Evaluation of a rhodamine-WT dye/glycerin mixture as a tracer for testing direct injection systems for agricultural sprayers

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TECHNICAL NOTE:

EVALUATION OF A RHODAMINE-WT DYE/GLYCERIN MIXTURE AS A TRACER FOR TESTING DIRECT INJECTION SYSTEMS FOR AGRICULTURAL SPRAYERS

J. D. Luck, S. A. Shearer, B. D. Luck, F. A. Payne

ABSTRACT. The purpose of this study was to provide valuable insight regarding the use of Rhodamine WT (red) dye as a tracer for evaluating injected concentrations. More specifically, the effects of mixing the dye with glycerin to simulate the viscosity of a pesticide (e.g., glyphosate) or injecting the dye/glycerin mixture into deionized (DI) tap water on developing appropriate calibration equations were evaluated. Test results indicated that mixing the dye in a solution of glycerin and DI water significantly affected absorbance measurements compared to the dye mixed solely in DI water. The error in estimating absorbance was 7.4% between the two calibration equations. Therefore, any calibration curves must include a solution containing glycerin to compensate for this. Absorbance results also indicated that potable tap water could be used to simulate the spray carrier as opposed to the DI water. A calibration curve was developed for the simulated pesticide (dye/glycerin/DI water solution) injected into the carrier (tap water) for solutions ranging from 2,000:1 carrier:pesticide to 500,000:1; an overall dilution range of 250:1. This dilution range exceeded typical pesticide tank-mixed dilutions which were on the order of 11:1 for the application of glyphosate for corn or soybeans. The regression model standard error for predicting the dye concentration based on absorbance measurements was 5.3x10^-6.

Keywords. Pesticide application, Precision agriculture, Spraying equipment, Pesticides.

The development of variable-rate pesticide application technologies has received significant attention in recent years and could provide solutions to various spray application errors. Direct chemical injection, an alternative to tank mixing, is one type of variable-rate technology that has been extensively tested over the years. The chemical concentrate and carrier are typically pressurized separately and combined in a mixing chamber ahead of the spray nozzle. The two most common performance factors related to direct injection systems are lag time (time delay between injection and discharge) and mixing uniformity of the chemical and carrier prior to discharge. Accurate methods for evaluating direct injection system performance are essential for the continuing development of these systems.

One method for performance evaluation utilizes fluorescent tracer dyes which are injected into the carrier stream. The resulting effluent concentrations are then estimated based on absorbance measurement determined by spectrophotometry. Preliminary calibration is typically required to estimate effluent concentrations based on absorbance measurements using mixtures of carrier and dye concentrate at known concentrations. Smart and Laidlaw (1976) conducted an evaluation of several fluorescent dyes for use in environmental water tracing. The study recommended either using either Rhodamine WT (orange), lissamine FF (green), or amino G acid (blue) dye for water tracing studies based on sensitivity, minimum detectability, photochemical decay rates, and adsorption losses.

More recently, researchers have chosen a variety of fluorescent dyes to evaluate direct injection systems for spray application. Xu (1993) utilized a red dye (Rhodamine B) to assess the performance of a single nozzle direct injection system for pesticide application (which
determined an optimal detection wavelength of 522.5 nm for the dye). Zhu et al. (1998a) used an oil-soluble tracer, UVITEX OB, to evaluate lag time and mixture uniformity for direct in-line injection sprayers. Mixture uniformity in the supply lines and spray pattern from an injection sprayer were evaluated by Zhu et al. (1998b) using a water-soluble Acid Yellow 7 dye along with the UVITEX OB dye. In a related study, Zhu et al. (1998c) studied factors contributing to lag time on injection sprayers including: number of active nozzles, boom size, travel speed changes, and pesticide viscosity, where the UVITEX OB dye was also used.

Sumner et al. (2000) developed a system using string collectors to evaluate lag time on injection sprayers. Cotton string collectors (typically used in aerial applications) were used to collect a solution of Rhodamine-B dye which had been injected into the carrier. Luck (2010) also used Rhodamine B dye to evaluate the response characteristics of a high pressure direct nozzle injection system.

Evaluating the effects of temperature and viscosity on accurate metering of pesticides has also been identified as an important component for evaluating direct injection systems (Gebhardt et al., 1984). To compensate, some researchers have utilized glycerin as a viscosity modifier (Xu, 1993; Luck, 2010), however the effects of glycerin on absorbance measurements to estimate these injected tracer concentrations has not been well documented.

The goal of this study was to provide information regarding absorbance measurements for tracers containing glycerin solutions. Specific objectives were to 1) develop calibration equations for predicting tracer concentrations based on absorbance measurements, 2) determine the effects of glycerin on absorbance readings, and 3) determine the effects of carrier type [deionized (DI) versus tap water] on absorbance measurements.

**MATERIALS AND METHODS**

For the purposes of this project, glyphosate was used as the reference pesticide because of its extensive use in U.S. grain crop production. Glyphosate is a very popular pesticide for no-till producers and others who grow glyphosate-resistant crops. Because of EPA regulations, producers must follow label rates when applying chemicals which provide minimum and maximum tank-mix concentrations. For instance, pre-emergence treatments for corn and soybeans are allowed within a range of 710 to 1420 mL per acre of glyphosate mixed with 37.9 to 75.7 L of water (Monsanto, 2002). The resulting minimum and maximum allowable ratios of carrier to glyphosate would be 107:1 and 27:1, respectively. By observing allowable rates for treatments to glyphosate-resistant corn and soybeans, the maximum allowable ratio of water to glyphosate would be 10:1 (post-emergence soybeans) while the minimum allowable ratio was 107:1 (pre-emergence corn and soybeans).

Applications at concentrations above the maximum ratio could result in crop damage (post-emergence treatments), while applying at concentrations below the minimum ratio would not be effective at controlling weed competition. Therefore, the desired operating range for the proposed direct injection nozzle was between 10:1 and 107:1, and as such, it was necessary to measure concentrations over an 11:1 range to characterize the maximum and minimum allowable carrier to glyphosate ratios.

A spectrophotometer (SPm) (Evolution 60, Thermo Electron Scientific Instruments, LLC, Madison, Wis.) was used to conduct the Rhodamine WT (RhoWT) dye absorbance tests. The SPm essentially determines absorbance readings of a given media by passing light through a sample at a predetermined wavelength and comparing the light intensity entering and exiting the sample (Thermo Scientific, 2007). RhoWT dye was chosen as the tracer because of its extensive use as a surrogate for direct injection systems.

All tests were conducted in a laboratory with a controlled temperature ranging from 18°C to 21°C. RhoWT dye was mixed (by volume) with DI water at concentrations ranging from 1:1 to 1 ppm in 15-mL centrifuge tubes. The tubes were sealed and mixed for 30 s on setting 10 using a vortex mixer (Mini Vortexer, Thermo Fisher Scientific Inc., Pittsburgh, Pa.). The tubes (sealed) were allowed to set for 30 min to allow any air bubbles to surface. A 1-mL cuvette was filled from each mixture and placed in the SPm where three measurements were taken per sample using DI water as the blank cuvette at a wavelength setting of 522.5 nm (Xu, 1993).

Glycerin and DI water were mixed (73% glycerin, 27% DI water by mass) to simulate the viscosity of glyphosate (Luck, 2010). RhoWT dye was mixed into the glycerin/DI sample (Thermo Scientific, 2007). RhoWT dye was chosen with the SPm for the RhoWT/glycerin/DI water mixtures.

The RhoWT/glycerin/DI water solution at a concentration of 2000:1 was mixed with DI water and ordinary tap (potable) water (KAWC, 2010) to produce dilutions from 2000:1 to 500,000:1. SPm measurements (three per sample) were recorded and regression lines were fit to the data. A linear regression analysis was performed using MS Excel to develop calibration equations for predicting absorbance based on the RhoWT concentrations. The standard errors of the regression were calculated according to procedures outlined by Haan (2002). SAS software was used to determine if the trendline slopes were significantly different using the proc glm procedure.

**RESULTS AND DISCUSSION**

A plot of the absorbance measurements versus RhoWT concentrations is shown in figure 1. As expected, the SPm was not able to record absorbance measurements for high dye concentrations (above 50:1). Therefore, further absorbance tests were limited to the linear range of the response. The linear regression models were based on Beer’s Law which has been discussed by others (Xu, 1993) as a model for comparing tracer concentrations to light absorbance. Beer’s Law essentially states that the absorbance of a solution shares a linear relationship with its
concentration, with zero absorbance at concentrations equal to zero. Therefore, a regression model with a zero intercept was developed from the absorbance data and is shown in figure 2 with a model SE of $4.12 \times 10^{-6}$ for RhoWT dye concentrations ranging from 2000:1 to 500,000:1.

The absorbance test results for the RhoWT dye mixed with DI water and glycerin/DI water are shown in figure 3. Regression models for both solutions resulted in a good fit ($R^2$ of 0.999) with low SE values (0.009 for the RhoWT/DI water and 0.01 for the RhoWT/glycerin/DI water). Results of the SAS analyses indicated that the trendline slopes were significantly different ($p<0.0001$), meaning that the use of glycerin as a viscosity modifier affected the absorbance. Comparing predicted absorbance values from the two calibration equations in figure 3 produced a 7.4% error when calculating absorbance based on these data. Therefore, calibration equations should be developed from a solution containing the appropriate amount of glycerin.

Absorbance tests results for the carrier type (DI water vs. tap water) are shown in figure 4 with results of the linear regression analyses. Results of the statistical analysis in SAS indicated that the trendline slopes were not significantly ($p=0.37$) different. Therefore, DI water was not necessary as a carrier, and potable tap water (KAWC, 2010) could be used as a substitute.

A final calibration curve was generated for the simulated pesticide (RhoWT/glycerin/DI water) that was injected into tap water as the carrier (fig. 5). The resulting model had a low SE value ($5.3 \times 10^{-6}$) for the range of concentrations from 2000:1 to 500,000:1. This also provided an overall dilution range of about 250:1, which exceeded the required range of 11:1 for typical tank-mixed pesticide concentrations.

**CONCLUSIONS**

Test results showed that using glycerin as a viscosity modifier to simulate pesticides significantly affected absorbance measurements with a 7.4% error in absorbance predictions using a calibration equation developed without the addition of glycerin to the dye/water mixture. Therefore, any calibration curve must include a solution containing the desired concentration of glycerin to

**Figure 1.** Raw absorbance data for concentrations of Rhodamine WT dye in DI Water.

**Figure 2.** Calibration curve for determining Rhodamine WT concentration in DI Water based on absorbance.

**Figure 3.** Results of linear regression on absorbance readings for glycerin added to the RhoWT dye/DI Water mixture.

**Figure 4.** Plot of data illustrating the effects of DI water vs. tap water on absorbance readings.
compensate for this. Absorbance results also indicated that potable tap water could be used to simulate the sprayer carrier as opposed to DI water. A calibration curve was developed for the simulated pesticide (Rhodamine WT/glycerin/DI water) injected into the carrier (tap water) for solutions ranging from 2000:1 to 500,000:1, an overall dilution of 250:1. This range far exceeded the desired range of typical pesticide tank-mixed solutions which were estimated to be approximately 11:1. The regression model had a low standard error ($5.3 \times 10^{-6}$) in predicting the Rhodamine WT/glycerin/DI water mixture concentration.

**REFERENCES**


