations occurred in the air flow, the rate of evaporation was affected in both methods, although droplet evaporation was more severely affected than that of the liquid film on the filter paper. It was therefore necessary to monitor the air flow in the vicinity of the samples throughout the study using an anemometer (Model 441 of Kurz Instruments, Carmel Valley, California), so that measurements can be done only when the fluctuations were within the usually observed range of 0.15 to 0.25 m/sec.

RESULTS AND DISCUSSION

Comparative evaporation characteristics of liquids in the two techniques

With both techniques, the residual amounts, expressed as % of initial amounts, were subjected to curvilinear regression analysis to determine the constants A, B and C in the equation:

$$Y = A + Be^{-Ct} \quad \dots\dots\dots(1)$$

where Y = residual wt. % in the gravimetric method, or the residual volume % in the droplet method; t = time in minutes; A, B and C are constants characteristic of the liquids (Table 5 and 6). With both techniques the liquids evaporated following an exponential decay curve (Figures 3 and 4).

In the gravimetric method, the evaporation occurred from the surface of the filter paper, whereas in the droplet method, evaporation occurred from the surface of a sphere. This suggests that the pattern of evaporation is likely to be different in the two tech-

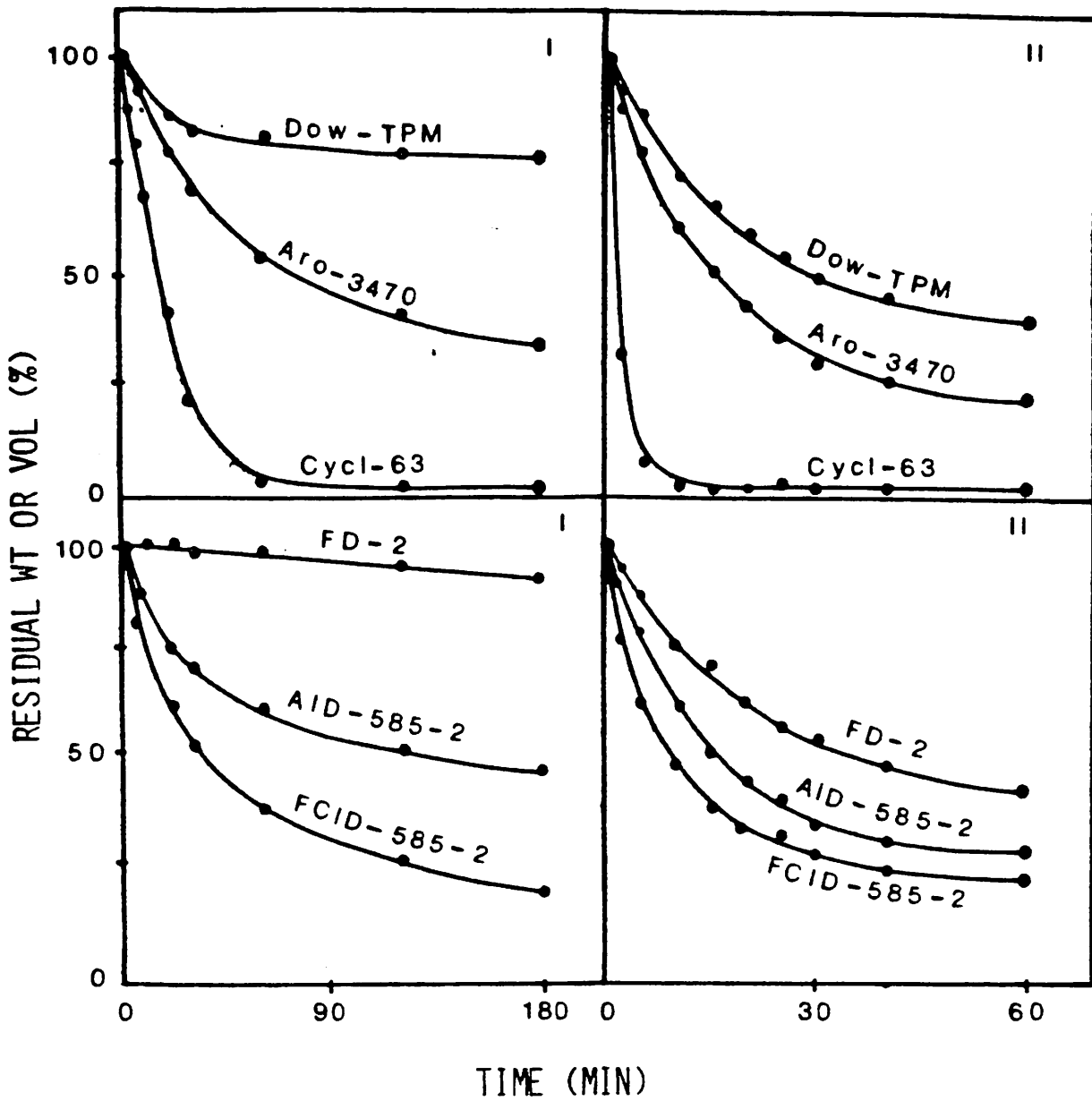
Table 5. Curvilinear regression for evaporation characteristics of pesticide formulations and diluent oils: Gravimetric Method.

Liquid	Regression Equation	R ² (%)	A _g	B _g	C _g
Cycl-63	y = 0.40 + 105e ^{-0.0458t}	99.8	0.40	105	0.0458
Aro-3470	y = 34.0 + 66.0e ^{-0.0200t}	99.9	34.0	66.0	0.0200
Dow-TPM	y = 78.6 + 19.2e ^{-0.0436t}	97.2	78.6	19.2	0.0436
FCID-585-1	y = 24.6 + 73.0e ^{-0.0299t}	99.6	24.6	73.0	0.0299
FCID-585-2	y = 23.3 + 72.6e ^{-0.0276t}	99.2	23.3	72.6	0.0276
FC-1	y = 23.7 + 76.8e ^{-0.0386t}	99.6	23.7	76.8	0.0386
FD-1	y = 77.9 + 22.4e ^{-0.0042t}	99.9	77.9	22.4	0.0042
FD-2	y = 77.2 + 23.5e ^{-0.0024t}	98.7	77.2	23.5	0.0024
AID-585-1	y = 57.6 + 40.9e ^{-0.0268t}	99.1	57.6	40.9	0.0268
AID-585-2	y = 50.0 + 46.8e ^{-0.0264t}	98.9	50.0	46.8	0.0264
ZE-UC-19-DIL	y = 48.0 + 50.0e ^{-0.0303t}	98.7	48.0	50.0	0.0303
ZE-AJ-DIL	y = 48.3 + 49.5e ^{-0.0341t}	98.8	48.3	49.5	0.0341

Table 6. Curvilinear regression for evaporation characteristics of pesticide formulations and diluent oils: Droplet Method.

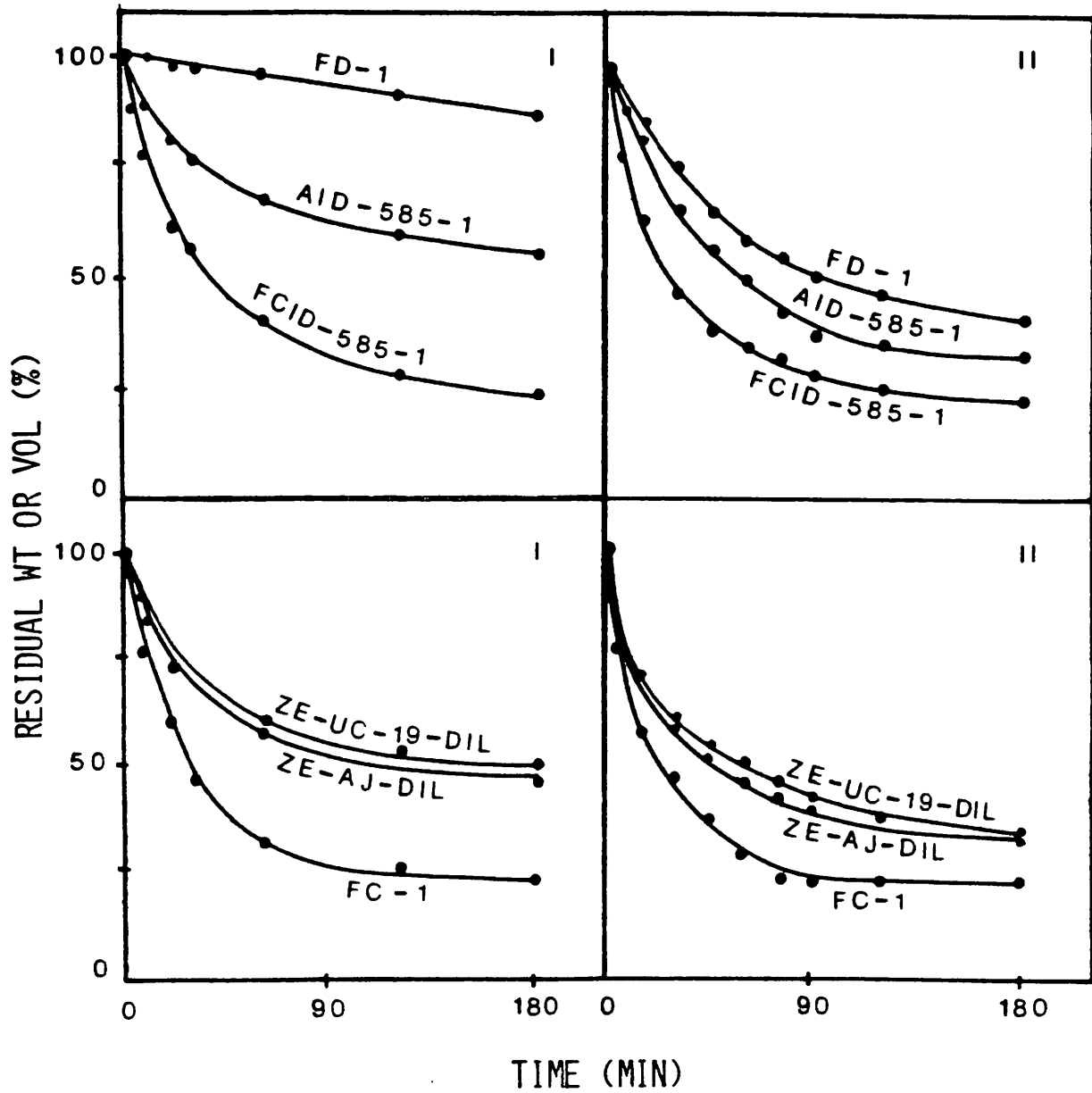
Liquid	Regression Equation	R ² (%)	A _d	B _d	C _d
Cycl-63	y = 1.22 + 98.7e ^{-0.56t}	100	1.22	98.7	0.56
Aro-3470	y = 20.6 + 78.1e ^{-0.0634t}	99.9	20.6	78.1	0.0634
Dow-TPM	y = 37.3 + 62.2e ^{-0.0520t}	99.8	37.3	62.2	0.0520
FCID-585-1	y = 26.7 + 69.6e ^{-0.11t}	98.9	26.7	69.6	0.11
FCID-585-2	y = 26.8 + 69.4e ^{-0.11t}	98.9	26.8	69.4	0.11
FC-1	y = 22.7 + 72.9e ^{-0.12t}	98.2	22.7	72.9	0.12
FD-1	y = 40.0 + 59.5e ^{-0.0540t}	99.9	40.0	59.5	0.0540
FD-2	y = 41.6 + 58.5e ^{-0.0485t}	99.9	41.6	58.5	0.0485
AID-585-1	y = 31.7 + 67.4e ^{-0.0652t}	99.5	31.7	67.4	0.0652
AID-585-2	y = 27.8 + 72.3e ^{-0.0716t}	99.9	27.8	72.3	0.0716
ZE-UC-19-DIL	y = 36.9 + 54.4e ^{-0.0845t}	94.2	36.9	54.4	0.0845
ZE-AJ-DIL	y = 37.4 + 54.9e ^{-0.11t}	94.7	37.4	54.9	0.11

FIG. 3. VARIATION OF RESIDUAL AMOUNTS (%) WITH TIME



I : Filter paper method
II : Droplet method

FIG.4. VARIATION OF RESIDUAL AMOUNTS (%) WITH TIME



I : Filter paper method
II : Droplet method

niques. This is in fact reflected in the evaporation rates (Tables 7 and 9), calculated from dy/dt of the curvilinear regression equation (1). It is evident that with all 12 liquids evaporation occurred faster from the droplet than from the filter paper. This is also shown in the short time period (60 min) required for the droplet to reach a residual volume percent, close to the limiting value. However, the liquid film on the filter paper evaporated at a slower rate and hence, even after 3 h the residual weight percents were much higher than the limiting values. However, the 3 h period was chosen because the rate of evaporation at 3 h was quite comparable to that of the droplet evaporation at 60 min (Tables 7,9). In fact, this time period is shown to be adequate for obtaining meaningful curvilinear relationships, evaporation rates and half-lives ($T_{1/2}$) (Tables 5 to 11; Figures 3 and 4).

With either technique, the initial evaporation rates and half-lives varied markedly with the nature of the formulations and diluent oils. However, the two methods are comparable for all practical purposes. For example, the high volatility of Cycl-63 and of formulations containing appreciable amounts of Cycl-63 is well demonstrated in both the techniques. Also the least volatile liquids are those of Dow-TPM and formulations containing Dow-TPM, and this is clearly shown in both the methods. The relative evaporation characteristics of formulations and oils are represented in Table 11 where the 12 liquids were grouped in four distinct categories in the order of increasing volatilities, as indicated by their distinctly different initial evaporation rates, (i.e. those at 1 min.), $T_{1/2}$ values and A and B. With both methods, the constants A_g and A_d , which represent the amount left over after evaporation at the final time, i.e., 3 h in the gravimetric method and 1 h in the droplet method, is inversely related to the evaporation characteristics of liquids. For example, the most volatile Cycl-63 has the smallest value for A_g and A_d , whereas the three least volatile liquids FD-2, FD-1 and Dow-TPM have the largest values (Table 11). The inverse relationship is demonstrated by the plot of initial evaporation rate vs constant A in both methods (Figure 5). The linear regression equations indicated a fairly good correlation:

Table 7. Rate of Evaporation (dY/dt) of Oils and Pesticide Formulations, with time 't', as calculated from equation (1) on page 7. Gravimetric Method.

Time 't' (min.)	Rate (dY/dt)											
	Cycl-63	Aro-3470	Dow-TPM	FCID-585-1	FCID-585-2	FC-1	FD-1	FD-2	AID-585-1	AID-585-2	ZE-UC-19-DIL	ZE-AJ-DIL
1	4.59	1.29	0.80	2.12	1.95	2.85	0.093	0.057	1.07	1.20	1.47	1.63
3	4.19	1.24	0.73	2.00	1.84	2.64	0.092	0.057	1.01	1.14	1.38	1.52
5	3.82	1.19	0.67	1.88	1.75	2.44	0.091	0.057	0.96	1.08	1.30	1.42
7	3.49	1.15	0.62	1.77	1.65	2.26	0.091	0.056	0.91	1.03	1.23	1.33
9	3.18	1.10	0.57	1.67	1.56	2.09	0.090	0.056	0.86	0.97	1.15	1.24
12.5	2.71	1.03	0.49	1.50	1.42	1.83	0.089	0.056	0.78	0.89	1.04	1.10
17.5	2.16	0.93	0.39	1.29	1.24	1.51	0.087	0.055	0.69	0.78	0.89	0.93
22.5	1.72	0.84	0.31	1.11	1.08	1.24	0.085	0.054	0.60	0.68	0.77	0.78
27.5	1.36	0.76	0.25	0.96	0.94	1.03	0.083	0.054	0.52	0.60	0.66	0.66
30	1.22	0.72	0.23	0.89	0.88	0.93	0.082	0.053	0.49	0.56	0.61	0.61
35	0.97	0.66	0.18	0.77	0.76	0.77	0.081	0.053	0.43	0.49	0.52	0.51
40	0.77	0.59	0.15	0.66	0.66	0.63	0.079	0.052	0.38	0.43	0.45	0.43
45	0.61	0.54	0.12	0.57	0.58	0.52	0.077	0.051	0.33	0.38	0.39	0.36
55	0.39	0.44	0.08	0.42	0.44	0.35	0.074	0.050	0.25	0.29	0.29	0.26
75	0.16	0.29	0.03	0.23	0.25	0.16	0.068	0.048	0.15	0.17	0.16	0.13
105	0.04	0.16	0.01	0.09	0.11	0.05	0.060	0.044	0.07	0.08	0.06	0.05
135	0.01	0.09	0.00	0.04	0.05	0.02	0.053	0.041	0.03	0.04	0.03	0.02
165	0.00	0.05	0.00	0.02	0.02	0.01	0.047	0.038	0.01	0.02	0.01	0.01

Table 8
 Linear Regression Equations for The plot of Rate (dy/dt) versus Curvilinear Regression Constants
 A, B, or C of Equation (1), on Page 7. Gravimetric Method.

Time 't' (min.)	Regression equation					
	Rate R versus 'A'	R ² (%)	Rate R versus 'B'	R ² (%)	Rate R versus 'C'	R ² (%)
1	R = 3.63 - 0.0449 A	83.1	R = -0.789 + 0.0443 B	86.3	R = -0.240 + 66.7 C	53.3
5	R = 3.12 - 0.0382 A	86.0	R = -0.618 + 0.0374 B	88.2	R = -0.141 + 56.0 C	53.6
9	R = 2.68 - 0.0324 A	88.5	R = -0.495 + 0.0317 B	90.6	R = -0.064 + 46.4 C	52.8
17.5	R = 1.96 - 0.0231 A	93.6	R = -0.225 + 0.0219 B	91.1	R = 0.074 + 32.1 C	52.9
27.5	R = 1.36 - 0.0155 A	97.3	R = -0.143 + 0.0149 B	95.9	R = 0.120 + 19.5 C	45.0
30	R = 1.24 - 0.0140 A	97.5	R = -0.116 + 0.0134 B	95.6	R = 0.128 + 17.4 C	43.7
35	R = 1.04 - 0.0115 A	97.3	R = -0.0746 + 0.011 B	94.5	R = 0.145 + 13.5 C	38.9
40	R = 0.86 - 0.0094 A	95.5	R = -0.0376 + 0.009 B	91.7	R = 0.151 + 10.5 C	35.0
55	R = 0.51 - 0.0052 A	82.4	R = 0.0179 + 0.005 B	76.6	R = 0.152 + 4.59 C	18.8
75	R = 0.26 - 0.0023 A	54.0	R = 0.0400 + 0.002 B	48.2	R = 0.128 + 0.93 C	2.5
105	R = 0.09 - 0.0005 A	12.3	R = 0.0433 + 0.000 B	10.0	R = 0.091 - 0.82 C	8.3
135	R = 0.04 - 0.0000 A	0.0	R = 0.0353 + 0.000 B	0.0	R = 0.067 - 1.13 C	42.8

Table 9. Rate of Evaporation (dY/dt) of Oils and Pesticide Formulations, with time 't', as calculated from equation (1) on page 7. Droplet Method.

Time 't' (min.)	Rate (dY/dt)											
	Cycl-63	Aro-3470	Dow-Tpm	FCID-585-1	FCID-585-2	FC-1	FD-1	FD-2	AID-585-1	AID-585-2	ZE-UC-19-DIL	ZE-AJ-DIL
1	31.6	4.65	3.07	6.86	6.84	7.76	3.04	2.70	4.12	4.82	4.22	5.41
3	10.3	4.09	2.77	5.50	5.49	6.10	2.73	2.45	3.61	4.18	3.57	4.34
5	3.36	3.61	2.49	4.42	4.40	4.80	2.45	2.23	3.17	3.62	3.01	3.48
7	1.10	3.18	2.25	3.54	3.53	3.78	2.20	2.02	2.78	3.14	2.54	2.80
9	0.36	2.80	2.03	2.84	2.84	2.97	1.98	1.83	2.44	2.72	2.15	2.24
12.5	0.05	2.24	1.69	1.94	1.93	1.95	1.64	1.55	1.95	2.12	1.60	1.53
17.5	0.00	1.63	1.30	1.12	1.11	1.07	1.25	1.21	1.40	1.48	1.05	0.88
22.5	0.00	1.19	1.00	0.64	0.64	0.59	0.95	0.95	1.01	1.03	0.69	0.51
27.5	0.00	0.87	0.77	0.37	0.37	0.32	0.73	0.75	0.73	0.72	0.45	0.29
35	0.00	0.54	0.52	0.16	0.16	0.13	0.49	0.52	0.45	0.42	0.24	0.13
45	0.00	0.29	0.31	0.05	0.05	0.04	0.28	0.32	0.23	0.21	0.10	0.04
55	0.00	0.15	0.19	0.02	0.02	0.01	0.16	0.20	0.12	0.10	0.04	0.01

Table 10. Linear Regression Equations for The Plot of Rate (dY/dt) versus Curvilinear Regression Constants A, B or C of Equation (1), on Page 7. Droplet Method.

Time 't' (min.)	Regression equation					
	Rate R versus 'A'	R ² (%)	Rate R versus 'B'	R ² (%)	Rate R versus 'C'	R ² (%)
1	R = 24.8 - 0.606 A	74.4	R = - 29.5 + 0.536 B	69.3	R = 0.346 + 55.8 C	99.5
3	R = 9.73 - 0.176 A	84.8	R = - 5.48 + 0.148 B	71.3	R = 2.910 + 13.9 C	84.0
5	R = 4.48 - 0.0363 A	24.6	R = 1.74 + 0.025 B	13.5	R = 3.320 + 0.80 C	1.90
7	R = 2.50 + 0.0081 A	1.40	R = 3.59 - 0.013 B	3.90	R = 3.100 - 3.02 C	30.6
9	R = 1.64 + 0.0214 A	11.2	R = 3.77 - 0.022 B	14.1	R = 2.730 - 3.86 C	57.5
12.5	R = 0.963 + 0.025 A	24.0	R = 3.17 - 0.022 B	22.6	R = 2.110 - 3.56 C	79.0
17.5	R = 0.512 + 0.021 A	32.9	R = 2.25 - 0.016 B	24.1	R = 1.440 - 2.65 C	82.8
22.5	R = 0.275 + 0.017 A	34.0	R = 1.59 - 0.012 B	20.6	R = 1.000 - 1.93 C	70.5
27.5	R = 0.139 + 0.013 A	32.0	R = 1.14 - 0.009 B	16.7	R = 0.702 - 1.42 C	56.5
35.0	R = 0.038 + 0.009 A	29.5	R = 0.71 - 0.006 B	13.4	R = 0.422 - 0.90 C	42.6

Table 11. Relative evaporation characteristics of pesticide formulations and diluent oils.

Liquid	Category	Gravimetric method						Droplet method					
		Initial Rate*	Final Rate*	T _{1/2} (g) (min)	A _g	B _g	C _g	Initial Rate*	Final Rate*	T _{1/2} (d) (min)	A _d	B _d	C _d
FD-1	I	0.093	0.047	- b	77.9	22.4	0.0042	3.04	0.16	34	40.0	59.5	0.0540
FD-2		0.057	0.038	-	77.2	23.5	0.0024	2.70	0.20	40	41.6	58.5	0.0485
Dow-TPM		0.800	0.000	-	78.6	19.2	0.0436	3.07	0.19	30	37.3	62.2	0.0520
Aro-3470	II	1.29	0.05	76	34.0	66.0	0.0200	4.65	0.15	16	20.6	78.1	0.0634
AID-585-1		1.07	0.01	-	57.6	40.9	0.0268	4.12	0.12	20	31.7	67.4	0.0652
AID-585-2		1.20	0.02	150	50.0	46.8	0.0264	4.82	0.10	17	27.8	72.3	0.0716
ZE-UC-19-DIL		1.47	0.01	120	48.0	50.0	0.0303	4.22	0.04	17	36.9	54.4	0.0845
ZE-AJ-DIL		1.63	0.01	120	48.3	49.5	0.0341	5.41	0.01	17	37.4	54.9	0.1100
FCID-585-1	III	2.12	0.02	40	24.6	73.0	0.0299	6.86	0.02	10	26.7	69.6	0.1100
FCID-585-2		1.95	0.02	40	23.3	72.6	0.0276	6.84	0.02	10	26.8	69.4	0.1100
FC-1		2.85	0.01	23	23.7	76.8	0.0386	7.76	0.01	9	22.7	72.9	0.1200
Cycl-63	IV	4.59	0.00	17	0.4	105	0.0458	31.6	0.00	1.5	1.22	98.7	0.5600

* Rates were calculated from the curvilinear regression equation (1), using, Rate = dY/dt.

^a T_{1/2}(g): Time for the residual wt. to reach 50% of the initial value, in the gravimetric method.

T_{1/2}(d): Time for the residual vol. to reach 50% of the initial value, in the droplet method.

^b Values are not calculated because T_{1/2} was not reached in the time interval studied.

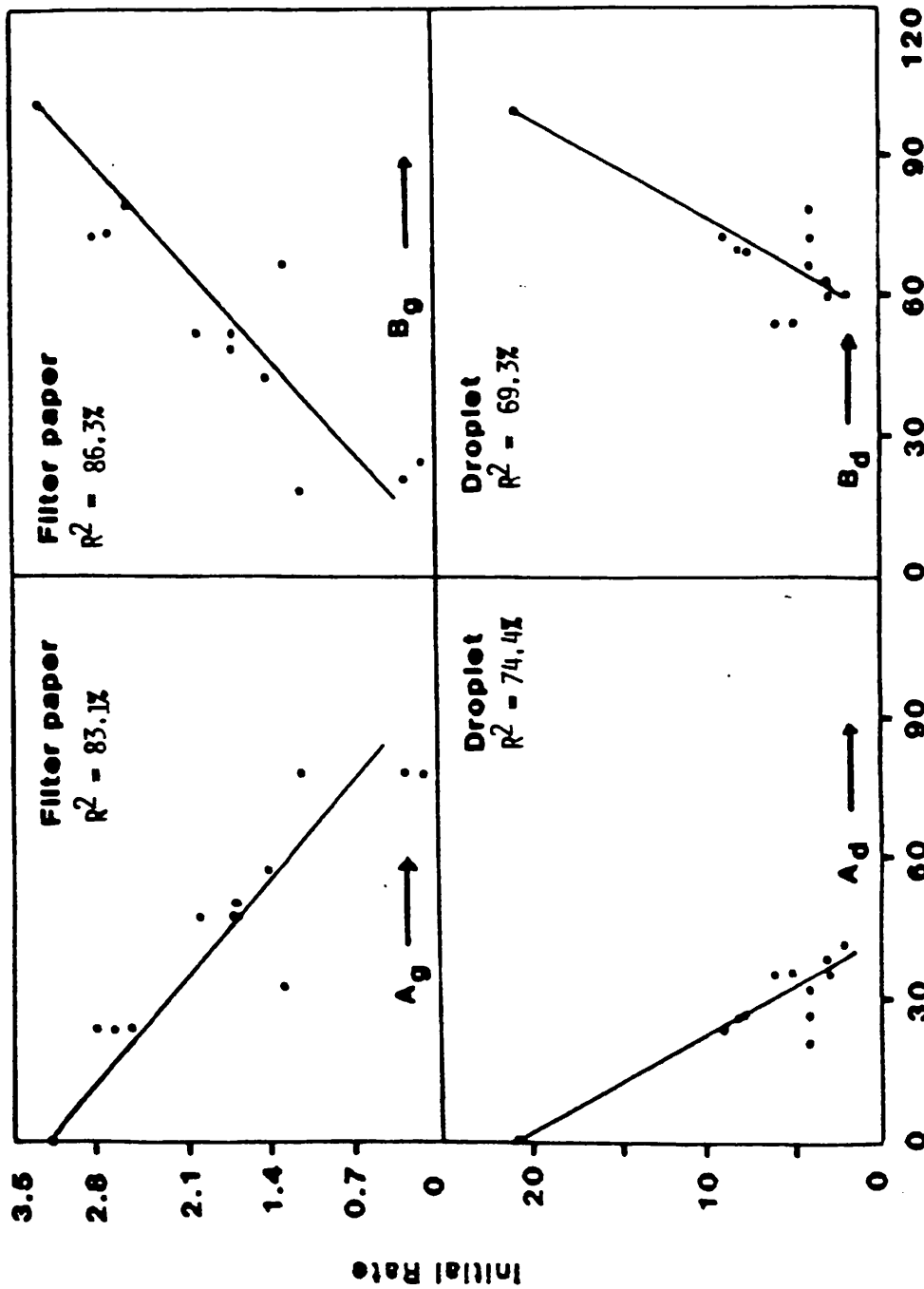
Category I Liquids of low volatility

Category II Liquids of medium volatility

Category III Liquids of high volatility

Category IV Liquids of extremely high volatility

FIG. 5. CORRELATION OF INITIAL RATE OF EVAPORATION WITH CURVILINEAR REGRESSION CONSTANTS 'A' AND 'B'



$$\text{Rate(g)} = 3.34 - 0.0358 A_g \quad (R^2 = 83.1\%)$$

$$\text{Rate(d)} = 18.0 - 0.394 A_d \quad (R^2 = 74.4\%)$$

Constant B also appears to be related to the volatility of liquids, but unlike A, B is directly related to the volatility. For the highly volatile Cycl-63, B is the greatest in both methods (Tables 5, 6 and 11). For the next three formulations, i.e. category III, B is slightly smaller but greater than for the rest, although this trend is not fully evident in the droplet method. For the three least volatile liquids in category I, B is the lowest in the gravimetric method, but again, this is not clearly indicated in the droplet method. The direct relationship between the initial rate and constant B is demonstrated by the plot of rate vs B (Fig. 5) according to the equations:

$$\text{Rate(g)} = -0.101 + 0.0338 B_g \quad (R^2 = 86.3\%)$$

$$\text{Rate(d)} = -16.1 + 0.331 B_d \quad (R^2 = 69.3\%)$$

The correlation is about the same for the constants A_g and A_d , and the results indicate that measurement of either the residual amounts at time 't', or the constants B, or the initial rates of evaporation would provide adequate information on the relative volatility of pesticide formulations and diluent oils.

The inverse and direct proportionalities of A and B respectively with the volatile nature of the liquids indicate the inverse relationship between A and B. Accordingly, when B was plotted against A (Figure 6), the relationship was found to be linear according the same equation in both methods;

$$B_g = 100 - 1.03 A_g \quad (R^2 = 99.1) \quad (\text{Gravimetric Method})$$

$$B_d = 99.1 - 1.06 A_d \quad (R^2 = 94.0) \quad (\text{Droplet Method})$$

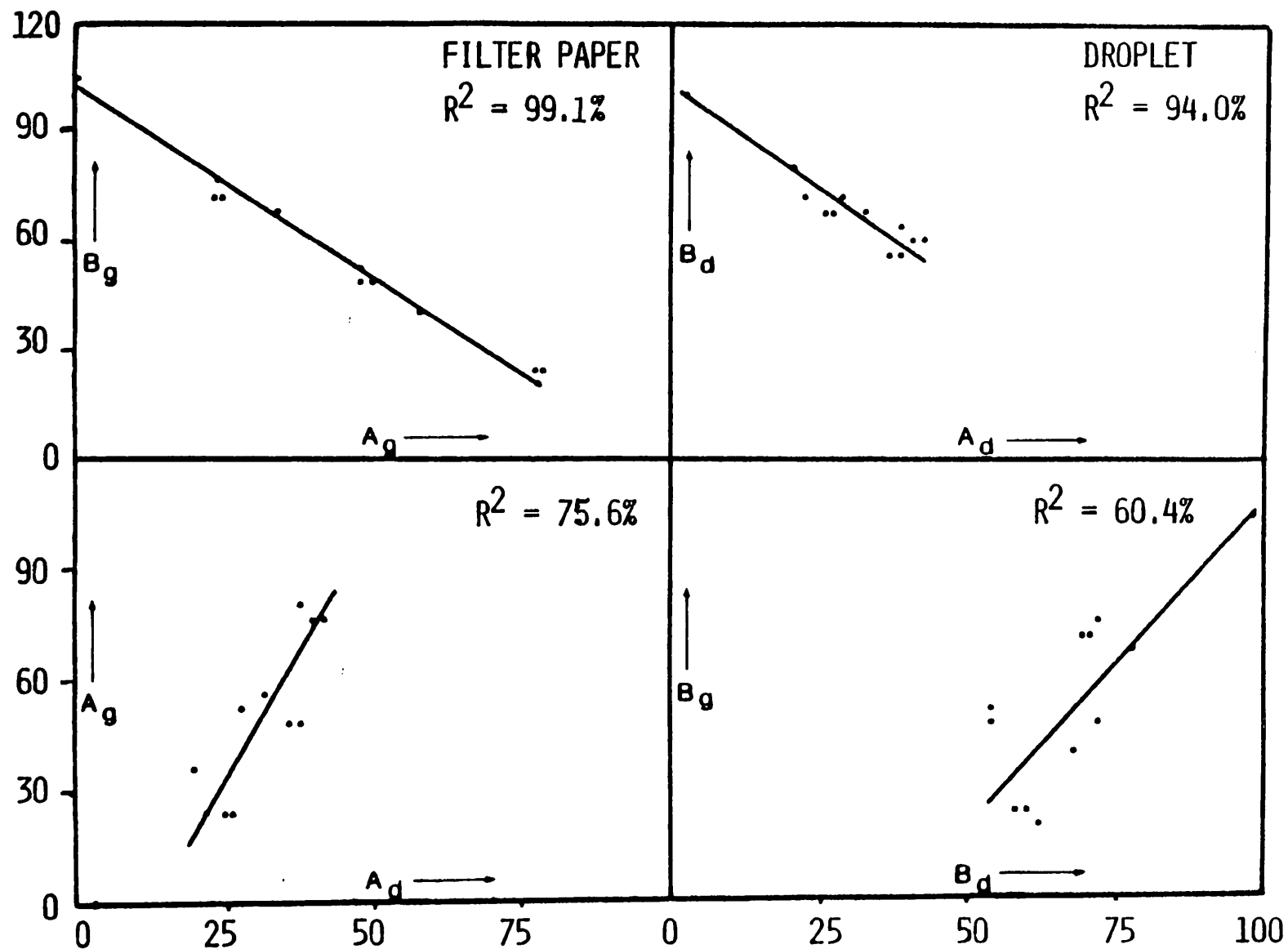
This probably indicates the similar comparative behaviour of the liquids in the two methods.

The exponent C_g does not appear to bear any simple relationship with evaporation rates of liquids (Table 8) or with the constants A_g or B_g , as shown below:

$$C_g = 0.0409 - 0.000295 A_g \quad (R^2 = 30.0\%)$$

$$C_g = 0.0124 - 0.000280 B_g \quad (R^2 = 28.8\%)$$

FIG.6. CORRELATION BETWEEN CURVILINEAR REGRESSION CONSTANTS



However, in the droplet method, the initial evaporation rate (that at 1 min.) correlates well ($R^2 = 99.5\%$), (Table 10), and moderately well with A_d and B_d , as indicated below:

$$C_d = 0.424 - 0.0104 A_d \quad (R^2 = 68.4\%)$$

$$C_d = -0.50 + 0.0091 B_d \quad (R^2 = 62.6\%)$$

Since both methods provided exponential decay curves for the evaporation characteristics of most liquids (except for FD-1 and FD-2), the constants A, B and C might possibly indicate some relationship between the two methods. Accordingly the A_g, B_g & C_g values from the weight method were correlated with the corresponding A_d, B_d & C_d values from the droplet method (Figure 6). When fitted into a linear regression equation:

$$A_g = -11.4 + 1.94 A_d \quad (R^2 = 75.6\%)$$

$$B_g = -58.4 + 1.65 B_d \quad (R^2 = 60.4\%)$$

$$C_g = 0.0216 + 0.0487 C_d \quad (R^2 = 25.8\%)$$

The data indicated some correlation between the two methods, although the A values correlated better than the B values. Correlation was non-existent for the C values. These findings indicate that the evaporation characteristics of liquids exhibit some form of relationship between the two techniques. The fact that correlation was not the best indicates that the pattern of evaporation is different in the two methods. In the gravimetric method, the liquids tend to occupy the empty crevices of the filter and this seemed to have retarded the evaporation processes. As a result the rate was slower than in the droplet method. The retardation in the rate appears to be much more pronounced for liquids of low volatility than for those of high volatility. This is reflected in the wider range of values for the regression constants A and B in the filter paper method than for those in the droplet method. For example, liquids in the categories II, III and IV in Table 11 provides A_g and B_g values of approximately the same order as A_d and B_d values. However, for liquids in category I, the filter paper method provides A_g and B_g values which are markedly different from A_d and B_d values of the droplet method.

The reason for the unusually low evaporation rates of liquids in category I in the filter paper method could also be due to the hygroscopic nature of the three liquids FD-1, FD-2 and Dow-TFM, causing absorption of moisture into the filter paper, thus providing an

apparently low evaporation rate. In the droplet method however, the absence of a filter causes a much slower absorption and retention of moisture, thus providing a more realistic evaporation rate. It is likely that the filter paper method is not highly recommended for hygroscopic liquids and formulations.

Comparative precision of the two methods

Tables 3 and 4 present results in "Mean \pm SD" of three measurements. It is evident that results from the gravimetric method are much less variable, with the standard deviations being consistently lower than those of the droplet method. This is partly due to the greater accuracy of the weighing technique than the visual measurements of the diameter of a rapidly evaporating droplet. It is also partly due to the slower rate of evaporation from the filter paper, which facilitates more reliable measurements at the time when readings are being taken.

CONCLUSIONS

In summary, the present study indicates the suitability of the gravimetric method for comparing the evaporation characteristics of spray vehicles and oil-based pesticide formulations. In both methods, the liquids evaporated following an exponential decay. Although evaporation occurred faster from the droplet surface than from the filter paper, the relative evaporation characteristics of liquids were similar in both methods, i.e. those which were highly volatile in one method were also found to be highly volatile in the other. Similar behaviour was also observed with formulations of low volatility.

With either method, the evaporation characteristics of a liquid were inversely related to the curvilinear regression constant A, i.e. which represents the residual amounts measured at 3 h in the gravimetric method, or at 1 h in the droplet method. This indicates that measurement of either the residual amounts or the initial rates of evaporation would provide equally satisfactory information on the volatile nature of pesticide formulations and diluent oils.

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