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Surfactant assisted spectrophotometric determination of glyphosate in its formulation

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ABSTRACT

A simple, selective and surfactant assisted spectrophotometric method was developed for the determination of glyphosate herbicide in its formulation. The absorption spectra of glyphosate-ninhydrin Ruhemann's purple colored complex obtained in basic medium of pH 8 and at a temperature of 100°C showed maximum absorption at 570nm. The effect of various categories of surfactants showed that the absorption of colored complex was found maximum in presence of Tx-100.

KEYWORDS

Glyphosate;
Pesticides;
Determination.

INTRODUCTION

Glyphosate[N-(phosphonomethyl) glycine] is a non-selective broad spectrum systematic herbicide used to kill weeds especially perennials[1]. Due to its relatively low toxicity to mammals; it is commonly being used for agriculture, horticulture and silviculture purposes including home garden maintenance[2]. The extensive use of this herbicide is concerned with environmental contamination problems which affects human health. Hence, the determination of glyphosate in crops, soil, water, food materials, vegetables and fruits has been of great importance[3]. A number of classical and instrumentation methods such as gas, liquid, ion and thin layer chromatography[4-8], capillary electrophoresis[9-11], High performance liquid chromatography[12], oscillopolarographic titration[13] etc. have been developed for the determination of glyphosate. However, the emphasis has always been to develop an easy, simple, cheap and a reliable method. The proposed surfactant assisted spectro-photometeric determination of glyphosate gave the impression as simple, selective, sensitive and a reliable method. The method is based on the reaction of glyphosate with the chromogenic reagent ninhydrin. The resultant and purple colored product showed maximum absorption at 570nm.

EXPERIMENTAL

Apparatus

The absorbance of solutions were measured with single beam Spectronic $20D^+$ spectrophotometer (Thermo Fisher Scientific) at 340-720nm using glass cell and the pH was measured using a digital pH meter (Elico, L-I 120, India).

Reagents

All reagents and chemicals used were of analytical reagent grade. Glyphosate ($C_3H_8NO_5P$) {71% extra pure (Excel Crop Care Limited, India)}, ninhydrin

($C_9H_6O_4$) (Qualigens, India), Triton X-100 (Tx-100) (CDH, India), N-cetyl-N,N,N-trimethyl ammonium bromide ($C_{19}H_{42}NBr$) (CTAB) and sodium dodecyl sulphate ($C_{12}H_{25}SO_4Na$) (SDS) (E-Merck, India) were used in this study.

Solutions

Solutions under study were prepared in demineralized water (DMW). A standard stock solution of glyphosate (0.01 M) was prepared by dissolving weighed amount of glyphosate in double distilled water and 10 ml of stock solution was further diluted to 100 ml using DMW. Similarly, 0.1 M stock solution of ninhydrin, Tx-100, SDS and CTAB were prepared by dissolving required amounts of each in DMW.

Procedure

Determination of λ_{max} for glyphosate-ninhydrin colored complex intensity

1 ml of 0.1 M NaOH and 1 ml of 1.0×10^{-3} M glyphosate solution was added in 16 ml of DMW. The solution was heated at 100°C for 5 min in closed tube and 2 ml of 1×10^{-2} M ninhydrin was added. The final volume of the solution was maintained constant at 20 ml by adding DMW. The mixture was again heated on the water bath for 30 min at 100°C. Now, the absorbance of the solution was observed at different wavelength ranging from 460 to 660 nm. The further studies were done at 570 nm.

Effect of pH on glyphosate-ninhydrin color intensity

A series of glyphosate solutions of varying pH in the range of 5 to 11 were prepared, keeping the concentration of glyphosate constant (1×10^{-4} M). Solutions were heated at a temperature of 100°C for 5 min and 1×10^{-2} M ninhydrin solution was added. The solution mixture was again heated on water bath for 30 min at 100°C. The final volume of the solution was maintained constant at 20 ml. The absorbance was taken at wavelength 570nm.

Effect of temperature on glyphosate-ninhydrin color intensity

Ethanol (3 ml) was added in 1 ml of 1×10^{-4} M glyphosate solution. The pH of the solution was adjusted to pH 8. Now, the solution was heated at a temperature of 100°C for 5 min and 1×10^{-2} M ninhydrin was added. The solution was again heated at different temperature ranging from 60-100°C. The final volume of the solution was maintained constant at 20 ml. The absorbance of the solution was observed at 570nm.

Effect of Tx-100, SDS and CTAB on glyphosate-ninhydrin color intensity

Various concentrations of each Tx-100, SDS or CTAB solutions ranging from 1×10^{-3} to 2.5×10^{-2} M were added in a mixture of 1 ml (1×10^{-4} M) glyphosate solution and 3 ml ethanol. The pH of the solutions was adjusted to pH 8. Now, the solutions were heated at a temperature of 100°C for 5 min and 1×10^{-2} M ninhydrin was added. The mixture was again heated on the water bath for 30 min at 100 °C. The final volume of the solution was maintained constant at 20 ml. The absorbance of the solution was observed at 570 nm.

Effect of glyphosate concentration in presence of Tx-100, SDS and CTAB on glyphosate-ninhydrin color intensity

Various concentration of glyphosate ranging from 0.1×10^{-4} to 0.6×10^{-4} were added in each 1.5×10^{-4} M Tx-100, SDS or CTAB solutions. Now, 3 ml of ethanol was added and the pH of the mixture was maintained at pH 8. The resultant solutions were heated at 100°C for 5 min and 1×10^{-2} M ninhydrin was added. The mixture was again heated on the water bath for 30 min at 100°C. The absorbance of the solution was observed at 570 nm.

Effect of ninhydrin concentration in presence of Tx-100, SDS and CTAB on glyphosate-ninhydrin color intensity

3 ml of ethanol and 1.5×10^{-4} M Tx-100, SDS or CTAB was added 0.5×10^{-4} M glyphosate solution. After maintaining the pH of the solution at pH 8 and heating the solution for 5 min at 100°C, different concentration of ninhydrin ranging from 0.5×10^{-2} to 1.25×10^{-2} M was added. The mixture was again heated on the water bath for 30 min at 100°C. The absorbance of the solution was observed at 570 nm.

RESULTS AND DISCUSSION

When glyphosate is reacted with a ninhydrin, Ruhemann's purple colored complex is formed. The

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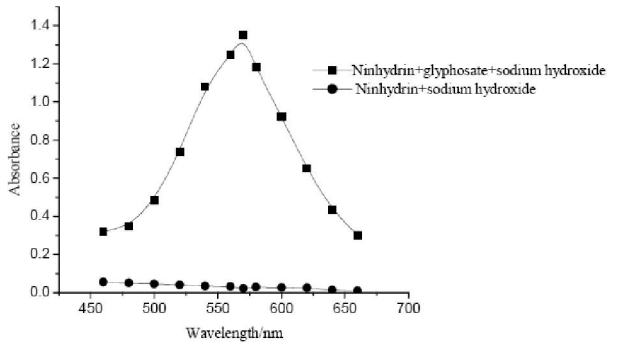

Figure 1 : Absorption spectra of both reaction product and reagent blank of glyphosate and ninhydrin in the presence of sodium hydroxide. Concentration of glyphosate=1.0×10^{-4}M

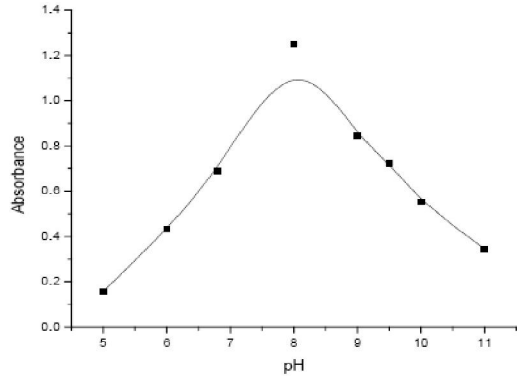

Figure 2 : Effect of pH on glyphosate-ninhydrin color intensity

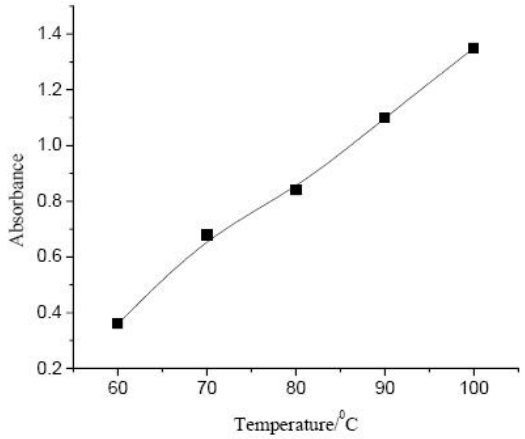

Figure 3 : Effect of temperature on ninhydrin-glyphosate color intensity

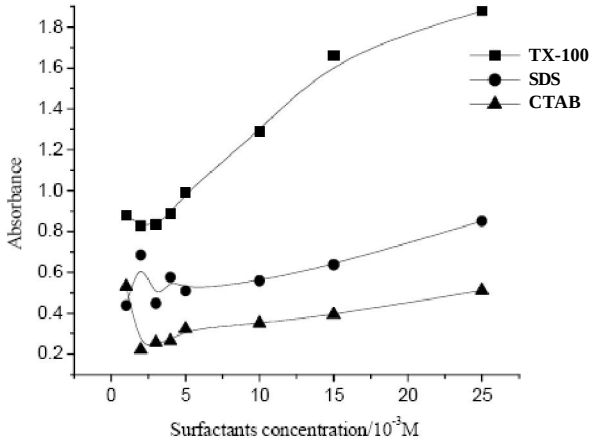

Figure 4 : Effect of surfactants concentration on glyphosate-ninhydrin color intensity

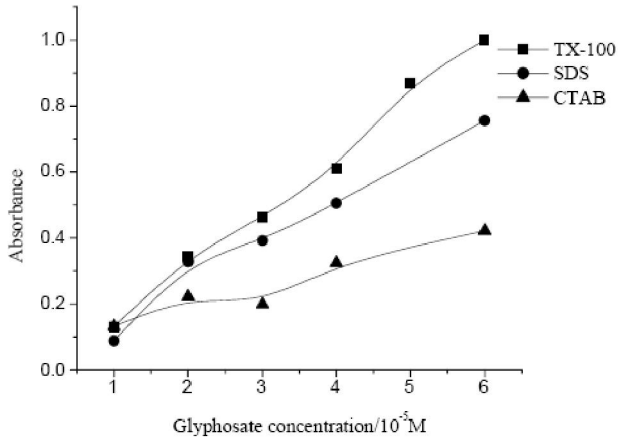

Figure 5 : Effect of glyphosate concentration on glyphosate-ninhydrin color intensity

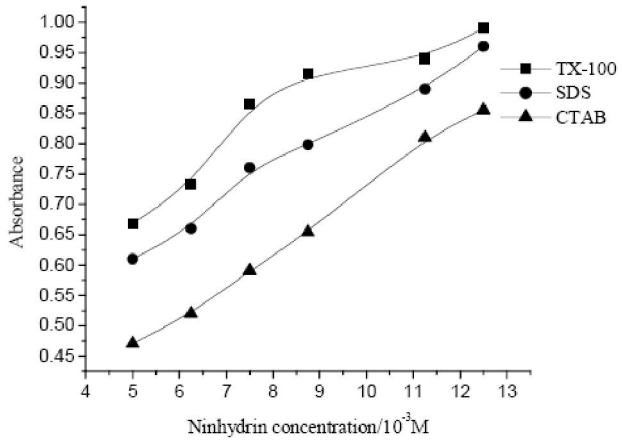

Figure 6 : Effect of ninhydrin concentration on glyphosate-ninhydrin color intensity

absorption spectra of colored product showed maximum adsorption at 570 nm, while the corresponding reagent blank showed practically negligible absorbance over entire wavelength ranging from 460-660 nm. The absorption spectra of glyphosate-ninhydrin colored complex and with the corresponding reagent blank are shown in Figure 1.

Generally, pH of the solutions influences the absorption of the colored complex. Thus, the effect of pH on the glyphosate-ninhydrin colored complex develop-

ment was studied. The maximum absorbance was observed in basic medium at pH 8 as shown in Figure 2. In general, there was an increase in absorbance upto pH 8 after that there was a gradual decrease in absorbance. Hence, to obtain the maximum absorbance subsequent studies were performed at pH 8. The pH of the solution was adjusted with sodium hydroxide/acetic acid.

The effect of temperature on intensity of glyphosate-ninhydrin colored complex showed that the absorbance of the color solution increases with increase in temperature as shown in Figure 3. The absorption of color was found maximum at 100°C, however at higher temperature the absorbance decreases which may be due to the dissociation of colored complex. It is necessary to heat the reagents solution on water bath for about 3 min at 100°C for colored development. The colored complex was cooled to room temperature, which can sustain the color on heating upto 100°C and 6 hrs at room temperature.

The effect of different categories of surfactants viz. Tx-100 (non-ionic), SDS (anionic) and CTAB (cationic) on the absorbance of glyphosate-ninhydrin complex color development was studied at fixed pH 8 and at a temperature of 100°C. Maximum absorbance of glyphosate-ninhydrin colored complex was observed in non ionic surfactant Tx-100. However, the order of absorption was found to be Tx-100>SDS>CTAB. It is apparent from Figure 4 that the addition of surfactant increases the absorption of colored complex.

Effect of glyphosate concentration on color development showed a linear increase in absorbance with Tx-100, SDS and CTAB as shown in Figure 5. However, maximum absorption was observed in presence of Tx-100. The order of linear absorbance corresponding to the surfactants was observed to be Tx-100>SDS>CTAB.

Concentration of ninhydrin in presence of Tx-100, SDS and CTAB also affects the color of glyphosate-ninhydrin complex formation. As shown in Figure 6, the absorbance of the solution increases with the increase in the concentration of ninhydrin and reached approximately constant at a concentration of 1.125×10^{-2} M. However, maximum absorption was observed in presence of Tx-100. The order of absorbance corresponding to the surfactants was observed to be Tx-100>SDS>CTAB.

CONCLUSION

Method for the spectrophotometeric determination of glyphosate in presence of various surfactants was developed. It was observed that the absorbance of the glyphosate-ninhydrin color was increased in presence of the surfactants. Hence, the surfactant assisted spectrophotometeric determination of pesticide could be applicable to environmental samples.

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