# Solubility study of hazardous pesticide (chlorpyrifos) by gas chromatography

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## Abstract

Solubility data of a hazardous pesticide like chlorpyrifos are important in order to determine its residual toxicity from soil and to understand its controlled release characteristics. In this paper, solubility of chlorpyrifos was measured by using gas chromatography in pure water, methanol, and water–methanol mixtures at 298.15, 303.15, and 308.15 K. The results indicate that chlorpyrifos is more soluble in methanol than in water. The solubility of chlorpyrifos in water can be enhanced by adding methanol to water. The effect of temperature on the solubility of chlorpyrifos was observed at higher methanol content in the mixture. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Solubility; Chlorpyrifos; Residual toxicity

## 1. Introduction

Chlorpyrifos (see Scheme 1), an organo-phosphorous compound, is a well-known pesticide found in commercial market and has been used as a liquid formulation in controlling pests like white grub and holotrichi consanguine blanch, which generally affect the groundnut crop. However, when chlorpyrifos is applied to plants or mixed with soil, it will produce hazardous effects to the environment, especially to the ozone layer in the atmospheres [1]. Leaching of the applied pesticide may pollute the surface/ground-water, ultimately resulting in adverse effects on the biological systems. Therefore, residual contamination of the pesticide is an important factor. In order to determine the residual toxicity of chlorpyrifos, it is appropriate to choose a proper solvent mixture to ensure complete extraction of the pesticide from the samples of interest.

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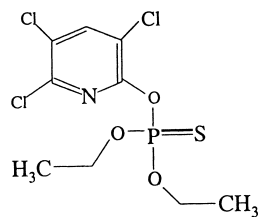
Scheme 1. Structure of chlorpyrifos.

Solubility data of pesticides in a well-defined media are important in agricultural industries [2–5]. A search of the literature indicates that virtually no solubility data of chlorpyrifos in aqueous-organic mixtures are available. In an effort to reduce its toxicity and to reduce the quantum of application, we are presently studying its encapsulation by using polymeric matrices for its controlled release (CR) [6,7]. Chlorpyrifos has a low solubility in water and its solubility can be enhanced by adding methanol to it. The solubility data of chlorpyrifos will be useful in selecting the in vitro dissolution medium after its formulations in order to develop the new CR formulations. For these reasons, we present here the results of solubility of chlorpyrifos in the binary mixtures of methanol and water using gas chromatographic (GC) technique. To understand the effect of temperature on solubility of pesticide, experiments were carried out at 298.15, 303.15, and 308.15 K.

## 2. Materials and methods

A 85 mass% pure technical grade and 99.6% pure analytical grade samples of chlorpyrifos were procured from Rallis Research Center, Bangalore, India. Methanol (HPLC grade) and the AR grade methyl isobutyl ketone (4-methylpentan-2-one) were purchased from s.d. fine Chemicals, Mumbai, India. Doubly distilled water was used and its purity was checked by comparing its density and conductivity at 298.15 K with the literature values, which agreed well.

Due to the highly toxic nature of chlorpyrifos, extreme precaution was taken to handle the product safely using appropriate personal protective clothing and nose coverings. Methanol–water mixtures were prepared by mixing the known volumes of methanol with water in a 50 ml volumetric flask. The amount of methanol transferred was calculated by subtracting the empty mass of the flask from the total mass of the volumetric flask+methanol. The mass measurements were performed on a single pan Mettler microbalance (Model AE 240, Switzerland) within the accuracy of ±0.01 mg. A total of nine compositions (including pure solvents viz., water and methanol) were used for mixing with chlorpyrifos. In each of these flasks, except in pure methanol, an excess amount (~10 g) of chlorpyrifos was added to ensure maximum solubility and the mixtures were manually shaken thoroughly at each temperature and allowed to stand for 8 h to attain maximum solubility. In case of pure methanol, chlorpyrifos was added and shaken thoroughly for 8 h until the undissolved granules were visually seen. The flasks were then immersed in a stirred circulation

constant temperature water bath (Grants, model Y14, UK) maintained at 298.15, 303.15, and 308.15 K within the accuracy of ±0.1 K at the desired temperature.

A 10 ml aliquot of the mixtures was taken from each system. The undissolved pesticide was removed from solvent by centrifugation (Remi R24, India) for 5 min at 10,000 rpm. Chlorpyrifos was completely extracted three times using the fresh 10 ml of methyl isobutyl ketone (MIBK). MIBK containing chlorpyrifos was then injected (2 μl) into GC (Hewlett Packard, HP 6890, USA) either directly or diluting it with MIBK depending upon the requirement.

The instrument was equipped with a flame ionization detector. A stainless steel column with a chromosorb W (HP) column (3% OV-101; 80/100 mesh; 1 m length; 1/8 in. o.d.) was used. The oven temperature was maintained at 463.15 K for 2.0 min, and temperature was increased at the rate of 303.15 K/min up to 533.15 K. Injection and detector temperatures were maintained at 533.15 and 553.15 K, respectively. This temperature range was selected for each set of measurements to avoid very short and excessively long retention times leading to large errors.

Pure nitrogen was used as a carrier gas with a flow rate of 35–40 ml/min. The flow rate of the carrier gas was measured at an ambient pressure by using the standard bubble flow meter within an accuracy of 0.5% of the reading. Known amounts of chlorpyrifos (~0.220 mg in 50 ml of MIBK) were injected into the GC column and the corresponding area was calculated automatically to establish the standard curve of multiple points. The unknown concentration of chlorpyrifos was subsequently calculated by measuring the area under the curve.

## 3. Results and discussion

All the experiments were performed in triplicate, but only the average values of solubility with deviations at different temperatures are presented in Table 1. Solubility data of chlorpyrifos in water–methanol mixture containing only up to 40% of methanol are presented in Fig. 1. Beyond 40% of methanol in the mixture, the solubility of chlorpyrifos increased

Table 1
Solubility results of chlorpyrifos in methanol–water mixture at different temperatures (each data point based on the average of three independent test results)

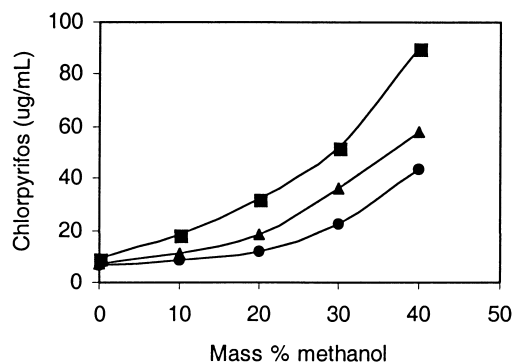| Mass% of methanol | Solubility of chlorpyrifos/(μg/ml) at | | |
|---|---|---|---|
| | 298.15 K | 303.15 K | 308.15 K |
| 0 | 6.36±0.58 | 7.18±0.63 | 9.07±0.98 |
| 10 | 8.25±0.98 | 11.5±0.81 | 18.2±0.91 |
| 20 | 11.6±1.63 | 18.2±1.96 | 32.1±2.38 |
| 30 | 22.2±1.12 | 36.3±1.85 | 51.7±1.37 |
| 40 | 43.3±13.1 | 58.2±15.2 | 90.4±19.2 |
| 50 | 290±21.9 | 399±30.2 | 522±29.6 |
| 60 | 456±59.9 | 618±59.9 | 865±42.2 |
| 80 | 4608±654 | 5201±338 | 9302±158 |
| 100 | 116498±7297 | 212511±7452 | 804651±8512 |

Fig. 1. Solubility of chlorpyrifos in methanol–water mixtures at (●) 298.15 K, (▲) 303.15 K and (■) 308.15 K.

considerably and hence, these data are not presented in the same figure. Chlorpyrifos was eluted at 3 min after the GC injection, whereas MIBK was completely eluted within 1 min. The instrument was PC-controlled and the data were processed using 'ChemStation' software (product number G2070AA) supplied with the instrument.

As can be seen in Fig. 1, the solubility of chlorpyrifos increased with an increasing amount of methanol in the mixture at all the temperatures. However, the incremental increase in solubility is more with increasing temperature. The effect of temperature on solubility is more prominent at higher concentrations of methanol in the mixture. Chlorpyrifos is a hydrophobic molecule (see Scheme 1), which results in its poor solubility of water. With an increment of 10 mass% of methanol in the mixture, its solubility also increases nearly by two-fold in lower methanol content (i.e. up to 20 mass% of methanol). However, at higher concentrations of methanol (i.e. beyond 20 mass%), its solubility increases considerably, thus, implying that higher amounts of methanol in the mixture act as a co-solvent to enhance its solubility due to specific interactions that can be attributed to the organic nature of methanol.

## 4. Conclusions

In an effort to develop the less hazardous products, we have undertaken a research to study the solubility of chlorpyrifos in water–methanol mixtures. Agro-industries have recognized the desirability to monitor the non-toxic concentration of chlorpyrifos in the environment to confirm the predicted safety factors. One of the greatest advantages of the GC method used here is that a minute quantity of the solute is sufficient for the measurements.

Encapsulation of chlorpyrifos by using a suitable and less expensive polymer is important to reduce its toxicity, a main concern of the farmers. Measuring the solubility of chlorpyrifos by GC can supply useful information and contribute to our further understanding of the behavior of chlorpyrifos in water–methanol mixture. Solubility enhancement of chlorpyrifos in higher methanol content is attributed to an increase in the organic nature of the system. Higher amount of methanol in water (>40 mass%) appears to be a favorable media for the

in vitro release study of chlorpyrifos-based CR formulations. These encapsulation studies are in progress and will be published later.

## Acknowledgements

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