THESIS

DETERMINATION OF THE WATER SOLUBILITY OF THE FUNGICIDE CHLOROTHALONIL

Submitted by
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WE HEREBY RECOMMEND THAT THE THESIS PREPARED UNDER OUR SUPERVISION BY JAMES L. HATHEWAY, JR. ENTITLED DETERMINATION OF THE WATER SOLUBILITY OF THE FUNGICIDE CHLOROTHALONIL BE ACCEPTED AS FULFILLING IN PART REQUIREMENTS FOR THE DEGREE OF MASTER OF SCIENCE.

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ABSTRACT

A UV-Visible spectrophotometric analytical procedure was developed and used to measure the water solubility of chlorothalonil at temperatures ranging from 8.5 to 37.5 °C. The effect of formulation chemicals present in BRAVO®500, a pesticide formulation containing chlorothalonil, on the apparent water solubility of chlorothalonil was also assessed. The water solubility was measured using a generator column technique while the apparent solubility enhancement of chlorothalonil by formulation chemicals in diluted formulation was evaluated by both generator column and batch shake techniques. A water solubility of 0.492 to 1.85 mg/L was found for a temperature range of 8.5 to 37.5 °C. The enthalpy of solution was found to be 7.96 kcal/mole. The apparent solubility enhancement due to formulation chemicals in dilute BRAVO®500 solution was 0.942 mg/L at 23 °C, which yielded a log K_{doc} of 4.24. Based upon these results and typical formulation application rates, it is unlikely that the formulation chemicals present in the BRAVO®500 formulation would increase the mobility of chlorothalonil in the environment.

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1. INTRODUCTION

1.1 Background

Since the 1980s, society has grown more concerned about the chemical contamination of the environment (Gerstl, 1990). Pesticides are one of many groups of chemicals which have met with severe scrutiny from the public and the agencies that control use and manufacture of pesticides. In 1993, a study was published by the National Research Council titled "Pesticides in the Diets of Infants and Children" (National Research Council, 1993). This along with EPA's recently completed evaluation of drinking water well contamination by pesticides (USEPA, 1990) are two examples of the growing concern about pesticides.

While pesticides have improved crop yields, they have also been shown to cause damage to the environment (Black and McCarthy, 1988; Kazuhiro et al., 1991; Aziz et al., 1991; Takagi et al., 1991) and, depending on the dose, hazards to human health (National Research Council, 1993). The human health effects and environmental fate of pesticides are two subjects which have been researched extensively. The requirements for registration of pesticides require both toxicity and environmental fate testing (USEPA, 1982).

Environmental fate is affected by several mechanisms including sorption, transport, volatilization, biodegradation, and plant uptake (Wagenet and Hutson, 1990; Arnold and Briggs, 1990). These fate mechanisms are governed by various physicochemical properties such as water solubility (S_W) and the octanol-water partition coefficient (K_{OW}), and these properties can thus be used to predict fate mechanisms. Therefore, it is important that accurate values of S_W and K_{OW} for pesticides are available in the literature.

1.2 Project Evolution

The research reported in this thesis was a part of an overall project to investigate various environmental aspects of pesticides used in the San Luis Valley of Colorado. The San Luis Valley is a major agricultural area and much research has been conducted at Colorado State University to evaluate pesticide contamination of ground water in the San Luis Valley. In particular, this overall study investigates the effects of formulation chemicals on the environmental behavior of pesticides with particular application to the San Luis Valley.

Little or no attention is usually directed towards formulation chemicals when conducting pesticide fate studies. Clearly, however, the physical or chemical behavior of a pesticide in aqueous solution must be altered by formulation type or composition because formulations contain pesticide concentrations that are substantially greater than the aqueous solubility. For example, the solubility of chlorothalonil is reported as 0.6 mg/L yet a formulation contains chlorothalonil at 500,000 mg/L. The formulation type or composition is devised specifically to enable greater amounts of pesticide to be held in solution or in suspension. The question of whether pesticide behavior may be affected by formulation composition is raised in many instances, such as the results of a recent field monitoring effort by Niccoli et al. (1990) who reported that model predictions did not agree with field observations for the pesticide atrazine. Durnford et al. (1990) also found pesticides such as chlorothalonil in the groundwater of the San Luis Valley, when a model being used in the study indicated that chlorothalonil would not appear. It is unknown whether the formulation chemical aspects may be responsible for the discrepancies observed by Niccoli et al. (1990) and Durnford et al. (1990).

The research to be conducted for this thesis was initiated to evaluate whether formulation composition may affect the environmental fate of pesticides. In considering the potential effects of formulation composition on pesticide fate, two criteria were identified as being most likely to demonstrate formulation effects: pesticide water solubility and mass fraction of inert chemicals in the formulation. It seems reasonable to expect that a pesticide of relatively low water solubility would require a higher degree of pesticide-formulation interaction to achieve a given concentration of the pesticide in the formulation. Similarly, high amounts of inert material in a formulation signal a situation where it is particularly difficult to keep the pesticide in solution or suspension.

To evaluate whether formulation chemicals would affect pesticide fate, it was decided to focus on pesticides used heavily in the San Luis Valley with low water solubilities, high inert chemical composition, or both. Thompson (1990) identified eight pesticides that are used heavily in the San Luis Valley. These pesticides and the information from Thompson (1990) on water solubility and inert composition are listed in Table 1-1.

Table 1-1 Pesticides Heavily Used in the San Luis Valley, Colorado[a]

Pesticide (Trade Name)	**Water Solubility (mg/L)**	**Inert Chemical Composition (% by weight)**
Chlorothalonil (Bravo)	0.6 @ 25 °C	10 .0% to 59.6%
Bromoxynil (Buctril)	130 @ 25 °C	66.6%
2,4-D	890 @ 20 °C	Not Available
Diquat (Diquat)	700,000	64.7%
EPTC (Eptam)	375 @ 25 °C	12.2% to 90.0%
Mancozeb (Manzate)	0.5	20.0% to 25.0%
Fenvalerate (Pydrin)	0.1 @ 20 °C	70.0%
Metribuzin (Sencor)	1220	25.0% to 59.0%

[a] Taken from Thompson (1990)

Three of the pesticides listed in Table 1-1, chlorothalonil, mancozeb, and fenvalerate have water solubilities below 1 mg/L. Of the three low water solubility pesticides only two have relatively high inert chemical composition, chlorothalonil and fenvalerate. For purposes of this work, chlorothalonil was chosen as the study pesticide.

The initial objective of this research was to evaluate the soil sorption and mobility of chlorothalonil. In considering the experiments that would lead to an understanding of the effects of formulation chemicals on soil behavior, it was apparent that a fundamental understanding of the solubility of chlorothalonil in water and of the effect of formulation chemicals on the apparent water solubility of chlorothalonil would first be needed. Therefore, the research presented herein, was focused on evaluating the water solubility and the effect of formulation chemicals on the apparent water solubility of chlorothalonil.

1.3 Project Description

Chlorothalonil is a pesticide used heavily in the San Luis Valley in Colorado (Thompson, 1990). It has been found that organochlorine pesticides are usually poorly degradable and remain in the environment for a long period of time (Kawamoto and Urano, 1989). The persistence of organochlorine chemicals in the environment would suggest that chlorothalonil might make a good chemical to study when evaluating factors that affect the environmental fate of pesticides.

The value of S_W for chlorothalonil that is reported in the literature is not supported by experimental data. Also, the reported S_W value dates back to the 1960's, which precedes the routine use of the generator column approach developed in the 1970's to determine more accurate values of S_W. Thus, the accuracy of the reported value of S_W for chlorothalonil is unknown.

Chlorothalonil is applied to crops in the San Luis Valley in a formulation. When formulated, inert chemicals are added to the chlorothalonil to enhance the fungicide's ability to protect against the target fungi. The effect of these formulation chemicals on the apparent water solubility is evident because of the high holding capacity of the formulation.

The purpose of this study was to evaluate the water solubility of chlorothalonil. In particular, this study evaluated reported water solubility values for chlorothalonil and compared these literature values with values determined experimentally with a saturation column. The effects of formulation chemicals were also evaluated as to their ability to enhance the apparent water solubility of chlorothalonil.

2. LITERATURE REVIEW

2.1 Environmental Fate Prediction Applications

The use of environmental fate prediction equations for soil sorption primarily involves water solubility (S_W) and the octanol-water partition coefficient (K_{OW}) (Briggs, 1981; Karickhoff et al., 1979; Gerstl, 1990; Kanazawa, 1989; Green and Karickhoff, 1990; and Kawamoto and Urano, 1989). Water solubility is considered to be among the most important properties controlling the transport and fate of organic pollutants and pesticides in aquatic systems (Chiou et al., 1986). From the above references, it is obvious that much research has been done to develop predictive equations which describe sorption by soil based on a given property of the chemical. Most often these equations correlate S_W and K_{OW} to the partition coefficient which describes sorption to the organic carbon fraction in the soil (K_{OC}) (e.g., Green and Karickhoff, 1990).

Accurate values of S_W are also important to help plan experiments and interpret the results from these experiments. For example, in order to accurately ascertain an enhancement in the apparent water solubility, an accurate value for S_W needs to be known. Also, it is important to stay below the S_W for sorption experiments and S_W is useful for interpreting groundwater data.

Use of predictive equations can prove to be advantageous if appropriately applied. Time and money can be saved because a sufficient understanding of the chemical's behavior can be obtained to allow for appropriate environmental action to take place. The equations can be used in predictive models to estimate concentrations in the soil, water and air. They also can be used as a reference for experimentally derived values and for the design of experiments (Gerstl, 1990). A drawback to using these equations is that they are usually developed for certain conditions and chemicals and these chemicals/conditions may not accurately describe the situation being evaluated.

In soil sorption analysis of pollutants, the one soil constituent which has proven to have the most correlation is the organic carbon content of the soil (Enfield and Bengtsson, 1988). The partitioning of pollutants onto the organic carbon is described by the partition coefficient K_{oc}. The K_{oc} value was developed as a normalizing factor so that different soils could be compared (Green and Karickhoff, 1990). The sorption coefficient, K_D can be found by multiplying K_{oc} by the organic carbon content of the soil (e.g., Kanazawa, 1989).

$$K_D = K_{oc} f_{oc} \tag{2-1}$$

Correlations have been found between S_w and K_{oc}, as well as between K_{ow} and K_{oc}. Both relationships have been explored by various researchers (e.g., Green and Karickhoff, 1990). For the purposes of this review, the focus will be on the correlations between S_w and K_{oc}. S_w has been found to be useful in predicting sorptive behavior of compounds (Chiou et al., 1986). The r^2 values presented with some of the equations is the coefficient of determination. In the case of the regression equations presented, r^2 represents how well the regression equation may predict the partition coefficients, where 1 is a good correlation and 0 means the equation is not helpful in predicting a partition coefficient.

Several classes of chemicals have been studied resulting in the development of several predictive equations. In an attempt to compile the work that had been done with respect to predicting the behavior of chemicals in the soil, Gerstl (1990) reviewed data generated by several researchers. From this review, Gerstl found a general equation for the thirteen classes of chemicals. This equation appeared as,

$$\log K_{OC} = A \log S_W + B \qquad (2\text{-}2)$$

Organochlorine pesticides, such as chlorothalonil, are usually poorly degradable and remain in the environment for a long period of time (Kawamoto and Urano, 1989). In research conducted by Kawamoto and Urano (1989), equation 2-3, based on 10 principle organochlorine pesticides, including chlorothalonil was developed. This equation appeared as:

$$\log K_{OC} = 3.788 - 0.464 \log S_W \quad (r^2 = 0.798) \qquad (2\text{-}3)$$

where S_W is in ppm. It appears that a value of S_W of 0.6 mg/L was used for chlorothalonil, based on a visual inspection of a plot presented in the paper. Kanazawa (1989) worked with 15 other pesticides and found the relationship,

$$\log K_{OC} = 3.01 - 0.356 \log S_W \quad (r^2 = 0.787) \qquad (2\text{-}4)$$

where S_W is also in ppm.

Karickhoff et al. (1979) found that the fate of hydrophobic organic pollutants (compounds with S_W less than a few ppm) was highly dependent upon their sorptive behavior. The sorption of a chemical not only controls its movement through the soil, but can also be involved with the degradation of the pollutant through surface associated chemical and biological processes. In the study by Karickhoff et al. (1979) of aromatic hydrocarbons and chlorinated hydrocarbons having a range of S_W of 500 ppt to 1800 ppm, the equation developed was,

$$\log K_{OC} = 0.44 - 0.54 \log X_W \quad (r^2 = 0.94) \qquad (2\text{-}5)$$

where X_W is expressed as a mole fraction.

Briggs (1981) derived theoretical equations based on the equation:

$$\log K_1 = a \log K_2 + b \qquad (2\text{-}6)$$

developed by Collander, in which K_1 and K_2 are two organic solvent - water partition coefficients. Briggs then compared the theoretical equations to experimentally-based derived equations. The theoretical equation he found was:

$$\log K_{om} = 0.3 - 0.52(\log [S_w] + 0.01T_m - 0.25) \qquad (2\text{-}7)$$

where $[S_w]$ is the molar solubility, K_{om} represents the partition coefficient based on organic matter content rather than organic carbon content, and the term $(0.01T_m - 0.25)$ represents the energy needed to break up the crystal structure of a solid, where T_m is the melting point in degrees Celsius. Briggs found that equation 2-8 developed for 38 chemicals from various classes was much as predicted by equation 2-7,

$$\log K_{om} = 0.8 - 0.51(\log [S_w] + 0.01T_m - 0.25) \quad (r^2 = 0.77) \qquad (2\text{-}8)$$

When Briggs adapted equation 2-7 to K_{oc} by multiplying K_{om} by the factor 1.724 and the term of $[S_w]$ was replaced by S_w (by assuming a molecular weight of 200) the equation became,

$$\log K_{oc} = 3.1 - 0.52 \log S_w \qquad (2\text{-}9)$$

Figure 2-1 shows a comparison between four of the regression equations presented here for K_{oc} and S_w. Each equation was plotted over the range for which it was developed. Equation 2-5 presented by Karickhoff et al. (1979), was modified using the values 1.724 and 200 given by Briggs (1981) so that S_w units of mg/L could be used. The modified equation is:

$$\log K_{oc} = 4.24 - 0.54 \log S_w \qquad (2\text{-}10)$$

In the plot, it is evident that there is fairly good agreement between the equations presented.

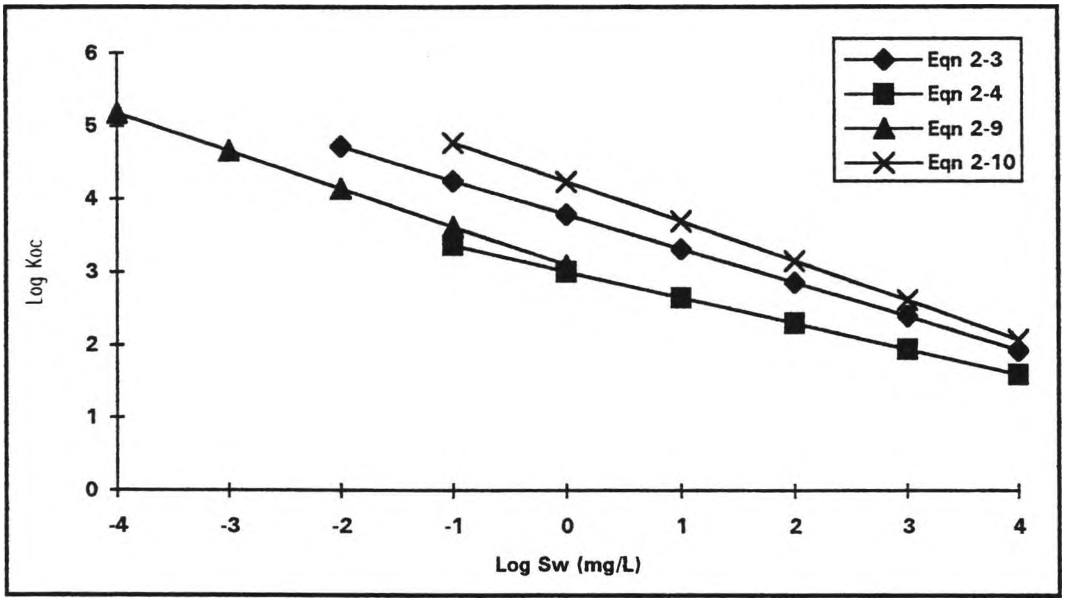

Figure 2-1 Plot of Regression Equations for K_{OC}

2.2 Solubility Enhancement by Dissolved Organic Matter

In the last decade, it has been recognized that constituents in water can increase the apparent solubility and therefore the soil mobility of a given hydrophobic chemical (Enfield and Bengtsson, 1986; Kile et al., 1990). The primary theory behind this idea is that a hydrophobic chemical, with a high affinity for the organic phase in solution (such as dissolved organic matter, DOM), will bind with that phase or the DOM will cause a change in the solvency of the solvent (Chiou et al., 1986). Chiou et al. (1986) also pointed out that size, polarity, and molecular configuration of the DOM may be important factors when determining the effectiveness of DOM for interaction with pesticides. Lee and Farmer (1989) and Carter and Suffett (1982) also reported that solution parameters like pH and ionic strength can play a role.

Most of the work reviewed studied naturally occurring organic acids as DOM. Landrum et al. (1984) stated that humic substances in water can increase the apparent water solubility of nonpolar compounds, bind organic compounds (either with covalent bonds, as charge transfer complexes, by hydrogen bonding or by van der Waals interaction), hydrolyze pesticides, interfere with polyaromatic hydrocarbon analysis in water, photosensitize pollutant degradation, and reduce the bioavailability of various compounds to aquatic organisms. Much like environmental fate considerations, K_{ow} and S_w play important roles in how a chemical will behave in the presence of DOM (Chiou et al., 1986; McCarthy and Jiminez, 1985; and Landrum et al., 1984). In general, K_{dom}, the partition coefficient for DOM and the chemical of concern, increases with a decrease in S_w or an increase in K_{ow} (Chiou et al., 1986; Landrum et al., 1984).

Most of the papers presented the equation,

$$C_{bound} = K_{dom} (C_{aqueous}) \tag{2-10}$$

where C_{bound} is the concentration of the chemical bound to the DOM (mg chemical/ g DOM) and C_{free} is the concentration of the chemical truly dissolved in water (mg/L) (e.g., Carter and Suffet, 1982). This equation is the same as that used when describing the partitioning of a chemical between solvent and soil in a water- soil system (equation 2-1). Chiou et al. (1986) and Kile et al. (1990) also presented an equation describing solubility enhancement.

$$S_w{}^* = S_w (1 + XK_{dom}) \tag{2-11}$$

Here $S_w{}^*$ is the apparent water solubility in water containing X g/mL DOM and S_w is the solubility in pure water.

Several methods have been used to determine the partitioning of a hydrophobic compound with DOM (Hassett and Millcic, 1985). One such method is solubility enhancement. In this method it is important for the solute to have a low water solubility and a high compatibility with the organic phase. The principle theory of solubility enhancement is that a cosolute can produce an enhancing effect on solute solubility either by changing the solvency of the medium or by direct solute interaction, either by adsorption or by partitioning (Chiou et al., 1986). Chiou et al. speculated that a partitioning interaction is most likely. The method employs adding an amount, in excess of the water solubility, of the solute of interest to a cosolute solution containing the DOM and evaluating the solution to see if an amount in excess of the water solubility is measured (e.g., Chiou et al., 1986). The equilibrium dialysis technique was the method most used in the literature reviewed (e.g., Kukkonen and Oikari, 1991). In this method, a dialysis bag containing DOM is placed in a container dosed with the chemical of interest. The pores in the bag are small enough to prevent diffusion of the DOM out of the bag and large enough to allow the chemical to move freely. After equilibrium is achieved, samples are analyzed from inside and outside the bag. The bound portion is found through mass balance, because the aqueous phase should be the same inside and outside of the bag (McCarthy and Jiminez, 1985). Another method used for differentiating between humic-bound and aqueous chemicals was the use of a reverse phase separation technique (Landrum et al., 1984; Morehead et al., 1986). For naturally occurring humic materials at a pH > 5, the idea was that the bound pollutant would pass through the column with the humic material and the aqueous pollutant would be retained by the column. At a pH greater than 5, the humics are ionized, which prevents them from sorbing to the reverse-phase media. Several values were presented for the partition coefficients in the various papers. Table 2-1 presents a sampling of these values.

There have also been some equations developed which predict these partition coefficients. Lee and Farmer (1989) presented the equation,

$$\log K_{doc} = 0.75 - 0.48 \log [S_w] \qquad (r^2 = 0.843) \qquad (2\text{-}12)$$

where $[S_w]$ is in mol/L. This equation was based on five nonionic pesticides ranging in solubility from 8.5×10^{-3} mmol/m^3 to 269 mmol/m^3 and the dissolved organic carbon was from peat derived humic acid at pH = 6.4. Eadie et al. (1990) presented the equation,

$$\log K_{doc} = 3.9 - 0.19 \log S_w \qquad (r^2 = 0.64) \qquad (2\text{-}13)$$

where S_w units were reported as μmol, after evaluating five chemicals with solubilities ranging from 0.0020 to 4.3 μmol. This solubility unit is missing a parameter. Solubility values were found for these compounds. After converting these known solubility values, it appears that the units should be in μmol/L.

Figure 2-2 shows a plot of the K_{doc} equations 2-12 and 2-13 presented here compared with the K_{oc} equation (2-3) developed by Kawamoto and Urano (1989). Equations 2-12 and 2-13, respectively, were both adjusted by assuming a molecular weight of 200 g/mol so that the units of S_w would all be in mg/L for accurate comparison. The adjusted equations are:

$$\log K_{doc} = 3.29 - 0.484 \log S_w \qquad (2\text{-}14)$$

$$\log K_{doc} = 3.77 - 0.19 \log S_w \qquad (2\text{-}15)$$

Each equation was plotted over the range for which it was developed. It was found that there is at most a 13 % difference between the log K_{doc} values found using the predictive equations, over a range of four log units. When comparing the K_{oc} versus the K_{doc} values, there is at most a 15% difference over the three log units which the equations had in common. It is interesting to note that the predictive equations appear to be similar on the surface as is seen by the percent comparison.

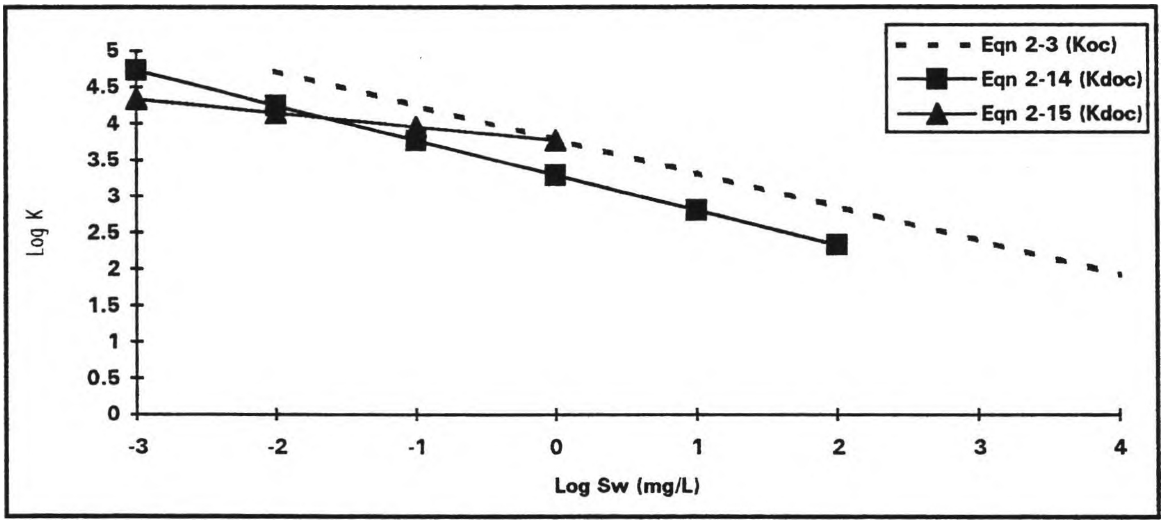

Figure 2-2 Comparison Between Predictive Equations for K_{oc} and K_{doc}

When evaluating the research that has been done, it becomes apparent that DOM should be of concern when evaluating the environmental fate of a hydrophobic chemical because of its ability to enhance the mobility of that chemical. In the study by Enfield and Bengtsson (1988), blue dextran, the study macromolecule, eluted from the column quicker than tritiated water. This result was exactly reversed from the predicted result that the blue dextran would be retained by the soil. The size of the macromolecule appeared to play a role in that it was only able to move through the larger pores and thus move more quickly through the column. This demonstrates that chemical transport can be facilitated by macromolecules which behave like hydrophilic compounds. The movement of these macromolecules with a water carrier may enhance movement of hydrophobic pollutants through soils. This may explain the underestimation of pollutant migration in soil by several models. Based on these results, DOM must be accounted for in models when predicting pollutant movement in soil.

Table 2-1 Reported Partition Coefficients for Organic Compounds and DOM

Compound[a]	log K_{dom}	DOM source	Method[b]	Reference
p,p'-DDT	4.82	Sanhedron Soil Humic Acid	Solubility Enhancement	Chiou et al., 1986
	4.27	Sanhedron Soil Fulvic Acid	Solubility Enhancement	Chiou et al., 1986
	4.12	Suwannee River Humic Acid	Solubility Enhancement	Chiou et al., 1986
	4.13	Suwannee River Fulvic Acid	Solubility Enhancement	Chiou et al., 1986
DDT	4.26[c]	Great Lakes Water	Reverse Phase Separation	Eadie et al., 1990
	4.8[d]	New Jersey Pond Humic Acid	Equilibrium Dialysis	Carter and Suffet, 1982
	5.4[d]	Aldrich Commercial Humic Acid	Equilibrium Dialysis	Carter and Suffet, 1982
B(a)P	4.57[c]	Great Lakes Water	Reverse Phase Separation	Eadie et al., 1990
	4.3 - 5.3	Finland Surface Water	Equilibrium Dialysis	Kukkonen and Oikari, 1982

[a] B(a)P - Benzo(a)pyrene

[b] An explanation of these methods can be found in section 2.2

[c] For dissolved organic carbon of suspended particles

[d] Approximate average value from several experiments

2.3 Physicochemical Properties of Chlorothalonil

Chlorothalonil is a contact protectant fungicide used to protect a large number of crops in many countries (Satoh, 1979; O'Neill, 1991; Camoni et al., 1991; and Walls et al., 1986). In the San Luis Valley of Colorado, it is used on potatoes (Thompson, 1990). Throughout the world it is used on fruits and other vegetables, golf courses, and ornamental plants (Reduker et al., 1988; Camoni et al., 1991; and ISK Biotek, 1993).

The chemical structure of chlorothalonil (2,4,5,6-tetrachloro-1,3-benzenedicarbonitrile, Chemistry Abstract Service Number 1897-45-6) is shown in Figure 2-3. The molecular weight of chlorothalonil is 265.90. The reported water solubility is 0.6 ppm at 25 C in most references (Hazardous Substances Data Bank [HSDB], 1989; Pesticide Manual, 1991; and Agrochemicals Handbook, 1987), but it has also been reported as ranging between 0.6 ppm and 1.2 ppm (Farm Chemicals Handbook, 1992). The earliest reference to water solubility traced back through reference books was a value of "~ 0.6 ppm" by Turner et al. (1963-4). However, in this reference, the value of S_w was given without any technical data to support the number.

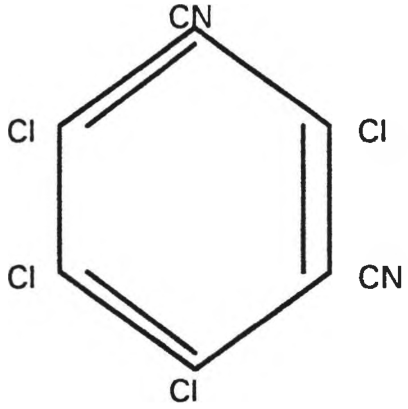

Figure 2-3 Chemical Structure of Chlorothalonil

Other data for chlorothalonil which has been found in reference materials includes a half-life in soil of 1.5 to 3 months (HSDB, 1989), K_{ow} of 4.37 X 10^2 (HSDB, 1989), bulk density of 40 lbs/ft^3 (Fermenta, 1988) and a specific gravity of 1.8 (Fermenta, 1988). It is clear that the density and specific gravity values are inconsistent, but the values were reported directly from the source. Davies (1988) working with aquatic system behavior of chlorothalonil reported a log K_{ow} of 4.38, which is nearly two log units higher than the value, log K_{ow} = 2.64, found in the

HSDB. No experimental procedure was immediately available for either value presented here, therefore no explanation for this discrepancy can be given.

BRAVO® 500 is a formulation that contains chlorothalonil as the active ingredient. It is described as a flowable formulation. This means that it is a liquid formulation consisting of finely ground active ingredient suspended in liquid and mixed with water for application (Farm Chemicals Handbook, 1992). The formulation is dispersible in water with a density at 20 °C of 10.3 lbs/gal, pH of 6-8, specific gravity of 1.24, and an active ingredient concentration of 500 g/L which constitutes 40.4% by weight of the formulation (Fermenta, 1988).

Information about the composition of the inactive portion of BRAVO® 500 was unavailable due to proprietary concerns. While the pesticide literature gives qualitative information about what is meant by flowable, details about the techniques used to prepare flowable formulations could not be located. In considering BRAVO® 500, it was postulated that it's ability to increase the solution's holding capacity was attributed to the presence of organic surfactants, inorganic colloids, or organic colloids, and that these materials carried the chlorothalonil in either the sorbed or coated state. For purposes of this work, it was assumed that the holding capacity of the solution was attributed to organic matter. It was found that the distribution of organic matter content in the formulation, fell within a factor of two of the percentages for chlorothalonil and formulation chemical content for BRAVO® 500.

Although not the primary focus of this review, some of the literature found explored the effects of chlorothalonil in the environment. Kazuhiro et al. (1991) explored the behavior of chlorothalonil in the soil and determined that chlorothalonil was degraded by many species of common soil microorganisms, but the chlorothalonil was toxic to those organisms unless sorbed to the soil. They also stated that the soil ecosystem and vegetation could be damaged by chlorothalonil accumulation in the soil. This persistence (soil accumulation) is in qualitative agreement with the relatively large half-life (1.5-3 months) reported by HSDB (1989). Davies (1988) conducted work on aquatic systems exploring the disappearance of chlorothalonil from these systems. He concluded that chlorothalonil was associated with nonfilterable residue in streams; a general reference to DOM. He found that chlorothalonil is readily biodegraded in stream water (half-life of 80 hours at 15 °C) at low concentrations (initial doses of 20 μg/L, approximately 2% of S_W), and cannot be regarded as a persistent pollutant in stream water. The difference between the conclusions by Kazuhiro et al. (1991), HSDB (1989), and Davies (1988) about the half life of chlorothalonil is possibly due to the mediums and concentrations used to assess the persistence in the environment.

2.4 Methods of Solubility Determination

Initially, it may appear that water solubility determination is an easy process. In reality, S_W for a crystalline hydrophobic compound can be a very difficult property to measure. The primary problem found in water solubility measurement is getting the crystalline material dissolved and equilibrated in solution, and then separating the solid from the aqueous phase (Karickhoff and Brown, 1979). Other factors can also cause problems like degradation, sorption, and volatilization.

One method to minimize some of these problems and to achieve saturation is the saturation generator column, which is described in May (1978). Briefly, beads coated with the crystalline compound of interest are placed in a column and water is run through the beads. As the water passes through the beads, the large surface area allows for the compound to dissolve from the coated beads into the water facilitating saturation. After a suitable conditioning time for the column, the water solubility can be found by analyzing the effluent. This method appears to be the most suitable for finding water solubilities for hydrophobic crystalline compounds.

Historically, a method was used where large chunks of the compound were placed into water and stirred continuously over several days or weeks. While this method may work, it is impractical for many applications and has been replaced by other methods like the generator column. A different approach is to coat the inside of a container with the compound of interest by first dissolving it into a volatile solvent and then rotating the container on its side allowing the solvent to evaporate. When the sides of the container have been adequately coated, water is added to the container and the solution is stirred or swirled gently in controlled temperature conditions, allowed to equilibrate and analyzed (see Green and Karickhoff, 1979).

After evaluating the methods reviewed above, the generator column appears to be the most appropriate for this study. The column was adapted for use in this study.

3. EXPERIMENTAL PROCEDURE

3.1 Experimental Overview

The research conducted for this thesis was conducted as a first step towards developing a research capability within the Environmental Engineering Laboratories of the Departement of Civil Engineering at Colorado State University on the environmental behavior of pesticides. Research involving pesiticides within the Environmental Engineering Laboratories was made possible throuh the acquisition of major analytical instrumentation. Unlike conventional wastewater parameters, which can be analyzed with reasonable precision in a relatively straightforward fashion, research with pesticides requires greater attention to laboratory techniques and is complicated by numerous experimental challenges that are not encountered when working with conventional parameters (Standard Methods, 1992).

Initial effort was required to select and develop an analytical technique. The Environmental Protection Agency (EPA) has established procedures for analysis of pesticides which requires a gas chromatograph. A gas chromatograph was available for use in the laboratory, but the method outlined by the EPA is time consuming and generates waste hexane solvent. Therefore, it was decided to explore alternative analysis methods which could take less time and generate less waste, such as fluorometry and spectrophotometry.

It was recognized from the beginning that there would be challenges to overcome and that these uncertainties would need to be solved when encountered. For instance, it was unknown if the formulation chemicals would interfere with analysis, or if there would be chemical degradation in the samples. These unknowns, when encountered, were dealt with and solved to minimize their effects on the research.

3.2 Materials

Technical grade chlorothalonil (97% pure) and BRAVO® 500 formulation were received from ISK Biotek and used as received without further purification. BRAVO® 500, as mentioned in Chapter 2, is 40.4% by weight chlorothalonil. The formulation is a very dense greyish solution. Pesticide grade methylene chloride, methanol, and hexane were obtained from Baxter Scientific. De-ionized (DI) water was prepared from tap water by ion exchange and granular activated carbon adsorption using a system from Continental Water Systems Corporation. Industrial grade nitrogen gas was received from General Air Service and Supply. Glass beads, 60 - 80 mesh, were purchased from All-Tech Associates, Inc.

BRAVO® 500, as mentioned earlier, is termed as a flowable pesticide. A flowable is defined by the Farm Chemicals Handbook (1992) as "a liquid formulation consisting of finely ground active ingredient suspended in a liquid." Flowables are mixed with water for application to a crop. It is a dense liquid, with a coarse texture. Because no literature could be found as to the nature of the formulation chemicals, it was postulated that they were organic in nature, and could be characterized by nonpurgeable organic carbon (NPOC) analysis, which is described later. The results of NPOC analysis, presented later in this thesis, indicated that organics other than chlorothalonil were present in the formulation chemicals. The formulation is highly turbid, and dilutions greater than 1 mg/L of chlorothalonil were visually turbid.

The DI water used was assumed to have a negligible NPOC content because of the high degree of treatment it received, therefore it was not initially analyzed. Also, the carbon cartridges, which are used, in part, to generate the DI water were replaced before any NPOC analysis was conducted. Towards the end of the experiments an NPOC analysis of technical grade chlorothalonil in DI water was prepared and the results indicated that there was a significant contribution by the DI water to the NPOC analyses, in which an average value of 0.892 mg/L NPOC was found in the DI water. The results of the experiments reported in this thesis, are not believed to have been affected, because all experiments were conducted within three months of the time that the cartridges were replaced. The high NPOC value in the DI water was found six months after installation of the cartridges, and three months after the completion of the experiments. This indicates that the carbon cartridges may have reached the adsorptive capacity after the experiments had been completed.

3.3 Analytical Method Development

Three methods for analysis were available for use in the laboratory during the time that the research was conducted. The instruments available were a fluorometer, uv-visible spectrophotometer, and a gas chromatograph. The fluorometer was considered because it is ordinarily very sensitive for detection of aromatic compounds (Sawyer and McCarty, 1978). The spectrophotometer, although less sensitive, would give a large range of the spectrum for use in detection and is also sensitive to aromatic compounds. The gas chromatograph is the method recommended by the EPA for the detection of chlorothalonil, but it generates waste solvent due to the extractions needed.

Analysis using a fluorometer, equipped with a fixed excitation and emission filter, was the first method attempted. Chlorothalonil standards ranging in concentration from 0.06 to 6 mg/L were prepared in methylene chloride and were to be used to calibrate the fluorometer. However, a measurable response was not obtained when the fluorometer was used to analyze these standards. It was suspected that this might be due to the particular combination of excitation and emission filters on the fluorometer. Turner Designs, the company that manufactured the fluorometer was contacted and it was confirmed that chlorothalonil would not fluoresce under the conditions of our instrument.

The UV-Visible spectrophotometer was then targeted for use. Standards were again prepared in methylene chloride and analyzed. In contrast to the fluorometer, it was found that the UV-Visible spectrophotometer did give measurable absorbances to chlorothalonil. Therefore, it appeared that this would be a viable analytical approach. To analyze the spectra generated, three types of techniques were attempted. The first method was a maximum peak method, which could be taken directly from the spectra. At low concentrations, though, it was found that this value was affected by background variations in the sample. A method by which the area under the peak was estimated was then attempted. This method was dismissed because of the high degree of estimation that the method employed, which would lead to the introduction of error. It was then decided to try a net absorbance method, which is described later. This method was eventually settled on, because it gave results with the highest precision. The development of the net absorbance method provided a method which could be used as an alternate to the gas chromatograph.

During the course of this research, another student was working in the lab with chlorothalonil. A method was devised by this student, according to the EPA methods, for the gas chromatograph. After the procedure had been developed, the gas chromatograph was used on a limited basis for this research.

3.4 Solubility Test Procedures

a) Gross Determination

A gross determination for the respective solubilities of chlorothalonil in methylene chloride and methanol was conducted. The purpose of this determination was not to achieve high precision on the solubility value but rather to obtain an order-of-magnitude estimate of the solubility to determine the feasibility of using these solvents for standard preparation. The approach was to add enough chlorothalonil to a given amount of solvent so that an equilibrium could be attained between the solid and solvent phases of chlorothalonil and a solubility could be determined.

Two centrifuge tubes were filled with 6 mL of methylene chloride. A solubility of 15,000 ppm was assumed and 0.1g and 0.2 g were added, respectively. These masses were selected to correspond to an exact assumed solubility and twice the amount of the assumed solubility of chlorothalonil. The tubes were allowed to sit, undisturbed and covered with para-film for 24 hours. Inspection of both tubes after this period indicated that some volatilization of the solvent had occurred and that an excess of chlorothalonil was present. The aforementioned volatilization led to larger solubility values than assumed. The tubes were centrifuged for 15 minutes at 3500 rpm. A 4 mL aliquot of methylene chloride was withdrawn and placed in a tared aluminum weighing pan. The liquid portion of the sample was allowed to evaporate for 24 hours, at which time the contents were weighed. The solubility was found by dividing the mass of the residue by the volume of the aliquot.

The same procedure was followed for methanol with one exception. Based on an assumed solubility of 1000 ppm, 0.05 g and 0.1 g of technical grade chlorothalonil were added to 50 mL and 100 mL of methanol, respectively.

The approximate value found for solubility in these two solvents was higher than the assumed value because of the volatility of the solvents, and the resulting reduction in volume of liquid in the tubes.

b) Saturation Column (Technical Grade Solubility)

The saturation column approach for evaluating the aqueous solubility of an organic chemical was developed by May (1978). The basic theory behind the generator column is to run a volume of solvent over glass beads coated with the solute of interest. The relatively high surface area of the beads increases the rate at which the solute dissolves into the solvent and enables the generation of a saturated solution.

The final experimental setup is shown in Figure 3-1. For this experiment a high pressure (5000 psi maximum pressure) - low flow (ranging from 0.05 to 1.5 mL/min) Eldex pump was purchased from Eldex Laboratories in Napa, California. Stainless steel tubing 7.5 cm long and 4.6 mm i.d. was used for the column and stainless steel tubing of 0.1cm i.d. and 18 in. long was used for the delivery of water from the pump to the column. A teflon tube 0.24 cm i.d. was used to deliver the water from the reservoir to the pump. A teflon tube 12 in. long, like the delivery tube, was used between the column and collection vessel. Care was taken to minimize the length of this tube to minimize sorptive losses or other interactions of the generated solution with the walls of the tubing. A 10 micron filter was placed on the influent end of the pump to prevent solids from entering the pumping mechanism.

Four runs were made initially without temperature control. Variability in the results of these runs led to the introduction of a constant temperature waterbath for control. The column was placed in a water bath to maintain a constant temperature. The temperatures used were, 8.5 ± 0.25 °C, 23 ± 0.25 °C, and 37.5 ± 0.64 °C. The 0.25 °C temperature interval for the first two temperatures was based on a conservative estimate of the 95% confidence interval, as there was no noticeable change in the temperature readings. There were noticeable temperature changes during the high temperature run. Temperatures were taken at the start and completion of each sample collection and ranged from 36 to 39 °C, for all five samples. The value of ±

0.64 °C is based on the average and standard deviation for the temperatures recorded during this period.

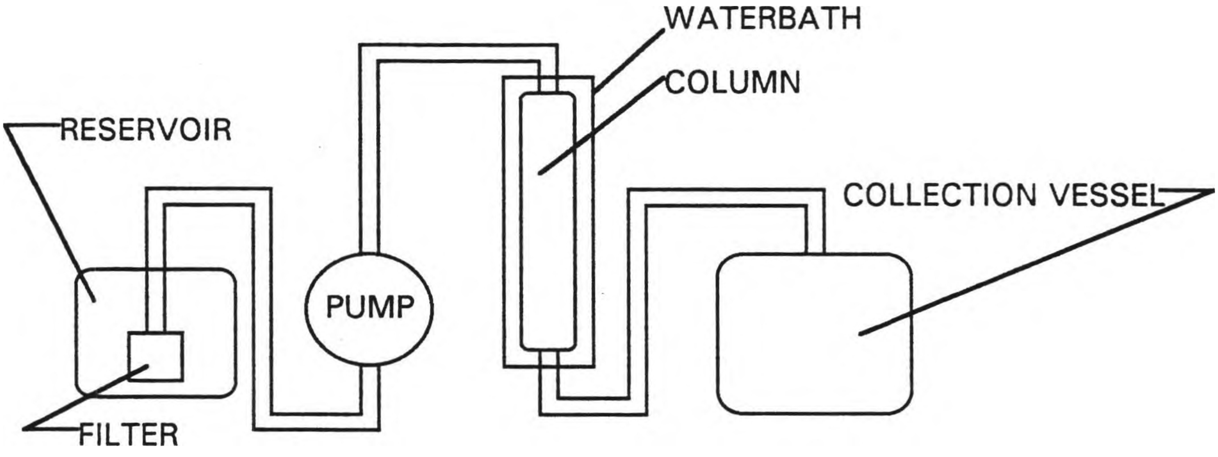

Figure 3-1 Saturation Column Schematic

Coating of Beads: Approximately 1% by weight technical grade chlorothalonil, based on bead mass, was dissolved in 10 to 30 mL methylene chloride to which 10 g of 60-80 mesh glass beads were added. The volume of methylene chloride was selected as necessary to completely cover the beads. The methylene chloride was evaporated from the beads with nitrogen gas. The sides of the evaporation vessel were occasionally washed with additional methylene chloride to wash the chlorothalonil into the beads. Care was taken to ensure that chlorothalonil coated the beads, rather than the sides of the container.

Column Preparation: The coated beads were added to the column, placing glass wool on the influent and effluent sides of the column. The column was conditioned by running approximately 70 mL of water through the column before collection of effluent samples for analysis. A void volume of $0.5\ cm^3$ was estimated by assuming a bead porosity of 0.4. The 70 mL used for conditioning corresponded to approximately 140 pore volumes. High and low flow comparisons in water solubility were conducted to determine an optimum flow rate. The pump was run at approximately 1 mL/min, which was within the range, 0.1 mL/min to 5.0 mL/min, used by May (1978). Effluent samples were collected for analysis at selected time intervals in 10 mL flasks containing 0.5 mL of methanol. Analytical results were corrected for the change in volume. Methanol was used to help decrease sorption of chlorothalonil onto the walls of the collection flask.

c) Saturation Column (BRAVO® 500 Solubility)

In an attempt to evaluate the extent of the solubility enhancement due to the formulation chemicals, a dilute solution of Bravo® 500 was prepared and run through the column.

The glass beads were prepared as previously described. A stock solution of BRAVO®500 with a target concentration of 100 mg/L chlorothalonil was prepared by adding 247.5 mg of formulation, at a concentration of 500 g/L, to 1 L of de-ionized water. From the stock solution a 1mg/L solution (0.6 mg/L solution as measured by the spectrophotometer) was prepared for use in the reservoir. The reservoir solution was pumped through the generator column in the same manner as previously discussed for deionized water. Chlorothalonil concentration solutions for UV-Vis spectrophotometric analysis were collected in 10 mL flasks with 0.5 mL of methanol for stabilization. Following the collection of each 10 mL sample for spectrophotometric analysis, a 10 mL sample was collected for nonpurgeable organic carbon (NPOC) analysis.

d) Batch Shake Test with BRAVO® 500

A batch procedure was also used as a check for apparent solubility enhancement. 100 mL dilutions of chlorothalonil were prepared from the BRAVO formulation stock solution at 2, 5, 10 and 15 mg/L, respectively. The samples were shaken in 100 mL volumetric flasks for 24 hours to allow for an assumed equilibrium to occur between the aqueous phase and the associated (DOM-chlorothalonil) phase.

Before shaking, initial triplicate readings were made of chlorothalonil concentration and NPOC concentration. Chlorothalonil samples were diluted to a target concentration 1mg/L based on the expected concentration, to accommodate analysis. Samples were then shaken for 24 hours and again analyzed for NPOC and total chlorothalonil concentration. A gas chromatograph was used to check the concentration numbers.

In an effort to distinguish the bound phase from the aqueous phase, the reverse-phase separation technique was used as described by Landrum et al., (1984). The bound phase can be defined as the chlorothalonil which has been partitioned onto the DOM which is assumed to pass through the column. 20 mL of each sample was drawn into a syringe and passed through a C-18 Sep-Pak from All-Tech Associates, Inc. It was expected that the dissolved chlorothalonil would be adsorbed by the C-18 packing. The effluent from the Sep-Pak was analyzed by the spectrophotometer to determine the concentration of the bound chlorothalonil.

3.3 Analysis

3.3.1 Chlorothalonil

a) UV-Visible Spectrophotometer

The UV-Vis spectrophotometer was used as the primary analytical instrument because of its ease and the quickness in obtaining results. An HP model 8452A diode array spectrophotometer was used. Samples were delivered to 3 mL cuvettes with standard silica windows, which were purchased from Fisher Scientific. The absorption spectra were recorded with the General Scanning software that came with the spectrophotometer. The software plotted the spectrum for analysis. Hardcopies of the spectrum were plotted on a 7470A HP Plotter. A typical plot for chlorothalonil in water is shown in Figure 3-2. Figure 3-2 shows that the absorbance maximum occurs at a wavelength of approximately 230 nm.

As previously discussed, undiluted BRAVO® 500 is an extremely thick, turbid suspension. Turbidity was not visually evident in the samples of BRAVO® 500 formulation that were diluted to a chlorothalonil concentration of 1 mg/L. Given the turbidity of the undiluted formulation, there was a concern as to the effect of turbidity on sample analysis. It was found however, that in working with samples of BRAVO® 500, with target chlorothalonil concentrations at or below 1 mg/L, that problems with sample analysis were not encountered.

Calibration Curve Preparation: A 50 mg/L stock solution of technical grade chlorothalonil was prepared in methanol. Dilutions of 0.05, 0.1, 0.15, 0.2, 0.3, 0.5, and 1.0 mg/L were prepared from the stock solution and diluted in de-ionized water. Triplicate readings of each sample were taken on the spectrophotometer.

Each sample was read after rinsing the cuvette three times with the sample. Net absorbance was measured and plotted versus concentration. Chlorothalonil gave a strong peak at 234 nm in the spectrum. The net absorbance was found by first estimating a baseline by drawing a tangent to the bottom of the curve. An absorbance value at 234 nm on the baseline was then estimated by linear interpolation on the tangent line. The value on the baseline was then subtracted from the peak value at the same wavelength. (See Appendix 2) A linear relationship was found through linear regression so that unknown concentrations could be determined. The equation used was

$$\text{Concentration (ppm)} = 5.072 * (\text{Net Absorbance}) \quad (r^2 = 0.99) \quad (3\text{-}1)$$

The data and calibration curve can be found in Appendix 3.

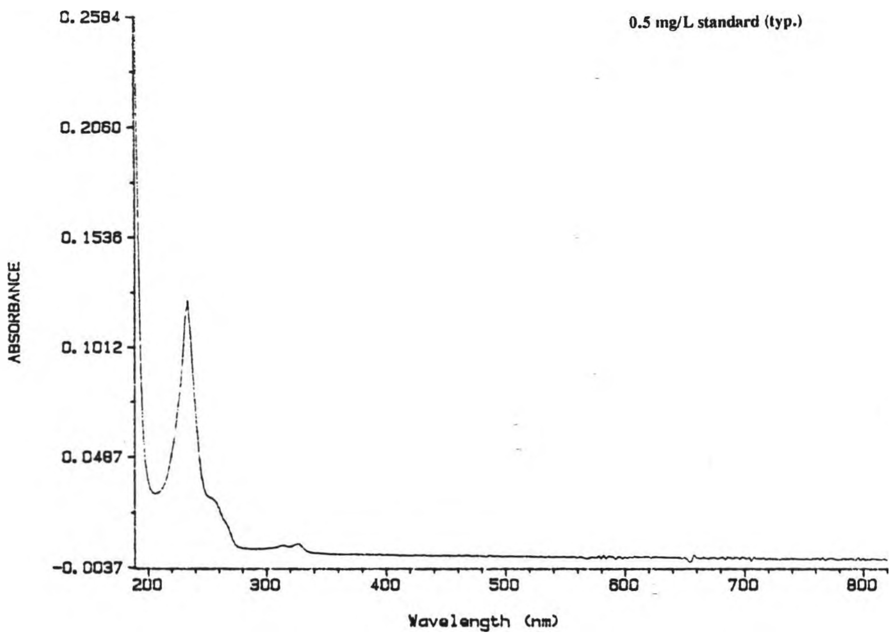

Figure 3-2 Typical Spectrum for Chlorothalonil from UV-Visible Spectrophotometric Analysis

Sample Analysis: Initially, technical grade samples were extracted into methylene chloride and analyzed. Extractions were done by adding 20 mL of methylene chloride to 20 mL of effluent from the column. The mixture was swirled in a separatory funnel for 10 minutes and allowed to separate for 10 minutes. The methylene chloride was withdrawn and analyzed. Later it was found that chlorothalonil could be analyzed in water allowing for the direct measurement of the samples. All water solubility values reported here are a result of direct analysis of water samples. Cuvettes were rinsed three times with the sample, as the volume allowed, and read in the spectrophotometer.

b) Gas Chromatograph

An HP Model 5890A Series II model gas chromatograph (GC) was used. The GC was equipped with an electron capture detector. A SUPELCO packed glass column, dimensions 4 mm I.D. and 2 meters in length, with 100/120 mesh packing material was used. Oven temperature was 250 °C, injector temperature was 250 °C, and detector temperature was 250 °C. A calibration curve was developed by making dilutions of 0.05, 0.5, and 1 mg/L in hexane (Wurtz, 1994). The operating software was HP Chemstation, Version A.03.01.

Triplicate extractions with hexane were used for water samples. To accomplish this, 20 mL of water were added to 10 mL of hexane. The mixture was shaken for 3 minutes and allowed to separate for 10 minutes. Water was collected and then hexane was collected. This procedure was followed two more times so that a total of 30 mL of hexane was collected. 6.9 μL of the combined extract were injected into the GC and analyzed. A sample of the data given by the gas chromatogram can be seen in Appendix 4.

3.3.2 Nonpurgeable Organic Carbon (NPOC)

A DC-80 total organic carbon analyzer from Rosemount Analytical Inc. was used with a model 3300 CO_2 infrared analyzer from Milton Roy. This method was used to characterize the formulation chemicals, represented as organic matter, as NPOC. This was confirmed when values larger than the chlorothalonil contribution were read. Nonpurgeable organic carbon is the carbon which is not in carbonate form (inorganic carbon). This analysis was done in an attempt to characterize the formulation chemicals, due to the lack of information with respect to the inert ingredients.

Before direct injection into the instrument, the samples were purged for 8 - 10 minutes to eliminate inorganic carbon species. The sample was injected with a 1 mL Hamilton Gas Tight syringe purchased from Baxter Scientific. The instrument was calibrated according to the directions by preparing a 10 mg/L TOC solution with reagent grade potassium hydrogen phthalate added to water. The average is taken by the instrument and used for a reference for internal calibration.

To determine how much carbon from technical grade chlorothalonil is contributed when an analysis with the TOC analyzer is performed. To accomplish this a solution with 0.76 mg/L chlorothalonil was prepared and was found to have an average NPOC value of 1.16 mg/L. Knowing that chlorothalonil is 36% carbon (a 0.274 mg/L contribution here), this value immediately raised questions. The deionized (DI) water used was analyzed and a value of 0.892 mg/L was found. Subtracting the DI water from the total value gave 0.268 mg/L, indicating that carbon in the chlorothalonil is almost completely released. The high NPOC value for the DI water was not found until near the end of the project. It is not believed that this was a problem before the detection of this high value.

3.4 Data Manipulation for DOM Interaction Analysis

An attempt to assess the bound chlorothalonil value was made by the reverse-phase separation technique. It was assumed that the non-chlorothalonil organic matter content of the formulation would pass through a reverse-phase column, and thus the concentration of the chlorothalonil-DOM complex could be found by analyzing the effluent from the Sep-Pak. Total chlorothalonil concentration of the sample was found using the spectrophotometer. The concentration of the bound chlorothalonil divided by the aqueous chlorothalonil, found by subtracting the bound chlorothalonil concentration from the total chlorothalonil concentration in the solution fed to the Sep-Pak, will give a value for an expected partition constant (i.e., equation 2-10). Taking the results from the batch shake test, a plot can be made of bound cholorothalonil versus aqueous chlorothalonil. The slope of this plot is the partition constant, K_{dom}. The NPOC analysis is used as a description of the chemicals present in the formulation.

4. RESULTS

4.1 Solubility

a) Gross Determination

The apparent solubility of chorothalonil in methylene chloride was found to be ≥25,000 mg/L. For methanol, an apparent solubility of ≥1,200 mg/L was found. These values are reported as ≥ because the experimental procedure did not involve rigorous confirmation of equilibrium. If true saturation was not attained, the numbers presented here may be smaller than the actual solubility values.

b) Saturation Column

Results of the initial saturation column runs, where separation funnel techniques were used (described in 3.3.1), can be found in Table 4-1. In this table, maximum absorbance values are compared to net peak absorbance values. There were no temperature controls for the generation of this data. Runs were also conducted without temperature control which were analyzed by direct analysis. Table 4-2 and Table 4-3 are examples of the results obtained from these runs. Table 4-4 shows a run with the saturation column, in a constant temperature water bath ($T=23 \pm 0.25$ °C). This data was analyzed by direct measurement with the spectrophotometer. Solubility was evaluated at high and low flow rates. The apparent solubility for high and low flow conditions was found to be 0.907 ± 0.032 ppm and 0.913 ± 0.024 ppm, respectively. The value for all data was 0.910 ± 0.017 ppm. The ± was estimated using the equation:

$$\pm = (t_{\alpha/2})(s)/n^{1/2} \quad (4\text{-}1)$$

where t is the student t statistic, α is the confidence interval, s is the standard deviation, and n is the total number of samples. Values represented as ± correspond to a 95% confidence interval (i.e., $\alpha = 1 - 0.95$) about the mean. A null hypothesis test showed that there was no appreciable difference between the high and low flow conditions, suggesting that the column could be run at the higher flow rate without affecting the solubility.

Table 4-1 Comparison Between Maximum and Net Peak Values at a Chlorothalonil Concentration of ~ 1 mg/L

Sample	Maximum Peak Absorbance (M)	Net Peak Absorbance (N)	Ratio (M/N)
1	0.205	0.202	1.015
2	0.229	0.226	1.013
3	0.264	0.255	1.035
4	0.250	0.242	1.033
5	0.259	0.250	1.036
6	0.250	0.246	1.016
7	0.241	0.236	1.021
8	0.206	0.206	1.000
9	0.254	0.253	1.004
10	0.244	0.244	1.000
11	0.224	0.223	1.004
12	0.235	0.234	1.004
13	0.225	0.224	1.004

Table 4-2 Saturation Column Data for Chlorothalonil Water Solubility without Temperature Control (9/7/93)

Sample	Concentration (mg/L)	Sample	Concentration (mg/L)		
1	0.900	7	0.745		
2	1.01	8	0.522	Average	0.810
3	0.877	9	0.717	Std Dev	0.134
4	0.877	10	0.731	±	0.085
5	0.948	11	0.877		
6	0.820	12	0.692		

± is in mg/L and is based on the mean and standard deviation for a 95% confidence interval

Table 4-3 Saturation Column Data for Chlorothalonil Water Solubility without Temperature Control (9/9/93)

Sample	Concentration (mg/L)	Sample	Concentration (mg/L)		
1	1.02	14	0.958		
2	1.05	15	0.970		
3	1.00	16	0.968		
4	1.02	17	0.907		
5	0.995	18	0.909	Average	0.948
6	0.878	19	0.882	Std Dev	0.051
7	0.971	20	0.922	±	0.021
8	0.920	21	0.946		
9	1.04	22	0.908		
10	0.945	23	0.881		
11	0.934	24	0.947		
12	0.875	25	0.896		
13	0.959	26	0.946		

± is in mg/L and is based on the mean and standard deviation for a 95% confidence interval

Table 4-4 Saturation Column Data for Chlorothalonil Water Solubility[a]

Low Flow Concentration (mg/L)[b]			High Flow Concentration (mg/L)[c]			All Data (mg/L)		
0.901	Mean	0.913	0.946	Mean	0.907	0.901	Mean	0.910
0.868	Std Dev	0.031	0.849	Std Dev	0.038	0.868	Std Dev	0.034
0.945	Std Error	0.010	0.940	Std Error	0.013	0.945	Std Error	0.008
0.888	±[d]	0.024	0.925	±	0.032	0.888	±	0.017
0.889			0.867			0.889		
0.892			0.873			0.892		
0.942			0.940			0.942		
0.944			0.920			0.944		
0.947						0.947		
						0.946		
						0.849		
						0.940		
						0.925		
						0.867		
						0.873		
						0.940		
						0.920		

[a] Temperature = 23 ± 0.25 °C

[b] Low flow rate = 0.59 mL/min

[c] High flow rate = 1.18 mL/min

d ± is in mg/L and is based on the mean and standard deviation for a 95% confidence interval

Tests were also conducted to evaluate the effects of temperature variation on the water solubility of chlorothalonil. At 8.5 ± 0.25 °C and 37.5 ± 0.64 °C values of 0.492 ± 0.003 mg/L and 1.85 ± 0.050 mg/L, respectively, were found. The results of this test can be found in Table 4-5.

Table 4-5 Water Solubility Dependence on Temperature

Temperature (°C)	Sample	Concentration 1 (mg/L)[a]	Concentration 2 (mg/L)[a]	Average Concentration
37.5 ± 0.64	1	1.91	1.92	
	2	1.82	1.83	
	3	1.85	1.87	1.85 ± 0.050
	4	1.91	1.94	
	5	1.74	1.75	
8.5 ± 0.25	1	0.496	0.495	
	2	0.495	0.487	
	3	0.497	0.494	0.492 ± 0.003
	4	0.491	N/A[b]	
	5	0.489	0.486	

[a] Duplicate measurements were taken for each sample
[b] N/A - data not available
± is based on the average and standard deviation for a 95% confidence interval

c) Saturation Column (BRAVO® 500 Solubility)

The data found in Table 4-6 shows the results from the saturation column run using the dilution of BRAVO® 500 in place of deionized water as the solvent. The average chlorothalonil concentration in the effluent was found to be 0.942 ± 0.05 mg/L while the average NPOC was found to be 2.33 ± 0.24 mg/L at a temperature of 23 ±0.25 °C. Initial values in the table refer to the start of the experiment and final values at the conclusion of the experiment. The run was conducted over a period of 36.6 hours.

4.2 Batch Shake Test with BRAVO® 500

The results from the batch shake test can be found in Table 4-7. UV-Visible spectrophotometric analysis of the samples collected from the batch shake vessels after 24 hours gave a concentration of 0.98 ± 0.05 mg/L, 2.32 ± 0.29 mg/L, 4.09 ± 0.28 mg/L, and 5.78 ± 1.21 mg/L for the 2, 5, 10, and 15 mg/L samples, respectively. GC analysis of the samples collected after 24 hours gave readings of 1.45, 4.35, 7.98, and 14.4 mg/L, respectively for the same dilutions listed above. These comparative results will be discussed later. To differentiate between the bound and aqueous phases of chlorothalonil, the reverse phase separation technique was used. The analysis on the Sep-Pak effluent yielded results of 0.0169, 0.0262, and 0.200 mg/L for the 5, 10, and 15 mg/L samples, respectively. Due to these unexpectedly low values, the original samples were analyzed on the spectrophotometer without dilution, yielding 0.792, 0.748, and 0.788 mg/L, respectively.

Table 4-6 Formulation Saturation Column Results[a]

Sample	Chlorothalonil Concentration (mg/L)	NPOC Concentration (mg/L)	Sample	Chlorothalonil Concentration (mg/L)	NPOC Concentration (mg/L)
1	0.870	2.45	9	0.874	1.80
2	0.861	1.94	10	0.869	2.05
3	0.844	2.41	11	0.894	1.87
4	0.937	2.86	12	0.945	3.72
5	1.28	2.84	13	0.886	3.06
6	0.944	1.91	14	0.964	2.24
7	1.15	1.98	15	0.941	1.91
8	0.930	2.24	16	0.941	2.75

[a] T = 23 ± 0.25 °C

± is based on the average and standard deviation for a 95% confidence interval

Reservoir Concentrations:

Initial NPOC Concentration = 2.82 mg/L
Final NPOC Concentration = 1.86 mg/L
Average Effluent NPOC = 2.33 ± 0.24 mg/L

Initial Chlorothalonil Concentration = 0.61 mg/L
Final Chlorothalonil Concentration = 0.71 mg/L
Ave. Effluent Chlorothalonil = 0.942 ± 0.05 mg/L

Table 4-7 Results of Formulation Batch Shake Test

Target Chlorothalonil Concentration (mg/L)	Initial UV Chlorothalonil Concentration (mg/L)	Final UV Chlorothalonil Concentration (mg/L)	GC Chlorothalonil Concentration (mg/L)	Initial NPOC (mg/L)	Final NPOC (mg/L)	UV Chlorothalonil Concentration Sep-Pak (mg/L)[a]	UV Chlorothalonil Concentration w/o dilution (mg/L)[b]
2	0.91	0.95	1.48	2.24	1.99		
	0.95	0.98	1.43	1.96	1.83	N/A	N/A
	0.96	0.99		2.12	1.87		
AVE	0.94 ± 0.06	0.98 ± 0.05	1.45	2.11 ± 0.35	1.89 ± 0.22		
5	2.65	2.44	4.33	1.96	1.76	pH=7.0	
	2.71	2.21	4.38	2.08	1.95	0.0169	0.792
	2.82	2.31		1.96	1.84		
AVE	2.72 ± 0.21	2.32 ± 0.29	4.35	2.00 ± 0.17	1.84 ± 0.24		
10	5.35	3.99	7.92	4.42	3.53	pH=6.7	
	5.46	4.09	8.04	4.28	3.51	0.0262	0.748
	5.52	4.21		4.41	3.61		
AVE	5.44 ± 0.22	4.09 ± 0.28	7.98	4.37 ± 0.19	3.55 ± 0.12		
15	5.45	5.46	14.2	3.93	3.78	pH=6.1	
	5.19	5.53	14.5	3.86	3.62	0.200	0.788
	5.77	6.34		3.86	3.52		
AVE	5.47 ± 0.72	5.78 ± 1.21	14.4	3.88 ± 0.11	3.64 ± 0.34		

[a] Measurement made on effluent from reverse phase separation using a Sep-Pak

[b] Samples measured on spectrophotometer without dilution

± based on the average and standard deviation for a 95% confidence interval

5. DISCUSSION

5.1 Solubility

a) Gross Determination

The values found for the solubility of technical grade chlorothalonil in methanol and methylene chloride proved that these would be good solvents for standard preparation. The high solubility allowed for a stock solution to be made easily, so that subsequent dilutions at or near the water solubility of chlorothalonil could be quickly made.

b) Maximum Peak versus Net Peak Quantitation

Initially, when evaluating the best way to interpret the spectrophotometer readings, it appeared that using the maximum peak values would be an appropriate method, because the absorbance value was readily available from any analysis. It was later found that using the net absorbance values, although time consuming, might give more reproducible results.

A general trend was observed when evaluating the spectra that were generated from sample analysis. At high concentrations, the maximum peak values remained fairly consistent, in that background changes were negligible and the net absorbance value was large. At low concentrations, while background fluctuations may have been similar to those that occurred at high concentrations, the relative magnitude of these fluctuations were more apparent in the maximum peak values. The net absorbance values, while smaller in magnitude, gave results which factored out these background fluctuations. Figure 5-1 demonstrates this general trend. In this figure it can be seen that M is the maximum peak absorbance value = A - 0, and N is the net absorbance value = A - Ab, where Ab is the value absorption value on the baseline and A is the maximum value for the spectra.

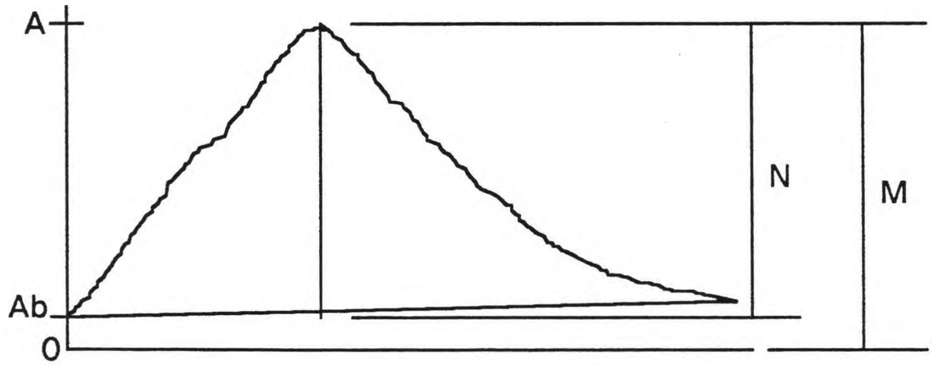

Figure 5-1a Hypothetical Spectra for High Chlorothalonil Concentration (~1 mg/L)

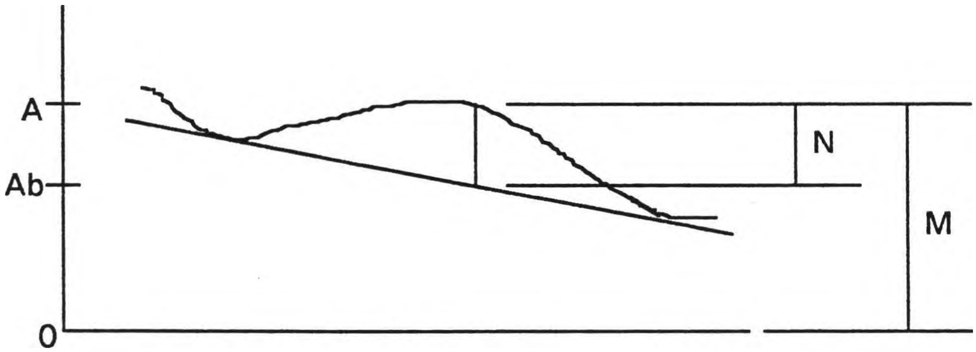

Figure 5-1b Hypothetical Spectra for Low Chlorothalonil Concentration (~0.1 mg/L)

Figure 5-1 Hypothetical Examples Demonstrating the Difference Between Maximum Peak and Net Absorbance Values (M = Maximum Peak Value = A - 0, = Net Absorbance Value = A - Ab)

Table 4-1 which contains data from the initial column runs, compares both absorbance values. The ratio M/N demonstrates that there is fairly good agreement (all values fall within less than 4% of each other) between the maximum peak absorbance values and the net absorbance values at a high concentration. Figures 5-2 and 5-3, presents specific examples of the general trend noted above. For the three spectra shown in Figure 5-2 for a high concentration (1 mg/L) the maximum absorbance values (0.245, 0.244, 0.241) all fall within 1% of the mean maximum absorbance value of 0.243, while the net absorbance values (0.208, 0.209, and 0.210) fall within 0.5% of the average net absorbance value of 0.209, indicating that either method is applicable. However, for the three spectra shown in Figure 5-3, at low concentrations (0.1 mg/L), it was found that the maximum peak values (0.0395, 0.0366, and 0.0305) differed from the mean maximum absorbance value of 0.0355 by as much as 14% due to background variations, while the net absorbance values (0.00752, 0.00743, and 0.00752) varied from the mean net absorbance value of 0.00749 by less than 1%, regardless of background changes. Because of this, net absorbance was chosen as the preferred method of analysis.

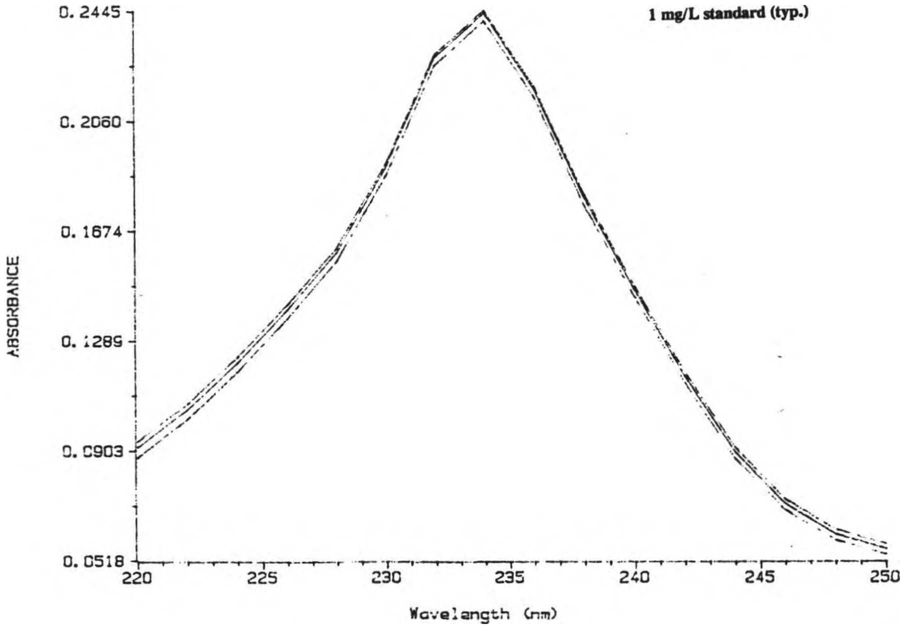

Figure 5-2 UV-Visible Absorbance Spectra From Triplicate Analyses on a 1 mg/L Chlorothalonil Standard in Water

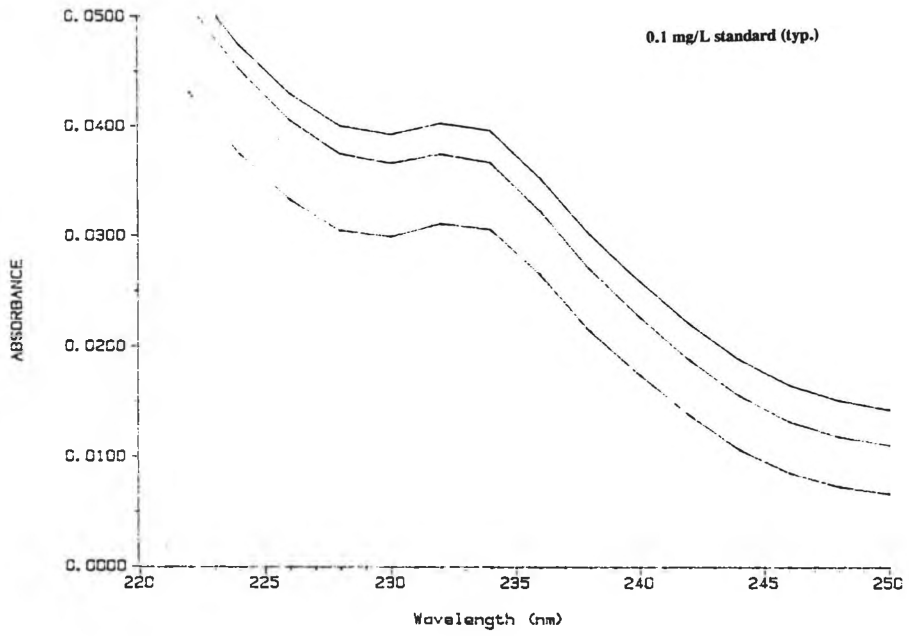

Figure 5-3 UV-Visible Absorbance Spectra From Triplicate Analyses on a 0.1 mg/L Chlorothalonil Standard in Water

c) Saturation Column (Technical Grade Solubility)

Without Temperature Control: Initially, the saturation column was operated without temperature control. It was found, as can be seen from Tables 4-2 and 4-3, that there were variations from the mean of up to 35.6% and 10.8%, respectively. This variation was much larger than was acceptable for this research. This led to the introduction of the constant temperature water bath for control.

With Temperature Control: The use of the saturation column in a constant temperature water bath yielded water solubility data for technical grade chlorothalonil which varied atmost 6.7% from the mean, with 14 of the 17 data points varying by less than 5% from the mean. This variation was deemed acceptable for the experimental data. The value of 0.910 mg/L found at 23 ± 0.25 °C is 150% larger than 0.6 mg/L, the value reported by Turner et al. (1963-4). A check for variation in S_W due to flow rates was also performed, to determine the optimum flow rate. Flows used were 0.59 and 1.18 mL/min. Based on a null hypothesis test, no significant difference for a 95% confidence interval was found in the concentrations due to the two flow rates, indicating that a flow rate of approximately 1 mL/min is acceptable for achieving saturation with the column used. Figure 5-4 shows the variation in data for the two flow rates.

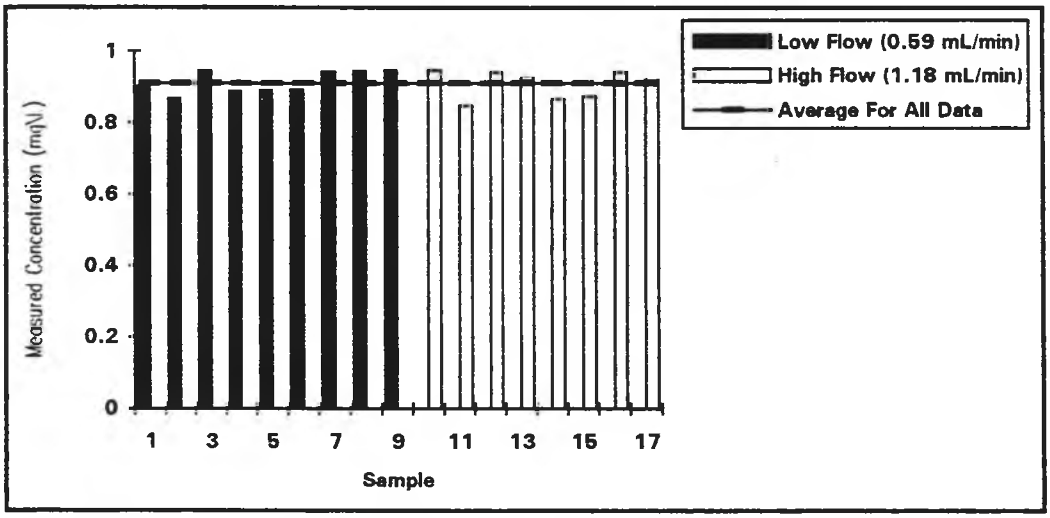

Figure 5-4 Chlorothalonil Water Solubility Variation at Two Flow Rates

d) Temperature Dependence of Water Solubility

The temperature variations in water solubility can be used to determine the enthalpy of solution. The equation used is

$$\ln [S_W] = -\Delta H/RT + b \qquad (5-1)$$

where $[S_W]$ is the molar solubility at temperature T, ΔH is the enthalpy of solution, R is the ideal gas constant, b is the y-intercept and T is the absolute temperature (May, 1978). Figure 5-5 shows the plot of this data.

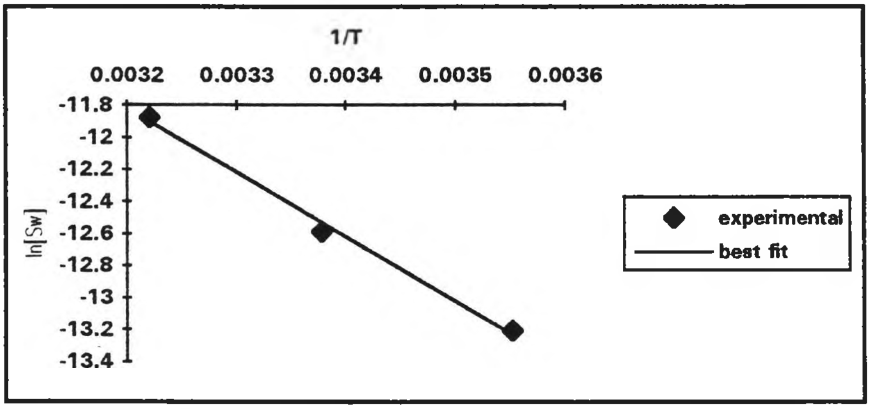

Figure 5-5 Solubility Variation With Temperature

The intercept was found to be 1.002 and the slope of this line was found to be -4010 K, with an $r^2 = 0.995$. The slope is equal to -ΔH/R. Substituting R = 1.986 cal/mole-K gives ΔH = 7.96 kcal/mole for temperatures between 8.5 ± 0.25 °C and 37.5 ± 0.64 °C. This falls within the range of 6.3 to 10.71 kcal/mole found by May (1978) for polyaromatic hydrocarbons for a temperature range of 5 to 30 °C. A value of 1.06 mg/L at 25 °C was estimated from the regression equation, because water solubility values are most often reported at this temperature.

e) Saturation Column (BRAVO® 500 Solubility)

Based upon data in Table 4-6, a slight difference was observed between technical grade solubility and the apparent solubility of chlorothalonil in the presence of formulation chemicals. The average chlorothalonil concentration of 0.942 ± 0.054 mg/L at 23 ± 0.25 °C determined from the formulation experiments is 0.032 mg/L larger than 0.910 ± 0.017 mg/L which was found for the technical grade chlorothalonil at the same temperature.

Using equation 2-10, a value for the partition coefficient to formulation DOM (described as DOC) can be estimated using the average NPOC value 2.34 mg/L found. The values used in the equation are taken from Table 4-6.

$$K_{doc} = (\text{bound chlorothalonil})/(\text{aqueous chlorothalonil}) \qquad (5\text{-}2)$$

$$\text{associated chlorothalonil} = (0.032\ \text{mg/L})/[2.34\ \text{mg/L} - 0.36(0.942\ \text{mg/L})]$$

$$= 16.0\ \text{mg/g}$$

$$K_{doc} = (16.0\ \text{mg/g})/(0.910\ \text{mg/L})$$

$$= 1.8 \times 10^4\ \text{mL/g}$$

Converting this value to log K_{doc} gives 4.24. This value is larger approximately 0.5 log units larger than the value log K_{doc} =3.78 found using equation 2-15.

Some aspects of this experiment were disturbing when trying to evaluate the effect of formulation chemicals on the apparent solubility. The first and foremost is the change in NPOC, which ranged from 1.86 mg/L to 2.82 mg/L in the reservoir over the 37 hours that this experiment was run. These numbers were based on duplicate analyses on single samples taken at the start and completion of the run. The range for the initial readings was 2.811 to 2.824 mg/L and for the final readings was 1.837 to 1.890 mg/L. This corresponds to a 34% change in NPOC concentration. The other observation that raised some questions was the change in the chlorothalonil concentration in the reservoir from 0.61 mg/L to 0.71 mg/L, a 16% increase. This is based on duplicate analyses on a single sample taken at the start and completion of the run.

These discrepancies are most likely due to experimenter error, because the reservoir had to be filled three times during the course of the experiment. Each time the reservoir needed to be filled, a new solution with a target chlorothalonil concentration of 1 mg/L was made from the stock solution. Great care was taken to maintain a high level of consistency when making each solution for use in the reservoir, such that it was assumed that there would be no greater than a 5% variation in the reservoir solutions. This was made difficult because the stock solution had a tendency to settle. The dilution of this stock to the target chlorothalonil concentration of 1 mg/L was made difficult by this settling, because it was difficult to ascertain that the same amount of chlorothalonil and inert ingredients were included in each dilution (heterogeneous effects), even though the steps to make each of the three solutions were identical.

The decrease of NPOC in the reservoir and increase in chlorothalonil may be related. This result may be described by the fact that the DOM may be causing a "masking" effect such that the spectrophotometer cannot detect all of the bound chlorothalonil, indicating that bound chlorothalonil may be a poor or non-light absorber. If this is occuring, as the DOM concentration decreases, more chlorothalonil is in the aqueous phase, allowing for the spectrophotometer to detect more chlorothalonil. However, the values obtained from this run indicate that the effects of this "masking" may be negligible, because there is a 5% agreement between the predicted log K_{doc} value and the calculated log K_{doc} value.

5.2 Batch Shake Test with BRAVO® 500

This set of experiments was designed to expand upon the results from the column test with the formulation. When evaluating Table 4-7, several observations can be made. For each dilution, the concentration of chlorothalonil, as measured by the spectrophotometer, was higher than the water solubility, found earlier for the technical grade chlorothalonil. While there is no other direct conclusion that can be made, there is a strong indication that solubility enhancement is occuring due to the formulation chemicals.

Partition values were found with equation 5-2, using the final readings from the spectrophotometer and the NPOC analyses. The results of these calculations can be seen in Table 5-1. The values in the table are presented when taking the NPOC from the chlorothalonil into account and when ignoring this contribution. These values may be artificially high, as compared to the log Kdoc value of 4.24 from the generator column. The artificially high values may be a result of kinetic factors and the desorption process. It has been demonstrated and discussed many times in the literature that the desorption process often gives a different isotherm than the sorption process, because hydrophobic compounds have a tendency to remain sorbed to the colloidal material (Green and Karickhoff, 1990).

Table 5-1 log Kdoc values from Batch Shake Test

Target Concentration	Spectrophotometer with[a]	Spectrophotometer without[b]	GC with[a]	GC without[b]
2 mg/L	4.58	4.67	5.50	5.64
5 mg/L	5.92	6.18	6.31	6.59
10 mg/L	5.99	6.23	6.34	7.06
15 mg/L	6.17	6.54	6.61	n/a[c]

[a] log K_{doc} values found with the carbon contribution from the chlorothalonil

[b] log K_{doc} values found when subtracting out the carbon contribution from the chlorothalonil

[c] n/a - Expected carbon contribution from the chlorothalonil larger than the measured value

Even though these values are higher, they may give a rough estimate of what the actual association values are. In performing the calculation, it was assumed that the aqueous concentration was 0.91 mg/L, based on the water solubility value found earlier. It was necessary to make this assumption because the results from the reverse-phase separation were questionable. This assumption gives a conservative estimate for the values. These values are conservative because at most the aqueous phase concentration will be 0.91 mg/L (the water solubility found for technical grade chlorothalonil). If the aqueous concentration is less than the aqueous solubility, the resulting K_{doc} values will be larger. The high values may also be due to the samples not being at equilibrium after the 24 hour time period. For future work, analyses should be conducted to confirm equilibrium between the bound and aqueous phase concentrations. Problems with the NPOC analysis also need to be resolved, so that the formulation chemicals are more accurately described.

Figure 5-6 presents a comparison of the results given by the spectrophotometer and the GC on the same samples. There was a large discrepancy between the spectrophotometer analysis and GC analysis, which can be seen in Figure 5-6. This can be observed by noticing that the initial and final spectrophotometer readings are fairly close, while the GC reading is noticeably different from these readings. The difference between the spectrophotometer and GC readings varied between 1.5 and 2.5 times. This again lends credence to the theory that the formulation chemicals may be causing a "masking" effect, as the GC gave values which were much closer to the target values. The "masking" effect only appears to have caused a problem in this set of experiments, due to the differences noted between the GC and spectrophotometric analyses. This may indicate that bound chlorothalonil is a poor or non-light absorber. Another explanation may be that the samples which were diluted to 1 mg/L and analyzed by the spectrophotometer were not at equilibrium, such that the chlorothalonil had not completely desorbed from the dissolved organic matter.

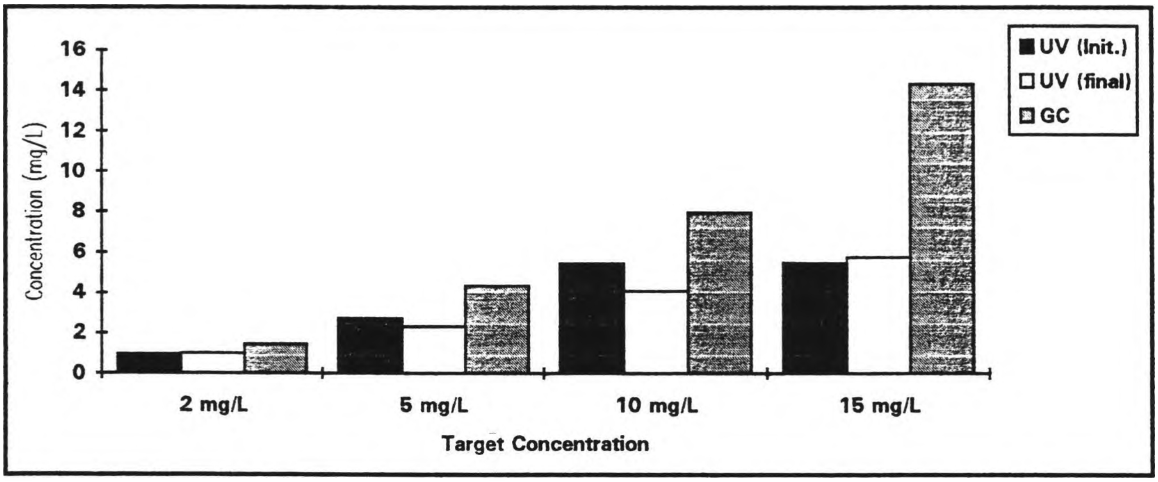

Figure 5-6 Comparison Between Spectrophotometric and GC Chlorothalonil Analyses[a]

[a] Samples for spectrophotometric analysis diluted to a target chlorothalonil concentration of 1 mg/L to fit the range of the calibration curve. Results were then corrected for the dilutions that were made.

A decrease in NPOC in each sample was observed over the 24 hour duration of the run, but a marked difference between NPOC values, corresponding to the relative increase in expected chlorothalonil concentration, in the four dilutions was not achieved. The initial NPOC readings for the 2, 5, 10, and 15 mg/L samples were 2.11 ± 0.35, 2.00 ± 0.17, 4.37 ± 0.19, and 3.88 ± 0.11 mg/L, respectively. The final NPOC concentrations for the 2, 5, 10, and 15 mg/L samples were 1.89 ± 0.22 mg/L, 1.84 ± 0.24 mg/L, 3.55 ± 0.12 mg/L, and 3.64 ± 0.34 mg/L, respectively. This corresponds to 10%, 8%, 19% and 6% decreases in NPOC, respectively. Surprisingly, an increase in NPOC of the same magnitude as the target concentration values was not achieved, as is demonstrated by Figure 5-7. This may mean that there is a highly heterogeneous distribution of chlorothalonil and NPOC in the formulation. The decrease in NPOC over time may be attributed to microbial activity, oxidation, random variation due to heterogeneities, or photodegradation.

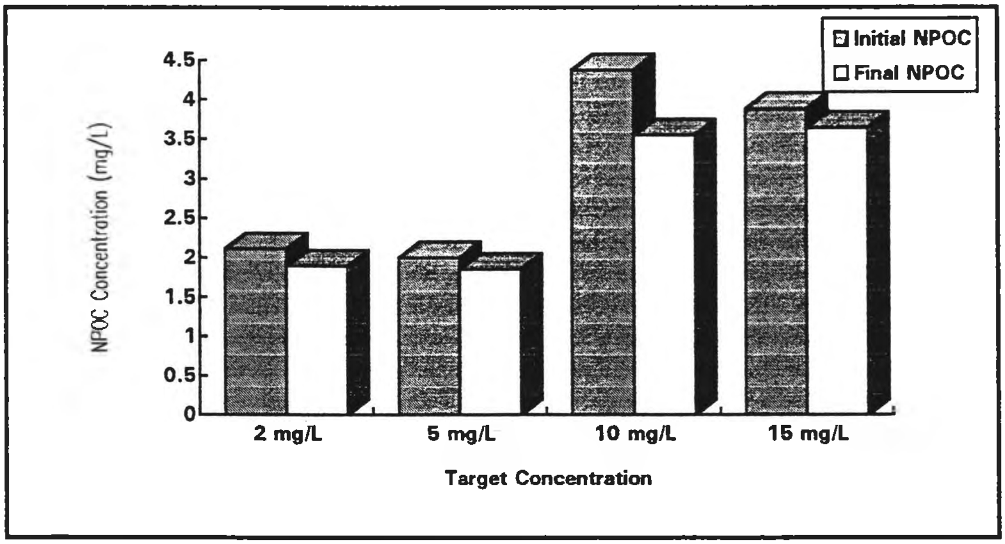

Figure 5-7 Initial and Final NPOC Data

The reverse-phase separation techniques described by Landrum et al. (1984) to differentiate between bound and aqueous chlorothalonil gave results for the 5, 10, and 15 mg/L samples of 0.0169, 0.0262, and 0.200 mg/L, respectively. These values came from a spectrophotometric analysis of the effluent from the separation cartridges. Assuming that the bound chlorothalonil should pass through the column, these values were unexpectedly low. One would have expected values of approximately 4.1, 9.1 and 14.1 mg/L because the fraction that should have been retained by the column would be near the known water solubility for chlorothalonil of 0.91 mg/L. This raises questions as to the validity of this method for separating the bound chlorothalonil from the aqueous phase chlorothalonil. There may also have been interference from the formulation chemicals during the analysis with the spectrophotometer. Further exploration is needed to determine a method which is suitable for separating the bound chlorothalonil from the aqueous phase chlorothalonil.

The results of the spectrophotometric analysis of the 5, 10, and 15 mg/L solutions without dilution, were 0.792, 0.749, and 0.788 mg/L, respectively. This analysis was conducted when the values for the reverse phase separation were unexpectedly low. It was initially thought that only the aqueous phase chlorothalonil was being detected, however turbidity in the samples prevented any conclusions from being made. It is interesting that the values were fairly close to the water solubility value of 0.91 mg/L, found with the generation column. Due to the turbidity in the samples, the values would be expected to be artificially high because of the light scattering affect of this interference. More work needs to be done to discount the effects of the turbidity, because spectrophotometry is not a good method for turbid samples.

5.3 Interpretation of Experimental Results

Chlorothalonil has been found in the groundwater in the San Luis Valley of Colorado, even though models have predicted that chlorothalonil should not leach to the groundwater (Durnford et al., 1990). These findings suggest that a factor not accounted for in the models, such as the potential interaction with formulation chemicals, is enhancing the mobility of chlorothalonil. The work that is reported in this thesis was done to evaluate how the environmental behavior of chlorothalonil is affected by the presence of formulation chemicals. It was found that the formulation chemicals cause an increase in the apparent water solubility of chlorothalonil, however a broader interpretation is needed. In order to accomplish this, the application of chlorothalonil to a crop needs to be explored.

Chlorothalonil, when applied in the BRAVO®500 formulation on a per acre basis, is mixed with a volume of water ranging from 5 gallons to 150 gallons, based on the label instructions (ISK Biotek, 1993), resulting in chlorothalonil concentrations of 26,700 mg/L to 423 mg/L, respectively. These concentrations are significantly higher than the values found from the solubility experiments, which ranged from 0.91 mg/L to 1.85 mg/L for temperatures ranging from 23 to 37.5 °C (77 to 100°F). (This temperature range, coincidentally, encompasses the temperature range which might be encountered during the growing season.) The volume of water required is a relatively small amount when considered on a square foot of soil basis, giving volumes of 0.4 mL/ft^2 to 13 mL/ft^2. The small amount of water that delivers the formulation would lead one to believe that chlorothalonil penetration into the soil caused by the suggested application procedures is extremely unlikely.

Enfield and Bengtsson (1988) conducted work which evaluated the movement of macromolecules through the soil. What they found was that macromolecules, or immiscible substances such as micelles or colloidal materials, moving along with a water carrier, may under certain circumstances enhance the movement of hydrophobic chemicals through soils. This might explain why various models underestimate chemical mobility in the soil. Figure 5-8 was developed and presented by Enfield and Bengtsson (1988), on a theoretical basis, to demonstrate the significance of the presence of macromolecules and the resulting relative mobility of a given organic chemical. The equation describing the effective velocity of the total fluid was:

$$R^*(\delta C^*/\delta t) = D^*(\delta^2 C^*/\delta x^2) - V^*(\delta C^*/\delta x) \qquad (5\text{-}2)$$

where R^* is the retardation of the chemical relative to the velocity of the total fluid, C^* is the total mass concentration of the mobile pollutant over all phases (bound and aqueous phases), D^* is the effective dispersion coefficient coefficient for the total fluid, and V^* is the effective velocity of the total fluid.

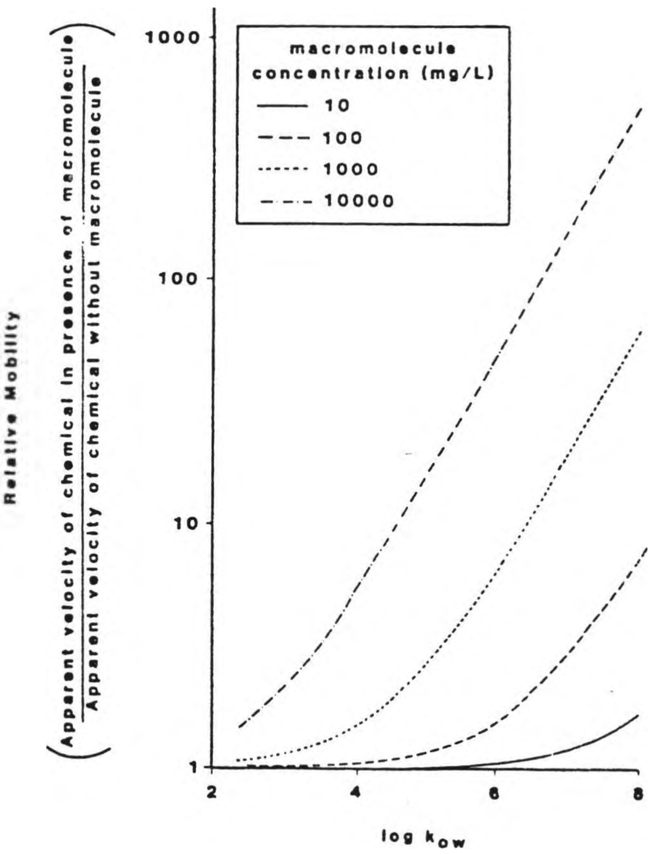

Figure 5-8 Relative Mobility of a Hydrophobic Compound as a Function of Octanol-Water Partition Coefficient and Amount of Organic Carbon in the Mobile Phase (taken directly from Enfield and Bengtsson, 1988)

This figure was based on several assumptions including: (1) ignoring dispersion in equation 5-2 giving

$$R^*(\delta C^*/\delta t) = -V^*(\delta C^*/\delta x) \tag{5-3}$$

(2) the density of the macromolecule was equal to the density of water; (3) the partition coefficient to the macromolecule organic carbon is the same as the partition coefficient to the soil organic carbon times the weight fraction (F) of carbon occupied by the macromolecules ($K_{doc} = FK_{oc}$); (4) the weight fraction (F) occupied by the organic carbon is 0.02; (5) the total porosity of the soil is 0.5; and (6) the particle density of the soil is 2.65. Figure 5-8 demonstrates the importance of the macromolecule on the

mobility of hydrophobic chemicals (Enfield and Bengtsson, 1988). It can be seen that the relative mobility of a hydrophobic compound can be significantly altered by the macromolecules in the mobile phase. The degree by which the mobility is altered was related to the octanol-water partition coefficient for purposes of the work by Enfield and Bengtsson (1988).

Assuming that irrigation or a rain event occurs after application, where 1" of water is added to the crop, one might expect mobility to increase. The added moisture would lead to chlorothalonil concentrations of approximately 4 to 270 mg/L if the applied chlorothalonil were completely dissolved within the 1" of applied water. Assuming that the formulation chemical concentration is approximately two times the chlorothalonil concentration, as was found in this research, DOM concentrations of 8 to 540 mg/L would be present. Taking these DOM concentrations and the value log $K_{ow} = 2.64$, found in the literature, and assuming that the DOM present in BRAVO®500 behaves in the same way as the macromolecules modeled by Enfield and Bentsson (1988) it appears from Figure 5-8 that these DOM concentrations would only lead to less than a 5% increase in the relative mobility. Therefore, it is unlikely that natural moisture conditions and reasonable irrigation practices would enhance the mobility of chlorothalonil due to formulation chemicals in the environment. Similarly, in the case of nonuniform application of the formulation, where larger amounts of chlorothalonil are deposited in certain locations than would be expected, increases in formulation DOM of up to 1000 mg/L would only provide a 10% increase in the relative mobility due to the formulation chemicals in the event that water is applied to the crop after being treated with the formulation.

Even though the formulation chemicals do not appear to increase the relative mobility, other factors may contribute to the mobility of chlorothalonil, such as naturally occuring macromolecules like humic materials. Also, no interpretations can be made, based on this research, as to the environmental accumulation, biodegradation or chemical reactions that may occur to chlorothalonil in the environment and how these factors are affected by formulation chemicals.

6. CONCLUSIONS AND RECOMMENDATIONS

The water solubility of chlorothalonil was evaluated using a saturation column. The presence of formulation chemicals was investigated as to the ability of these chemicals to enhance the apparent water solubility of chlorothalonil. Technical grade chlorothalonil and BRAVO® 500 were used as received from ISK Biotek in Mentor, Ohio. A UV-Visible spectrophotometric analysis technique was developed and samples were evaluated primarily by this technique for chlorothalonil concentration and by a TOC analyzer used to describe the formulation chemicals.

Evaluation of the effluent from the saturation column, gave the result of 0.910 ± 0.017 mg/L at 23 ± 0.25 °C, which is higher than the reported water solubility of 0.6 mg/L found in much of the literature. The saturation column provided repeatable results, substantiating its use for solubility determinations. Temperature variations in solubility gave results of 0.489 ± 0.003 mg/L and 1.85 ± 0.050 mg/L at 8.5 ± 0.25 °C and 37.5 ± 0.64 °C, respectively. The saturation column approach as well as batch shake tests were used for the solubility enhancement evaluation. The effluent from the saturation column when using the formulation, gave 0.942 ± 0.054 mg/L chlorothalonil, which is 3.5% larger than the technical grade solubility. A log K_{doc} of 4.24 was found from this data which is approximately 0.5 log units larger than the value of 3.78 calculated from equation 2-15. The ± values were based on the standard deviation and reflect a 95% confidence interval about the mean.

The batch shake tests provided evidence of solubility enhancement as demonstrated by Table 4-4, and partition coefficients were calculated for each sample. The log K_{doc}s which ranged from 4.58 to 7.06 were larger when compared to the value found with the generator column. These values may have been high for several reasons. One may be due to the fact that the samples, which were diluted for spectrophotometric analysis, had not reached equilibrium when they were analyzed. Another may be because that this was a desorption experiment, and it has been found that hydrophobic chemicals don't always completely desorb from colloidal materials. NPOC analysis on technical grade chlorothalonil in water found that the carbon in the chlorothalonil did contribute according to the amount present in the compound (36% of chlorothalonil is carbon). The biggest problem was an inability to determine the concentrations of the bound chlorothalonil and the aqueous chlorothalonil. Because of this the aqueous concentration was assumed to be the water solubility of chlorothalonil determined earlier. This gave a value on the low end of the scale, because the chlorothalonil concentration could only decrease.

The use of a reverse-phase separation technique, initially expected to separate the bound chlorothalonil from the aqueous chlorothalonil, gave results which were much lower than expected, raising questions about the use of this technique to find the concentration of bound chlorothalonil. Undiluted analyses of the samples from the batch shake test on the spectrophotometer which were then conducted, gave results near the water solubility. This may be a reading of the aqueous concentration, but turbidity in the samples prevents any conclusive results from being drawn.

Based on an article written by Enfield and Bengtsson (1988) and the suggested application methods for potatoes, it seems unlikely that the formulation chemicals contribute to the relative mobility of chlorothalonil in the environment. It may be possible, though, that chlorothalonil mobility may be enhanced by naturally occuring DOM. However, no interpretations can be made as to the environmental accumulation, biodegradation or chemical reactions that chlorothalonil may undergo in the environment.

For future investigations, several recommendations can be made. The first would be to evaluate chlorothalonil-DOM interaction by using technical grade chlorothalonil and known DOM like humic materials. This would be helpful in evaluating solubility enhancement by these dissolved materials and in evaluating the ability of naturally occuring DOM to enhance the relative mobility of chlorothalonil in the environment.

When dealing with the formulation, a comparative evaluation between analyses by the spectrophotometer and gas chromatograph is needed. This experiment, through limited comparison, found discrepancies between the two analytical methods. The GC gave chlorothalonil concentrations which were closer to the target values than the spectrophotometer in the presence of formulation chemicals. Conducting a time series analysis to cofirm equilibrium exists between the bound and aqueous phases before any analysis is done may help eliminate this discrepancy. In evaluating the DOM in the formulation, a time series analysis on the inert chemicals would be useful to determine if degradation is occuring. If so, to determine the degradation rate of these chemicals and the resulting effective availability for interaction with the chlorothalonil in solution. An accurate assessment of the inert chemicals is needed so that the results can be more conclusive with regards to a partition coefficient. The composition of the inert chemicals was not released due to proprietary concerns of the company. Also, a method needs to be developed to separate the bound chlorothalonil from the aqueous phase chlorothalonil.

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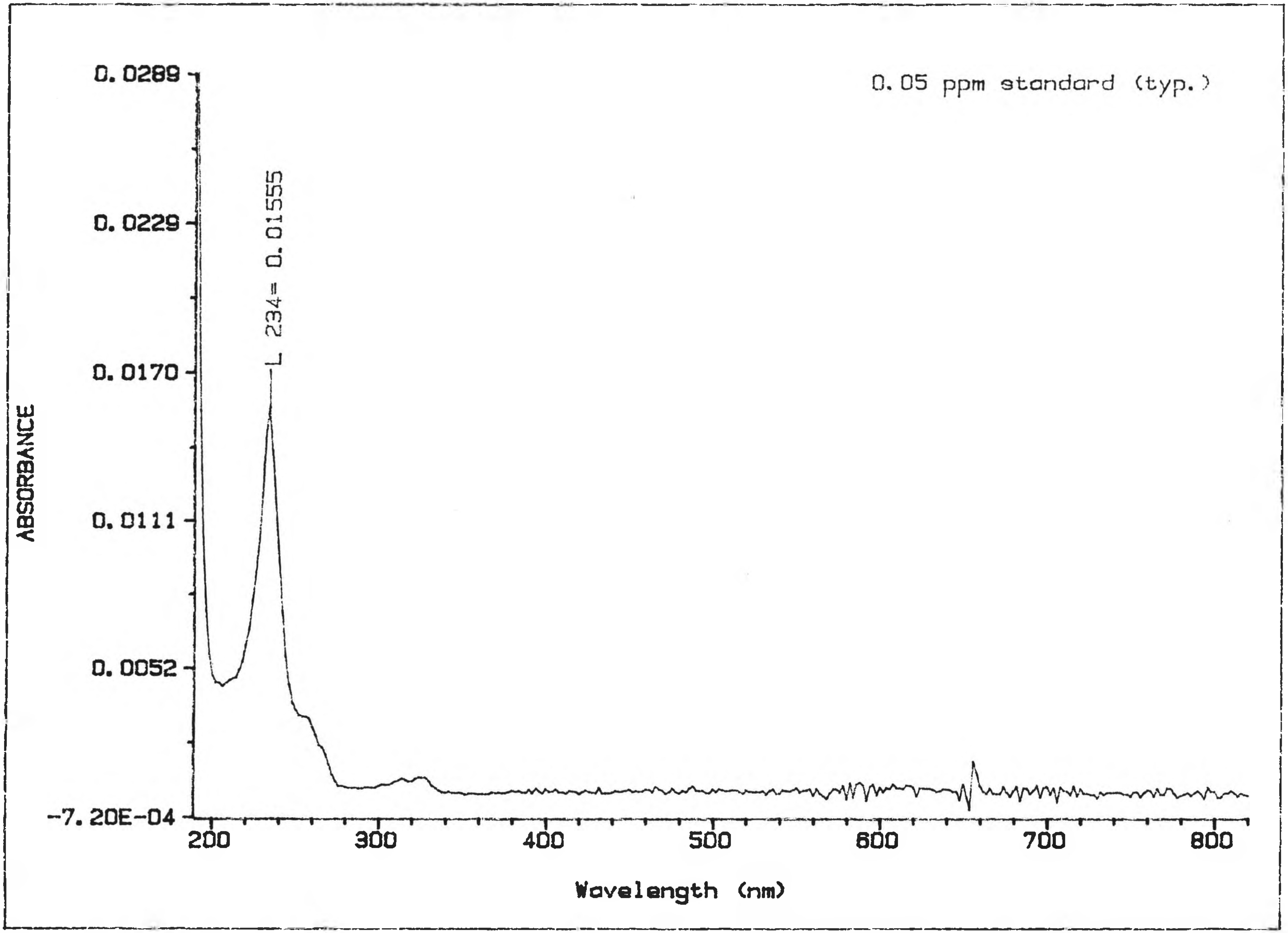
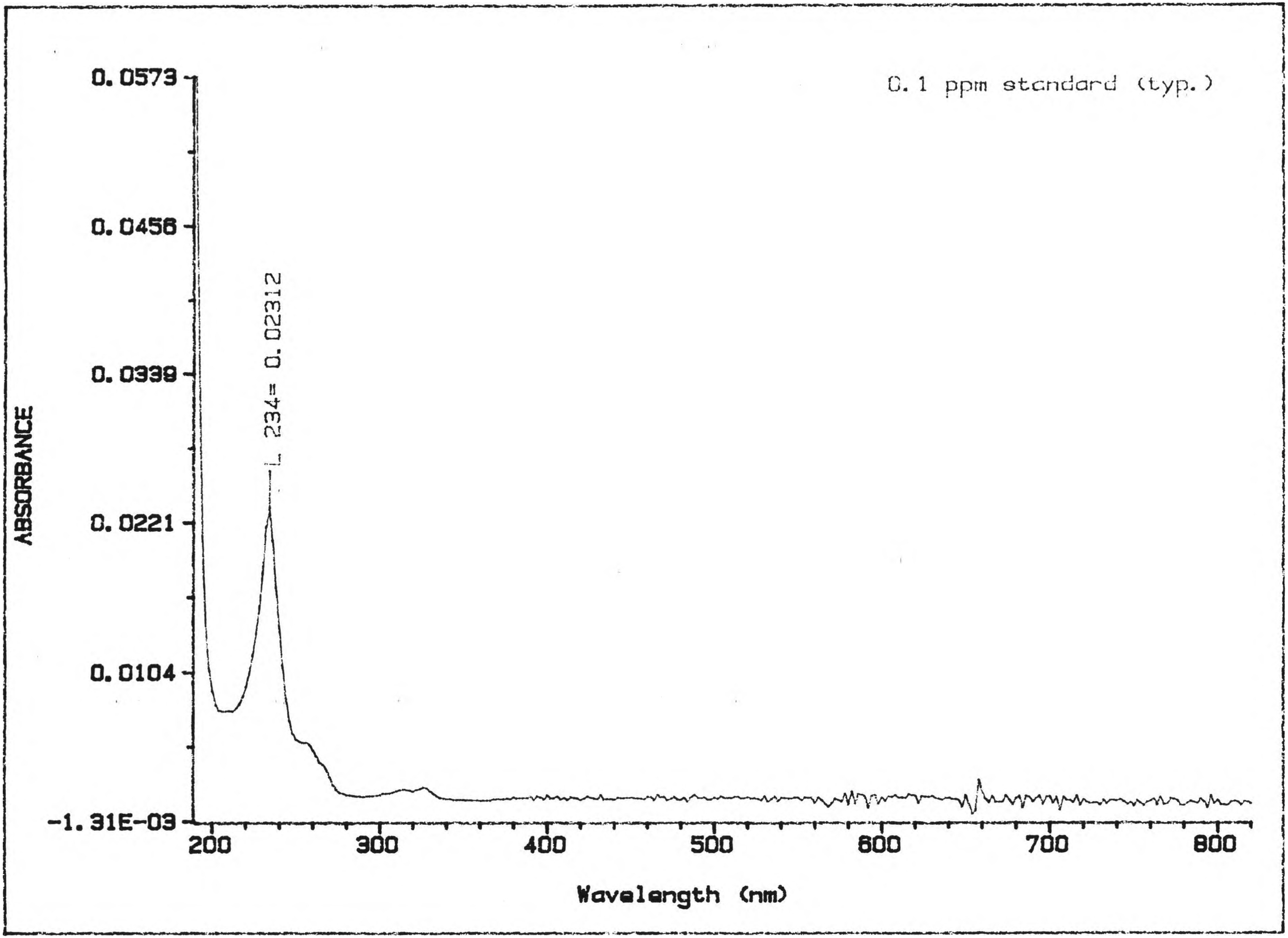
APPENDIX 1 - RANGE OF SPECTRA OF CHLOROTHALONIL IN WATER USED FOR CALIBRATION CURVE PREPARATION (typ.)

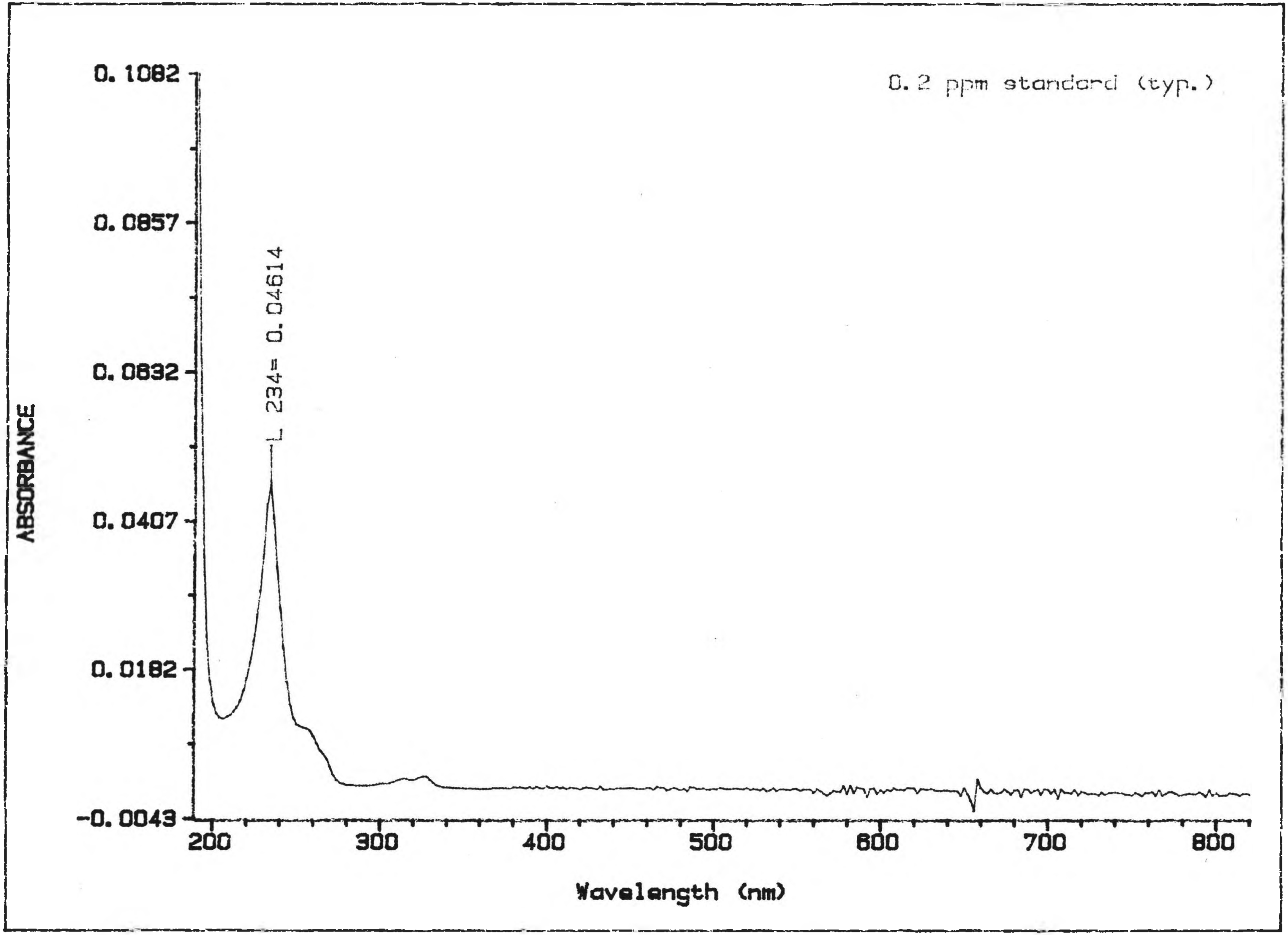
B


0.05 ppm standard (typ.)
L 234= 0.01555
ABSORBANCE
0.0289
0.0229
0.0170
0.0111
0.0052
-7.20E-04
200
300
400
500
600
700
800
Wavelength (nm)

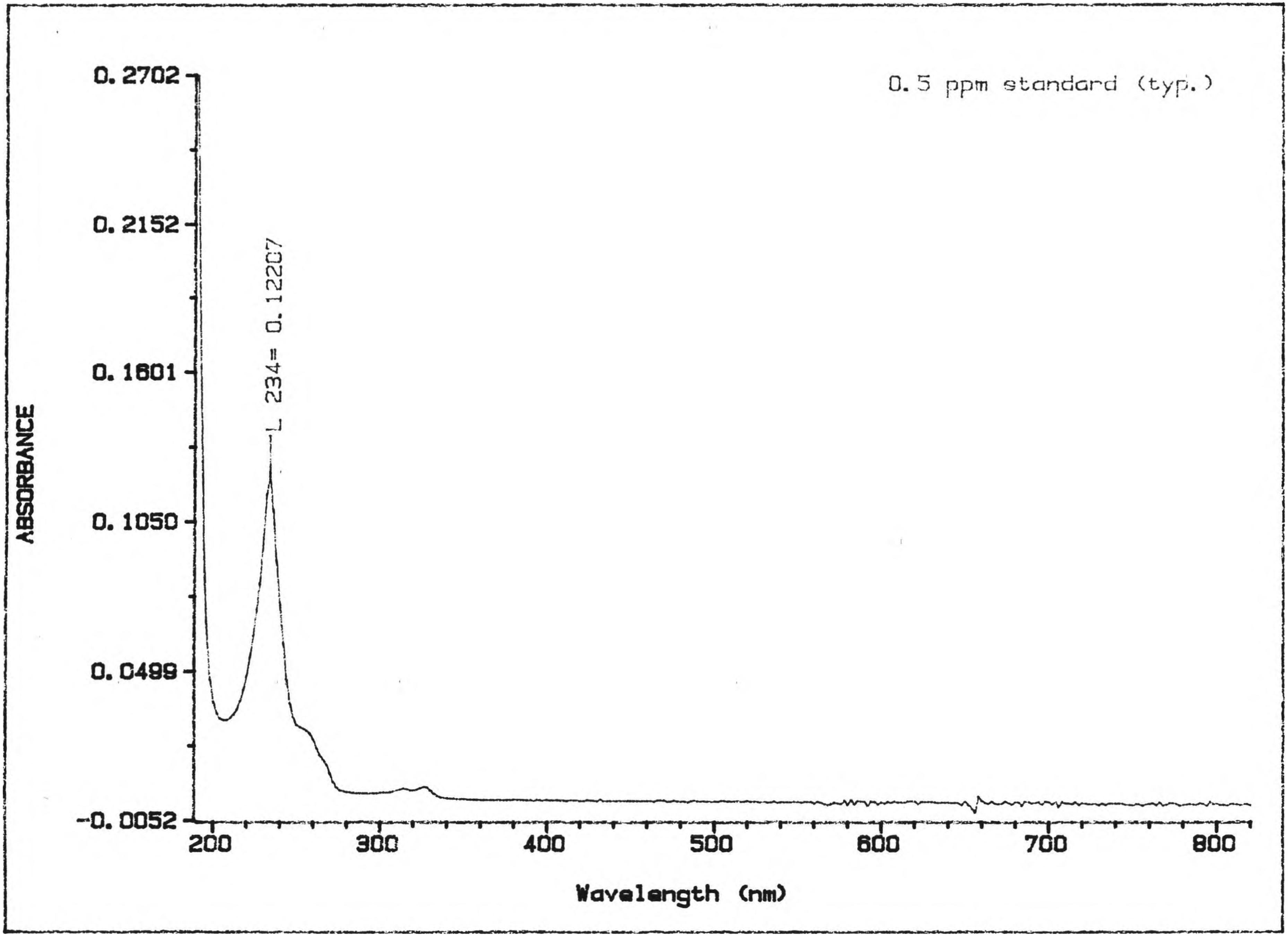
C


0.1 ppm standard (typ.)
L 234= 0.02312
ABSORBANCE
0.0573
0.0456
0.0339
0.0221
0.0104
-1.31E-03
200
300
400
500
600
700
800
Wavelength (nm)

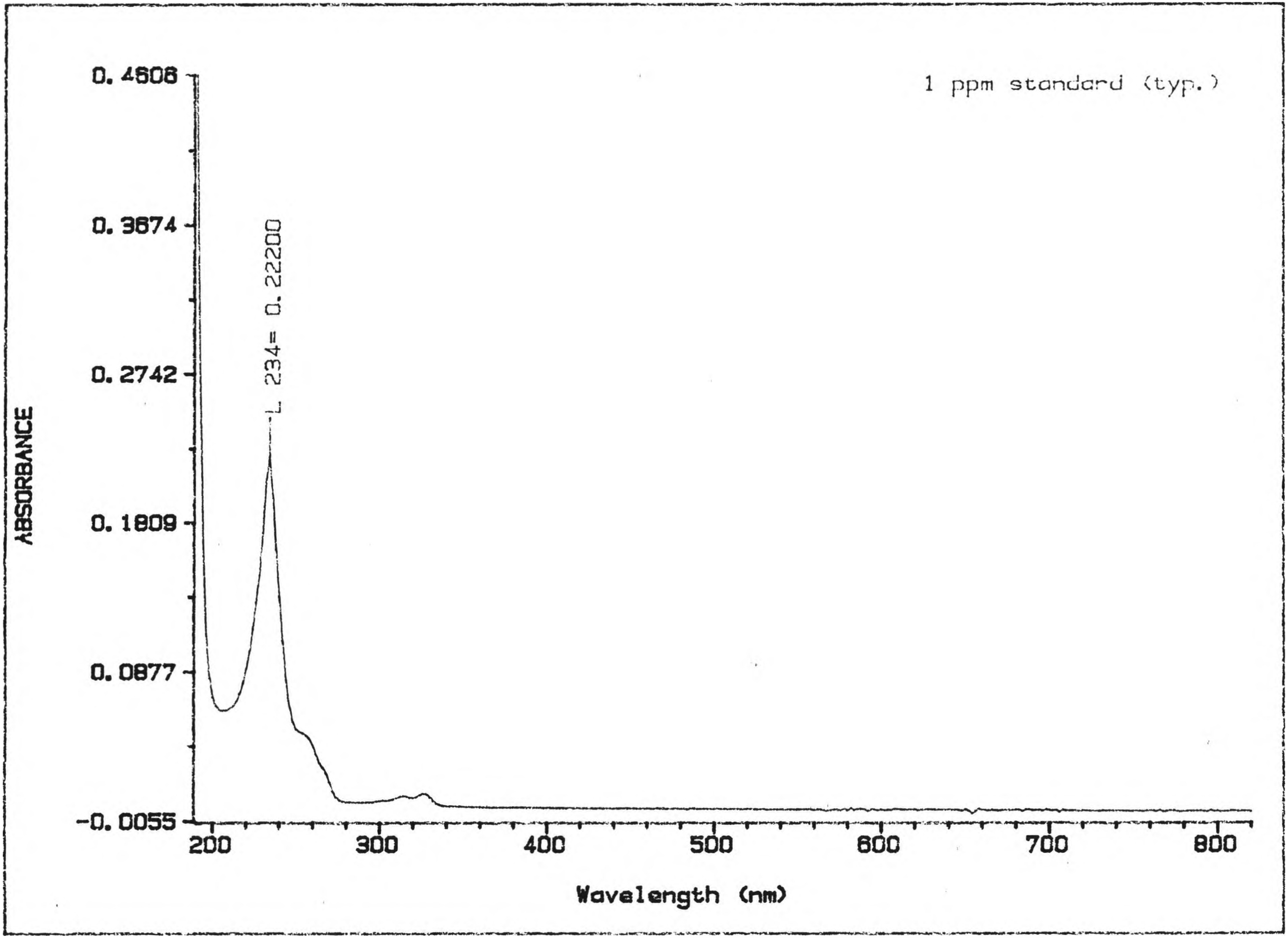
D


0.2 ppm standard (typ.)
L 234= 0.04614
ABSORBANCE
0.1082
0.0857
0.0632
0.0407
0.0182
-0.0043
200
300
400
500
600
700
800
Wavelength (nm)

E


0.5 ppm standard (typ.)
L 234= 0.12207
ABSORBANCE
0.2702
0.2152
0.1601
0.1050
0.0499
-0.0052
200
300
400
500
600
700
800
Wavelength (nm)

F


1 ppm standard (typ.)
L 234= 0.22200
ABSORBANCE
0.4608
0.3674
0.2742
0.1809
0.0877
-0.0055
200
300
400
500
600
700
800
Wavelength (nm)

APPENDIX 2 - NET PEAK METHOD

Calculations

1) Baseline Calculation

The baseline was visually estimated while on screen so that a range of values could be determined for use when drawing the baseline by hand.

Interpolation

204	0.03186
234	X
276	0.00627

This gives $X = 0.02120$

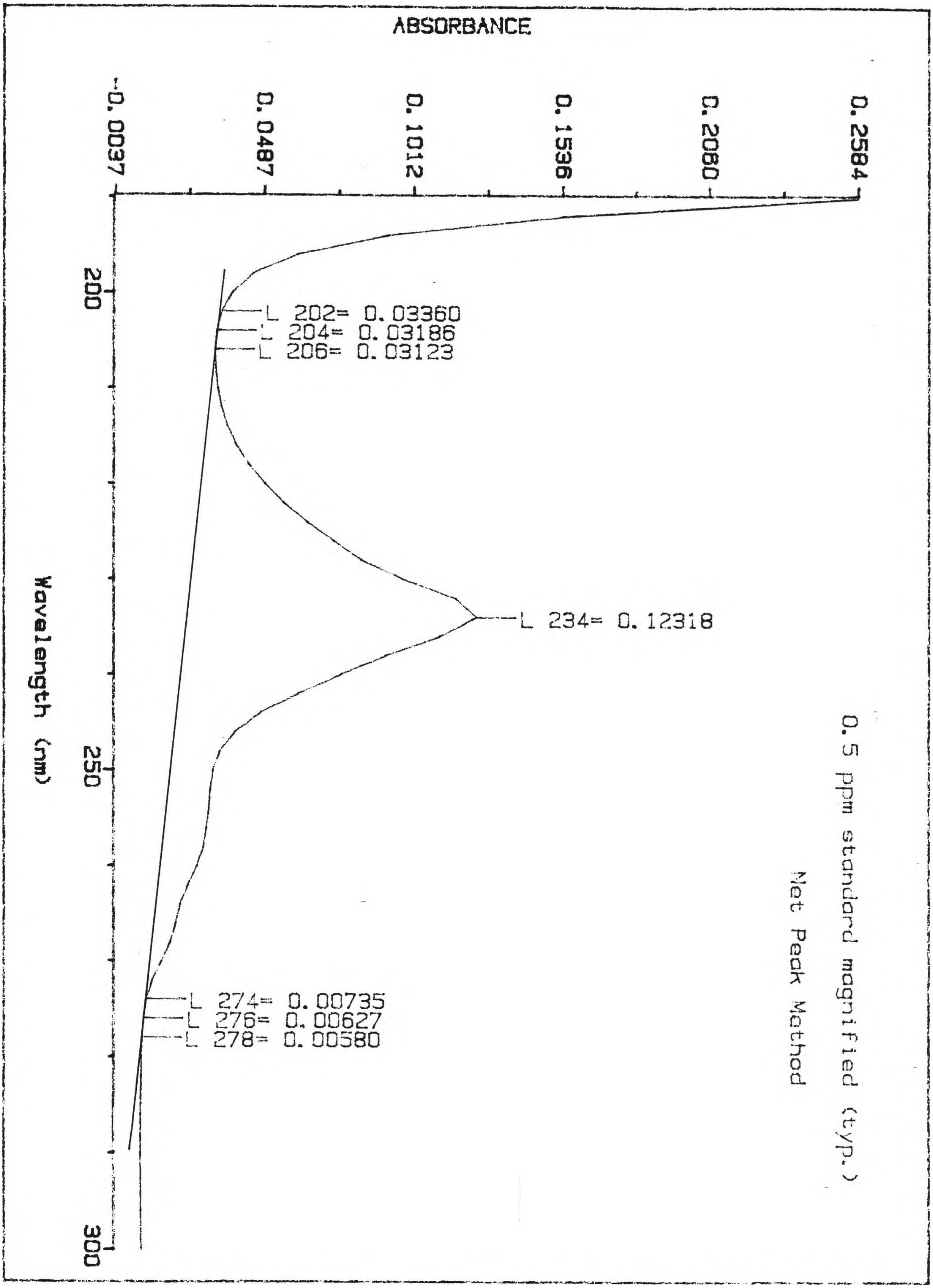
2) Net Peak

$\Delta = 0.12318 - 0.02120$
$\Delta = 0.10198$

3) Calibration Curve Point

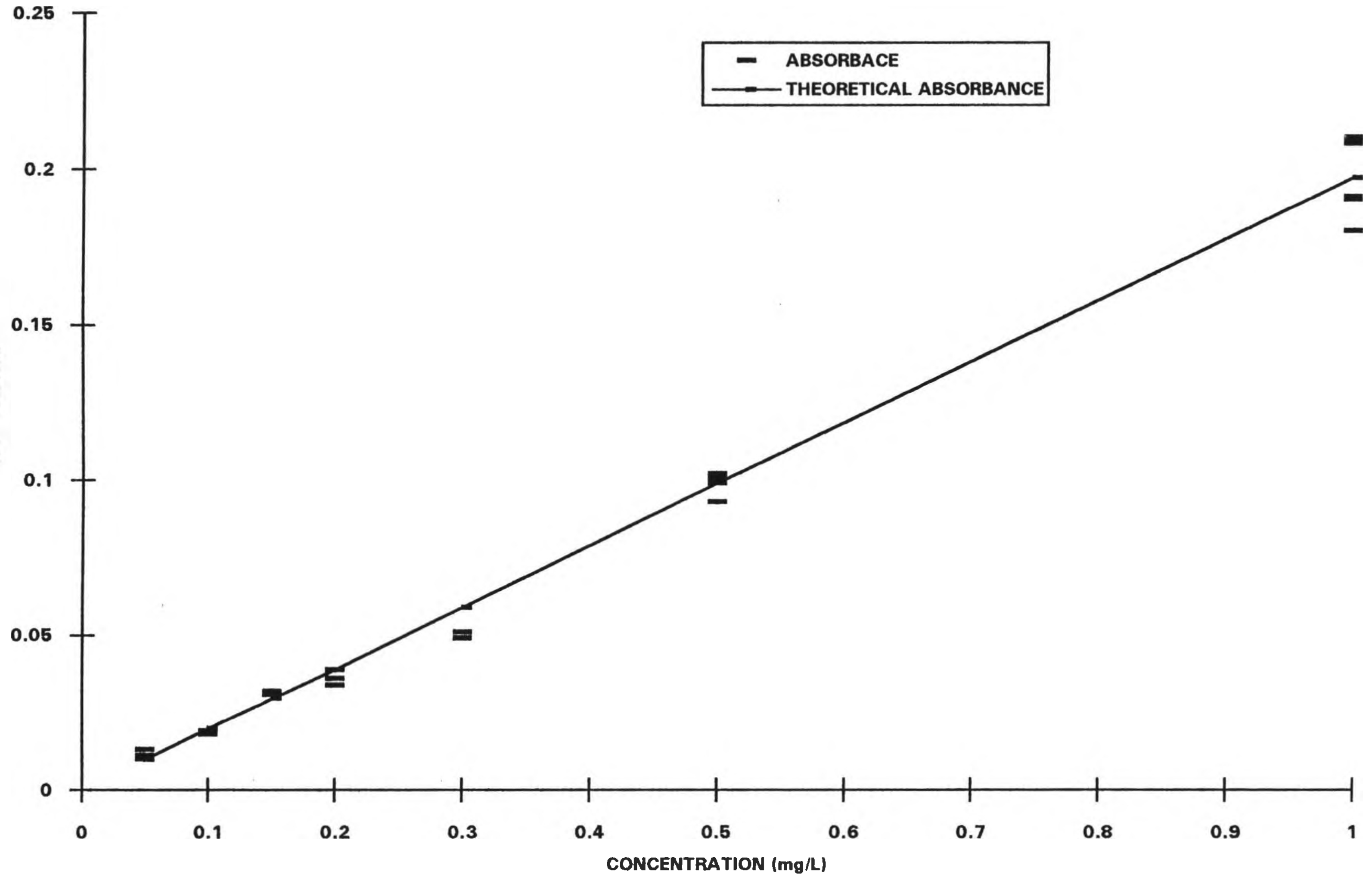
$(C, A_{net}) = (0.50, 0.102)$

I


ABSORBANCE
-0.0037
0.0487
0.1012
0.1536
0.2080
0.2584
Wavelength (nm)
200
250
300
L 202= 0.03360
L 204= 0.03186
L 206= 0.03123
L 234= 0.12318
L 274= 0.00735
L 276= 0.00627
L 278= 0.00580
0.5 ppm standard magnified (typ.)
Net Peak Mathod

APPENDIX 3 - CALIBRATION CURVE AND DATA

Target Concentration (mg/L)	Net Absorbance	Target Concentration (mg/L)	Net Absorbance	Statistics	
1	0.208	0.2	0.034	Slope	5.072
	0.209		0.036	Intercept	0
	0.210		0.034	R^2	0.990
	0.180		0.039		
	0.191		0.039		
	0.190	0.15	0.032		
0.5	0.099		0.031		
	0.093		0.031		
	0.101	0.1	0.018		
	0.100		0.018		
	0.102		0.019		
	0.099	0.05	0.010		
0.3	0.051		0.013		
	0.049		0.011		
	0.049				



ABSORBACE
THEORETICAL ABSORBANCE
NET ABSORBANCE
0.25
0.2
0.15
0.1
0.05
0
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
CONCENTRATION (mg/L)

APPENDIX 4 - TYPICAL GC DATA AND CHROMATOGRAM

```
===============================================================================
                             Area Percent Report
===============================================================================

Data File Name    : C:\HPCHEM\1\DATA\T4EXT28.D
Operator          : Andy Wurtz                      Page Number       : 1
Instrument        : ANALYZER1                       Vial Number       :
Sample Name       :                                 Injection Number  :
Run Time Bar Code:                                  Sequence Line     :
Acquired on       : 03 Nov 93   04:37 PM            Instrument Method: PEST.MTH
Report Created on: 04 Nov 93   01:58 PM             Analysis Method  : PEST.MTH

Sig. 2 in C:\HPCHEM\1\DATA\T4EXT28.D
    Pk#  Ret Time        Area           Height      Type   Width      Area %
   |---|----------|--------------|--------------|----|---------|----------|
     1     0.544         797801         234275  BB    0.053      9.8148
     2     3.034          41959            528  PB    0.941      0.5162
     3     4.745          75006           5406  BB    0.207      0.9227
     4     6.724          76936           4621  BV    0.259      0.9465
     5     7.403        7136828         340319  VB    0.315     87.7997

Total area = 8128529

===============================================================================
```

Sig. 2 in C:\HPCHEM\1\DATA\T4EXT28.D