

Measurement of Spray Deposit Amount Using Spectrophotometer and Food Dye as Tracer

J. Y. Rhee, S. Y. Ahn

Abstract: Measurement of spray deposit is necessary for evaluation of a chemical application technology. However it is not easy and time consuming. A simple method for measuring the deposition amount of spray using a tracer and a spectrophotometer was developed. Various materials were tested to determine an adequate tracer. Food dye was selected as a tracer, because it was cheap and easily treatable. Using NIRS(Near Infrared Reflection Spectrophotometer), a regression curves between maximum absorbance of a solution and concentration of the tracer were obtained. Yellow food dye solution showed a peak of spectrum at 452 nm, and absorbance of peak showed a tendency to increase as concentration increased. Green or pink food dye were tested and judged to be good tracers. However, tracer concentration should not exceed certain limits in order to measure maximum absorption. Using spraying liquid with known tracer concentration and known amount of washing liquid, spray deposit amount on real targets on leaves could be estimated at less than 13% error level.

Keywords: Deposition, NIR, Spectrophotometer, Tracer, Food Dye, Pesticide Spray

Introduction

Measurement of spray deposit on targets is necessary for evaluation of chemical application technology. Spray deposit measurement using the water sensitive card is the most popular way, which measures size of droplets and counts their numbers. However, measurement of spray deposit is not only difficult but also inaccurate due to variability in spread factor at each droplet size level with respect to impaction direction and droplet sizes as well as superposition of droplet images. Also, the water sensitive card shows different impaction efficiency because it has different surface characteristics and shape from those of natural targets such as leaves and stems. Spray deposit amount can be analyzed precision chemical analyzer such as HPLC but it requires considerable amounts of money and time.

This study was accomplished to find a convenient and quick method for measuring spray deposit quantitatively using a tracer and a spectrophotometer. Determination of a proper tracer and development of spray deposit measurement procedure are the main contents of this study.

Lee et al.(1996) used the water sensitive card to compare coverage characteristics of a boom sprayer for paddy field. They could evaluate relative coverage ratio but could not measure amount of spray deposits. Suh et al. (1994) also used the water sensitive card to

evaluate amount of spray deposits but they could not count droplets smaller than 25 μm . Derksen and Gray (1995) used fertilizer with Zn and Mn as a tracer because Zn and Mn were not detectable on natural apple leaves and photo-disintegrative. They evaluated deposition characteristics of air-carrier orchard sprayer using an argon plasma atomic emission spectrometer. Bouse (1994) used 0.1% v/v Triton X-100 and fluorescent dye to evaluate deposition characteristics of swirl type hollow cone nozzle and narrow-angle flat spray nozzle. They used water as diluent and measured deposit amount using a fluorometer. Gupta and Duc (1996) used spectrophotometer and fluorescent sodium and *Bacillus thuringensis* as tracers to investigate deposition characteristics of hand-held electrostatic sprayer. Dante and Gupta (1991) used digital fluorometer and Fluorescein-Natrium as tracer. They washed the artificial targets and fluorescence of solution was measured to estimate amount of spray deposition.

Materials and Methods

1. Determination of Tracer

Edible sodium, sugar, urea, and food dyes were selected as tracers. Absorbances of the selected materials were compared. Tracer should be water-soluble and could not be found on leaves (target). Some components in leaves could be leached out into washing distilled water and give effect on absorbance of tracer solution. Leaves were cut 1 cm wide and 1 cm long in square shape and submerged in distilled water of 50 ml. After 5 minute long agitation, maximum absorbance of the water was compared to that of pure distilled water.

When too much washing water is used, maximum absorbance could be too small to measure. In such

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case, concentration of tracer could be increased by boiling the washing water but boiling should not give effect on absorbance. To find out boiling effect on absorbance, 500 ml of yellow dye solution with low concentration (0.0001 g/ml) were boiled and 10 ml of solution was sampled at 30 min interval. Absorbance of boiled dye solution were compared to that of unheated dye solution with the same concentration.

2. Calibration of Concentration of Solution

Absorbance Measurement

Absorbance of solution were measured by a near-infrared spectrophotometer (NIR Systems model 6500, NIR System, Inc) as shown in fig. 1 and data were analyzed by MS Excel Program.

When light with energy level of P_0 were illuminated on sample solution in a cuvette with uniform concentration, outgoing light may have energy level of P . Then transmittance of the sample, T could be defined as follows.

$$T = P/P_0 \quad (1)$$

Absorbance is defined as logarithmic value of reversed transmittance as shown.

$$A = -\log_{10} T = \log \frac{P_0}{P} \quad (2)$$

At low concentration, absorbance is known to be proportional to concentration. It is so called Beer's law and could be expressed as equation (3).

$$A = \log \frac{P_0}{P} = \epsilon bc \quad (3)$$

Here A : Absorbance
b : Depth of sample
c : Concentration of sample solution
 ϵ : Absorbance coefficient

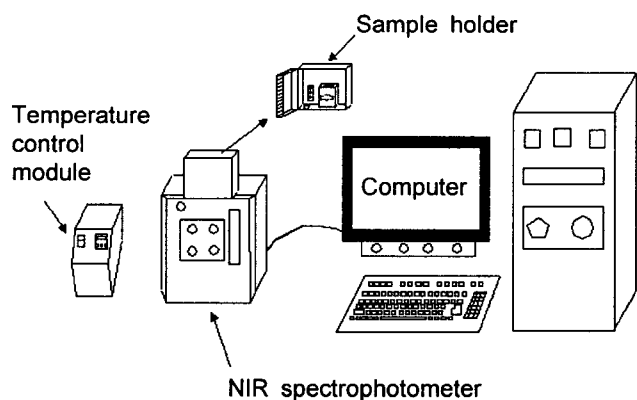


Fig. 1 NIR spectrophotometer.

Development and validation of a regression equation

A relation between maximum absorbance and concentration of yellow food dye solution was investigated to determine proper range of concentration. This experiment was accomplished with repetitions of two.

An experiment to verify the regression equation was designed. Yellow dye solution with known concentration was sprayed over sesame leaves. After spraying, the leaves were washed by distilled water. Because the initial concentration and amount of washing water were known, the concentration of the washing water could be known. Error between real concentration and estimated concentration using the regression equation and measured absorbance data were calculated.

Yellow dye of 0.02 g, 0.04 g, 0.06 g, 0.08 g, 0.10 g respectively were solved in distilled water of 10 ml. The dye solutions with various concentration were sprayed over leaves. The leaves were washed by distilled water of 100 ml. If washing was perfect, the washing solution would have concentration of 0.0002, 0.0004, 0.0006, 0.0008 and 0.001 g/ml. Evaluation of the regression equation was accomplished by R^2 and concentration error.

Results and Discussion

1. Determination of a Tracer

Fig. 2 showed the absorbance spectrums of tracer candidates such as salt, sugar(white, yellow), urea, yellow food dye. Only yellow food dye solution showed apparent peak of absorbance at 450 nm. Yellow food dye solution was judged as best tracer among the candidates.

Noise in absorbance spectrum due to leaching out of some components from leaves was investigated and shown in fig. 3. An absorbance spectrum of agitated solution with cut leaves was nearly the same as that of pure distilled water. Error of maximum absorbance at 450 nm was only 0.001271 and negligible. In other words, measurement of maximum absorbance from pieces of cut leaves was possible if yellow food dye was used as a tracer.

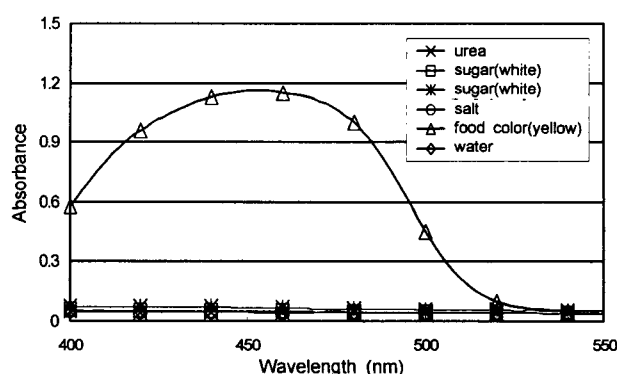


Fig. 2 Infrared absorbance spectrums of various solutions.

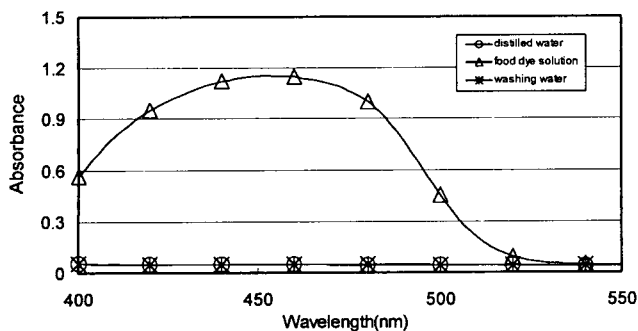


Fig. 3 Effect of leaf cutting and agitation in water on NIR spectrum of food dye solution between 400nm and 550nm.

2. Calibration and Validation of a Regression Equation

Fig. 4 showed detail shape of absorbance spectrums between 400~550 nm at various concentration levels. Fig. 5 showed a relationship between concentration of yellow dye solution and maximum absorbance of it.

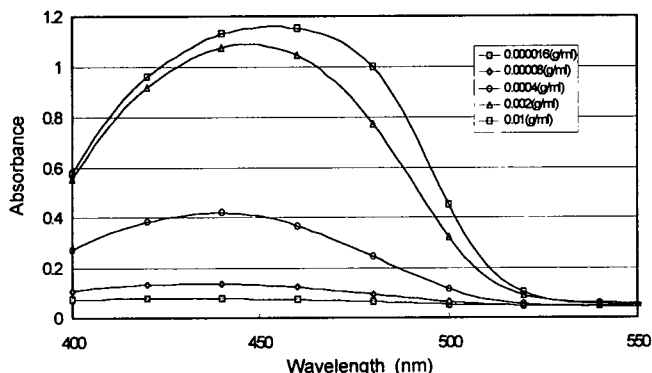


Fig. 4 Infrared absorbance spectrum of yellow dye solution between 400nm and 550 nm at various concentration levels.

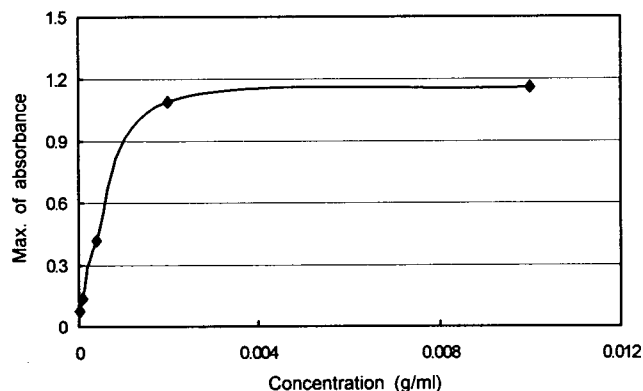


Fig. 5 Change of maximum absorbance of yellow dye solution and concentration of it.

As shown in fig. 5, maximum absorbance of solution showed small increment when concentration of solution was larger than 0.002 g/ml. Therefore, concentration of washing solution should be less than 0.002 g/ml to prevent absorbance saturation.

Maximum absorbance were measured at concentration range between 0.0002 and 0.02 g/ml, at every 0.0002 g/ml difference. Absorbance data below concentration of 0.0002 g/ml were used again. A regression equation for concentration range below 0.0016 g/ml was developed as equation (4). R² of equation (4) was calculated to be high value as 0.9947. Another linear regression equation was developed which was applicable when concentration of solution was 0.0008 g/ml because error between measured and predicted absorbance of equation (4) was systematic. The linear regression was shown in equation (5) and fig. 7. Its R² was 0.9933 slightly less than that of equation (4). Here A(c) represented maximum absorbance and c, concentration of yellow dye.

$$A(c) = -500275c^2 + 1487.6c - 0.0158 \tag{4}$$

$$A(c) = 1153.2c + 0.03 \tag{5}$$

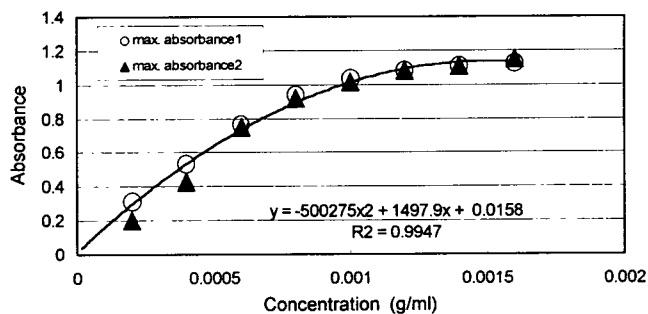


Fig. 6 Parabolic regression curve of concentration with maximum absorbance of yellow dye solution.

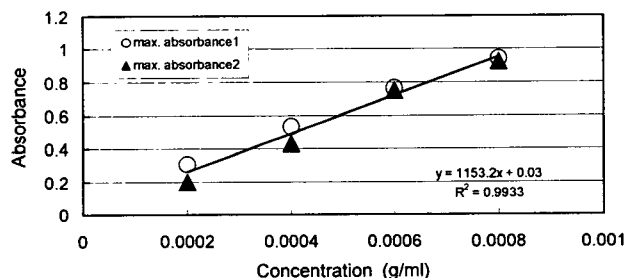


Fig. 7 Linear regression curve of concentration with maximum absorbance of yellow dye solution.

The developed regression equation (5) was used to estimate amount of spray deposit. Error between known concentration and estimated concentration by equation (5) was less than 7 percent as shown in table 1 and fig 8.

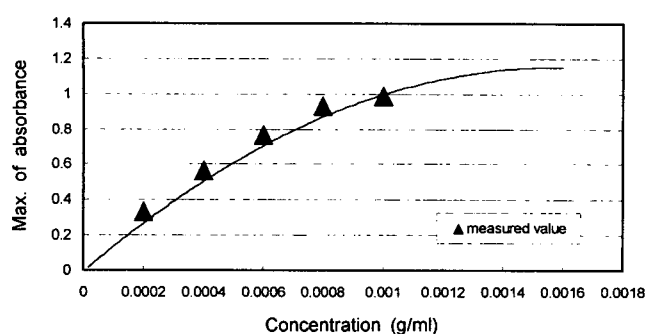


Fig. 8 Comparison of a regression curve and measured values.

3. Properties of Food Dyes as a Tracer

In fig. 9 absorbance spectrums of yellow dye solution at the same concentration but one was distilled and the other was boiled were shown with little difference. In other words, boiling did not change absorption characteristics of food dye solution.

Absorbance spectrums of pink and green dye solution were also investigated. Pink dye solution showed a peak at 530 nm (Purple color) as in fig. 10. The absorbance peak of pink dye solution was sharper than that of yellow dye solution. R^2 of a regression equation for pink dye solution was greater than 0.99 so that pink dye could be used as tracer (fig. 11).

Green color is mixture of yellow and green. An absorbance spectrum of green dye solution (fig. 12) showed two peaks at 440 nm (yellow) and 635 nm (blue-green). Regression equations using the peak values separately had R^2 greater than 0.99 (fig. 13). Any food dye which had unique peaks at certain wavelengths was judged to be adequate as a tracer when absorbance characteristics of solution was measured.

Proper concentration of tracer (yellow dye) was estimated to be between 0.0002–0.0008 g/ml because absorbance of solution showed saturation tendency at high concentration and non-linearity. It was necessary to control amount of washing water to get proper concentration. When washing solution showed too low concentration to be measured for absorbance, concentration could be increased by boiling the solution as long as the amount of washing solution was larger

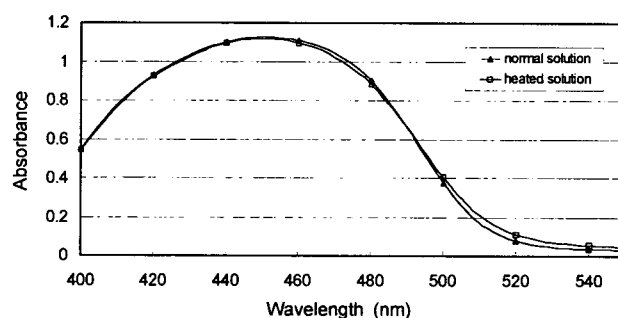


Fig. 9 Comparison of absorbance spectrums between normal solution and boiled solution.

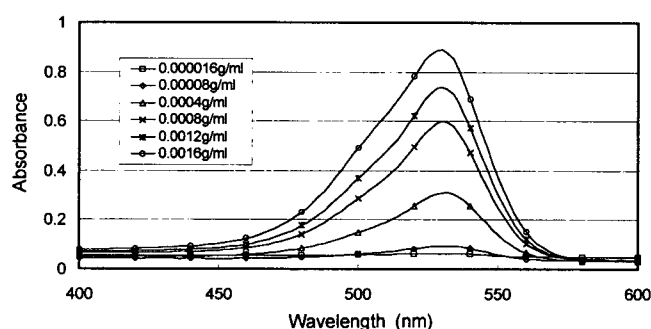


Fig. 10 Infrared spectrums of pink dye solution.

than the capacity of measuring cuvette for NIR spectrophotometer. The spectrophotometer in this study had a cuvette of which depth and volume were 4mm and 5 ml respectively.

Absorbance spectrums of yellow food dye using a cuvette with 10 mm depth were measured at concentration range from 0.0004 g/ml to 0.0016 g/ml, at 4 different levels. According to Beer's law the absorbance spectrums achieved using cuvettes with 4mm depth and 10 mm depth should show some proportionality. The result was summarized in table 2. According to the result, Beer's law were valid when concentration was less than 0.0004 g/ml in case of yellow solution. As concentration range increased, proportional constant decreased. Therefore, when the cuvette depth was changed, another regression equation should be developed.

Table 1 Error value of regression equation

Max. of Absorbance	Predicted concentration A(g/ml)	Measured concentration B(g/ml)	Absolute error (g/ml) A-B	Relative error A-B / B × 100(%)
0.334450	0.000230	0.0002	0.000030	13.22
0.566770	0.000429	0.0004	0.000029	6.85
0.766485	0.000636	0.0006	0.000036	5.73
0.929857	0.000854	0.0008	0.000054	6.27
0.987908	0.000950	0.0010	0.000050	5.31

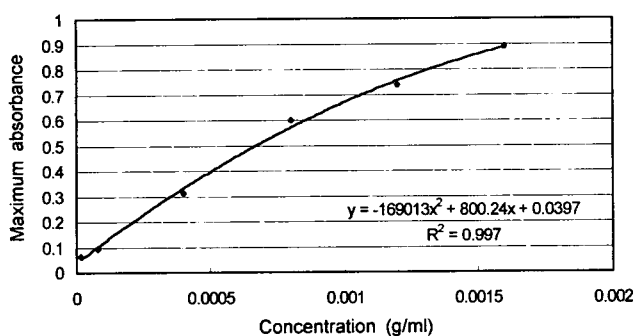


Fig. 11 Regression curve of concentration with maximum absorbance of pink dye solution.

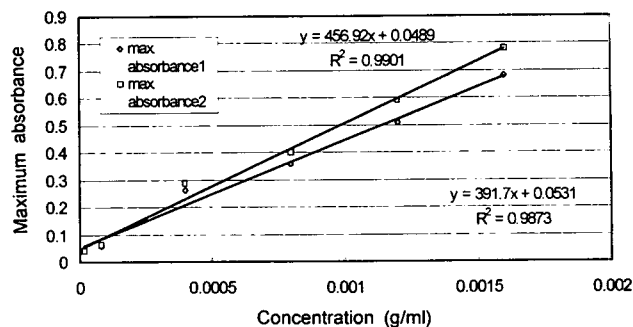


Fig. 13 Regression curve of concentration with maximum absorbance of green dye solution.

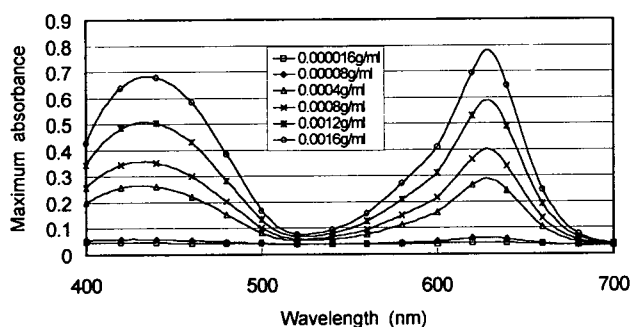


Fig. 12 Infrared spectrums for the solution of the green dye solution.

In order to use the proposed method, water and food dye solution should be well mixed at a known concentration C_0 . Let the solution to be sprayed over target with surface area of $S \text{ cm}^2$, then the target was washed with distilled water of $X \text{ ml}$, and finally concentration of washed solution was measured to be C_f . The spray deposit $D(\text{ml}/\text{cm}^2)$ on the target per unit area can be calculated as the following equation:

$$D = \frac{C_f}{C_0} \cdot \frac{X}{S} \quad (6)$$

Conclusions

This study was conducted to develop a quantitative measurement method of spray deposit on real target using a NIR spectrophotometer. Several materials were tested as tracers and yellow food dye was selected as a most convenient tracer. The detail procedure for

measuring spray deposit was developed.

This method could not supply information on numbers and size of droplets but on amount of sprayed solution. Natural target could be used so that impaction mechanism is not distorted by artificial target. Once spraying solution with known concentration over a target, the target would be washed by known amount of distilled water and then the amount of deposit could be estimated from the amount of washing solution and measured concentration of solution by a NIR spectrophotometer.

Important result could be summarized as follows.

1. Salt, sugar, urea and food dye(yellow) were selected as tracer candidates and tested. Yellow food dye was determined as a proper tracer because it showed apparent peak of absorbance at 452 nm.

2. Absorbance characteristics of yellow food dye solution was neither affected by leaching of cut leaves in washing solution not boiling the solution.

3. Yellow food dye showed saturation of absorbance when its concentration was larger than 0.002 g/ml . A regression equation for concentration(c) range from 0.000016 to 0.0016 g/ml was developed using maximum absorbance(A) at 450 nm as the following.

$$A(c) = -500275c^2 + 1487.6c - 0.0158$$

$$R^2 = 0.9947$$

4. Validity of the regression equation was evaluated by spraying solution with known concentration over sesame leaves, and error of spray deposit was evaluated to be less than 13%.

5. Pink and green food dye were also investigated as a tracer. They showed unique peaks at certain wavelength and judged to be adequate as a tracer.

Table 2 Comparison of maximum absorbances for 4mm and 10mm thickness cuvette

Concentration(g/ml)	0.0004	0.0008	0.0012	0.0016
Max. absorbance with 4mm cuvette	0.420842	0.920885	1.084198	1.154205
Max. absorbance with 10mm cuvette	1.06425	1.187701	1.191325	1.192516
Magnification ratio	2.528859	1.289739	1.098808	1.033193

6. Absorbance spectrums using different sized NIR cuvette showed proportionality only at very low concentration. Therefore a regression equation developed for a certain sized cuvette could not be used to estimate concentration using absorbance data measured with different sized cuvette.

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