Evaluation of Methodologies for Field Studies of Spray Deposition

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ABSTRACT

USING Rhodamine-B and copper as tracers, four common methods of deposition assessment, i.e., combinations of fluorometry and colorimetry on leaf and mylar targets were compared for use on citrus. Merits and limitations of each method were identified. All were found to be reliable; however, considering limitations in the lab and in the field, colorimetric analysis of leaf samples appeared to be the most desirable method for deposition or residue assessment in citrus spraying.

INTRODUCTION

Almost all research studies dealing with efficiency of spray application require some quantitative method of deposition assessment. The methods used have been based on visual judgement, optical measurement, and chemical analysis. They usually have involved the use of tracer materials which often employ a fluorescent dye that could be seen under ultra-violet light or an element or compound that could be isolated and measured by chemical analysis. Deposition has been assessed using plant leaves, fruit, and twigs or artificial targets such as paper, mylar, film, glass, or metal.

Each method has some merit and its suitability is determined by the nature of the crop, chemical application technique, and degree of reliability sought. The objective of this study was to examine several common methods of deposition assessment simultaneously, and identify their merits, limitations, and reliabilities for spraying studies on citrus leaves.

DEPOSITION ASSESSMENT METHODS

Visual judgement of deposition patterns (Staniland, 1959; Edwards et al., 1961; Bullock et al., 1968) is simple, fast, and adequate for determining large differences in spray coverage but is too subjective for more detailed studies. Therefore, attempts have been made to find quantitive methods for more reliable deposition assessment.

Liljedahl and Strait (1959) developed an instrument that could measure the reflected light from a fluorescent dye deposit (on a paper strip) and provide a continuous recording of deposition for an entire swath. Carlton et al. (1982) collected spray deposits on 35 mm film and ran through a colorimeter which could provide a continuous readout across the spray swath. Whitney and Roth (1985) employed string as spray collector and used it along with a fluorometer for analysis. Sistler et al. (1982) developed an image analyzer that could measure the percent coverage, droplet size, and number of droplets per unit area. These methods have been used mostly in aerial application and on field crops. In general, they are fast and more sophisticated than visual judgement but do not necessarily result in more reliable measurements of deposition.

Chemical analysis involving various instrumental measurements is laborious but provide more reliable results. In a drift study, Yates et al. (1974) used a fluorometer to analyze fluorescent spray deposits on mylar sheets and a gas chromatograph to measure pesticide residues on alfalfa crop. Whitney (1981) studied fluorometry for deposition assessment on citrus trees. Byers et al. (1984) sprayed chelated copper on apple trees and analyzed deposits by atomic absorption spectrophotometry. Whitney et al. (1986) employed colorimetry to trace copper deposits on mylar targets placed inside the citrus trees.

MATERIALS AND METHODS

Preliminary Tests

It was intended to compare deposition on leaf samples with that collected on mylar targets by means of visual judgement, fluorometry, and colorimetry. Testing of several water soluble fluorescent dyes including Fluorescein, Uranine, and Rhodamine-B* revealed that their dried residues on citrus leaves do not fluoresce under both long and shortwave ultra-violet light; therefore, visual judgement of deposition patterns could not be accomplished. The dyes were photosensitive and their fluorescence diminished by time. Rhodimum-B (Rh-B) was found to be the least sensitive and most stable; therefore, it was selected as the fluorescent tracer for the test. It should be noted that Rhodamine-B is on the EPA's list of Inert Ingredients of Toxicological Concern (U.S. EPA, 1987).

To find the dry state decay rate of Rhodamine-B fluorescence, 15 filter papers (Whatman No. 4) were

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*Trade and company names used in this paper are solely for providing specific information. Their mention does not constitute an endorsement over other products not mentioned.

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dipped in a Rh-B solution (95 mg/L) and hung in the dark to dry. They were then hung outside and exposed to sunshine. Three papers were collected at every 1 h time interval and their fluorescence measured (see Analysis Procedure). The following equation for the rate of decay was established:

$$FL = 0.107513 \times EXP(-0.005251 \times Te); \quad (R^2 = 0.97^{**}) \quad [1]$$

where

FL = fluorescing Rhodamine-B concentration, mg/L

Te = exposure time to sunshine, min

Copper as the tracer for colorimetry was found to be very stable and not photosensitive. It could be dissolved and washed off a target surface with a nitric acid solution. To determine the effects of soaking time and shaking on the removal of copper and Rh-B, 12 leaves were dipped in a copper and Rh-B solution and dried. Each 3 leaves were shaken for a different number of shakes (0, 5, 15, 50); then sampled after 1, 2, 4, and 8 min. Solution samples were analyzed as explained later. Shaking did not have any significant effect on the removal of deposits. Soaking for 1 min dissolved nearly all the copper deposits but the Rh-B concentration increased as follows:

$$RF = 1.641 \times (1 - EXP(-0.7775 \times Ts)); \quad (R^2 = 0.98^{*}) \quad [2]$$

where

RF = relative concentration of fluoresing Rh-B

Ts = soaking time, min

Therefore, it was decided to soak the samples uniformly for at least 5 min before taking solution samples for analysis.

Field Tests

Twelve 3-tree plots of orange trees were flagged to be sprayed in a completely random design (3 speed levels, 4 replications). The trees were set 7.6 x 7.6 m, hedged both ways, and were 5 to 6 m high. The center tree of each plot was selected for sampling. Twelve sampling locations (3 heights (H), 2 azimuths (A), 2 radii (inside and outside)) were identified on each sampling tree (Fig. 1). On each location, three mylar strips (76 x 51 mm) were stapled, at random, to the end of three clipped leaves. Three nearby leaves were washed on the tree (with 0.05N nitric acid solution), dried, and stapled for later identification (Fig. 1). The washing was done to remove residual copper which existed at detectable levels from previous spray applications (copper is commonly used as a fungicide for citrus).

Using a FMC Model 9100 airblast sprayer, a spray mix containing both of the tracers was applied to two sides of the trees. The tank concentrations of Rhodamine-B and copper (in the form of 50% cupric hydroxide) were 66 and 1321 mg/L, respectively. The sprayer was nozzled to discharge a total of 37.5 L/min at 827 kPa pressure. The material was applied at three speeds of 6.31, 1.58, and

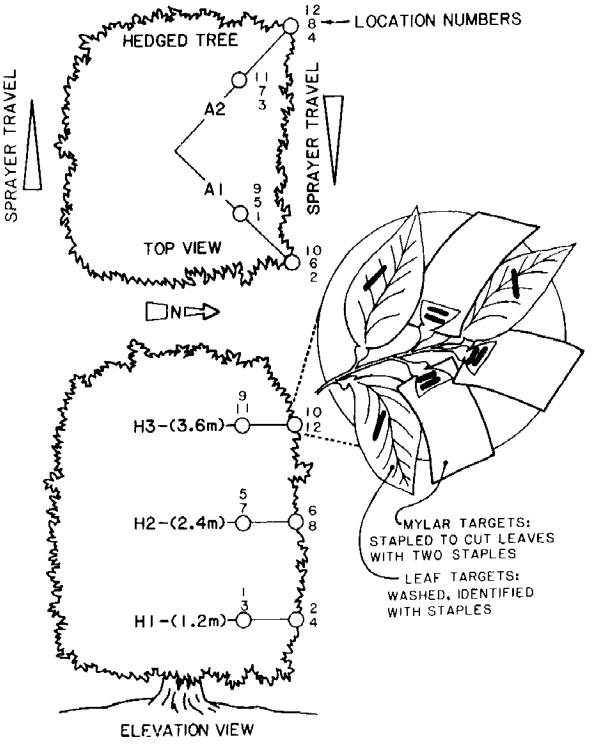

Fig. 1—Sample (target locations).

0.63 km/h to give application rates (volume) of 470, 1880, and 4700 L/ha, respectively. As soon as the targets dried, they were picked, individually placed inside Zip-Loc plastic bags with the respective sampling locations recorded. Leaf samples were stored in a refrigerator to minimize deterioration and dehydration.

Analysis Procedure

Prior to analysis of samples, the bags containing leaves were run through an area meter (LI-3000, LI-COR, Inc.) and surface area of leaf samples were recorded. Depending on the expected amount of deposition, 25 or 50 mL of 0.05N nitric acid solution was poured into each plastic bag, the bag was sealed and laid on the bench for about 5 min to bring the deposit into solution. It was then shaken a few times and samples of the solution were taken for fluorometric and colorimetric analyses.

A Turner Model 111 fluorometer was used for fluorometry. The method involved: (a) taking 5 mL sample of the solution in a 12 x 75 mm cuvette; (b) placing the cuvette inside the instument, (c) waiting about 15 s for stablization of the fluorescence dial, and (d) reading the dial (0 to 100). Calibration curves, prepared earlier, were used to relate the dial reading to Rhodamine-B concentration by the following equation:

$$\frac{CF2}{CF1} = \frac{FR2}{FR1} \quad \text{(Blank set to zero)} \quad [3]$$

or

$$CF2 = \frac{CF1}{FR1} \times FR2 = SX \times FR2 \quad [4]$$

where

CF1 = concentration of Rh-B in standard solution, mg/L
CF2 = concentration of Rh-B in the sample solution, mg/L
FR1 = fluorescence reading for standard solution
FR2 = fluorescence reading for the sample solution (normalized for the wash volume)
SX = slope of the calibration curve, mg/L

The values of SX for four sensitivity ranges of the instrument (1X, 3X, 10X, 30X) were 0.007437, 0.002659, 0.001247, and 0.000351 mg/L, respectively. The ranges could provide Rhodamine-B concentration measurements from 0.7 to 0.0007 mg/L. The general purpose ultra-violet light source (#10-850) had a wavelength of 360 nm. The primary filter (#1-60 plus #58) and the secondary filter (#23A) had wavelengths of 546 and 570 nm, respectively.

A Hach Model DR-100 colorimeter was used for copper colorimetry. The method involved: (a) taking 10 mL of the solution in a cuvette, (b) clipping a reagent powder pillow and pouring its contents into the cuvette, (c) shaking the sample a few times, (d) adding a drop or two of 6 N sodium hydroxide to adjust the pH, (e) waiting for at least 2 min for full color development, (f) placing the cuvette inside the instrument, and (g) reading copper concentration. The instrument had a reading range of 0 to 3 mg/L; therefore, samples with higher concentrations had to be diluted 2 or 4 times in order to be read by the instrument.

The presence of copper in a solution did not affect the fluorescence reading, but the purple color of Rhodamine-B directly affected the copper reading. Although the effect was less than 1%, colorimetric readouts were corrected as follows:

$$CC2 = CC1 - (CF2 \times Sc) \quad \ldots\ldots\ldots\ldots\ldots\ldots [5]$$

where

CC2 = corrected copper concentration, mg/L
CC1 = colorimeter reading, mg/L
Sc = slope of the colorimeter reading vs. Rhodamine-B concentration line (Sc = 2.206)

The quantities of Rhodamine-B and copper were normalized by dividing them by the unit area of the sample as follows:

$$QFC = CFC2 \times \frac{Vn}{As} \quad \ldots\ldots\ldots\ldots\ldots\ldots [6]$$

where

QFC = quantity of Rh-B or copper per unit area, $\mu g/cm^2$
CFC2 = concentration of Rh-B (CF2) or copper (CC2) in sample solution, mg/L
Vn = volume of nitric acid solution, mL
As = sample surface area of both surfaces, cm^2

The variation in deposition was expressed as the coefficient of variability (CV), i.e., deposit standard deviation expressed as percentage of deposit mean.

RESULTS AND DISCUSSIONS

Rhodamine-B and copper deposits on leaf and mylar targets (LF, LC, MF, MC) were all significantly affected by spray volume and increased as spray volume increased. However, the amount of the increase was not proportional to the volume increase and it averaged 2.22 and 3.86 times for volume increases of 4 and 10 times, respectively (Fig. 2). Variation in all depositions decreased as spray volume increased (Fig. 3). The variation among 3 subsamples was less than the variation among locations.

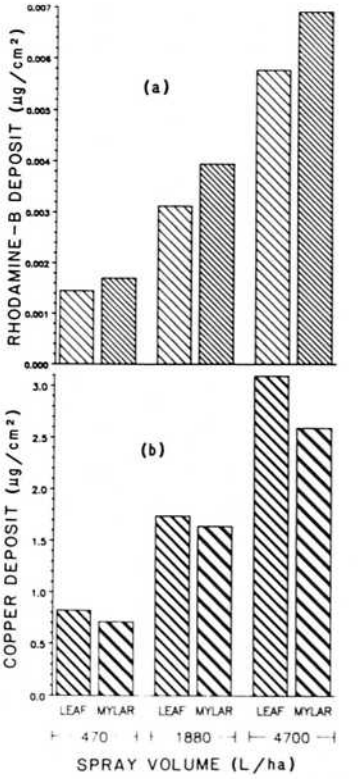

Fig. 2—Spray volume effect on deposits: (a) Rhodamine-B deposits, b) copper deposits.

The effect of target (sample) location on all depositions was significant (Table 1). Targets at 2.4 m height received more deposition than other targets; also outside radius samples had more deposits than inside ones (Table 1). The tank concentration of Rhodamine-B

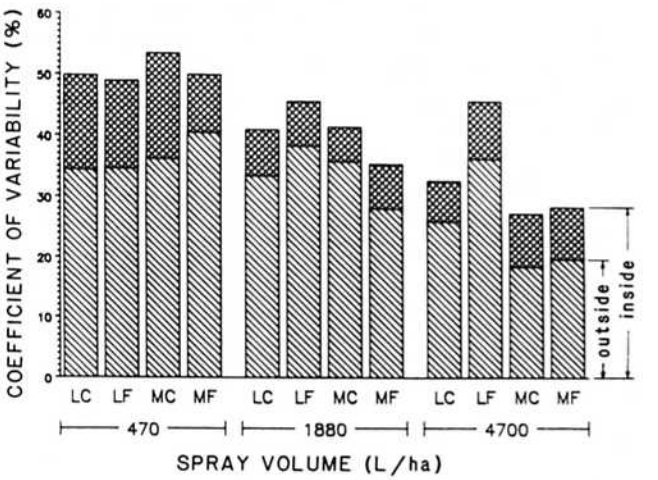

Fig. 3—Variability of deposits.

TABLE 1. EFFECT OF SAMPLE LOCATION ON DEPOSITS

Sample location			Deposit means*			
No.†	Radius in/out	Hgt., m	LF, $\mu g/cm^2$	LC, $\mu g/cm^2$	MF, $\mu g/cm^2$	MC, $\mu g/cm^2$
1	I	1.2	0.00321cd	1.58d	0.00361fg	1.45fg
3	I	1.2	0.00286d	1.53d	0.00354g	1.53ef
5	I	2.4	0.00329bcd	1.87bc	0.00438cd	1.71bcd
7	I	2.4	0.00289d	2.20a	0.00449bc	1.87ab
9	I	3.6	0.00328bcd	1.85bc	0.00341g	1.31g
11	I	3.6	0.00292d	1.83bc	0.00354g	1.41fg
2	O	1.2	0.00370bc	1.74cd	0.00401de	1.55def
4	O	1.2	0.00362bc	1.89bc	0.00398ef	1.73abc
6	O	2.4	0.00486a	2.02abc	0.00504a	1.88ab
8	O	2.4	0.00384b	2.09ab	0.00485ab	1.90a
10	O	3.6	0.00337bcd	1.96abc	0.00459bc	1.69cde
12	O	3.6	0.00345bcd	2.02abc	0.00457bc	1.75abc

*Means followed by same letter (in each column) are not significantly different (at 5%) using Duncan's Multiple Range Test. LF, LC, MF, and MC are deposit means for leaf Rh-B, leaf copper, mylar RH-B, and mylar copper, respectively.
†See Fig. 1.

was 1/20th of the copper, but the measured deposits showed further decrease in this ratio which was due to degradation of Rhodamine-B fluorescence. For all volumes, the variation in deposits of inside samples was greater than that of the outside ones (Fig. 3).

As shown in Fig. 2 and Table 2, there was less fluorescing Rh-B deposit on leaves than on mylar targets but the trend was reversed for copper deposit. Part of the difference in the amount of deposits may have been due to the difference in surface characteristics of leaves and mylar targets. However, the inconsistency in the differences was hypothesized to originate from residual copper deposits and inadequate soaking of leaves. Washing of the sample leaves to remove residual copper deposits before spraying (see Materials and Methods) may have been insufficient. Also, due to time constraint and experimental errors, leaves may not have been soaked and treated properly during analysis. The variabilities (CV) of both fluorescing Rh-B and copper deposits on leaves were greater than that on mylar targets, and LF was the most variable deposit (Table 2). Comparatively less variability of mylar target deposits may have been due to the better control of processes for mylar target analysis which were exercised more vigorously after completion of leaf target analysis. Also uniform size of mylar targets may have resulted in less variability even though no correlation between the leaf size and amount of deposit could be established.

Despite the problems mentioned above, there were very good correlations among all four kinds of deposits. Figs. 4 to 7 show correlations between LF and MF, LC and MC, LF and LC, and MF and MC, respectively. All of the four methods were found to be useful for deposition assessment.

Fluorometry is simple, fast, inexpensive, and reliable, but photosensitivity of common water soluble fluorescent dyes (degradation) is serious problem and requires very careful calibration. It is very difficult to control exposure of samples to light and the inherent difference in the exposure (due to difference in location on the tree) would result in more variability and error of the test. Colorimetry is simple, not as fast and sensitive as fluorometry, but more reliable when degradation of a fluorescent tracer is a problem. Copper deposits are stable and not photosensitive; therefore, unlike fluorometry, it does not involve time constraint for analysis. There is no need for laborious calibration procedure; however, adding the reagent is time consuming. The price of the colorimeter is far less than the price of the fluorometer, but the latter is a more versatile and sensitive instrument.

The use of mylar targets does not offer any advantage for fluorometry but, for colorimetry, it alleviates the problem of residual copper deposit on the leaves. Mylar

TABLE 2. DEPOSITS ON LEAF AND MYLAR TARGETS

Statistics	LF	LC	MF	MC
Mean, $\mu g/cm^2$	0.00344038	1.88210061	0.00416719	1.64686089
Error mean sq.	0.00000124	0.26852845	0.00000064	0.11247440
CV, %	32.40	27.53	19.27	20.36
R^2	0.8569	0.8660	0.9310	0.9114

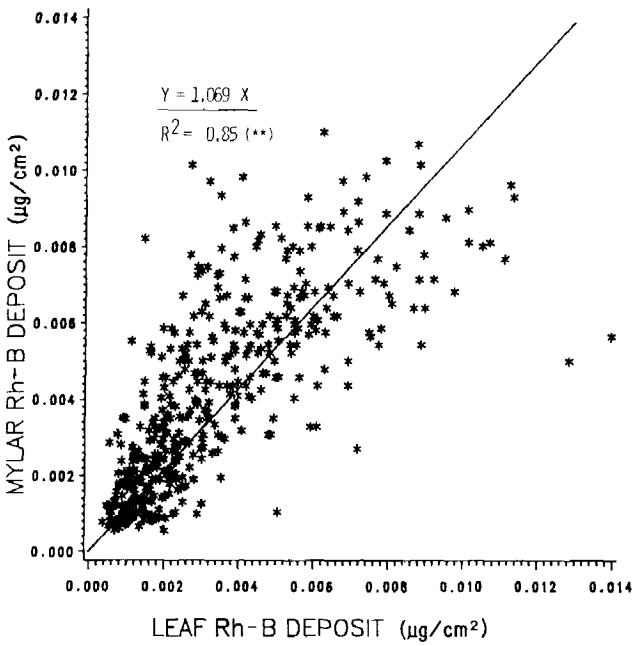

Fig. 4—Correlation between leaf and mylar Rh-B deposits.

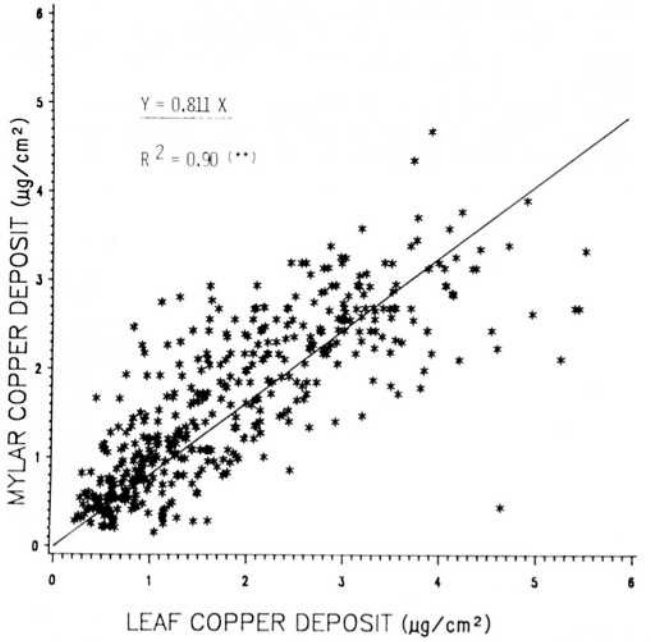

Fig. 5—Correlation between leaf and mylar copper deposits.

target preparation and installation require extra time and may not conveniently represent the surface characteristics of the leaf. If the trees or test area have not been sprayed with copper for some time (about 6 months), using leaf samples offers many advantages. Leaves eliminate the expenditure of time and resources needed for mylar targets. They are abundant and do not create limitations for sampling, but require area measurement, refrigeration, and time constraints for analysis. Using the U-V light and filters mentioned above, no interfering background fluorescence was detected for citrus leaves. However, there may be some interference with other dyes and leaves.

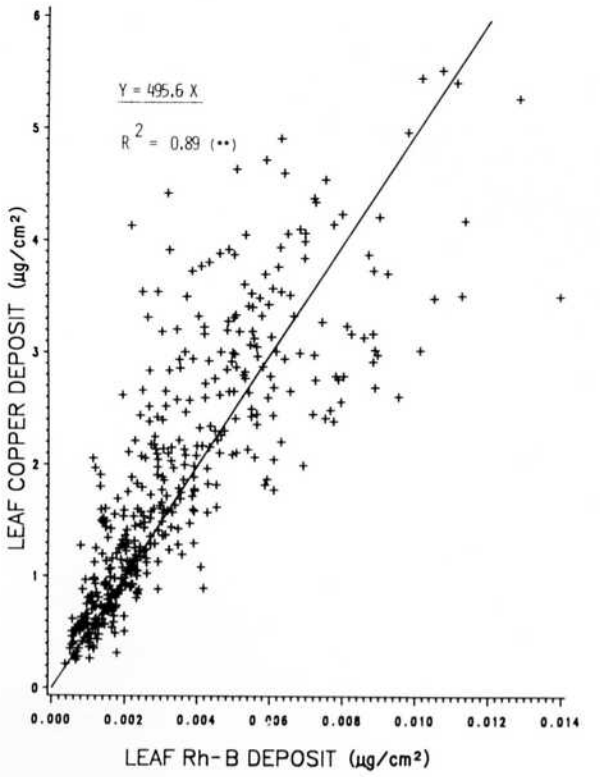

Fig. 6—Correlation between leaf Rh-B and copper deposits.

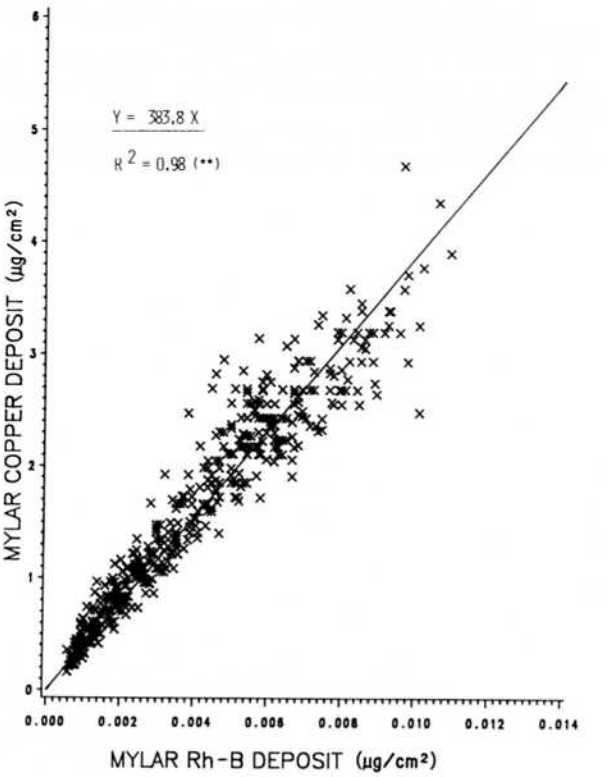

Fig. 7—Correlation between mylar Rh-B and copper deposits.

CONCLUSIONS

1. Correlations between colorimeter and fluorometer readings for both leaf ($R^2 = 0.89$) and mylar ($R^2 = 0.98$) targets were highly significant.
2. Correlations between leaf and mylar target deposits by both colorimetry ($R^2 = 0.90$) and fluorometry ($R^2 = 0.85$) were highly significant.
3. All four methods were found to be reliable; however, considering limitations in the field and in the lab, colorimetric analysis of leaf samples appears to be the most desirable method for deposition assessment in citrus spraying.

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