The Equilibrium Complexing of Atrazine to a Soil Fulvic Acid at Various pH Values, Ionic Strength, and Fulvic Acid Concentration

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ABSTRACT

The Equilibrium Complexing of Atrazine to a Soil Fulvic Acid at Various pH Values, Ionic Strength, and Fulvic Acid Concentration

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Two ultrafiltration methods were investigated so as to determine the binding of Atrazine to a soil fulvic acid. A continuous flow ultrafiltration method (CFUM) suffered from poor reproducibility of experimental data because of membrane rejection of Atrazine and poor control of pH. A version of a batch ultrafiltration method (BUM) was developed by the author and was successful at controlling experimental parameters and, hence, was reproducible. The BUM is simple and inexpensive but time consuming.

Using BUM, titration graphs were obtained for fulvic acid with Atrazine as titrant at various pH values, ionic strength and fulvic acid concentrations. Weighted average and differential stability functions were determined from the titration graphs.

The competition of copper (II) with Atrazine for the Type A fulvic acid sites was determined by using titration graphs. Binding studies were also conducted at fixed Atrazine and fulvic acid concentrations at varying pH values in the presence and absence of potassium chloride.

Atrazine was monitored by gas chromatography while copper (II) was analyzed for by ion selective electrode or atomic absorption methods.

ACKNOWLEDGEMENTS

I wish to thank my supervisors Drs. C.H. Langford and R.H. Zienius for their support during the course of my research work.

I would like to extend special thanks to Dr. D.S. Gamble for helping in the interpretation of the results of this thesis.

TO MY MOTHER, BROTHERS AND SISTERS,

AND THE MEMORY OF MY FATHER

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GLOSSARY OF SYMBOLS

SYMBOL	MEANING	DIMENSION
At	- Atrazine	none
AtH^+	- Protonated Atrazine	none
a_H	- Hydrogen ion activity	mole per litre
BUM	- Batch ultrafiltration method	none
C	- Concentration of free fulvic acid	mmole per gram
C_A	- Concentration of Type A functional groups	mmole per gram
C_B	- Concentration of bound fulvic acid	mole per litre
CFUM	- Continuous flow ultrafiltration method	none
C_{max}	- Influent concentration of Atrazine from the CFUM reservoir	µmole per litre
C_n	- Effluent Atrazine concentration in each fraction	µmole per litre
$\bar{C}_i$	- The uncomplexed portion of the i^{th} small component of FA	mole per litre
C'_n	- Concentration of free Atrazine inside the CFUM cell	µmole per litre
C_{OH}	- Concentration of standard NaOH	mole per litre
C_T	- Concentration of total fulvic acid	mmole per gram
C_l	- The concentration of free ligand inside the cell at the end of collecting fraction n	µmole per litre
ECD	- Electron capture detector	none
FA	- Fulvic acid	none
FA_i	- The i^{th} component of fulvic acid	none
GLC	- Gas liquid chromatography	none

SYMBOL	MEANING	DIMENSION
K_A	- The dissociation function for the ionization of the individual Type A functional group	mole per litre
$\bar{K}_A$	- The experimental weighted average equilibrium function	mole per litre
K_a	- Dissociation constant for protonated Atrazine	mole per litre
K_w	- Ion product constant	$mole^2$ per $litre^2$
K_0	- Differential equilibrium dissociation function for unprotonated Atrazine	mole per litre
$\bar{K}_0$	- Weighted average equilibrium dissociation function for unprotonated Atrazine	mole per litre
K_{0_i}	- Differential equilibrium dissociation function for i^{th} component of FA complexed to unprotonated Atrazine	mole per litre
K_1	- Differential equilibrium dissociation function for protonated Atrazine	mole per litre
$\bar{K}_1$	- Weighted average equilibrium dissociation function for protonated Atrazine	mole per litre
K_{1B}	- Dissociation constant for the protonated complex formed between Atrazine and FA	mole per litre
K_4	- Differential equilibrium formation function for the complex formed between copper(II) and fulvic acid	none
$\bar{K}_4$	- Weighted average equilibrium formation function between copper(II) and fulvic acid	none
L_b	- Amount of Atrazine bound in the sorption profile	µmole per gram

SYMBOL	MEANING	DIMENSION
L_d	- Amount of Atrazine bound in the desorption profile	µmole per gram
L_{tb}	- Total amount of Atrazine sorbed	µmole per gram
L_{td}	- Total amount of Atrazine desorbed	µmole per gram
M_T	- Concentration of total Atrazine	mole per litre
M_{TB}	- Concentration of total Atrazine bound	mole per litre
M_0	- Concentration of unprotonated Atrazine	mole per litre
M_{OB}	- Concentration of unprotonated Atrazine bound	mole per litre
M_{OB_i}	- Concentration of unprotonated Atrazine bound to the i^{th} small component of fulvic acid	mole per litre
M_1	- Concentration of protonated Atrazine	mole per litre
M_{1B}	- Concentration of protonated Atrazine bound	mole per litre
m_A	- Concentration of all Type A carboxyl groups that are ionized	mole per litre
m_{AH}	- Concentration of all Type A carboxyl groups that are unionized	mole per litre
m_C	- Concentration of copper(II) complex with fulvic acid	mole per litre
m_M	- Concentration of free copper(II)	mole per litre
m_{SH}	- Concentration of singly ionized fulvic acid chelation sites	mole per litre
m_{SH_2}	- Concentration of fully protonated fulvic acid chelation sites	mole per litre
N_B	- Normality of standard NaOH	equivalence per litre

SYMBOL	MEANING	DIMENSION
V_{e1}	- Volume of standard base at the equivalence point for the first Gran's function	millilitre
V_{e2}	- Volume of standard base at the equivalence point for the second Gran's function	millilitre
V_n	- Total volume up to fraction n for the sorption profile	millilitre
V_t	- Total volume up to fraction t for the desorption profile	millilitre
V'	- The apparent void volume of the CFUM filtration cell	millilitre
$\bar{V}_0$	- The average sample volume in the CFUM filtration cell	millilitre
Y_1	- First Gran's function	litre
Y_4	- Second Gran's function	litre
γ	- Activity coefficient	none
Γ	Quotient for activity coefficients	none
α_A	- The macroscopic degree of ionization for the Type A carboxylic acid group	none
α_{1B}	- Degree of dissociation of protonated Atrazine	none
σ	- Reflection coefficient	none
κ	- Thermodynamic differential equilibrium dissociation function for unprotonated Atrazine	mole per litre
χ_C	- Fraction of copper(II) complexed to fulvic acid	none

SYMBOL	MEANING	DIMENSION
X_{SH}	- Fraction of singly ionized FA chelation sites	none
X_{SH_2}	- Fraction of fully protonated FA chelation sites	none
X_T	- Fraction of total Atrazine bound to FA	none
X_0	- Fraction of unprotonated Atrazine bound to FA	none
X_1	- Fraction of protonated Atrazine bound to FA	none

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CHAPTER 1

INTRODUCTION

1.0.0 CONTAMINATING THE ENVIRONMENT

The environment is continually being sprayed with herbicides and pesticides so as to increase crop production and eliminate pests which are harmful for human survival. The short term economic gains obtained from the use of these chemical inhibitors may not necessarily be the answer for the future. Today, some of the materials that we consume are beginning to show trace levels of herbicides and pesticides which have been used extensively on edible crops. If these compounds are not biodegradable they can be transported by various means into our lakes, rivers and streams and, hence, even contaminate the water we drink and the fish we eat. These problems may not be critical at present, but, preventative measures must be implemented before these compounds attain toxic levels in the environment

1.1.0 ATRAZINE IN THE ECOSYSTEM

In 1952 Gast (1) introduced the herbicide, Atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine), to control weeds among corn, soybean and sorghum crops. The applications ranged from 0.4 to 2.0 kilogram per acre. Since the introduction of this weed killer, it has been used extensively by farmers in North America. Because of the continual use of this weedicide it is necessary to undertake studies of Atrazine in the soil environment.

The two main components of soils which are responsible for binding organic pesticides are clays and organic matter. The interactions between

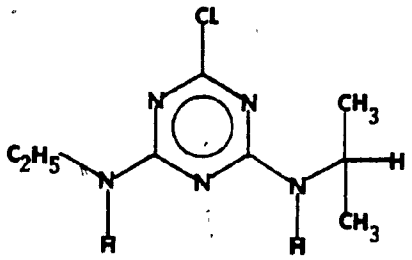
clay and Atrazine have been documented by Weber (2). However, data on organic matter-Atrazine interaction is scarce in the literature. In many publications (1,2,3,4,5,6), the organic component of soil was touted as being mainly responsible for binding organic compounds. In a laboratory experiment by Weber (6) it was found that Atrazine phytotoxicity decreased as the organic matter content increased in a soil. The organic matter in soils could also be responsible for transporting herbicide and pesticides into lakes and streams, eventually making them polluted (7). If these compounds are toxic thay can also be harmful to humans. Atrazine, with a LD_{50} value of 3,080 mg/kg is not toxic compared to other herbicides (8) being used today.

Because of the complexity of the organic molecules in soil organic matter it is not surprising to find a lack of research on herbicide-organic matter interactions. The editor of the "Environmental Science and Technology" says the overall structure of soil organic matter "is a mystery" (9). He added, "the mechanism by which they react chemically is also a mystery". A study of the interactions between Atrazine and fulvic acid (a component of soil organic matter) was undertaken so as to gather some information on the mechanism of binding.

This study is a part of a larger program where the water soluble portion of soil organics, fulvic acid, receives our priority attention because it could play a significant role in mobilization of pesticides. Atrazine is capable of hydrogen bonding in aquatic environments that are not ionic. Atrazine behaviour should be contrasted, for example, to that for Lindane (non-polar) or paraquat (ionic). They are the subject of related studies in these laboratories.

1.1.1 THE STRUCTURE AND CHEMISTRY OF ATRAZINE

The structure of Atrazine is shown as (I).



(I)

2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine

Since Atrazine contains nitrogens with lone pairs of electrons, it can become protonated in an acidic medium. In the older literature (10, 11,12), a monoprotonated species was observed from spectroscopic studies. The nitrogen containing the isopropyl group in (I) was said to be responsible for Atrazine protonation. The pKa for this species was determined to be 1.68. In a more recent study by Plust et al. (13) it is suggested that protonation takes place on the aromatic nitrogens rather than on the nitrogen containing the isopropyl group. Since the equivalent of one nitrogen was protonated on the heterocyclic ring, Plust et al. concluded that it was a weighted average of the three nitrogens on the ring which was protonated. A pKa value of 1.62 was reported by Plust et al. for Atrazine. The higher pKa value in the older literature was attributed to the neglect of activity corrections.

From the above discussion, it can be gathered that two species of Atrazine can exist in aqueous solution at low pH values, i.e., monoprotonated (or protonated) and unprotonated Atrazine. If unprotonated Atrazine is represented by At or M_0 and protonated Atrazine is represented by AtH^+ or M_1, then,

$$AtH^+ \overset{K_a}{\rightleftharpoons} At + H^+ \qquad (1\text{-}1)$$

$$K_a = \frac{M_o a_H}{M_1} \qquad (1\text{-}2)$$

If M_T represents the stoichiometric amount of Atrazine and α_{1B} the degree of dissociation of protonated Atrazine, then,

$$M_T = M_o + M_1 \qquad (1\text{-}3)$$

$$\alpha_{1B} = \frac{M_o}{M_T} \qquad (1\text{-}4)$$

$$\frac{1}{\alpha_{1B}} = 1 + \frac{M_1}{M_o} = \frac{K_a + a_H}{K_a} \qquad (1\text{-}5)$$

$$M_o = \frac{M_T K_a}{K_a + a_H} \qquad (1\text{-}6)$$

Accepting the pKa value of 1.62 by Plust et al., the distribution of unprotonated (α_{1B}) and protonated ($1-\alpha_{1B}$) species as a function of pH was determined from equation (1-5). Figure (1) shows the distribution of both species as a function of pH. Above a pH value of about 4, there are no protonated species present. At about a pH value of 0.1, there are no unprotonated species present. At a pH value of about 1.6, there are equal quantities of both species present.

If fulvic acid interacts with Atrazine below a pH value of 4, then, one would have to consider the chemistry and thermodynamics of four Atrazine species present in solution, i.e., unprotonated Atrazine, protonated Atrazine, unprotonated Atrazine complexes with fulvic acid, and protonated Atrazine complexes with fulvic acid. Above a pH value of 4, only two Atrazine species exist, i.e., unprotonated Atrazine and unproto-

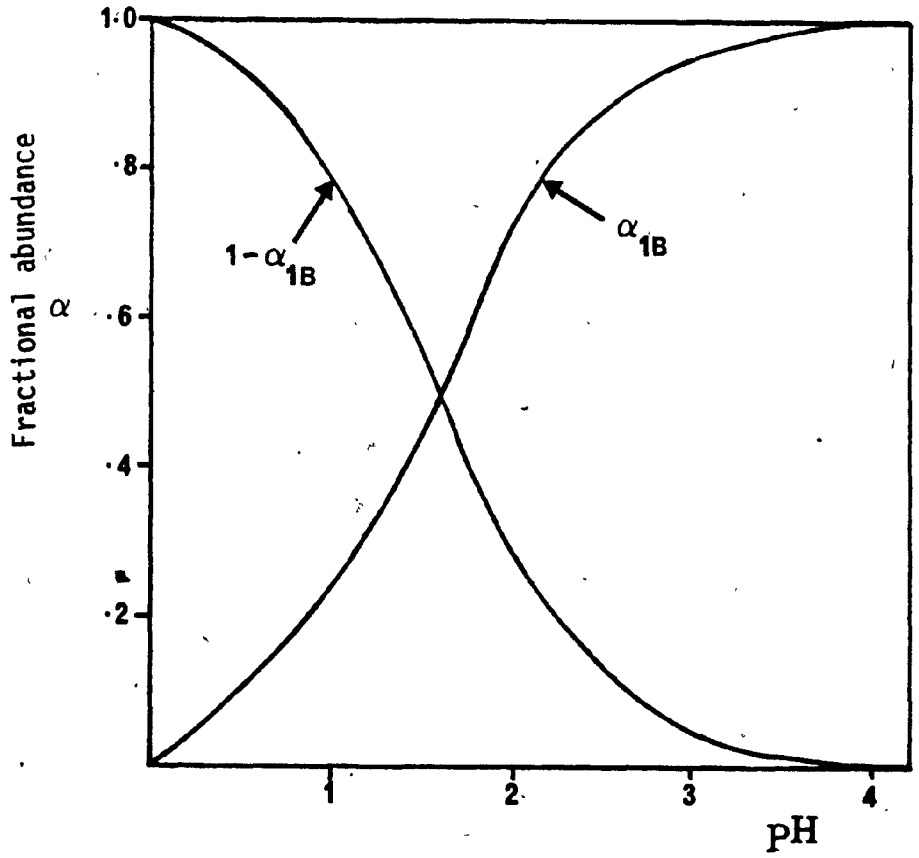


Figure (1): Fraction of Atrazine species as a function of pH.

$$\alpha_{1B} = \frac{(At)}{(At)_T}; \quad 1-\alpha_{1B} = \frac{(AtH^+)}{(At)_T}.$$

nated Atrazine complexes with fulvic acid.

1.2.0 ORGANIC MATTER CLASSIFICATION

Organic matter in soils and waters is derived from decayed plants, animals and microbes and their respective wastes (14). The decayed products can be subdivided into two categories: (a) nonhumic substances, and (b) humic substances. Figure (2) represents a classification of organic matter.

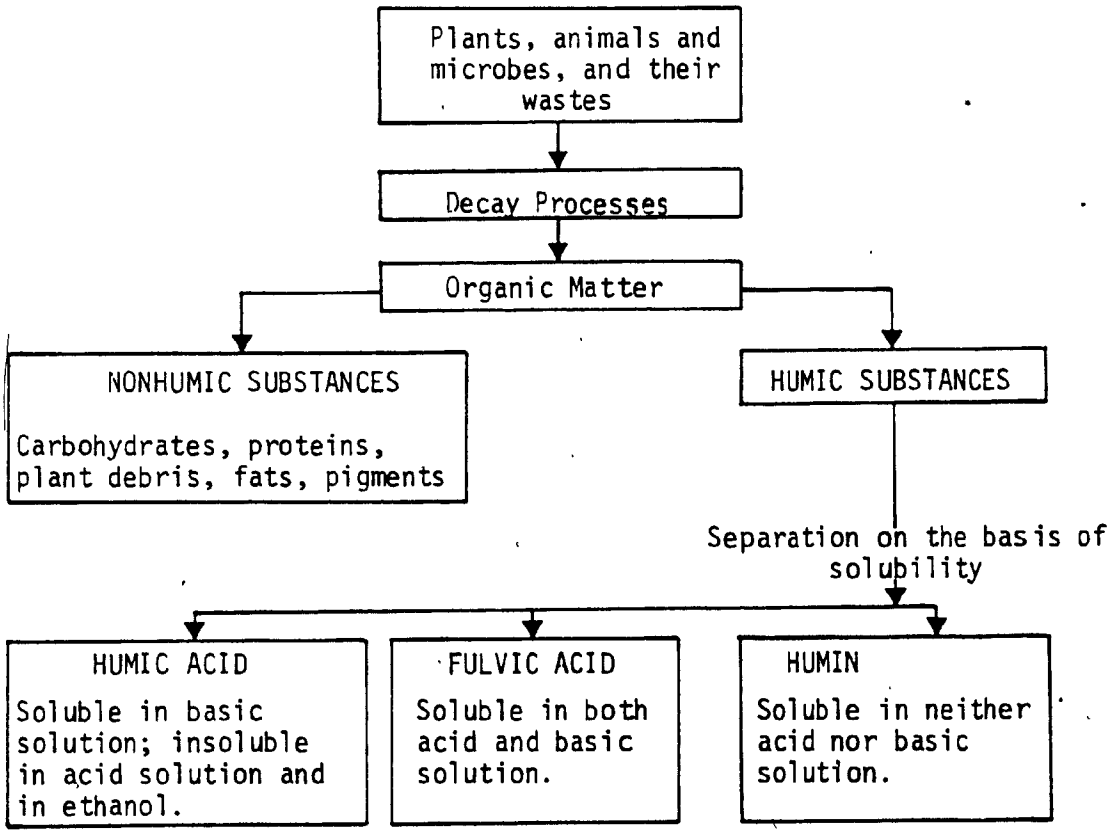


Figure (2): Classification of organic matter.

Most of the organic matter in soils and waters exists as humic substances. Only a minor part is nonhumic. It is generally thought that the humic substances are responsible for binding metals and organic compounds and transporting them into lakes and rivers (15). According to Upchurch et al. (16) it is also the humic substances present in the soils which decrease the phytotoxicity of herbicides.

Because of the environmental and economic impact of humic substances, detailed studies of their mechanisms of binding to other compounds are needed. As Figure (2) demonstrates, humic substances can be divided into three fractions: (a) humic acid (HA), which is soluble in dilute alkaline solution but is precipitated by acidification of the alkaline extract;

(b) fulvic acid (FA), which is that humic fraction which remains in the aqueous acidified solution, i.e., it is soluble in both acid and base; and (c) the humic fraction that cannot be extracted by dilute base and acid, which is referred to as humin (17). The three humic fractions are structurally similar, but, they differ in molecular weight, elemental analysis, and functional groups (17). The molecular weight range is from several hundreds to tens of thousands. The major oxygen-containing functional groups are carboxyls, hydroxyls and carbonyls. The FA fraction has the lowest weight of the three, but, it has the highest oxygen-containing functional group content per unit weight.

1.2.1 FULVIC ACID

Fulvic acid (FA) is the fraction of humic substance which has been considered partially responsible for transporting metal ions into lakes and rivers (18). This fraction is hydrophilic and as mentioned before, it is soluble at both high and low pHs'. The functional groups of FA can be protonated and deprotonated in the pH range common in natural waters (pH = 3 to 9) (18).

These functional groups are good ligand sites for forming complexes with metals, anions and organics. However, because of the heterogenity of the FA functional groups, it is very difficult to characterize completely all FA structures. The batch to batch variation of FA also adds to the complexity of characterizing the functional groups since particular molecules may be important in one batch but not in another (18). The present trend in research is to describe FA in terms of group properties.

Through extensive degradation studies on FA, Schnitzer (19,20,21) has proposed a partial chemical structure for FA. This structure is ambiguous,

since FA, initially, has a wide variety of monomers which are similar to the degraded products. Also, degradation reactions may produce products which are different from the true chemical components of the FA structure.

In addition to the degradation studies, determinations were done on the number and type of oxygen containing functional groups for FA (22,23). These include tests for total acidity, carboxyl group content, hydroxyl group content (both total and phenolic), and quinone and methoxyl group contents. These tests only contributed to the understanding of the chemistry of the FA molecule, and, hence, only a representative structure of the molecule can be given. Gamble (24), using the above knowledge of FA, has put forward a representative structure for an FA component (Figure (3)).

The FA used in this project was extracted from the same soil and under similar conditions as the Armadale FA1 batch which has been extensively characterized by Agriculture Canada (25,26,27). Gamble (28,29) thoroughly studied the acid-base equilibria of the FA1 fulvic acid. He treats it as a polyelectrolyte which has a number of chemically nonidentical acidic functional groups, whose respective dissociation constants are a function of the overall degree of ionization of the FA molecule.

According to Gamble, there are two types of acidic groups in FA extracted from the Armadale Prince Edward Island B horizon podzol soil. They are the Type A group which comprise 4.99 mmole acidic sites per gram of FA and the Type B group which comprise 2.72 mmole acidic sites per gram of FA. The Type A group includes 3.0 to 3.3 mmole/gm FA of highly acidic (Type 1) carboxylic groups (pK_A = 2.3 to 2.6) and 1.7 to 2.0 mmole/gm FA of moderately acidic carboxylic groups (pK_A = 4.5 to 5.7). The Type B group is weakly acidic (phenolic hydroxy groups) and has a pK_A range of about 9.4 to 9.7.

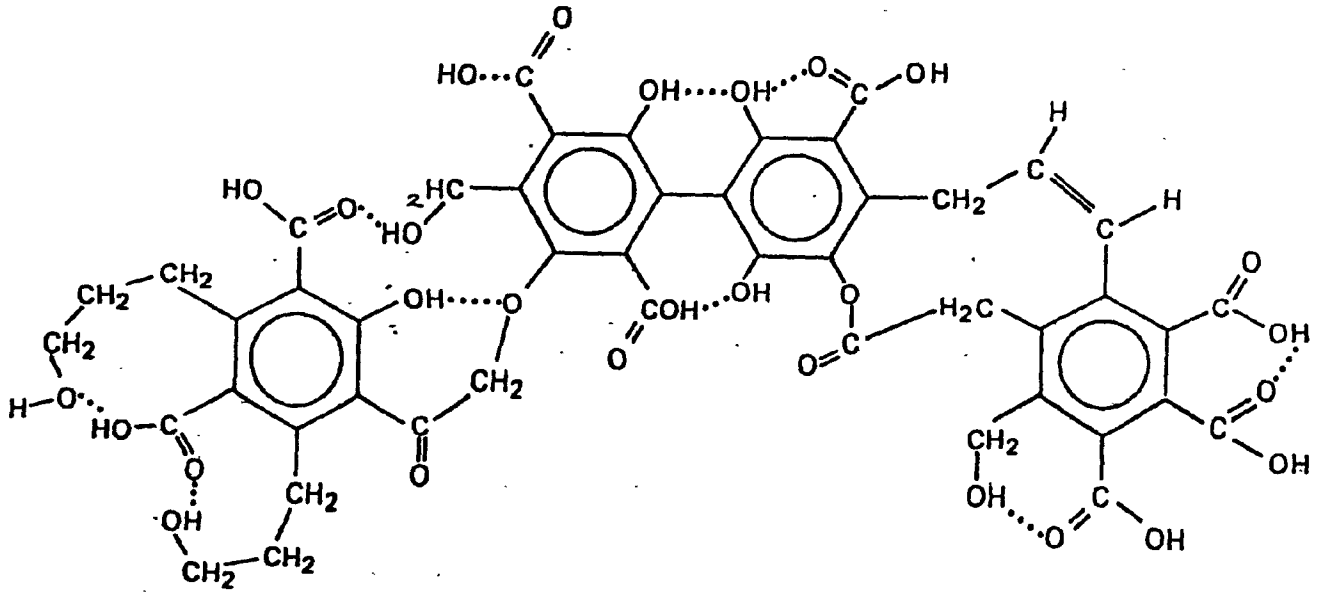


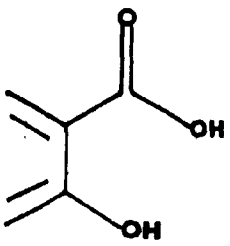
Figure (3): Structure of a representative component of a fulvic acid mixture.

From the Gamble acid-base model, the acid dissociation function (K_A) for the ionization of the individual Type A functional group can be calculated from equation (1-7),

$$K_A = -\frac{d((1-\alpha_A)\bar{K}_A)}{d\alpha_A} \qquad (1\text{-}7)$$

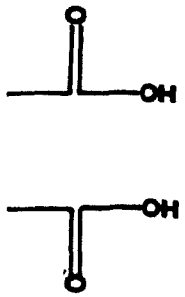
where α_A is the macroscopic degree of ionization for the Type A carboxylic sites, and $\bar{K}_A$ is the experimental weighted average equilibrium function. The K_A values obtained from acid-base titrations are useful for characterizing the acidic functional group.

The acidic sites of Armadale FA are also responsible for binding metal ions. Gamble (30) and Underdown et al. (31), using a potentiometric titration technique, determined the weighted average ($\bar{K}_4$) and differential (K_4) equilibrium functions for the complexing of Cu^{2+} to Armadale FA. The types of bidentate chelating sites are thought to be responsible for binding Cu^{2+}. These are the salicylic type (II) and dicarboxylic (or phthalic acid) type (III). There are three classes of the dicarboxylic sites: (a) the ortho dicarboxylic structure; (b) two carboxyls on the same polymer molecule, but not on the same ring; and (c) two carboxyls on different polymer molecules.



(II)

SALICYLIC TYPE



(III)

DICARBOXYLIC TYPE

In case (c), the bridging of Cu(II) between two FA molecules contributes to coagulation. Gamble et al. (31) determined the total copper (II) chelating-sites for the Armadale FA to be 5.43 mmole/gm FA.

Light scattering work done on the Armadale FA by Underdown et al. (32,33) has shown that FA has a large range of molecular weights (polydisperse). Light scattering measurements were made on fractions of FA solutions (0.100 gm/litre) after filtration through a series of polycarbonate micropore filters from 0.4 to 0.05 μm nominal pore size. The Rayleigh light scattering ratio at 90^0 (R_{90}) is given in Table (1). The smaller the R_{90} value the smaller the value of the weight average molecular weight ($\bar{M}_w$).

Table (1): Light scattering properties of fulvic acid fractions at a pH value of 3.5.

FRACTION	% TOTAL MASS	$10^6 R_{90}$	$10^{-3} \bar{M}_w$
I(>0.4μm)	3.6	1.64	8870
II(<0.4,>0.2μm)	2.0	0.926	3690
III(<0.2,>0.05μm)	24.1	0.169	58.0
IV(<0.05μm)	70.3	0.056	5.85

Electron microscope and x-ray fluorescence indicated that the 0.4 μm filter retained particles that contain significant amounts of Si. Fraction I is thought to be the ash content of the FA with absorbed organic matter. The distribution indicated by fractionation in Table (1), shows a small number of large molecules (fractions I and II) and a larger mass of material in a large number of small molecules (fractions III and IV). The wide range of $\bar{M}_w$ for a sample of Armadale FA in Table (1) indicates the high degree

of polydispersity of this FA.

Underdown et al. have shown that fractions I and II are large molecules with a closed association structure while fractions III and IV are non-aggregated species or unimers which are potentially capable of forming aggregates by an open association mechanism (33). For example, in Figure (4) where R_{90} is plotted against α (the degree of ionization of FA, i.e., for an α value of 0.4 the corresponding pH value is 5.0), the unfiltered sample shows some decrease in R_{90} with increasing α. This suggests a little disaggregation. The filtered sample where larger particles have been removed shows an increase of R_{90} with α which probably reflects "unfolding" of polymers as charge accumulates with α. In the low pH region, when α is small and charge is very low, high ionic strength induces extensive aggregation. This aggregation no doubt involves hydrogen-bonding.

The reason for FA aggregation below a pH value of 5 is surely due to the increase of protonation of the Type A carboxyl groups reported by Gamble. When these groups become protonated, they can be used to hydrogen bond to other groups which have lone pairs of electrons. For the case where there is no KCl in Figure (4), it is obvious that the protonated larger molecules are responsible for the limited aggregation formed below a pH value of 5. According to Underdown et al., the unimers contain an average of three acidic groups. When these groups are protonated they can take part via an open association mechanism to form aggregates, hence, the large increase in R_{90} for the high ionic strength case in Figure (4). The common effect of high ionic strength on coagulation of colloids is seen in the enhancement of aggregation by KCl (34,35).

Underdown et al. also studied the effect of copper (II) binding on

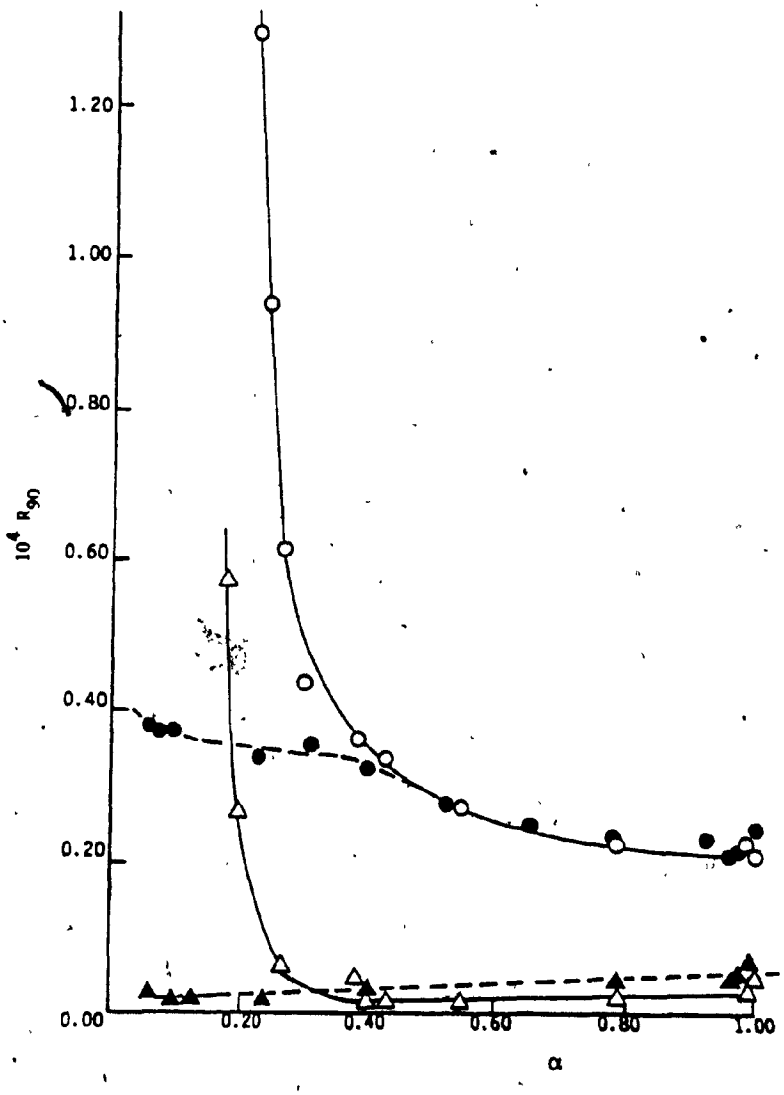


Figure (4): Dependence of 90° light scattering, R_{90}, on degree of ionization, α. (Reference (33)).

○ Not filtered/10^{-1} M KCl.
△ Filtered (0.2 μm)/ 10^{-1} M KCl.
● Not filtered/no KCl.
▲ Filtered (0.2 μm)/no KCl.

Armadale FA aggregation. For a solution containing 0.100 gm FA/litre, Figure (5) shows how the R_{90} scattering ratio changes as copper (II) is bound to FA molecules. The initial small change in R_{90} in Figure (5) was attributed to copper (II) binding to the salicylic type carboxyl groups (about 3.3 mmole per gm FA) in Armadale FA. When copper (II) binds to the salicylic type sites, there is not much increase in the particle size. Beyond these sites, copper (II) is used to connect (cross-link) aggregates which are already large, hence, the large increase in R_{90} at 2 mmole/gm FA at a pH value of 3.6 and at 3 mmole/gm FA at a pH value of 6.0. Underdown et al. also showed that the smaller particles (fractions III and IV in Table (1)) are responsible for the copper (II) binding and aggregate formation.

From the above work of Underdown et al. , one can say that FA aggregation is promoted by neutralization of anionic charge by H^+, increase of ionic strength, and Cu^{2+} with the effectiveness being in the same order.

From the above discussion of FA chemistry, the critical factors which will possibly influence the FA complexing ability and the stability constant determinations for metals, anions and organics are (a) the source of FA, (b) the method of isolation of FA, (c) the concentration of FA, (d) the ionic strength of the media, (e) the pH of the media, (f) the nature and concentration of other cations, (g) the method of analysis for the complex and (h) the method of data manipulation and stability constant calculations. There are some confusion in the literature as to the validity of cases (a), (b), and (g).

Even though the complexing properties of FA vary from sample to sample, the similarities are great enough so that findings in the litera-

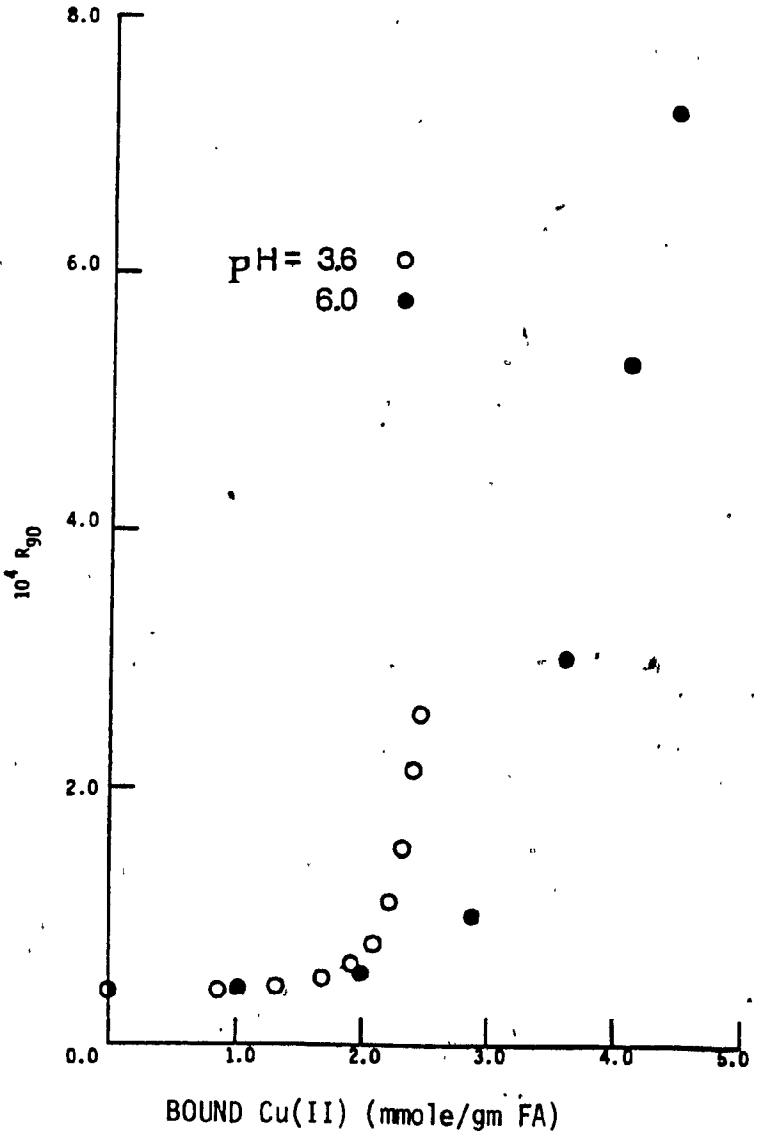


Figure (5): Variation of R_{90} with bound Cu(II); FA = 10^{-1} gm/litre, no background electrolyte: o pH = 3.6, ● pH = 6.0. (Reference (33)).

ture overlap substantially (36). Aggregation of the FA molecules affects the binding of weak complexes (37). If aggregation increases the hydrophobic character of FA, then, an increase of binding to nonpolar compounds might be expected. If aggregation is caused by hydrogen bonding between the FA molecules, then, a decrease in binding is expected for complexes

formed via hydrogen bonds.

1.3.0 METHODOLOGIES FOR COMPLEXATION STUDIES

The method chosen to analyze various species of a system will considerably affect the results obtained (37). Methods can be divided into two categories: (a) separation (separation of free and complexed species) and (b) nonseparation (distinguishes between free and complexed species in situ).

The separation methods include liquid chromatography (specifically gel filtration), ultrafiltration, and equilibrium dialysis. The nonseparation methods include electron paramagnetic resonance spectroscopy, ion exchange competition, ion selective electrode potentiometry, anodic stripping voltammetry and fluorescence spectroscopy. The separation methods are best for studying the binding of neutral species onto fulvic acid. They can also be used to study the binding of charged species. The same cannot be said for most of the nonseparation techniques since most of them are probes for charged species. However, lately, the fluorescence technique is beginning to gain popularity for monitoring organics which are bound onto humic substances (38,39,40,41). This technique may, however, probe a subfraction of FA. Both categories suffer disadvantages, some of which are adsorption problems, shift in equilibrium and restriction on the ionic strength of the media used.

The nonseparation method requires expensive instrumentation which was not available for the studies undertaken in the project. According to Rainville et al. (42) the equilibrium dialysis method does not separate the free from the complexed metal ions effectively. It was observed that complexed and uncomplexed FA molecules penetrated through the dialysis membrane (a cut off molecular weight of 1000), hence, making it difficult

to determine the true equilibrium concentration of free metal ion. The ultrafiltration method does separate more efficiently, but, it is more time consuming. The development of an ultrafiltration method will be the route taken in this project. The ultrafiltration method used by Grice et al. (43) for binding studies will be used as a guide in the development of a method.

1.4.0 THE PROBLEM AND THE RESEARCH PLAN

Little is known about the fate of pesticides in the environment. According to many researchers, it is the organic matter in the soils that is responsible for transporting these organic compounds into water bodies. It is also the organic content of soils that is responsible for decreasing the phytotoxicity of most herbicides.

An investigation of herbicide-organic matter interaction is, therefore, warranted. The interaction of Atrazine with fulvic acid will, therefore, be studied under various experimental conditions which resemble those of field conditions.

Binding studies will then be carried out under conditions of (a) varying ionic strength (b) varying FA concentrations (c) varying pH of the media (d) varying Atrazine concentrations and (e) in the presence of copper ions. Atrazine will be analyzed by Gas Chromatography and copper will be analyzed with an Ion Selective Electrode and by Atomic Absorption Spectroscopy.

The calculation of stability constants will follow the Gamble approach which is discussed in Chapter 2.

CHAPTER 2

THEORY

2.0.0 QUANTITATIVE MODELING OF THE SOLUTION PHASE COMPLEXING OF ATRAZINE BY FULVIC ACID

From the discussion in Chapter 1 the following postulates can be made about the complexing of Atrazine by fulvic acid in solution, and all must be taken into account in interpretation of the experimental results:

(a) The binding sites on the FA are not known to be discrete or unique, and cannot be identified with specific molecular structures.

(b) No stoichiometric relationships exist, which could be used for defining FA binding capacities for Atrazine.

(c) Labile complexes form, for which the law of mass action may be applied.

(d) The complexing equilibrium is influenced by protonation of the Atrazine.

The complexing and protonation reactions give four Atrazine species. M_0, M_1 and M_T were defined in equation (1-3) in Chapter 1. M_{0B} and M_{1B} are bound unprotonated and bound protonated Atrazine, respectively. Therefore, the total Atrazine bound is,

$$M_{TB} = M_{0B} + M_{1B} \qquad (2\text{-}1)$$

The fulvic acid concentration in gram/litre can be represented by C (free FA) and C_B (bound FA). The total FA, C_T, is

$$C_T = C + C_B \qquad (2\text{-}2)$$

But, from the experimental results $C_B \ll C$, therefore,

$$C_T \approx C \tag{2-3}$$

The loading of FA binding sites with Atrazine is given by,

$$x_0 = (M_{0B}/C) \tag{2-4}$$

for unprotonated Atrazine, and

$$x_1 = (M_{1B}/C) \tag{2-5}$$

for protonated Atrazine. The total fraction of Atrazine bound is given by,

$$x_T = x_0 + x_1 = (M_{TB}/C) \tag{2-6}$$

It is probable that the H^+ dissociation constants of complexed and free Atrazine are very similar, if not identical. Since direct experimental evidence for this is lacking, however, the distinction will be maintained here. Reaction (2-7) gives the complexed Atrazine case.

$$(AtH^+\text{-}FA) \overset{K_{1B}}{\rightleftharpoons} (At\text{-}FA) + H^+ \tag{2-7}$$

$$K_{1B} = \frac{M_{0B}\, a_H}{M_{1B}} \tag{2-8}$$

The degree of dissociation is given in the usual way by equation (2-9).

$$\alpha_{1B} = \left(\frac{K_{1B}}{K_{1B} + a_H}\right) \tag{2-9}$$

Correspondingly, the degree of protonation is,

$$(1-\alpha_{1B}) = \left(\frac{a_H}{K_{1B}+a_H}\right) \qquad (2\text{-}10)$$

The complexing equilibria of unprotonated and protonated Atrazine may be separately examined.

2.1.0 THE COMPLEXING OF UNPROTONATED ATRAZINE

Although complexing is usually described with stability functions, a dissociation function is found to be more convenient for this case. It is defined by equation (2-12) for the whole FA mixture.

$$(\text{At-FA}) \overset{\bar{K}_0}{\rightleftharpoons} \text{At} + \text{FA} \qquad (2\text{-}11)$$

$$\bar{K}_0 = \frac{M_0 C}{M_{0B}} \qquad (2\text{-}12)$$

It is necessary to describe the FA concentration in grams per litre, because no explicit stoichiometry exists for the binding sites. An important point is that $\bar{K}_0$ is a concentration quotient. The reason for this is that C and M_{0B} both describe the concentrations of mixtures, for which activities and activity coefficients cannot be defined.

In just the same way as has been done for FA-metal ion equilibria (31), $\bar{K}_0$ defined for the mixture may be related to the properties of the components of the mixture. For Atrazine complexing with the i^{th} small component of the FA, one has

$$(\text{At-FA}i) \overset{K_{0i}}{\rightleftharpoons} \text{At} + \text{FA}i \qquad (2\text{-}13)$$

$$K_{O_i} = \frac{M_O C_i}{M_{OB_i}} \tag{2-14}$$

where,

C_i = the uncomplexed portion of the i^{th} small component of the FA.

M_{OB_i} = molarity of the Atrazine bound to the i^{th} small component of the FA.

The components of the FA mixture are all accounted for by the material balance equations (2-15) and (2-16).

$$C = \sum_{i=1}^{n} C_i \tag{2-15}$$

$$M_{OB} = \sum_{i=1}^{n} M_{OB_i} \tag{2-16}$$

From equation (2-14),

$$C_i = K_{O_i}\left(\frac{M_{OB_i}}{M_O}\right) \tag{2-17}$$

Introducing this into equation (2-15),

$$C = \sum_{i=1}^{n} K_{O_i}\left(\frac{M_{OB_i}}{M_O}\right) \tag{2-18}$$

The properties of the system may be now related to those of its components, by substituting equation (2-18) into equation (2-12), giving equation (2-19).

$$\bar{K}_0 = \frac{(M_0)\sum_{i=1}^{n} K_{0_i}\left(\frac{M_{OB_i}}{M_0}\right)}{M_{OB}} \tag{2-19}$$

Therefore,

$$\bar{K}_0 = \left(\frac{1}{M_{OB}}\right)\sum_{i=1}^{n} K_{0_i} M_{OB_i} \tag{2-20}$$

For the loading of the i^{th} small portion of FA with Atrazine, let

$$(\Delta x_0)_i = \frac{M_{OB_i}}{C} \tag{2-21}$$

Introducing the definitions of x_0 and $(\Delta x_0)_i$ into equation (2-20) gives equation (2-22) and (2-23).

$$\bar{K}_0 = \left(\frac{C}{M_{OB}}\right)\sum_{i=1}^{n} K_{0_i}\left(\frac{M_{OB_i}}{C}\right) \tag{2-22}$$

$$\bar{K}_0 = \left(\frac{1}{x_0}\right)\sum_{i=1}^{n} K_{0_i}(\Delta x_0)_i \tag{2-23}$$

The complexing sites, although structurally nonidentical, are expected to have sufficiently closely spaced binding energies so that their equilibria overlap (28). Because of the anticipated continuum the summation of equation (2-23) may be replaced by an integration, as shown in equation (2-24).

$$\bar{K}_0 = \left(\frac{1}{x_0}\right)\int_0^{x_0} K_0 \, dx_0 \qquad (2\text{-}24)$$

The chemical meanings of $\bar{K}_0$ and K_0 are quite different, and should be carefully noted. According to equation (2-24), the experimental function $\bar{K}_0$ is a weighted average. The statistical weight factors are dx_0 and $1/x_0$. The average exists for the collection of binding sites represented by the range covering zero to x_0 moles of Atrazine per gram of FA. In contrast to this, K_0 is evidently a differential equilibrium function, defined by equation (2-25) for an infinitesimal portion of complex located at any point in the range covering zero to x_0. K_0 may be calculated in a very simple way using equation (2-26), which has been obtained by rearranging and differentiating equation (2-24).

$$K_0 = \left(\frac{M_0 \partial c}{\partial M_{0B}}\right) = f(x_0) \qquad (2\text{-}25)$$

$$K_0 = \frac{d(\bar{K}_0 x_0)}{dx_0} \qquad (2\text{-}26)$$

The effect of this calculation is to "undo the averaging" that is inherent in the experimentally measured $\bar{K}_0$.

The numerical values of $\bar{K}_0$ and K_0 depend on the chemical composition of the system, and this is not reflected in equations (2-24) and (2-25). A total list of the variables includes:

(a) fulvic acid concentration

(b) total concentration of all Atrazine species

(c) pH

(d) loading of FA with Atrazine

(e) mole fraction of free Atrazine protonated

and,

(f) mole fraction of bound Atrazine protonated

Because of the constraints imposed by these equilibria, there are only three independent variables out of this total of six- the equilibria protonation of free and bound Atrazine, and the Atrazine complexing. The total state of the system may be specified by choosing any three of the six variables, but some of them are of particular interest. For convenience, cases having constant FA concentrations will be considered. As for the two remaining variables, total loading of the FA with Atrazine and pH will be introduced into equation (2-24).

Using the definition of x_0 and x_1, equation (2-8) becomes,

$$K_{1B} = \frac{x_0 a_H}{x_1} \tag{2-27}$$

Therefore,

$$x_1 = \left(\frac{a_H}{K_{1B}}\right) x_0 \tag{2-28}$$

From the definition of x_T and equation (2-28),

$$x_T = x_0 + \left(\frac{a_H}{K_{1B}}\right) x_0 \tag{2-29}$$

Therefore,

$$x_T = \left(1 + \frac{a_H}{K_{1B}}\right) x_0 \qquad (2\text{-}30)$$

$$x_T = \left(\frac{K_{1B} + a_H}{K_{1B}}\right) x_0 \qquad (2\text{-}31a)$$

$$x_T = \left(\frac{1}{\alpha_{1B}}\right) x_0 \qquad (2\text{-}31b)$$

$$x_0 = (\alpha_{1B} x_T) \qquad (2\text{-}32)$$

Total Atrazine loading of the FA, and the degree of dissociation of the bound Atrazine are both experimental variables. Differentiating, therefore, gives two terms;

$$dx_0 = (\alpha_{1B} dx_T) + (x_T d\alpha_{1B}) \qquad (2\text{-}33)$$

This may be expressed in terms of pH variation. From equation (2-9),

$$\alpha_{1B} = K_{1B}(K_{1B} + a_H)^{-1} \qquad (2\text{-}34)$$

$$d\alpha_{1B} = -K_{1B}(K_{1B} + a_H)^{-2}\, da_H \qquad (2\text{-}35)$$

$$d\alpha_{1B} = -\left(\frac{K_{1B}}{K_{1B} + a_H}\right)\left(\frac{1}{K_{1B} + a_H}\right) da_H \qquad (2\text{-}36)$$

$$d\alpha_{1B} = -\alpha_{1B}\left(\frac{1}{K_{1B} + a_H}\right) da_H \qquad (2\text{-}37)$$

$$d\alpha_{1B} = -\alpha_{1B}\left(\frac{a_H}{K_{1B}+a_H}\right)\left(\frac{da_H}{a_H}\right) \qquad (2\text{-}38)$$

$$d\alpha_{1B} = -\alpha_{1B}(1-\alpha_{1B})\, d\ln a_H \qquad (2\text{-}39)$$

$$d\alpha_{1B} = -2.303\ \alpha_{1B}(1-\alpha_{1B})\ dpH \qquad (2\text{-}40)$$

Substituting into equation (2-33),

$$dx_0 = \alpha_{1B}dx_T + 2.303x_T\alpha_{1B}(1-\alpha_{1B})\ dpH \qquad (2\text{-}41)$$

From equation (2-26),

$$d(\bar{K}_0x_0) = K_0\ dx_0 \qquad (2\text{-}42)$$

Substituting from equations (2-33) and (2-41) in turn into equation (2-42) gives equations (2-43a) and (2-43b) respectively.

$$d(\bar{K}_0x_0) = \alpha_{1B}K_0dx_T + x_TK_0d\alpha_{1B} \qquad (2\text{-}43a)$$

$$d(\bar{K}_0x_0) = \alpha_{1B}K_0dx_T + 2.303x_TK_0\alpha_{1B}(1-\alpha_{1B})\,dpH \qquad (2\text{-}43b)$$

During the integration of equations (2-43), care must be taken in distinguishing between constants, and the variables to be included under the integral operations. The "General Working Equations (2-44)" result. In equation (2-44a), the second integral represents bound protonated Atrazine, exerting an influence on the unprotonated Atrazine equilibrium function $\bar{K}_0$. It only exists to the extent that the degree of dissociation is less than unity, that is, $\alpha_{1B} < 1$.

$$\bar{K}_0 = \left(\frac{\alpha_{1B}}{x_0}\right)\int_0^{x'} K_0 \, dx_T + \left(\frac{x_T}{x_0}\right)\int_{\alpha_{1B}}^{1} K_0 \, d\alpha_{1B} \qquad (2\text{-}44a)$$

$$\bar{K}_0 = \left(\frac{\alpha_{1B}}{x_0}\right)\int_0^{x_T} K_0 \, dx_T + 2.303\left(\frac{x_T}{x_0}\right)\int_{pH}^{pH'} K_0 \, \alpha_{1B}(1-\alpha_{1B}) \, dpH \qquad (2\text{-}44b)$$

In equation (2-44b), the same effect is described in terms of pH, with pH' being its value at which α_{1B} has effectively become ≈ 1. This will happen at about pH' ≈ 4.0. Correspondingly, the second integral only exists to the extent that pH < pH'. Equation (2-44a) should be useful for molecular level interpretations of the effect on $\bar{K}_0$, of protonating bound Atrazine. On the other hand, equation (2-44b) should be more useful for practical descriptions of pH effects on $\bar{K}_0$.

There are three ways in which K_0 may be calculated, and the choice is determined by the type of experiments to be described. Each type of calculation gives a K_0 having a different chemical meaning.

(a) x_T and α_{1B} both vary

In this case, $\bar{K}_0$ and K_0 are not state functions, but are defined for some particular experimental pathway. From equation (2-24),

$$K_0 = \left(\frac{d(\bar{K}_0 x_0)}{dx_0}\right) = f_0(x_T, \alpha_{1B}) \qquad (2\text{-}26)$$

(b) α_{1B} is constant, and x_T varies

From equation (2-44a),

$$\int_0^{x_T'} K_0 \, dx_T + \frac{x_T}{\alpha_{1B}} \int_{\alpha_{1B}}^{1} K_0 \, d\alpha_{1B} = \left(\frac{1}{\alpha_{1B}}\right) R_0 x_0 \tag{2-45}$$

$$K_0 = \frac{1}{\alpha_{1B}} \left[\frac{\partial (R_0 x_0)}{\partial x_T}\right]_{\alpha_{1B}} \tag{2-46}$$

For some particular value of α_{1B} as a parameter,

$$K_0 = f_0(x_T) \tag{2-47}$$

(c) x_T is a constant, and α_{1B} varies

From equation (2-44a),

$$\left(\frac{\alpha_{1B}}{x_T}\right) \int_0^{x_T'} K_0 \, dx_T + \int_{\alpha_{1B}}^{1} K_0 \, d\alpha_{1B} = \left(\frac{1}{x_T}\right) R_0 x_0 \tag{2-48}$$

$$K_0 = \left(\frac{1}{x_T}\right) \left[\frac{\partial (R_0 x_0)}{\partial \alpha_{1B}}\right]_{x_T} \tag{2-49}$$

For some particular value of x_T as a parameter,

$$K_0 = f_0(\alpha_{1B}) \tag{2-50}$$

pH is an alternate choice of the second variable. From equation

(2-44b),

$$\left(\frac{\alpha_{1B}}{X_T}\right)\int_0^{X_T'} K_0\, dX_T + \int_{pH}^{pH'} K_0\alpha_{1B}(1-\alpha_{1B})\, dpH = \left(\frac{1}{2.303X_T}\right)\bar{R}_0X_0 \qquad (2\text{-}51)$$

$$K_0\alpha_{1B}(1-\alpha_{1B}) = \left(\frac{1}{2.303X_T}\right)\left[\frac{\partial(\bar{R}_0X_0)}{\partial pH}\right]_{X_T} \qquad (2\text{-}52)$$

$$K_0 = \left(\frac{1}{2.303X_T\alpha_{1B}(1-\alpha_{1B})}\right)\left[\frac{\partial(\bar{R}_0X_0)}{\partial pH}\right]_{X_T} \qquad (2\text{-}53)$$

Since $\alpha_{1B} = f_{1B}(pH)$, then for some particular value of X_T as a parameter,

$$K_0 = f_0(pH) \qquad (2\text{-}54)$$

2.2.0 THE COMPLEXING OF PROTONATED ATRAZINE

The approach taken for the derivation of the dissociation function of protonated Atrazine is similiar to that in section 2.1.0 for the unprotonated form. Therefore, only the key starting and final equations for the protonated form of Atrazine will be presented.

$$(AtH^+\text{-}FA) \rightleftharpoons AtH^+ + FA \qquad (2\text{-}55)$$

$$\bar{R}_1 = \frac{M_1C}{M_{1B}} \qquad (2\text{-}56)$$

where $\bar{K}_1$ is the weighted average dissociation function for protonated Atrazine and M_{1B} is the concentration of bound protonated Atrazine. M_1 and C have the same meaning as before. The "General Working Equations (2-57)" are the result of the treatment in section 2.1.0 on the protonated Atrazine case.

$$\bar{K}_1 = \left(\frac{1-\alpha_{1B}}{\chi_1}\right)\int_0^{\chi_T'} K_1 \, d\chi_T + \left(\frac{\chi_T}{\chi_1}\right)\int_{(1-\alpha_{1B})}^{1} K_1 \, d(1-\alpha_{1B}) \qquad (2\text{-}57a)$$

$$\bar{K}_1 = \left(\frac{1-\alpha_{1B}}{\chi_1}\right)\int_0^{\chi_T} K_1 \, d\chi_T - 2.303\left(\frac{\chi_T}{\chi_1}\right)\int_{pH=4.00}^{pH'=0.10} K_1\alpha_{1B}(1-\alpha_{1B}) \, dpH \qquad (2\text{-}57b)$$

where K_1 is the differential dissociation function for the protonated Atrazine and χ_1 is the mole fraction of bound protonated Atrazine. The other symbols in equations (2-57) have the same meaning as before.

In equation (2-57a), the second integral represents bound unprotonated Atrazine, exerting an influence on the protonated Atrazine equilibrium function $\bar{K}_1$. This term only exists to the extent that the degree of protonation is less than unity, i.e., $(1-\alpha_{1B}) < 1$. In equation (2-57b), the same effect is described in terms of pH, with pH' being its value at which $1-\alpha_{1B}$ has effectively become ≈ 1. This will happen at about pH' ≈ 0.10. Correspondingly, the second integral only exists to the extent that pH > pH'. The pH limits for these integrals were taken from Figure (1).

Equation (2-57a) can be made to look similiar to equation (2-44a).

$$d(1-\alpha_{1B}) = -d\alpha_{1B} \qquad (2\text{-}58)$$

Therefore,

$$\bar{K}_1 = \left(\frac{1-\alpha_{1B}}{x_1}\right)\int_0^{x_T'} K_1 \, dx_T - \left(\frac{x_T}{x_1}\right)\int_{pH=4.00}^{pH=0.10} K_1 \, d\alpha_{1B} \tag{2-59}$$

Equation (2-57b) is similiar in form to equation (2-44b).

As with equations (2-57), there are three ways in which K_1 may be calculated. Each type of calculation gives a K_1 which has a different chemical meaning.

(a) x_T and $(1-\alpha_{1B})$ both vary

$$K_1 = \frac{d(\bar{K}_1 x_1)}{d(x_1)} = f_1(x_T,(1-\alpha_{1B})) \tag{2-60}$$

$\bar{K}_1$ and K_1 are not state functions since they depend on some experimental pathway.

(b) $(1-\alpha_{1B})$ is constant, and x_T varies.

From equation (2-59),

$$\int_0^{x_T'} K_0 \, dx_T - \left(\frac{x_T}{x_1}\right)\int_{pH=4.00}^{pH'=0.10} K_1 \, d\alpha_{1B} = \left(\frac{1}{1-\alpha_{1B}}\right) K_1 x_1 \tag{2-61}$$

$$K_1 = \frac{1}{1-\alpha_{1B}}\left[\frac{\partial(\bar{K}_1 x_1)}{\partial x_T}\right]_{(1-\alpha_{1B})} \tag{2-62}$$

For some particular value of $(1-\alpha_{1B})$ as a parameter,

$$K_1 = f_1(x_T) \tag{2-63}$$

(c) x_T is a constant, and $(1-\alpha_{1B})$ varies

From equation (2-59),

$$\left(\frac{1-\alpha_{1B}}{x_1}\right)\int_0^{x_T'} K_1\, dx_T - \int_{(1-\alpha_{1B})}^{1.0} K_1\, d\alpha_{1B} = \left(\frac{1}{x_T}\right)K_1 x_1 \tag{2-64}$$

$$K_1 = -\left(\frac{1}{x_T}\right)\left[\frac{\partial(K_1 x_1)}{\partial \alpha_{1B}}\right]_{x_T} = \left(\frac{1}{x_T}\right)\left[\frac{\partial(K_1 x_1)}{\partial(1-\alpha_{1B})}\right]_{x_T} \tag{2-65}$$

For some particular value of x_T as a parameter,

$$K_1 = f_1\,(1-\alpha_{1B}) \tag{2-66}$$

pH is an alternate choice of $(1-\alpha_{1B})$. From equation (2-57b),

$$\left(\frac{1-\alpha_{1B}}{x_1}\right)\int_0^{x_T'} K_1\, dx_T - \int_{pH=4.00}^{pH=0.10} \alpha_{1B}(1-\alpha_{1B})K_1\, dpH = \left(\frac{1}{2.303x_T}\right)K_1 x_1 \tag{2-67}$$

$$K_1 = -\left(\frac{1}{2.303x_T\alpha_{1B}(1-\alpha_{1B})}\right)\left[\frac{\partial(K_1 x_1)}{\partial pH}\right]_{x_T} \tag{2-68}$$

Since $(1-\alpha_{1B}) = f_{1B}(pH)$, then for some particular value of x_T as a parameter,

$$K_1 = f_1(pH) \qquad (2\text{-}69)$$

The unprotonated (K_0) and protonated (K_1) equilibrium functions derived here will be used to interpret the experimental results in Chapter 4. Since K_{1B} (equation (2-8)) will be assumed to be equal to K_a (equation (1-2)), then, the values that will be calculated for K_0 and K_1 in Chapter 4 will not be significantly different.

CHAPTER 3

EXPERIMENTAL

3.0.0 EQUIPMENT

3.0.1 pH METER

The pH meter used for pH adjustments was a Metrohm E300B instrument. It was equipped with a Fisher EA120-UX glass combination electrode.

3.0.2 POTENTIOMETER

Potentiometric measurements were made with a Concordia model 25A 5B digital meter using a Beckman number 41263 calomel glass electrode in combination with an Orion model 94-29A cupric ion selective electrode.

3.0.3 SHAKER

A mechanical shaker made by Eberbach Corporation was used to agitate the samples for 72 hours. It was also used in extraction of Atrazine from an aqueous media with benzene.

3.0.4 ATOMIC ABSORPTION SPECTROPHOTOMETER

A Perkin Elmer Flame Absorption instrument, model number 503, equipped with a Copper Hollow Cathode lamp was used to analyse total copper concentrations in samples. The wavelength used for analysis was 3247Å.

3.0.5 ULTRAFILTRATION STIRRED CELLS

An Amicon Ultrafiltration Stirred Cell, model 8050, was used for binding studies in the Batch Ultrafiltration Technique and the Model 8010 cell was used for binding studies in the Continuous Flow Ultrafiltration

Technique. Both techniques will be described later in the thesis.

Both methods used UM2 or YM2 membranes which had a molecular weight cutoff of 1000. Before use, each membrane was soaked in distilled water for at least one hour and then it was washed three times with fresh distilled water. The membrane was then mounted in its respective cell and conditioned by passing through approximately 25 millitres of 1.000 gm per litre of FA. The membrane was then ready to be used for binding studies by either technique. Conditioning was only done so as to make sure that the first sample in a batch was filtered through a membrane similiar to the other samples in the batch, i.e., a membrane which had FA solution previously passed through it. When a conditioned membrane was not in use it was stored in a 70% ethanol solution.

3.0.6 FRACTIONATING COLLECTOR

The eluate from the continuous flow method, which will be described later, was collected at ten minute intervals on a B. Braun Mekungen fractionating collector. The volume of each fraction was determined by taking the difference between the final weight of each partially filled test tube and the original weight of the empty test tube.

3.0.7 STIRRING PLATE

A Fisher model number 14-511-2 stirring plate was used to rotate the magnetic bar in the Amicon Stirred Cells. In order to prevent heat transfer to the cell a two centimeter thick piece of wood was covered with Whatman Filter paper and placed between the cell and the stirring plate. A one inch air gap was then left between the covered wood and the cell.

3.0.8 ROTARY EVAPORATOR

The solvent for each fraction of eluate collected was removed by a Buchi rotary evaporator. A water bath heated at 50°C was used to hasten the removal of benzene. The same bath heated at 65°C was used to remove water with the rotary evaporator.

3.0.9a GAS CHROMATOGRAPHY

The concentrations of unprotonated Atrazine were monitored with a Shimadzu Gas Chromatograph, Series GC 6-AM. An Electron Capture Detection system was used since nanogram levels of herbicide were being detected. Table (2) gives the experimental conditions for detecting the herbicide.

The carrier gas, nitrogen, was made free of contaminants (water vapor and large organic molecules) by passing it through molecular sieve and a drying agent.

3.0.9b GLC COLUMN PREPARATION

It has been well established that the response and resolution of a compound analysed by Gas Liquid Chromatography depends on many experimental parameters (44). However, one of the most important parameters which seems to affect response in a packed column is the liquid phase used to coat the solid support. Gamble et al. (45) used a column packed with 3% Carbowax 20M on Chromosorb W-HP to analyse for Atrazine. A similiar column was made to analyse for Atrazine, but, it was found to cause tailing of the compound and, hence, prevent accurate determination of peak area. Another column made of 3.5% OV-17 coated on Chromosorb W-HP gave more symmetrical Atrazine peaks and a better response. Both columns were prepared by the evaporative method (46,47).

Table (2): GLC experimental conditions for the analysis of Atrazine with an ECD.

Parameters	Conditions
Column	Single 4 ft x 1/8" stainless steel with 3.5% OV-17 on 80/100 mesh support.
Column Temperature	190 deg. C
Detector Temperature	260 deg. C
Injection Port Temperature	260 deg. C
Carrier Gas and Flow Rate	Nitrogen gas at 60 mls/min.
Attenuation *	4×10^2
Pulse	20 microsecond
Injection Type	10 µl Hamilton syringe onto insert liner (glass)
Sample	3 to 100 nanogram of Atrazine in methanol
Recorder	Fisher Scientific 5000 recorder operating at a speed of 1 in/min.

*----- Sensitivity of the instrument.

0.70 gram of OV-17 (or Carbowax 20M) was dissolved in 150 mls of toluene with stirring at room temperature. To the solution was added 20 grams of support material, slowly, with careful stirring. The mixture was allowed to stand at room temperature for ten to fifteen minutes with intermittent stirring. The beaker containing the mixture was placed on a warm hot plate (about 60 deg. C) under a stream of nitrogen gas so as to remove the toluene by evaporation. During the removal of the toluene the beaker was swirled so as to maintain uniform coverage of the particles. After

the solvent had been removed and the particles became free flowing, the contents of the beaker was gently poured onto a large watch glass, spread out, and left overnight to remove any traces of solvent.

A 4 ft x 1/8" o.d. stainless steel tube was then cut, plugged at one end with silanized glass wool and packed with the prepared packing. During the packing of the column, tapping the sides of the column was necessary in order to make the particles settle compactly without leaving any voids. The open end of the column was plugged with silanized glass wool. The column was then fitted with ferrules and placed in the Shimadzu Gas Chromatograph oven and conditioned overnight at 270 deg. C with carrier gas (nitrogen) flowing through at a rate of 60 mls per minute. After conditioning for more than 24 hours, the column was ready for use (46).

During the course of the project, four OV-17 columns had to be prepared because they deteriorate after about twenty five experimental runs (47).

3.1.0 GLASSWARE

50-ml conical flasks were used to equilibrate the Atrazine-FA solutions. Black #8 rubber stoppers were used to retain the solution in the flask.

The volume of each solution to be added in an equilibration study was measured with 10 or 50-ml Kimax burettes.

60-ml glass stoppered separatory funnels were used in the extraction process for Atrazine. Kimax 20-ml test tubes were calibrated for 10-ml volumes so as to collect fractions for the Batch Ultrafiltration Technique.

Since Atrazine is an organic compound it is very easy for it to be

contaminated with other organics. If these organics have the same retention times as Atrazine, then, the chromatogaphic peak of Atrazine will be obscured. The glassware was soaked overnight in regular laboratory detergent, soaked for ten minutes with chromic acid, rinsed several times with distilled water, rinsed with deionized water, and, then, dried in an oven at 110°C.

3.2.0 REAGENTS

3.2.1 BENZENE

The benzene used had to be of the highest quality since trace levels of Atrazine were being determined. Accusolv Grade benzene (GD-995) purchased from Anachemia satisfied the Gas Chromatographic requirement.

3.2.2 METHANOL

Methanol was used as a solvent to inject Atrazine into the Gas Chromatograph. Anachemia Accusolv Grade (GD-5730) met the requirements for the GC analyses.

3.2.3 WATER

Nanopurified water was used throughout this project. Distilled water was passed through a Barnstead nanopure column.

3.2.4 STANDARD COPPER (II) SOLUTION

15.8850 gm of copper wire was weighed into a 250-ml beaker. 20 ml of 6N HNO_3 was added to the beaker which was then heated until all the copper was in solution. 50 ml of water was, then, added to the dissolved copper. The solution was allowed to come to room temperature and, then, filtered through a Whatman 42 paper into a 500-ml volumentric flask. The flask was made up to the mark with nanopurified water. The resulting solution

had a concentration of 0.500 M copper. This solution was used for binding studies with FA.

3.2.5 STANDARD SODIUM HYDROXIDE SOLUTION

2.08 gm of sodium hydroxide pellets was weighed into a 125-ml Erlenmeyer flask. 10 ml of nanopure water was promptly introduced into the flask which was, then, swirled to hasten the solution of the base. 50 ml of water was further added to the solution which was allowed to cool to room temperature. The base was filtered through Whatman number 42 paper into a 1000-ml volumetric flask which was then diluted to the mark with nanopure water.

Potassium hydrogen phthalate, $KHC_8H_4O_4$, was dried for 2 hours in an oven at 110°C and then cooled in a desiccator. Three samples (accurately weighed to the nearest 0.5 mg), between 0.35 gram to 0.45 gram were placed into 250-ml Erlenmeyer flasks and dissolved with 30 ml nanopure water. 2 drops of phenolphthalein indicator was added to each flask which was, then, used to standardize the sodium hydroxide. The average concentration of the prepared base was 0.0503 M.

The reagents used in the project are described in Table 3.

3.2.6a AQUEOUS ATRAZINE STOCK SOLUTION

Pure Atrazine is an amorphous white solid with a m.p. range of 175-177°C; the vapour pressure at 20°C is 3.0×10^{-7} torr; at 25°C and a pH of 7.0, Atrazine has a solubility of 35 ppm in water; Atrazine is much more soluble in alcohols than in water (48,49). This compound was purchased pure (Table (3)) so there was no need for further purification.

Approximately 0.0940 gram of Atrazine was weighed out in a 25-ml

Table (3): Reagents used in the project

Reagent	Source	Concentration or form of use	Application
Atrazine (99.9% pure)	Poly Science Corp.	10^{-4} M	Standard solution
Potassium Chloride(A.R.)*	Fisher	Saturated solution	Filling glass electrode
Sodium Nitrate(A.R.)	Fisher	0.10 M	Electrolyte
Sodium Hydroxide(A.R.)	Fisher	1.0 M and 0.0503 M	Adjust pH and titration of FA
Hydrochloric Acid(A.R.)	Fisher	1.0 M	Adjust pH
Benzene (Pesticide Grade)	Anachemia	Neat	Extraction of Atrazine
Methanol	Anachemia	Neat	Solvent for injecting Atrazine into GC.
OV-17 (Nº 49211)	Pierce Chemical Co.	3.5 %	Used as liquid phase on GC column support
Chromosorb W-HP	Johns-Manville Corp.	Solid particles (80/100 mesh)	Used as support material in GC column
Buffers	Fisher	pH 4.00 and pH 7.00	Calibrate pH electrode
Copper Metal (99.9% pure),	Fisher	0.5000 M and lower	Standard solution
Ethanol (95%)	Fisher	70%	Used for washing Amicon YM2 and UM2 membranes
Toluene (Pesticide Grade)	Anachemia	Neat	Used for preparing column packing for GC
Nitric Acid (A.R.)	Fisher	6 M	Used to prepare standard copper solution

* --- Analytical Reagent.

beaker. The Atrazine was transferred to an Erlenmeyer flask which contained 4 litres of nanopure water heated to 55°C. The mixture was stirred for, at least, four hours with a magnetic bar at 55°C, after which time all the Atrazine will have been solubilized. The heat was removed and the Atrazine solution was stirred overnight at room temperature. The solution had an approximate concentration of 1.1×10^{-4} M with respect to Atrazine. Other stock solutions of Atrazine were similarly prepared.

This stock solution of Atrazine was used in equilibrium binding experiments between Atrazine and fulvic acid.

3.2.6b METHANOLIC ATRAZINE STANDARD SOLUTION

0.01000 gram of Atrazine was accurately weighed out on a Mettler balance and quantitatively transferred to a 100-ml volumetric flask. The contents were diluted with pesticide grade methanol. Atrazine was dissolved by shaking the flask until no more particles were seen. This solution contained exactly 100 nanogram Atrazine per microlitre of methanol (100 ng/µl).

Taking exactly 0.50, 1.50, 4.00, 7.50, 10.00 and 15.00 millilitres of the 100 ng/ul Atrazine stock solution and diluting it to 50.00 ml with pesticide grade methanol give concentrations of 1.00, 3.00, 8.00, 15.00, 20.00 and 30.00 ng/ul of Atrazine respectively. These standards were used in the GC method for the quantitative determination of Atrazine. Every three weeks new standard solutions were prepared even though the half-life for Atrazine is 116 years at pH 7 and 20°C (1).

3.2.6c ATRAZINE SPECIES IN AQUEOUS SOLUTION

Two species of Atrazine exist in aqueous solution in the pH range that will be studied in this project (1).

15.00 ml each of Atrazine stock solution prepared in Section 3.0.6a was added to fourteen Erlenmeyer flasks. Each flask was diluted to 45.00 ml with nanopure water and its pH adjusted with 0.1 M acid or 0.1 M base. More water was added to each flask in order to obtain a total volume of 50.00 ml. The pH range of the samples was from one to ten. The flasks were stoppered securely, packaged in boxes, and shaken at room temperature for 72 hours.

10.00 ml fractions of each sample were collected after passing through the Batch Ultrafiltration apparatus (described later). Each fraction was extracted quantitatively with 40.00 ml of pesticide grade benzene. 25.00 ml of each extract was placed in a round bottom flask and distilled on the rotary evaporator. The residue was cooled to room tmeperature and it was taken up in exactly 3.00 ml of pesticide grade methanol.

GC was used to analyse the residue for Atrazine. A calibration curve was prepared with the standards in Section 3.2.6b and the exact amount of Atrazine in each sample was determined. The result of an experiment is described in Section 4.0.1 of Chapter 4.

3.2.7a PREPARATION OF FULVIC ACID

Fulvic acid was prepared by K. Roach according to the standard procedure described in reference (50). The preparation is the following:

The fulvic acid was extracted from the Bh horizon of a podzol soil which was obtained from Armadale, Prince Edward Island, Canada. Fulvic acid from this location has been used by Schnitzer et al. (51,52) and Gamble (29) for characterization purposes and metal ion binding studies (53).

2 kg of air dried soil was extracted with 20 litres of 0.5 M NaOH solution under inert conditions (N_2 atmosphere). The extract was allowed

to stand overnight in a dark room at 5°C with occasional shaking. The insoluble material was removed by settling and centrifugation for 30 minutes at 2000 rpm. The soluble material was kept under nitrogen atmosphere at 5°C until it was ready to be purified.

Two columns filled with Dowex 50W cation-exchange resin (20-50 mesh) were used to obtain fulvic acid from the alkaline extract (50). The first column which was bigger was used as a roughing column whereas the second column was used as a finishing column. The eluate from the larger column was led to the head of the finishing column. During the purification process both the alkaline extract and the eluate from the second column were kept under nitrogen atmosphere.

The eluate flow rate was maintained at one drop per second. When the pH of the eluate became greater than seven, the columns were regenerated with 1.0 M HCl. Complete removal of Na^+ and Cl^- ions from the regenerated columns were ascertained by carrying out a flame test for Na^+ and a $AgNO_3$ test for Cl^-.

The purification of fulvic acid was complete when the iron content in the eluate was less than 10^{-2} mmoles/gm of FA. If the eluate had a greater concentration of iron than was expected, then, it was recycycled in the finishing column until the desired amount was obtained.

The purified FA solution was freeze-dried to obtain the brown powder of FA. This batch of fulvic acid was given a call number of FA8.

3.2.7b POTENTIOMETRIC TITRATION OF FULVIC ACID

0.1000 gm of the FA8 fulvic acid was dissolved in 50.00 ml of nanopure water. To the 250-ml beaker containing the solution was added a stirring bar. The beaker was mounted on a stirring plate and a pH electrode

was introduced into the fulvic acid solution. The lead of the electrode was connected to a Metrohm pH meter which, then, monitored both the pH and the voltage of the solution as standard 0.0503 M NaOH was added to the beaker. For every addition of standard base the corresponding pH and millivolt reading was recorded. During the course of the titration constant stirring was maintained and three minutes was allowed between each addition of base before a reading was taken. The result from this experiment is described in Section 4.0.2 of Chapter 4.

3.2.7c FULVIC ACID STOCK SOLUTION

(i) 0.7692 gm of FA was dissolved in 25 ml of nanopure water. The solution was transferred quantitatively to a 100-ml volumetric flask. The flask was carefully made up to the mark with water. The solution was allowed to stand for 2 days so as to make sure that all FA particles were dissolved. This solution was then used in the Continouous Flow Ultrafiltration Method (CFUM).

(ii) 2.0000 gm of FA was dissolved in 60 ml of nanopure water and transferred quantitatively to a 100-ml volumetric flask. The flask was diluted to mark with water and then transferred to a clean 100-ml brown bottle. This solution was allowed to stand for 2 days before use in the Batch Ultrafiltration Method (BUM).

3.3.0 BATCH ULTRAFILTRATION METHOD

The apparatus and procedure for the Continuous Flow Ultrafiltration Method (CFUM) will be described in Chapter 5. After extensive preliminary work, a Batch Ultrafiltration Method (BUM) was developed for binding studies. This technique is more time consuming than CFUM but, the results obtained

from it are more reproducible. In the BUM, one has a greater control of the experimental parameters (pH, metal ion concentration, ionic strength, time of equilibration for each concentration of Atrazine, etc.). The greatest disadvantage of the BUM is that it utilizes five to seven times more FA (depending on the number of samples prepared) than the CFUM.

3.3.1 PREPARATION OF BUM SAMPLES

A general outline of the BUM is as follows: fixed amounts of FA are added to 50-ml Erlenmeyer flasks with a 10-ml burette. Other reagents which have to be added in constant amounts to each flask (KCl, Cu^{2+}, etc.) are introduced quantitatively with 25-ml burettes. The Atrazine titrant is then added to each flask with a 50-ml burette. The volume of each sample is adjusted to 45.00 ml with nanopure water which is measured with a 50-ml burette. 1.0 M HCl or 1.0 M NaOH is added to each sample so as to obtain the desired pH of the experiment. The pH of the samples are monitored with the Metrohm pH meter which is calibrated with buffers of pH 4.00 and 7.00. The amount of base or acid added to each sample is measured exactly (to the accuracy of the 10-ml burettes). The samples are diluted to 50.00 ml with more nanopure water and, then, stoppered securely with black #8 rubber stoppers.

The same procedure as above is repeated for control samples. The only component that is missing in these controls is the FA solution. In all of the initial experiments done by the BUM there were corresponding controls. However, once the method had been established, only half the number of controls compared to samples were run.

Both the controls and the samples were packaged securely into carton boxes and oscillated for 72 hours on the shaker at room temperature.

3.3.2 BUM FILTRATION APPARATUS

Figure (6) illustrates the BUM filtration apparatus that was used to filter the equilibrated samples described in Section 3.3.1. The filtration cell was assembled as directed in the operation manual (54) with a YM2 membrane (Section 3.0.5). An FA sample was quantitatively transferred to the cell and the magnetic stirrer was turned on to 35 cycles/second. 10.00 ml of the sample was forced out of the cell at a helium pressure of 40 lb/in^2; the flow rate was, on the average, 10 ml per hour. After ten millilitres filtrate was collected from the sample, the cell was dismounted and the FA solution in the cell was used to condition membranes for future experiments. The cell was washed and dried and remounted with a control sample and again 10.00 ml was filtered off by the procedure above. The alternating filtration process of FA sample and control sample was repeated until all the samples of the experiment were completed.

The filtrates from the samples were almost free of FA since they were clear rather than yellow which is an indication of the presence of FA. Kwak et al. (55), also, found that these membranes almost completely reject fulvic acid and sodium fulvate.

By filtering off 20% of each equilibrated solution, the assumption is made that the equilibrium of the complex formed is not shifted significantly by change in dilutions. The ten millilitres of filtrate represent one fifth of the free Atrazine that exists in an equilibrated solution. The smaller the volume of filtrate taken the smaller the shift in equilbrium and, hence, the more true will be the measure of the equilibrium. However, in all equilibrium studies for weak binding complexes, there are always instrumental detection problems. This problem is enhanced tremendously if

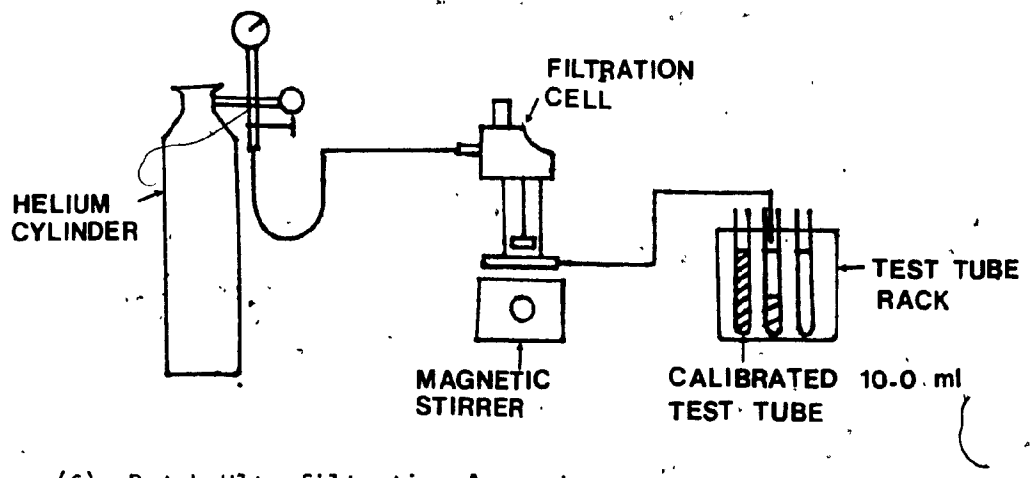


Figure (6): Batch Ultrafiltration Apparatus.

the titrant is insoluble in water-as is the case with Atrazine. In preliminary experiments it was found that a smaller fraction of filtrate gave Atrazine concentrations that fell below the linear detectable range of the GC used. Collecting fractions smaller than 10.00 mls was therefore avoided. The stability constants calculated from BUM experiments can, therefore, be termed apparent values. However, equilibrium shifts are typical for separation methods Section 1.3.0 and reference (18). Non-separation methods suffer less from equilibrium shifts, but their instrumentation is expensive and, hence, not available.

3.3.3 DETERMINATION OF ATRAZINE AND COPPER IN FILTRATE

(a) ATRAZINE

For experiments in which free Atrazine was sought, the work up procedure was as follows: the 10.00 ml filtrate was transferred to a 65-ml separatory funnel and it was extracted quantitatively with 40.00 ml pesticide grade benzene (preliminary work indicated that greater than 92% of Atrazine was extracted with this amount of benzene). Quantitative extraction meant placing the separatory funnels in a well secured carton

box which was then shaken vigourously for one hour on the shaker. Because a distinct layer was not formed between the aqueous and organic layers in some cases and also because of the possibility of water contamination, 20.00 ml of the benzene extract was pipetted out of the funnel and transferred to a 100-ml round bottom flask. The benzene in the extract was removed on the rotary evaporator and the residue in the flask was allowed to cool to room temperature. Each sample was taken up in 3.00 ml of pesticide grade methanol.

The Atrazine in the residue was analyzed for by GC using the conditions in Table (2). First, a calibration curve was prepared with the Atrazine standard solutions in Section 3.2.6b, then, the sample solutions were injected. The amount of Atrazine in each sample was determined by taking the area of the Atrazine peak and interpolating it on the calibration curve. Figure (7) shows a typical chromatogram with peak A representing the solvent (methanol); peak B is an impurity present in the solvent; and peak C is the Atrazine peak corresponding to 45 nanogram of the herbicide. Figure (8) shows a typical Atrazine calibration curve with peak area (square millimetres) plotted against nanograms of Atrazine. The least square fit for the straight line give values of 121 for the slope, 412 for the intercept and .996 for the correlation coefficient.

All experiments carried out below a pH of 4.0 had their filtrates adjusted to between pH 4.0 and pH 7.0, except where otherwise stated. Above pH 4.0, all Atrazine species exist in the unprotonated form and, hence, can be extracted with benzene. The protonated Atrazine species is not extractable with benzene since it is a charged species.

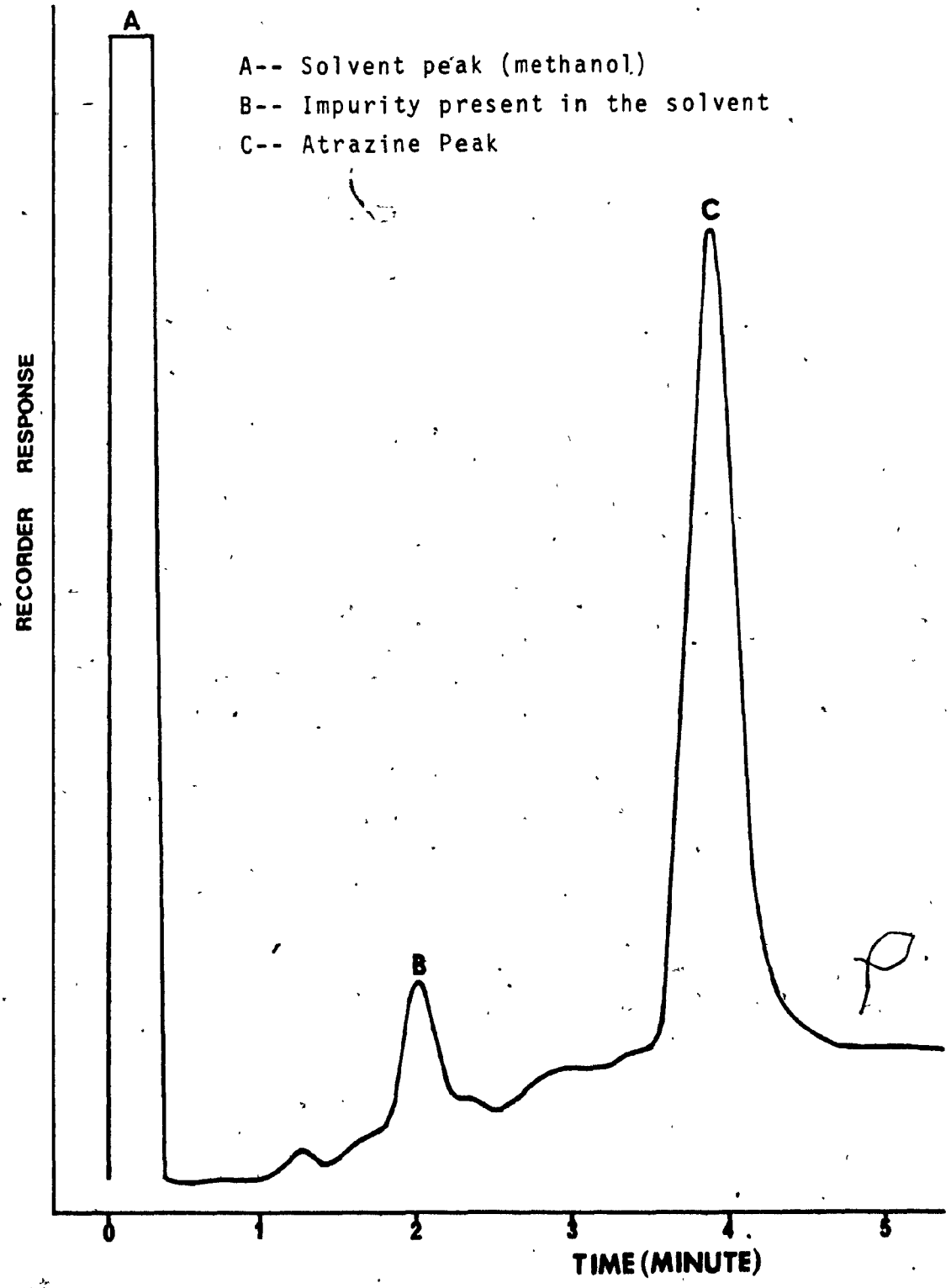


Figure (7): Typical Atrazine gas chromatogram. Peak C corresponds to 45 nanograms of Atrazine.

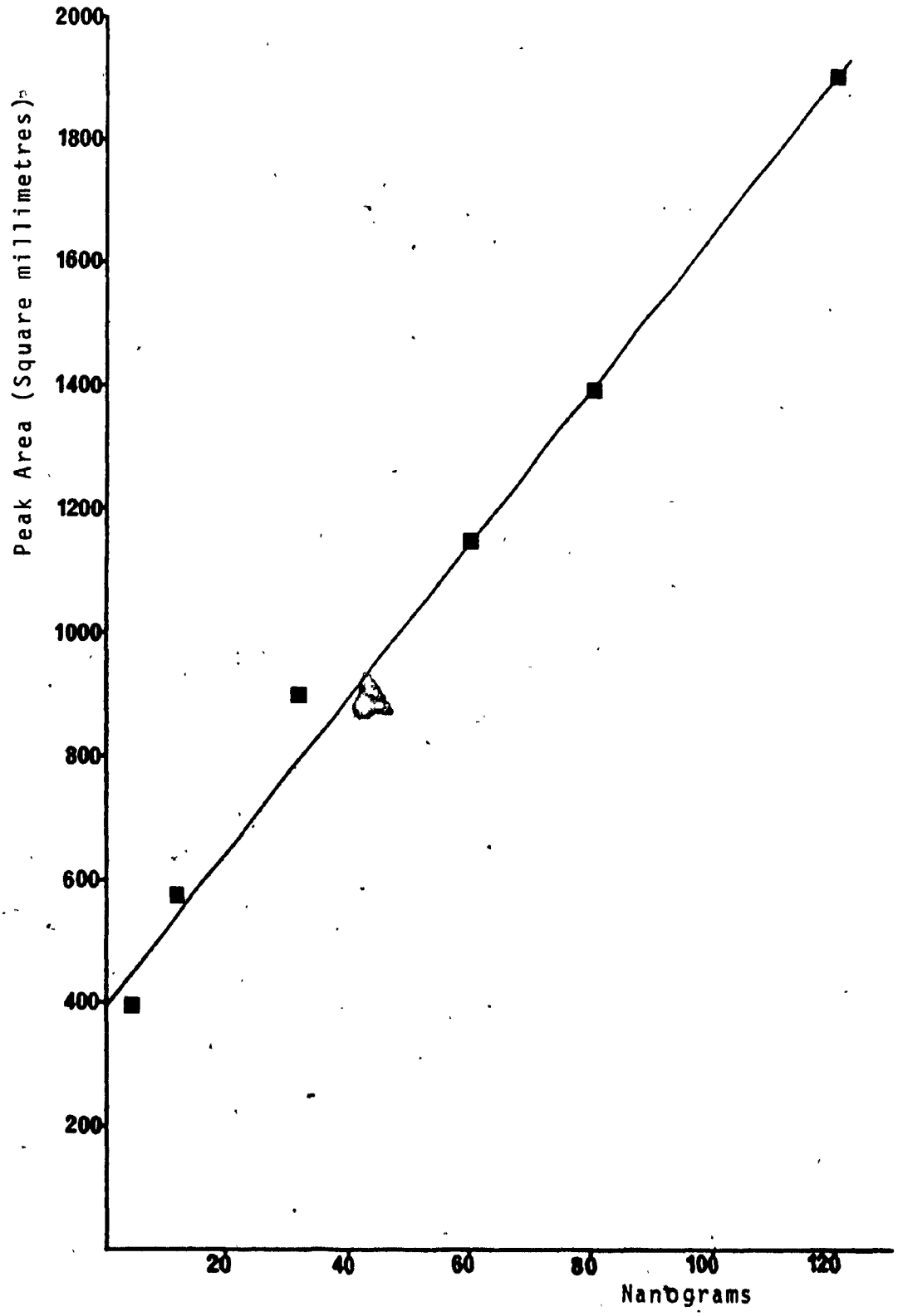


Figure (8): Typical calibration curve for Atrazine determination.

(b) COPPER

In filtrates for which both Atrazine and copper had to be analyzed, the extraction procedure described in part (a) was carried out first on the ten millilitres of filtrate. Atrazine was determined from the organic layer. Aliquots of the aqueous layer were used to analyze for total copper. In experiments which had a small range of copper concentrations, atomic absorption spectroscopy (AAS) was used to determine total copper. For experiments which had a large range of copper concentrations, a copper ion selective electrode, (ISE), was used to determine total copper.

(i) Determination of Copper by AAS.

Copper was analyzed at a wavelength of 3247 Å. The linear range for this wavelength using the Model 503 Flame AAS was 0 to 5 ppm. The concentration of copper in the sample filtrates was too high to be determined directly. Therefore aliquots of the filtrates were taken and diluted to 100 ml in a flask.

Using the 0.5000 M Cu^{2+} stock solution prepared as described in Section 3.2.4, standards containing 1.00, 2.00, 3.00, 4.00, and 5.00 ppm Cu^{2+} were made. These standards were compared with the copper standards purchased from Fisher Scientific; they were not significantly different.

Absorbance readings were taken for samples and standards on the AAS. A calibration curve was made with the standards and the concentrations of copper in the samples were calculated from the curve.

(ii) Determination of Copper by ISE.

Standards containing 0.048, 0.100, 0.477, 1.00, 3.18, 6.36, 10.0, and 20.0 ppm of Cu^{2+} and a background electrolyte concentration of 0.10 M $NaNO_3$

were prepared to obtain a calibration curve.

Aliquots of the aqueous layer of the filtrate of an experiment were added to 100-ml volumetric flasks. 2.00 ml of 5.0 M $NaNO_3$ was added to each flask which was, then, diluted to mark with nanopure water.

The potentiometer, copper selective electrode, and saturated calomel electrode described in Section 3.0.2 were assembled to determine the potentials of the standards and the samples. A plot of millivoltage reading versus the logarithm of the concentration of each standard was made and the concentration of the copper in each sample was, then, determined by interpolation (56).

3.3.4 BUM PROCEDURES

(a) Atrazine variation at constant pH and low ionic strength.

Table (4) gives the experimental conditions for the binding of Atrazine onto FA at pH 1.36. The FA sample #1 was prepared by the addition of the following reagents to a 50-ml Erlenmeyer flask: 5.00 ml Atrazine stock solution (Section 3.2.6a); 2.50 ml FA stock solution (Section 3.2.7c (ii)) giving a final concentration of 1.000 gm per litre; 40.00 ml nanopure water; and 2.50 ml of 1.0 M HCl. It is significant to note that the exact amount of acid or base needed for a particular pH was determined by preliminary tests. For cases in which the desired pH values had been overstepped, acid or base was added to the solution until the correct value was obtained, and appropiate volume corrections were made so as to still obtain a total volume of 50.00 ml. The remaining samples in Table (4) were similarly prepared and, then, they were subjected to the operations described in Sections 3.3.1 to 3.3.3.

Table (4)[a,b,c,d]: Values for Atrazine variation experiment at pH 1.36.

Fulvic Acid Solution			Control Solution	
#	Vol. of Stock Atrazine (ml)	Vol. of H_2O (ml)	Vol. of Stock Atrazine (ml)	Vol. of H_2O (ml)
1	5.00	40.00	5.00	45.00
2	7.50	37.50		
3	10.00	35.00	10.00	40.00
4	12.50	32.50		
5	15.00	30.00	15.00	35.00
6	20.00	25.00	20.00	30.00
7	22.50	22.50		
8	25.00	20.00	25.00	25.00
9	32.50	12.50		
10	37.50	7.50	35.00	15.00
11	40.00	5.00		
12	42.50	2.50		
13	45.00	0.00	45.00	5.00

a- Each FA sample had 2.50 ml of a 2.000 gm FA/100 ml solution.

b- The pH of each FA sample was adjusted to 1.36 with 2.50 ml of 1.0 M HCl.

c- The total volume of each sample was 50.00 ml.

d- The pH of the FA samples after equilibrium were 1.36.

The calibration curve for the Atrazine standards in Section 3.2.6b was fitted by linear regression to a straight line. The equilibrium concentrations for the total Atrazine in both the FA samples and the control samples were obtained by interpolating on the regression line. Similiar experiments were carried out at pH values of 1.72, 2.28, 2.77, 3.21, 3.50, 4.50, 6.00, and 8.00. The results of these experiments are described in Section 4.0.3 of Chapter 4.

(b) Atrazine variation at constant pH in the presence of 0.10 M KCl.

These experiments were designed and carried out in a similar fashion to those in Section 3.3.4a. The only exception was the addition of an electrolyte to the solutions so as to do binding studies in a high ionic strength medium.

2.00 ml of 2.50 M KCl was added to each solution. The final concentration of KCl in the solutions was 0.100 M. At low pH values (below pH 2) in the presence of the KCl there was visible precipitation of FA in the solutions; above a pH value of 2.6 in the high ionic media there was no visible precipitation of FA in solution.

Experiments were carried out at pH values of 1.27, 1.83, 2.77, 3.82, 4.55, 5.45, 6.48, 7.62, 8.49 and 10.25. The results for these experiments are described in Section 4.0.4 of Chapter 4.

(c) Effect of FA concentration on Atrazine binding at a pH value of 3.50.

These experiments were designed in the same way as those in Section 3.3.4a except that varying amounts of FA were used. Five concentrations of FA were studied - 0.2000, 0.4000, 0.6000, 0.8000, and 1.000 gm/litre. The results for these experiments are described in Section 4.0.5 of Chapter 4.

(d) Effect of FA concentration on Atrazine binding at a pH value of 3.50 in the presence of 0.100 M KCl.

These experiments were of similar design to those in Section 3.3.4c except that a higher ionic strength medium was used. FA concentrations of 0.2000, 0.4000, 0.6000, 0.8000, and, 1.0000 gm/litre were studied in the presence of 0.100 M KCl. The results for these experiments are also described in Section 4.0.5 of Chapter 4.

(e) Atrazine variation at constant pH in the presence of copper (II).

These experiments were designed to find out how FA aggregation affected the binding of Atrazine. The design was similar to that described in Section 3.3.4a except that constant amounts of copper(II) were added in each experiment and the amount of Atrazine was varied. Table (5) has the initial and final copper (II) concentrations for each experiment and their respective pH values.

Table (5): Equilibrium copper (II) concentration at different pH values.

pH	Initial Cu(II) Concentration (mole/litre) x 10^3	Final Cu(II) Concentration (mole/litre) x 10^3	Amount of Cu (II) bound (mole/litre) x 10^3
1.19	1.074	0.940	0.134
1.38	4.696	4.022	0.674
2.14	4.896	3.871	1.025
2.38	1.036	0.596	0.440
3.02	4.692	3.182	1.510
3.96	4.613	2.013	2.600
4.04	4.619	1.810	2.809
5.23	4.949	1.111	3.838

The uncomplexed copper in each solution was determined by the AAS procedure described in Section 3.3.3b(i). The results for these experiments are described in Section 4.0.6 of Chapter 4.

(f) Copper (II) variation at constant pH in the presence of a constant amount of Atrazine.

In these experiments FA was titrated with copper (II) in the presence of a constant amount of Atrazine. Duplicate experiments were carried out at a pH value of 3.86. A FA concentration of 0.1000 gm/litre was used

Table (6)[a]: Design of a pH variation experiment. Total volume = 50.00 ml.

	FA Solution				Control Solution			
#	pH	1.0 M HCl(ml)	1.0 M NaOH(ml)	H_2O	pH	1.0 M HCl(ml)	1.0 M NaOH(ml)	H_2O
1	0.99	8.00	--	24.50	1.12	6.00	--	29.00
2	1.08	6.00	--	26.50	1.28	4.00	--	31.00
3	1.22	4.00	--	28.50	1.52	2.00	--	33.00
4	1.49	2.00	--	30.50	1.80	1.00	--	34.00
5	1.75	1.00	--	31.50	2.09	0.50	--	34.50
6	2.00	0.50	--	32.00	2.38	0.25	--	34.75
7	2.80	0.00	--	32.50	2.61	0.15	--	34.85
8	3.14	--	0.50	32.00	2.74	0.10	--	34.90
9	3.72	--	1.00	31.50	3.08	0.05	--	34.95
10	4.50	--	1.50	31.00	5.75	0.00	--	35.00
11	5.28	--	2.00	30.50	8.78	--	0.05	34.95
12	6.53	--	3.00	29.50	9.50	--	0.01	34.90
13	9.38	--	5.00	27.50	9.77	--	0.15	34.85
14	10.15	--	7.00	25.50	9.95	--	0.20	34.80

a -- 2.50 ml of a 2.0000 gm/100ml of FA solution was added to each sample.

instead of 1.0000 gm/litre. The uncomplexed copper in each sample was determined by the ISE procedure in Section 3.3.3b(ii). The results from these experiments are described in Section 4.0.7 of Chapter 4.

(g) pH variation for constant Atrazine.

In these experiments a constant amount of stock Atrazine (15.00 ml) and FA (2.50 ml of 2.0000 gm/litre) was used in each sample. The pH values for an experiment were varied with acid or base and the volume of each flask was adjusted to 50.00 ml with water. Table (6) gives a typical experimental design. These experiments were worked up in the same way as those in Section 3.3.4a. The results for these experiments (triplicate) are described in Section 4.0.8 of Chapter 4.

(h) pH variation for constant Atrazine in the presence of 0.100 M KCl.

These experiments were designed in a similar fashion to those in Section 3.3.4g. The only exception was that 2.00 ml of a 2.50 M KCl was added to each solution. The filtrate from each sample was adjusted to pH values of between 4 and 6 before they were worked up as in Section 3.3.4a. The results from these experiments are described in Section 4.0.9 of Chapter 4.

CHAPTER 4

RESULTS AND DISCUSSION

4.0.0 RESULTS

The results for each experiment done in Chapter 3 will be described here. An integrated interpretation and discussion of all experimental results, taken together with relevant literature results will be given in Section 4.1.0.

4.0.1 EFFECT OF pH ON ATRAZINE SPECIATION

The pH variation study done in Section 3.2.6c on the extraction was to confirm how many species of Atrazine exist in aqueous solution. The solid line in Figure (9) represents the concentration of unprotonated Atrazine (M_0) recovered at each pH. The dashed line in the same figure represents the concentration of unprotonated Atrazine which can be theoretically obtained (equation (1-6) of Chapter 1) from the equilibrated Atrazine solution in the experiment ($M_T = 2.30 \times 10^{-5}$ M). Both the experimental and theoretical curve show the appearance of monoprotonated Atrazine (M_1) at a pH value of about 3.10. Below pH 3.10, the present experimentally determined unprotonated Atrazine was generally higher than the theoretically calculated unprotonated Atrazine.

At pH values between 7.00 and 1.90 the error bars in the experimental curve of Figure (9) are in the range of the theoretical curve. However, at lower pH values the error bars are outside the range of the theoretical curve. There is one plausible explanation for the observed difference. Unexpectedly high concentration of unprotonated Atrazine could be due to an experimental deficiency, i.e., in the extraction procedure described

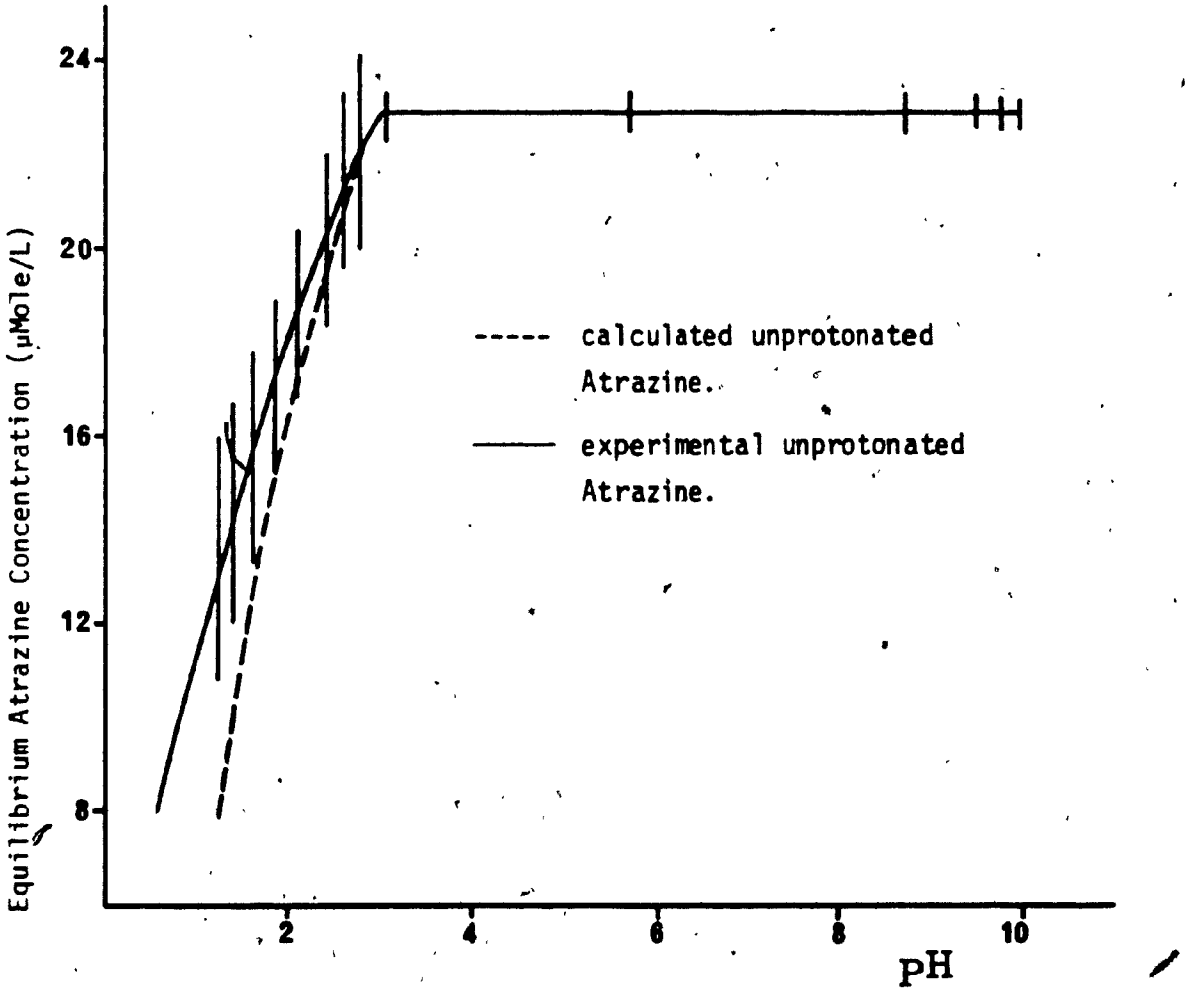


Figure (9): Unprotonated Atrazine as a function of pH. The stoichiometric concentration of the reagent was 23.00 μMoles/Litre.

in Section 3.2.6c, the equilibrium described in reaction (1-1) (Chapter 1) will be shifted to the right as unprotonated Atrazine is extracted from the aqueous layer; hence, more than the theoretical amount of unprotonated Atrazine will be observed in an experiment of this kind.

From the distribution diagram in Figure (1) of Chapter 1, it can be seen that the fraction of Atrazine monoprotonated, $(1-\alpha_{1B})$, starts at a pH value of about 4. The region of the curve (Figure (1)) between pH values of 3.1 and 4 indicates a very small amount of monoprotonated species is

present. It was difficult to detect any significant amount of monoprotonated species in solution between these pH values for the experiment in Figure (9). For example, the amount of Atrazine protonated between pH 3.1 and 4 is less than 3% which is within the experimental error indicated in Figure (9). Hence, monoprotonated Atrazine can be shown to appear at pH 4 rather than at pH 3.1 in Figure (9).

The equilibrium shift during the extraction process did not affect other experiments done in the project, since, they were all adjusted between pH values of 4 to 7 before extraction. In this way the stoichiometric amount of Atrazine, M_T, in each equilibrated solution was obtained as unprotonated Atrazine.

4.0.2 FULVIC ACID CHARACTERIZATION

The FA8 fulvic acid prepared in Section 3.2.7a was analyzed for carbon, hydrogen, and nitrogen content by Guelph Chemical Laboratories Limited. The results of the analysis are given in Table (7) together with those for FA1 batch prepared by the Chemistry and Biology Research Institute (CBRI), Research Branch, Agriculture Canada. From the data in the table it can be concluded that these two batches of fulvic acid are not significantly different as far as organic matter is concerned. Table (8) lists the metal ion content found in the FA8 fulvic acid. Atomic absorption spectroscopy was used to determine the amount of metal ion present in the fulvic acid. Also in Table (8) are the metal ion contents for the fulvic acid prepared by Underdown (33).

Table (7): Elemental analysis of two batches of fulvic acid prepared by the same procedure (Reference (50)).

Elements	FA8	FA1
% Carbon	49.52	49.50
% Hydrogen	4.60	4.50
% Nitrogen	0.58	0.80

Table (8): Metal ion concentration for the FA8 (Reference(50)) and Reference (33) fulvic acids.

	CONCENTRATION (mmole/gm FA)	
ION	FA8	REFERENCE (33)
Iron	3.0×10^{-3}	3.0×10^{-2}
Copper	$< 10^{-3}$	$< 10^{-4}$
Sodium	1.1×10^{-3}	6.5×10^{-2}
Potassium	5.7×10^{-4}	$< 2.6 \times 10^{-3}$
Aluminum	5.3×10^{-3}	1.95×10^{-2}
Magnesium	1.8×10^{-4}	3.7×10^{-3}
Calcium	1.1×10^{-4}	---*
Manganese	$< 10^{-3}$	$< 10^{-4}$
Silicon	$< 10^{-3}$	---*

* --- no values available for these ions.

4.0.2a DEGREE OF PROTONATION OF FA8 FULVIC ACID

From the experiment in Section 3.2.7b the titration curve for FA is given in Figure (10). Gamble et al. (28,29,30,57) have used similar acidometric titration curves to fully characterize the acidic functional groups of FA obtained from Armadale Prince Edward Island. The Type A

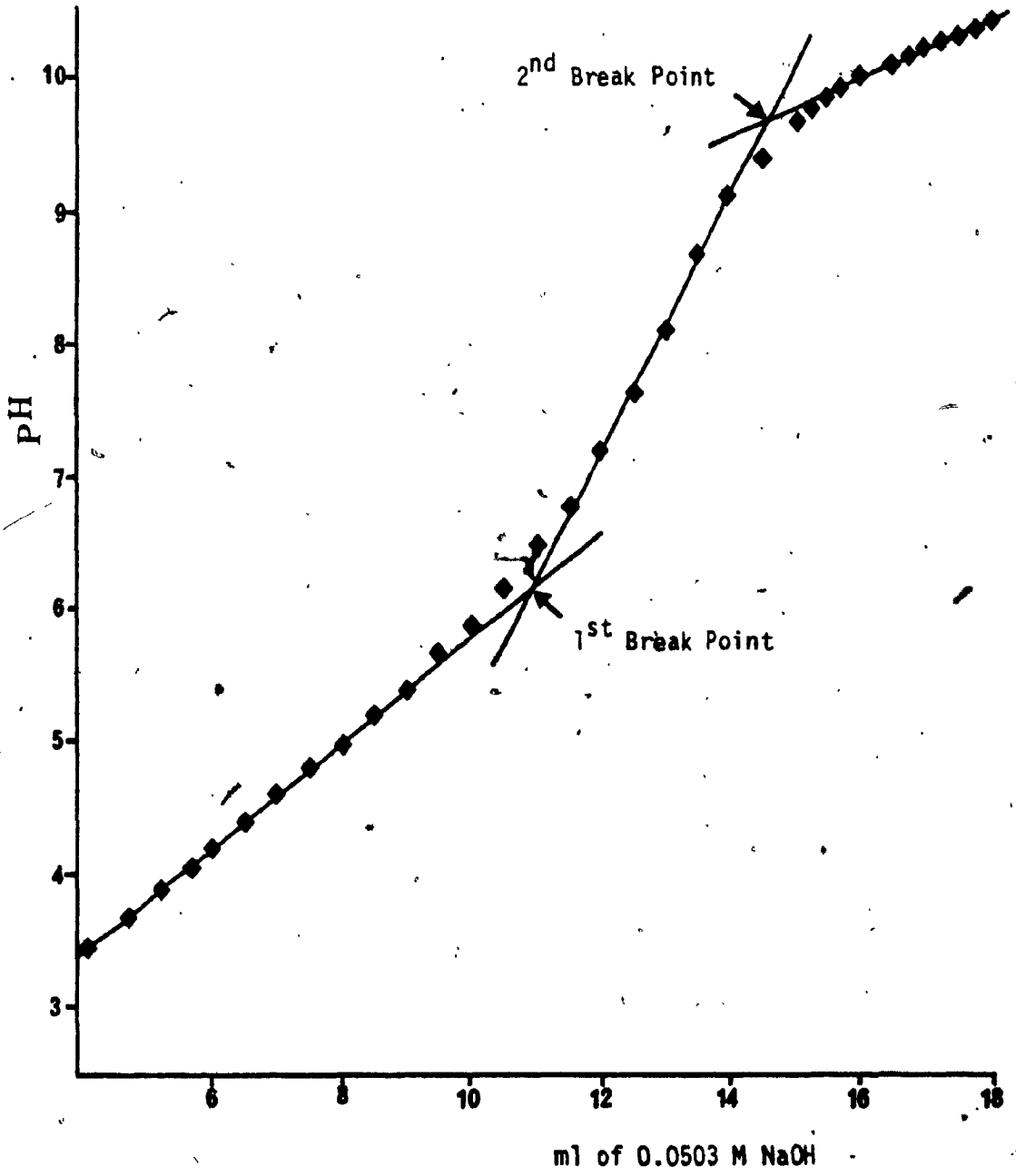


Figure (10): Titration curve for 0.1000 gm FA in 50.0 ml of water with 0.0503 M NaOH.

acidic functional groups (discussed in Section 1.2.1 of Chapter 1) are all those up to the first break point in Figure (10). The Type B acidic functional groups are those between the first and second break

points in Figure (10). According to Gamble (28), the Type A acidic groups has a subset of 3.0 mmole/gm FA of carboxylic groups which are highly acidic and which are referred to as the Type 1 acidic groups.

Using the data from the titration curve in Figure (10) for the FA8 fulvic acid, the macroscopic degree of ionization, α_A, for the whole FA mixture can be calculated. Burch et al. (57) have used equation (4-1) to calculate α_A.

$$\alpha_A = \frac{C_{OH}}{C_A} + \frac{a_H + K_W/a_H}{C_A} \qquad (4\text{-}1)$$

where,

C_{OH} – concentration of NaOH (mole/litre).

C_A – concentration of Type A functional groups (4.99 mmole/gm FA).

a_H – hydrogen ion activity (mole/litre).

K_W – ion-product constant (mole^2/litre^2).

Activity coefficients (58) were used to correct the hydrogen ion concentrations to activities at 25^{o}C. Figure (11) represents the curves for the dissociation (α_A) and the protonation ($1-\alpha_A$) of the FA8 fulvic acid as a function of pH.

The calculated α_A values are not significantly different from those values reported by Gamble (29).

The Type A groups are carboxyl groups (28) which are chemically non-identical but whose acid strengths are sufficiently closely spaced as to prevent the appearance of separate titration end points. However,

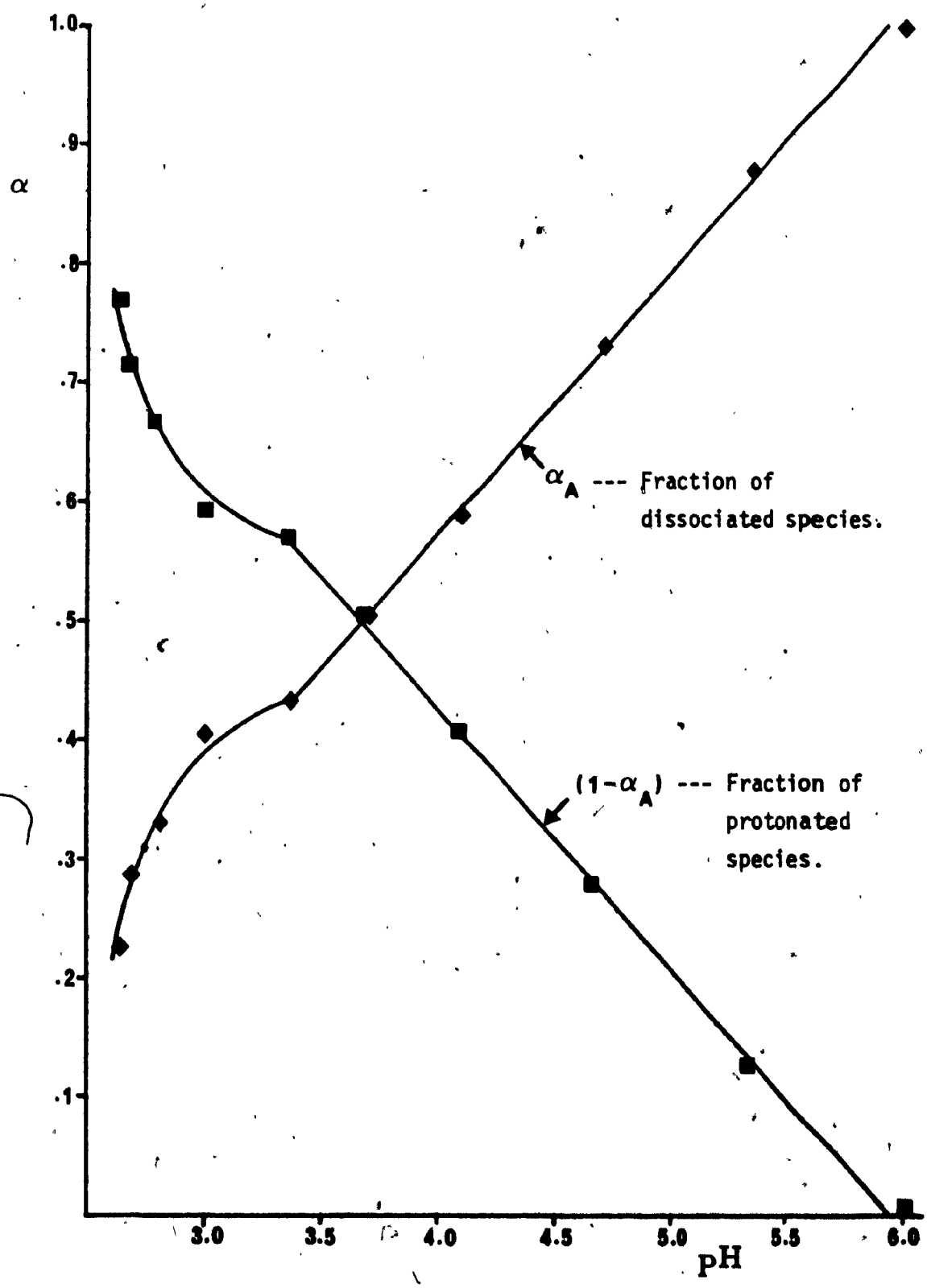


Figure (11): Distribution diagram for the different species of fulvic acid as a function of pH.

different dissociation constants will be observed experimentally as the α_A varies. For the Type A carboxylic group (AH) dissociation in reaction (4-2),

$$AH \overset{\bar{K}_A}{\rightleftharpoons} A + H^+ \qquad (4\text{-}2)$$

the weighted average dissociation function, $\bar{K}_A$, can be written as in equation (4-3):

$$\bar{K}_A = \frac{m_A a_H}{m_{AH}} \qquad (4\text{-}3)$$

where,

m_A — all Type A carboxyl groups that are ionized.

m_{AH} — all Type A carboxyl groups that are unionized.

If the degree of ionization of the Type A group is given by equation (4-4),

$$\alpha_A = \frac{m_A}{m_A + m_{AH}} \qquad (4\text{-}4)$$

then, it can be shown that,

$$\bar{K}_A = \frac{\alpha_A a_H}{1-\alpha_A} \qquad (4\text{-}5)$$

By using equation (4-5), $\bar{K}_A$ values were calculated and listed in Table (9).

Table (9): Ionization of Type A carboxyl groups in aqueous solution at 25°C.

$a_H \times 10^3$ (mole/litre)	α_A	$K_A \times 10^3$ (mole/litre)
1.01	0.408	0.696
0.488	0.420	0.354
0.437	0.430	0.329
0.201	0.496	0.198
0.0975	0.565	0.127
0.0786	0.588	0.112
0.372	0.659	0.0719
0.0236	0.708	0.0572
0.0184	0.733	0.0506
0.0124	0.782	0.0446

The hydrogen ion concentrations were converted to activity values before use in equation (4-5). The ionization constants obtained in this table are not very different from those reported by Gamble (29). Therefore, we can assume that Gamble's FA and FA8 are similar enough so as to expect each to behave in the same way to Atrazine.

4.0.2b FUNCTIONAL GROUP DETERMINATION FOR THE FA8 FULVIC ACID

Because the acid groups in FA are weak, it is quite difficult to obtain sharp equivalence points for them in an acid-base titration. Also complicating the end point detection are the spectrum of minutely different K_a's for the FA carboxylic acid groups. Gamble (29) has found that a better approximation to the Type A and Type B equivalence points can be obtained by using the Gran's function. Correction terms were used in the Gran's function (59) so as to remove any scatter near the equivalence

points.

Neglecting Gamble's correction terms to the Gran's function still gives reliable equivalence points. The Type A equivalence point can be obtained by using equation (4-6).

$$Y_1 = \left[\frac{Va_H}{\bar{K}_A}\right] = V_{e1} - V \qquad (4\text{-}6)$$

where,

Y_1 – first Gran's function

V – millilitre of standard base added.

V_{e1} – volume of standard base at the first equivalence point.

a_H and $\bar{K}_A$ have the same meaning as before. By plotting Y_1 versus V for the titration curve in Figure (10), V_{e1} is obtained on the V-axis when Y_1 is equal to zero. Figure (12) gives a plot of equation (4-6). V_{e1} was determined to 10.1 ml of 0.0503 M NaOH which correspond to 5.08 mmole Type A carboxylic groups per gram of FA8. This value is only 1.8% different from the value reported by Gamble (29).

Equation (4-7) was used to determine the end point of the Type B functional groups.

$$Y_4 = \left[\frac{K_W V_T}{N_B a_H}\right] V - V_{e2} \qquad (4\text{-}7)$$

where,

Y_4 – second Gran's function.

V_T —total volume of standard base added.

V_{e2} —volume of standard base at the second equivalence point.

N_B —normality of the standard base.

The other variables have their regular meaning. By plotting Y_4 versus V for the data after the second equivalence point in Figure (10), V_{e2} was obtained as 14.71 ml when Y_4 was equal to zero (Figure (13)). The sum of the Type A and the Type B groups in FA8 were found to be 7.40 mmole per gram of FA. Therefore, the amount of Type B groups in FA8 are 2.33 mmole per gram of FA. There was a 3.1% difference between the value reported here and that reported by Gamble (29).

Since replicate titrations were done on the Armadale FA by Gamble, there is less error in the value reported by him. Therefore, 4.99 mmole per gram FA for the Type A carboxyl groups will be used in calculations where it is needed in the remainder of the thesis.

4.0.3 ATRAZINE VARIATION AT CONSTANT pH AND LOW IONIC STRENGTH

From the experiments in Section 3.3.4a preliminary graphs were prepared by plotting the equilibrium total Atrazine concentration versus the volume of Atrazine stock solutions for both the FA solutions and the control solutions. For example, for the experiment at pH 1.36 in Table (4) of Chapter 3, the equilibrium total Atrazine concentrations are given in Table (10) for both solutions. A plot of the experimental total Atrazine concentrations versus the volume of Atrazine stock solutions for both the FA solutions and the control solutions is given in Figure (14). This preliminary graph indicates that the control solutions (solid squares)

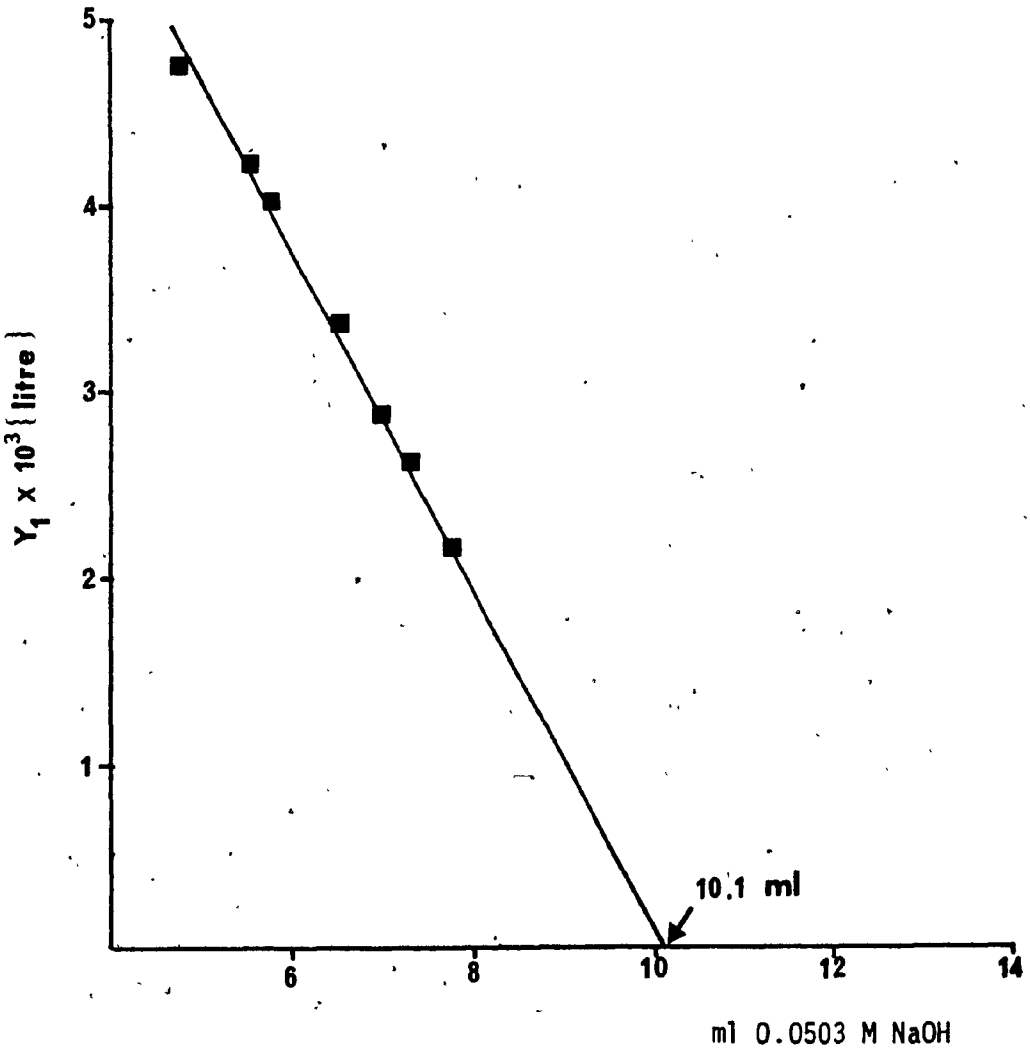


Figure (12): Gran's plot to determine the first equivalence point of FA8 using the data in Figure (10).

could be fitted to a straight line whereas the Atrazine in the FA solutions (solid diamonds and triangles) could be fitted to two separate straight lines. The control solutions were fitted by linear regression to an equation with intercept (b) 6.20, slope (m) 1.22 and correlation (r) 0.992. The first eight FA solutions were fitted to an equation with b = 3.05, m = 0.266 and r = 0.984. The last five FA solutions were fitted

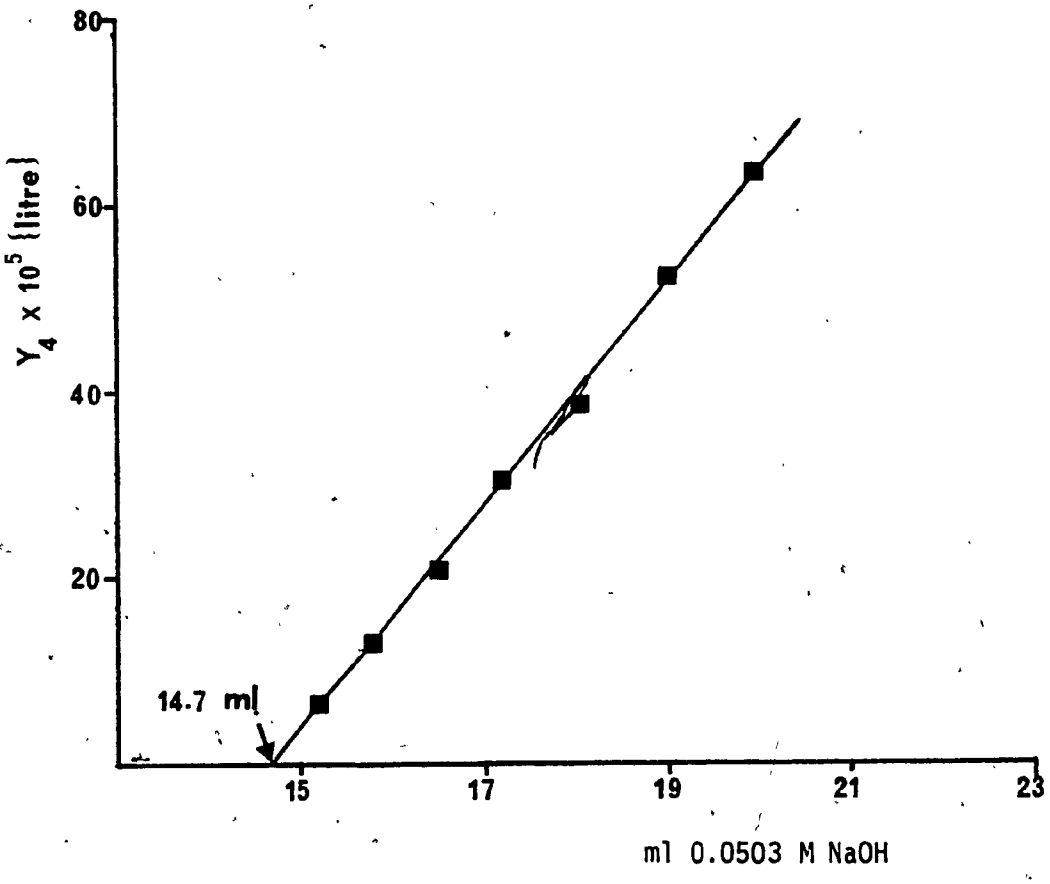


Figure (13): Gran's plot to determine the second equivalence point of FA8 using the data in Figure (10).

to another equation with b = -28.6, m = 1.28 and r = 0.991. From these equations the total Atrazine concentrations were calculated and then listed in Table (10). These calculated values and the corresponding stock solution volumes were used to prepare the titration graph in Figure (15). In both the preliminary (Figure (14)) and fitted (Figure (15)) titration graphs, the solid diamonds represent the points before the equivalence point and the solid triangles represent the points after the equivalence point. Similarly fitted titration graphs were prepared for experiments done at other pH values. These results are presented in Appendix (I).

Table (10): Equilibrium Atrazine concentrations for the experiment in Table (4) of Chapter 3.

	Fulvic Acid Solutions			Control Solutions		
#	Vol. of Atrazine Stock Solution (ml)	Experimental Free Atrazine (μMole/litre)	Calculated Free Atrazine (μMole/litre)	Vol. of Atrazine Stock Solution (ml)	Experimental Free Atrazine (μMole/litre)	Calculated Free Atrazine (μMole/litre)
1	5.00	4.70	4.37	5.00	12.10	11.67
2	7.50	5.04	5.04	10.00	17.50	17.97
3	10.00	5.50	5.70	15.00	21.20	24.27
4	12.50	6.20	6.36	20.00	30.00	30.58
5	15.00	6.80	7.04	25.00	35.50	36.67
6	20.00	8.70	8.38	35.00	49.49	48.86
7	22.50	9.10	9.04	45.00	62.10	61.04
8	25.00	9.65	9.70			
9	32.50	13.20	13.02			
10	37.50	19.50	19.42			
11	40.00	22.70	22.62			
12	42.50	24.50	25.82			
13	45.00	30.00	29.02			

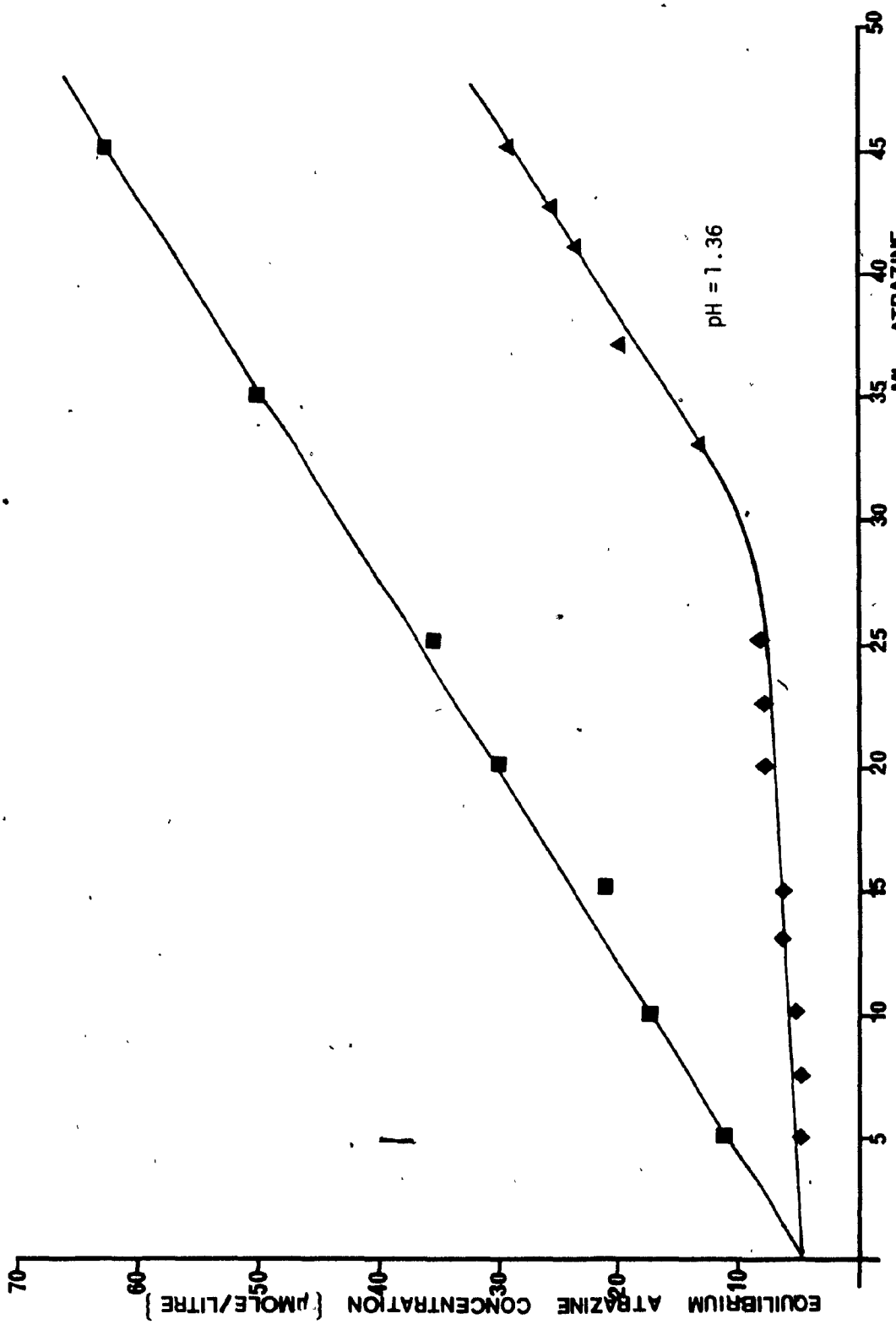


Figure (14): Preliminary titration graph for FA at a pH value of 1.36. FA = 1.0000 gm/litre.

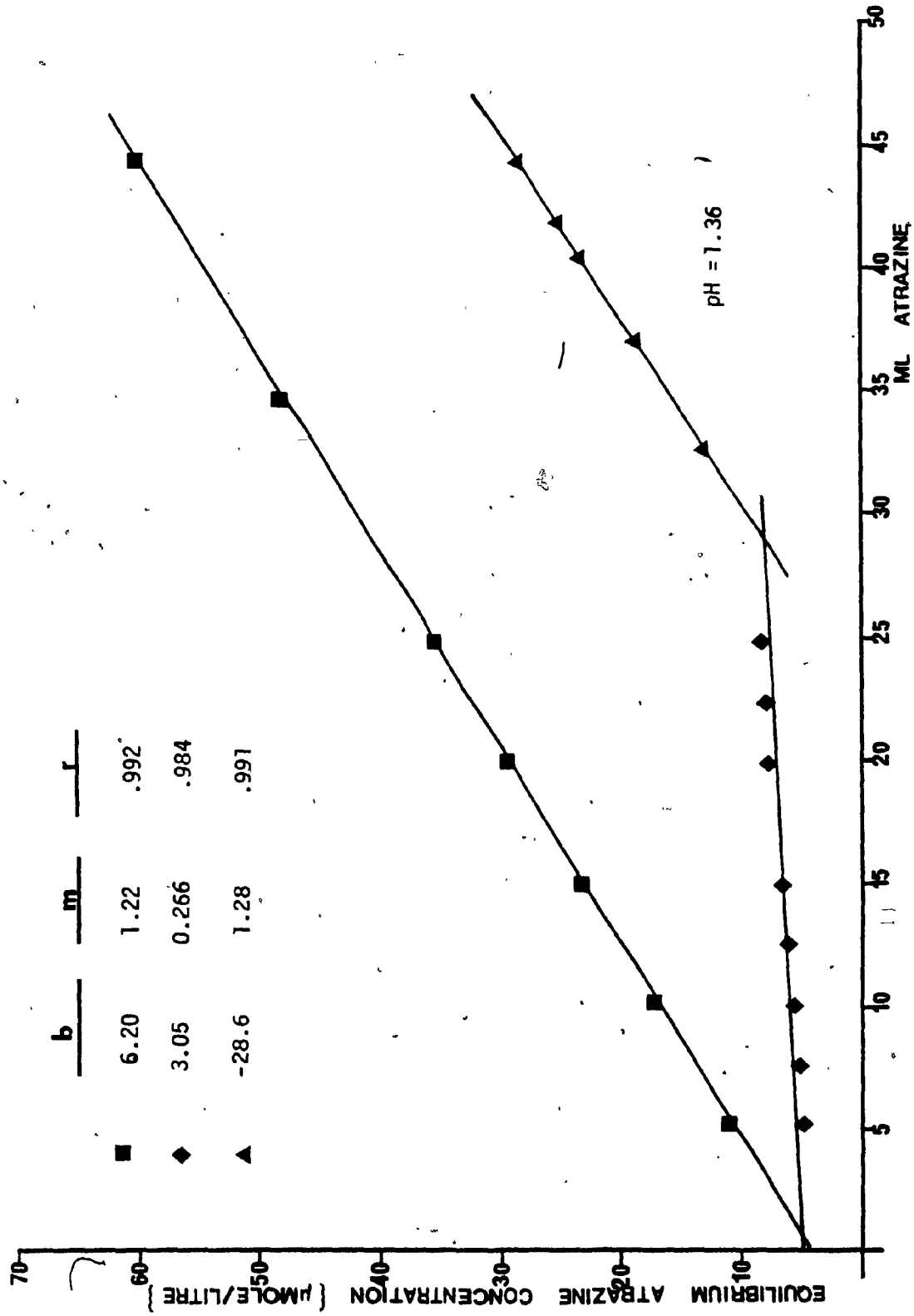


Figure (15): Fitted titration graph for FA at a pH value of 1.36. FA = 1.0000 gm/litre.

Using the titration graphs, tha amount of Atrazine bound for each volume of total Atrazine added to a sample can be obtained by subtracting the quantity of Atrazine in the FA solution from that in the control solution. Figure (16) shows the total Atrazine bound as a function of the volume of stock Atrazine added for seven of the nine pH values tested. It should be noted that titration graphs without solid diamonds in Appendix (I) (at pH values of 6.00 and 8.00) indicate that no Atrazine binds to FA at those particular pH values. Also, the graphs without solid triangles indicate that the equivalence points were not reached in these titrations.

Each curve in Figure (16) shows a maximum complexing capacity, C_L, at the plateau. At pH values of 1.36, 1.72, 2.28, 2.77, 3.21, 3.50 and 4.50 the respective complexing capacities from Figure (16) are 35.4, 31.6 12.8, 16.0, 14.0, 27.6 and 4.6 μmoles per gram FA. Figure (17) shows a plot of the complexing capacity versus the pH at which each experiment was done (solid squares).

4.0.3a CALCULATION OF EQUILIBRIUM FUNCTIONS IN A LOW IONIC STRENGTH MEDIUM

Since these experiments were all done at fixed pH values and varying Atrazine concentrations, then, the unprotonated equilibrium function, K_0, can be calculated from equation (2-46) of Chapter 2. The protonated equilibrium function, K_1, can be calculated from equation (2-62) of Chapter 2. For pH values of 4.00 and greater equation (2-62) does not apply, since no protonated Atrazine exist. Using the data from Figure (15) for the experiment done at pH 1.36, the relevant values needed to calculate K_0 and K_1 from equations (2-46) and (2-62), respectively, are

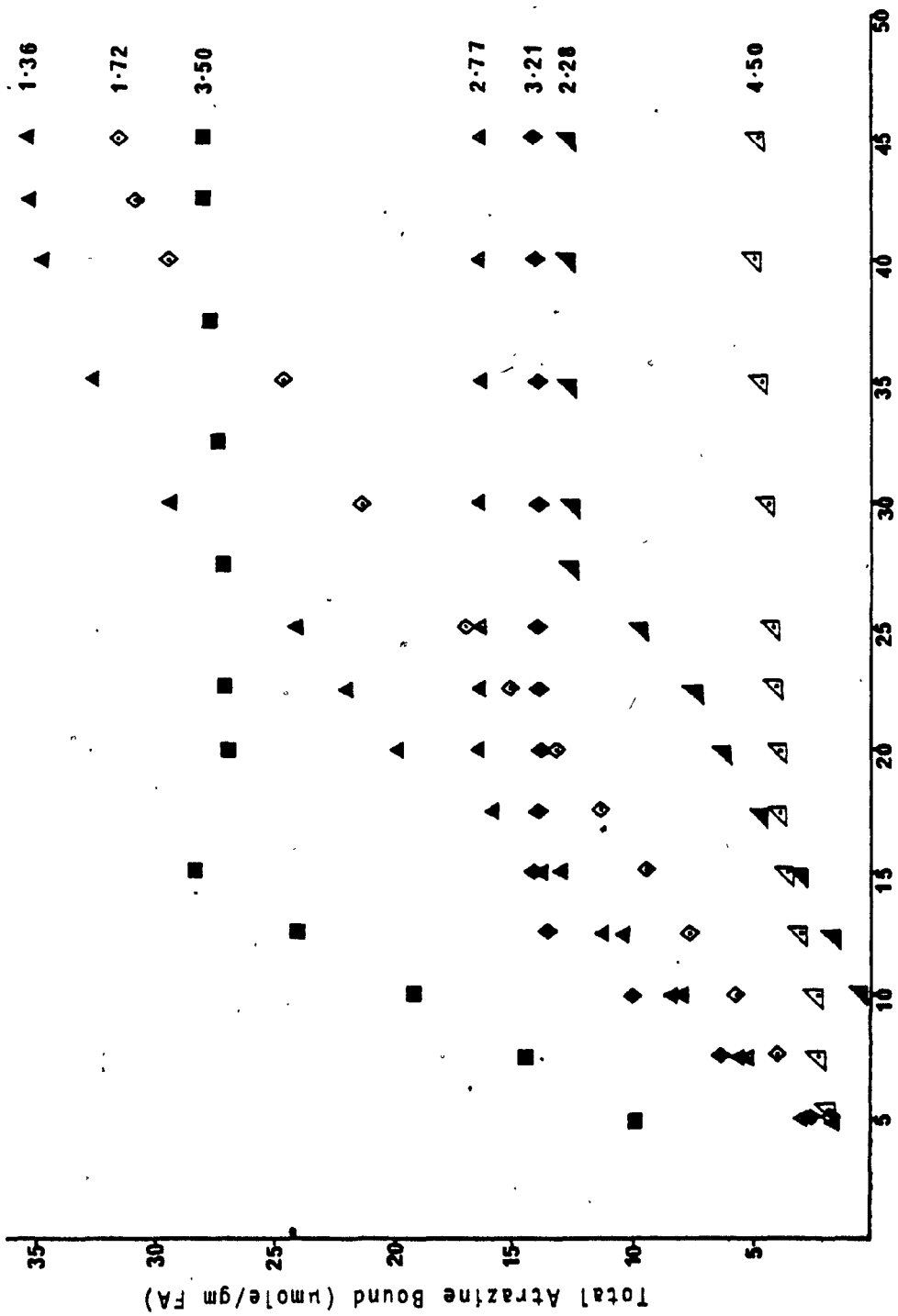
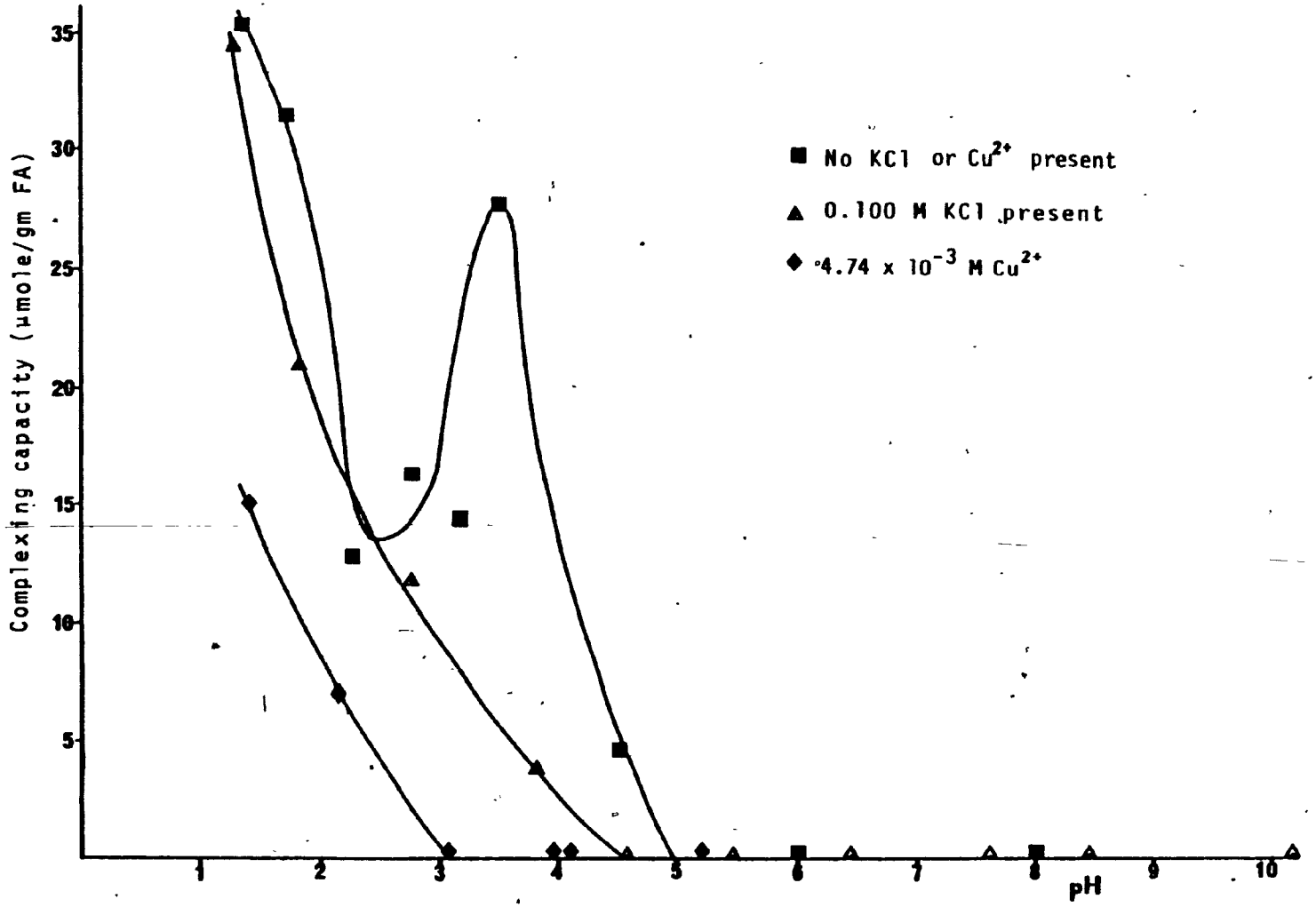


Figure (16): Total Atrazine bound as a function of volume of Atrazine titrant at various pH values. FA = 1.0000 gm/litre.



Figure(17) : Atrazine complexing capacity as a function of pH for various experimental conditions.
FA=1.0000 gm/litre.

given in Table (11). It should be noted that the parameters M_T, M_1, M_0, x_T, x_1, and x_0 have the same meaning as in Chapter 2. M_T is the experimentally determined total Atrazine; M_0 was obtained from equation (1-6) of Chapter 1; M_1 was obtained by the difference between M_T and M_0; the K_a value, as described before, is 2.45×10^{-2}. The concentration of FA, C, used was 1.0000 gram per litre which transforms to 4.99×10^3 μmole of Type A functional groups per litre. M_{TB}, total Atrazine bound, was obtained by subtracting M_T in the FA solution from M_T in the corresponding control solution; the amount bound is then expressed in μmole per litre; x_T was, then, obtained by dividing M_{TB} by 4.990×10^3 μmole of Type A functional groups per litre. M_{1B} was obtained by subtracting the quantity of protonated Atrazine, M_1, of the FA solution from that of the control; x_1, was, then, calculated similarly to x_T. This procedure was repeated in order to calculate x_0.

The above calculations were done, only, for solutions before the equivalence point in Figure (15). Beyond the equivalence point, x becomes independent of the Atrazine concentrations in solution.

From equations (2-4) and (2-12),

$$\bar{K}_0 x_0 = \left[\frac{M_0 C}{M_{0B}} \times \frac{M_{0B}}{C}\right] = M_0 \qquad (4\text{-}8)$$

and from equations (2-5) and (2-56),

$$\bar{K}_1 x_1 = \left[\frac{M_1 C}{M_{1B}} \times \frac{M_{1B}}{C}\right] = M_1 \qquad (4\text{-}9)$$

Table (11)[a]: Determination of protonated and unprotonated free and bound Atrazine from the total free Atrazine in solution. The data was taken from Figure (15) at pH 1.36.

#	Vol. of Stock Atrazine (ml)	FA Solution (μmole/litre)			Control Solution (μmole/litre)			Fraction Bound (10^4)		
		M_T	M_1	M_o	M_T	M_1	M_o	x_T	x_1	x_o
1	5.00	4.37	2.80	1.57	11.67	7.47	4.20	14.63	9.36	5.27
2	7.50	5.04	3.23	1.81	14.82	9.49	5.33	19.60	12.54	7.06
3	10.00	5.70	3.65	2.05	17.97	11.51	6.46	24.59	15.75	8.84
4	12.50	6.37	4.08	2.29	21.12	13.52	7.60	29.56	18.92	10.64
5	15.00	7.04	4.51	2.53	24.27	15.54	8.73	34.53	22.10	12.42
6	20.00	8.38	5.36	3.01	30.58	19.58	11.00	44.49	28.50	16.00

a - the symbols M_T, M_1, M_o, x_T, x_1 and x_o have the same meaning as in Chapter 2.

Hence, by plotting M_0 versus χ_T from Table (11), $\partial(\bar{K}\chi_0)/\partial\chi_T$ can be obtained as the slope for any point (χ_T, M_0) on the graph; K_0 can then be obtained from equation (2-46); α_{1B} was evaluated for each pH value from equation (2-9). Figure (18) represents the plots for the titration graphs in Figure (15) and Appendix (I). Since K_0 represents the dissociation equilibrium function, then, $1/K_0$ is the formation equilibrium function for the Atrazine-FA complex. Gibbs free energy values were calculated from the formation constant at 25°C. In all calculations, the hydrogen ion concentrations were corrected to activity values. From Figure (18) it can be seen that the graphs are all linear, therefore, they were fitted to linear least square equations in order to obtain the slopes. Table (12) shows the pH, the α_{1B}, the correlation coefficient (r) for the least square fit, $\partial(\bar{K}_0\chi_0)/\partial\chi_T$, K_0, and $(\Delta G^0 + RT\ \text{In}\Gamma)$ for the bound unprotonated Atrazine.

Similar calculations were done for the bound protonated Atrazine for the titration graphs of Figure (15) and Appendix (I). Figure (19) represents the graphs for the M_1 versus χ_T plots. Again, these graphs were linear, and, hence, fitted to linear least square equations. The results for these calculations are also listed in Table (12).

The K_0 values may be related to the thermodynamic equilibrium constant, κ_0, in the following way:

$$FA + At \overset{K_0}{\rightleftharpoons} (FA\text{-}At) \qquad (4\text{-}10)$$

$$K_0 = \left[\frac{M_{0B}}{CM_0}\right]\left[\frac{\gamma_{M_{0B}}}{\gamma_C \gamma_{M_0}}\right] \qquad (4\text{-}11)$$

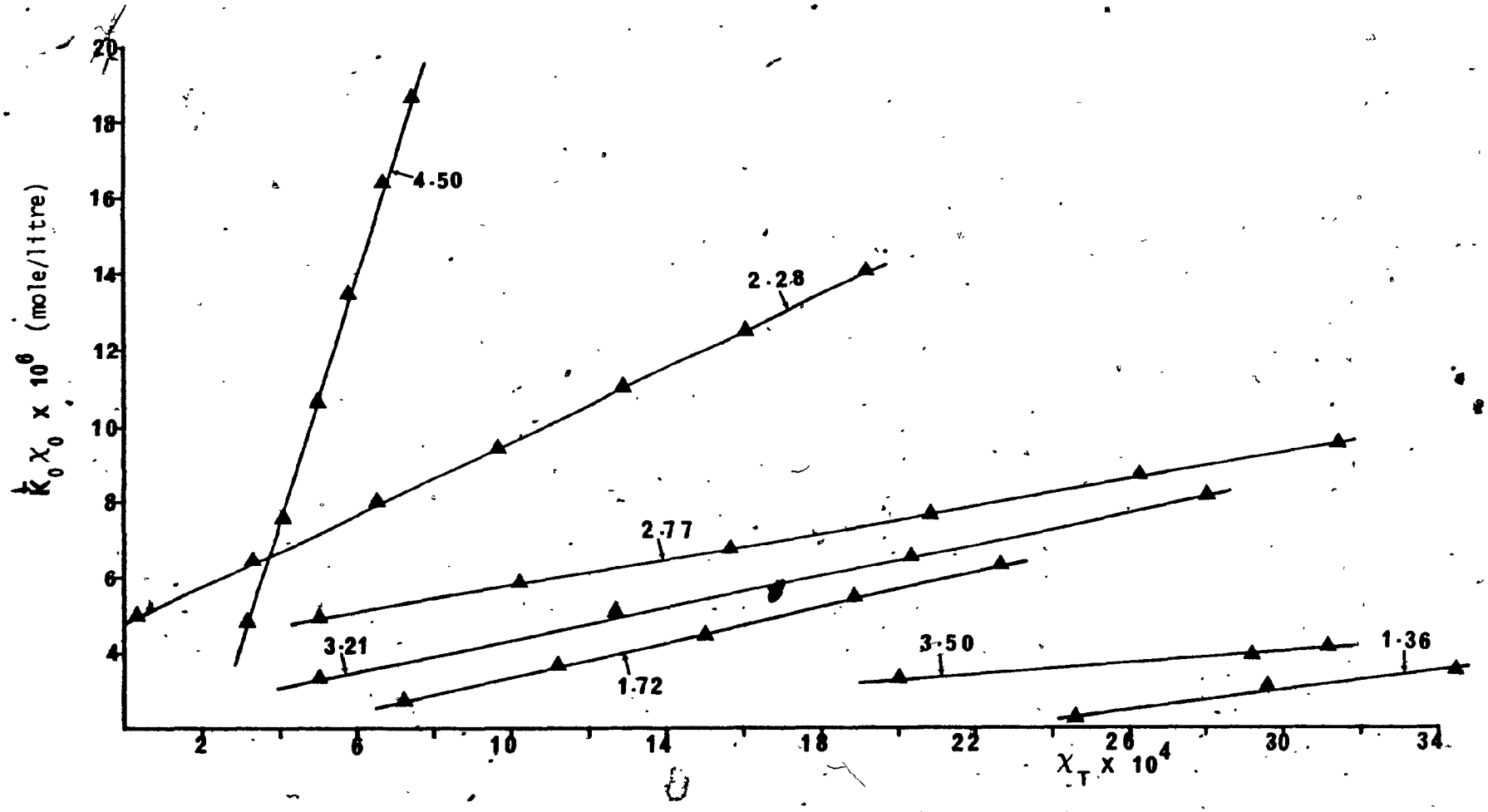


Figure (18): Calculation of $\partial(\bar{K}_0 X_0)/\partial X_T$, for the unprotonated Atrazine complex from a plot of $\bar{K}_0 X_0$ versus X_T at various pH values.

Table (12): Determination of the formation functions and free energies for complexed unprotonated and protonated Atrazine at various α_{1B} values.

Complexed Unprotonated Atrazine

pH	α_{1B}	$\frac{\partial(\bar{K}_o x_o)}{\partial x_T}$ (mole/l)	r	K_o (mole/l)	$1/K_o$ (1/mole)	$-(\Delta G^o + RT\ln\Gamma)$ (Kj/mole)
1.36	0.360	4.82×10^{-4}	0.999	1.34×10^{-3}	7.46×10^{2}	16.4
1.72	0.561	2.46×10^{-3}	0.999	4.39×10^{-3}	2.28×10^{2}	13.4
2.28	0.825	1.91×10^{-3}	0.999	2.32×10^{-3}	4.32×10^{2}	15.0
2.77	0.935	1.75×10^{-3}	0.999	1.87×10^{-3}	5.34×10^{2}	15.6
3.21	0.976	2.08×10^{-3}	0.999	2.14×10^{-3}	4.68×10^{2}	15.2
3.50	0.988	7.22×10^{-4}	0.999	7.32×10^{-4}	1.37×10^{3}	17.9
4.50	0.999	3.26×10^{-2}	0.999	3.26×10^{-2}	3.06×10^{1}	8.48

Complexed Protonated Atrazine

pH	α_{1B}	$\frac{\partial(\bar{K}_1 x_1)}{\partial x_T}$ (mole/l)	r	K_1 (mole/l)	$1/K_1$ (1/mole)	$-(\Delta G^o + RT\ln\Gamma)$ (Kj/mole)
1.36	0.360	8.57×10^{-4}	0.999	1.34×10^{-3}	7.46×10^{2}	16.4
1.72	0.561	1.93×10^{-3}	0.999	4.40×10^{-4}	2.21×10^{2}	13.4
2.28	0.825	9.99×10^{-3}	0.999	5.70×10^{-3}	1.76×10^{2}	12.8
2.77	0.935	1.20×10^{-3}	0.999	1.86×10^{-2}	5.37×10^{1}	9.87
3.21	0.976	5.42×10^{-5}	0.999	2.14×10^{-3}	4.67×10^{2}	15.2
3.50	0.988	1.05×10^{-5}	0.999	8.44×10^{-4}	1.19×10^{3}	17.5
4.50	0.999	-----	---	-----	-----	---

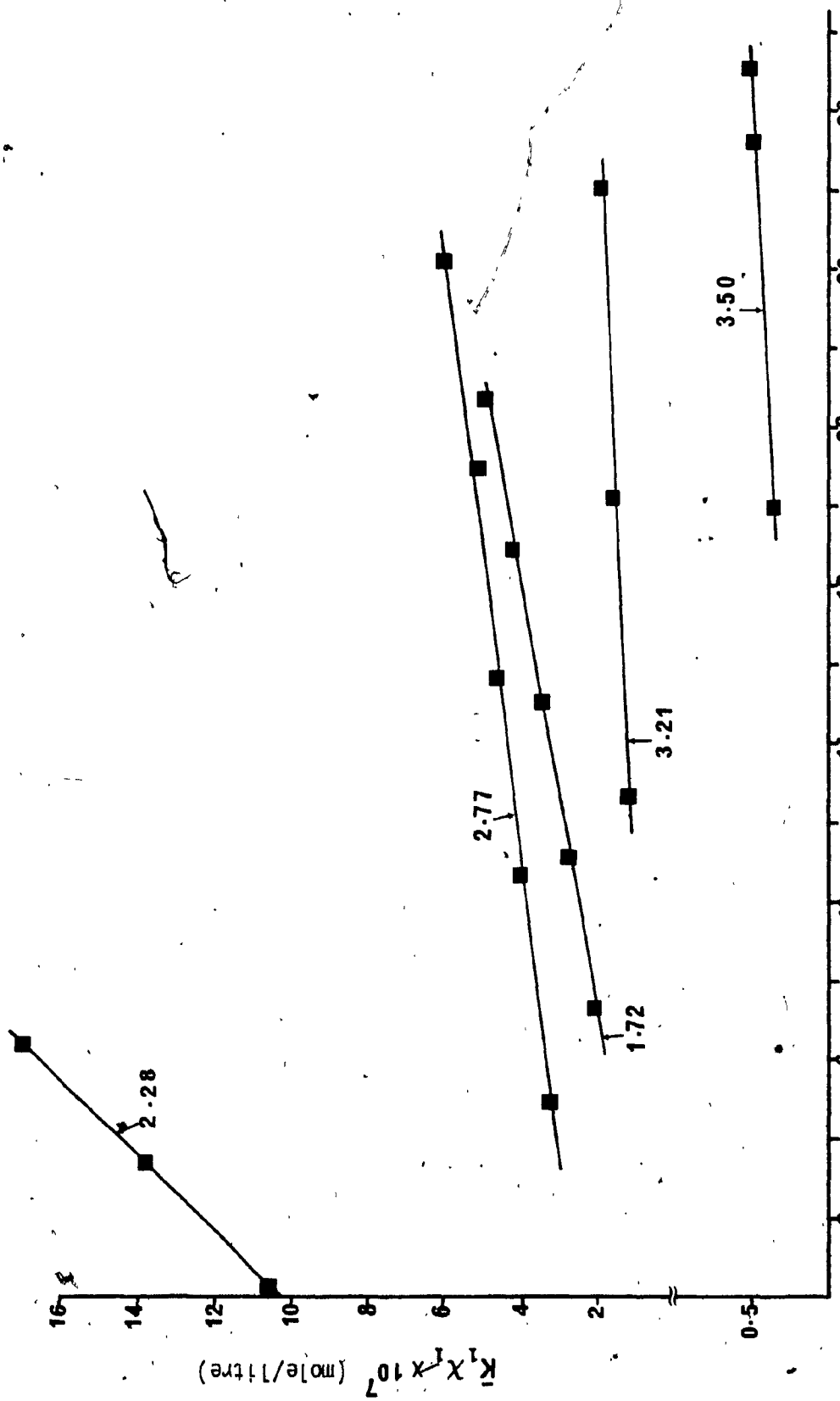


Figure (19): Calculation of $a(\bar{K}_1\chi_1)/a\chi_T$, for the protonated Atrazine complex from a plot of $\bar{K}_1\chi_1$ versus χ_T at various pH values.

Therefore,

$$\kappa_0 = (1/K_0)\left(\frac{\gamma_{M_{OB}}}{\gamma_C \gamma_{M_0}}\right) \qquad (4\text{-}12)$$

If,

$$\Gamma = \left(\frac{\gamma_{M_{OB}}}{\gamma_C \gamma_{M_0}}\right) \qquad (4\text{-}13)$$

Then,

$$\kappa_0 = (1/K_0)\,\Gamma \qquad (4\text{-}14)$$

$$\Delta G^o = -RT\ \ln(1/K_0)\Gamma \qquad (4\text{-}15)$$

Therefore,

$$-(\Delta G^o + RT\ \ln\Gamma) = RT\ \ln(1/K_0) \qquad (4\text{-}16)$$

Only for dilute solutions can Γ be assumed to be close to unity. Since the FA concentrations used in the project are considered to be reasonably high (31), then, the γ_C value in equation (4-13) is less than unity. Since no activity coefficients data are available for FA, an exact value for γ_C could not be obtained. Hence, the RTlnΓ term in equation (4-16) had to be retained and reported in Table (12). Similarly, the equation for the protonated Atrazine case can be derived.

4.0.4 ATRAZINE VARIATION AT CONSTANT pH AND HIGH IONIC STRENGTH (0.100 M KCl)

From the experiments done in Section 3.3.4b, preliminary titration graphs (similar to that in Figure (14)) were prepared so as to obtain the fitted titration graphs (similar to that in Figure (15)). The fitted

titration graphs are presented in Appendix (II). From these graphs, the amount of total Atrazine bound were determined as a function of the volume of stock solution added. Figure (20) shows a plot of total Atrazine bound versus the volume of stock solution added. pH values of 4.55, 5.45, 6.48, 7.62, 8.49, and 10.25 show no significant binding of Atrazine. From Figure (20), the complexing capacity at pH values of 1.27, 1.83, 2.77 and 3.82 are 34.4, 21.0, 11.9, and 3.85 μmole per gram FA, respectively. The triangles in Figure (17) shows a plot of the complexing capacity versus the pH at which each experiment was done.

4.0.4a CALCULATION OF EQUILIBRIUM FUNCTIONS IN A HIGH IONIC STRENGTH MEDIUM

Using the titration graphs in Appendix (II), the same calculations as were done in Section 4.0.3a were repeated here. Figure (21) represents the plot of $\bar{K}_0 x_0$ versus x_T for the complexed unprotonated Atrazine and Figure (22) represents the plot of $\bar{K}_1 x_1$ versus x_T for the complexed protonated Atrazine. Table (13) gives the calculated formation functions and free energies for these complexes. It should be noted here that Atrazine binding was observed at a pH value of 3.82 (see Figure (20)). However, no data points could have been obtained before the equivalence point in the titration graph (see pH 3.82 in Appendix (II)). Hence, no values for K_0 and K_1 can be reported for pH 3.82.

4.0.5 EFFECT OF FA CONCENTRATION ON ATRAZINE BINDING AT A pH VALUE OF 3.50 IN THE PRESENCE AND ABSENCE OF 0.100 M KCl

Appendix (III) shows the titration graphs for varying concentrations of FA in the absence of KCl at pH 3.50. The graph for the FA concentration of 1.0000 gram per litre is given in Appendix (I). No binding of Atrazine was observed at FA concentrations of 0.2000, 0.4000 and 0.6000 gram per

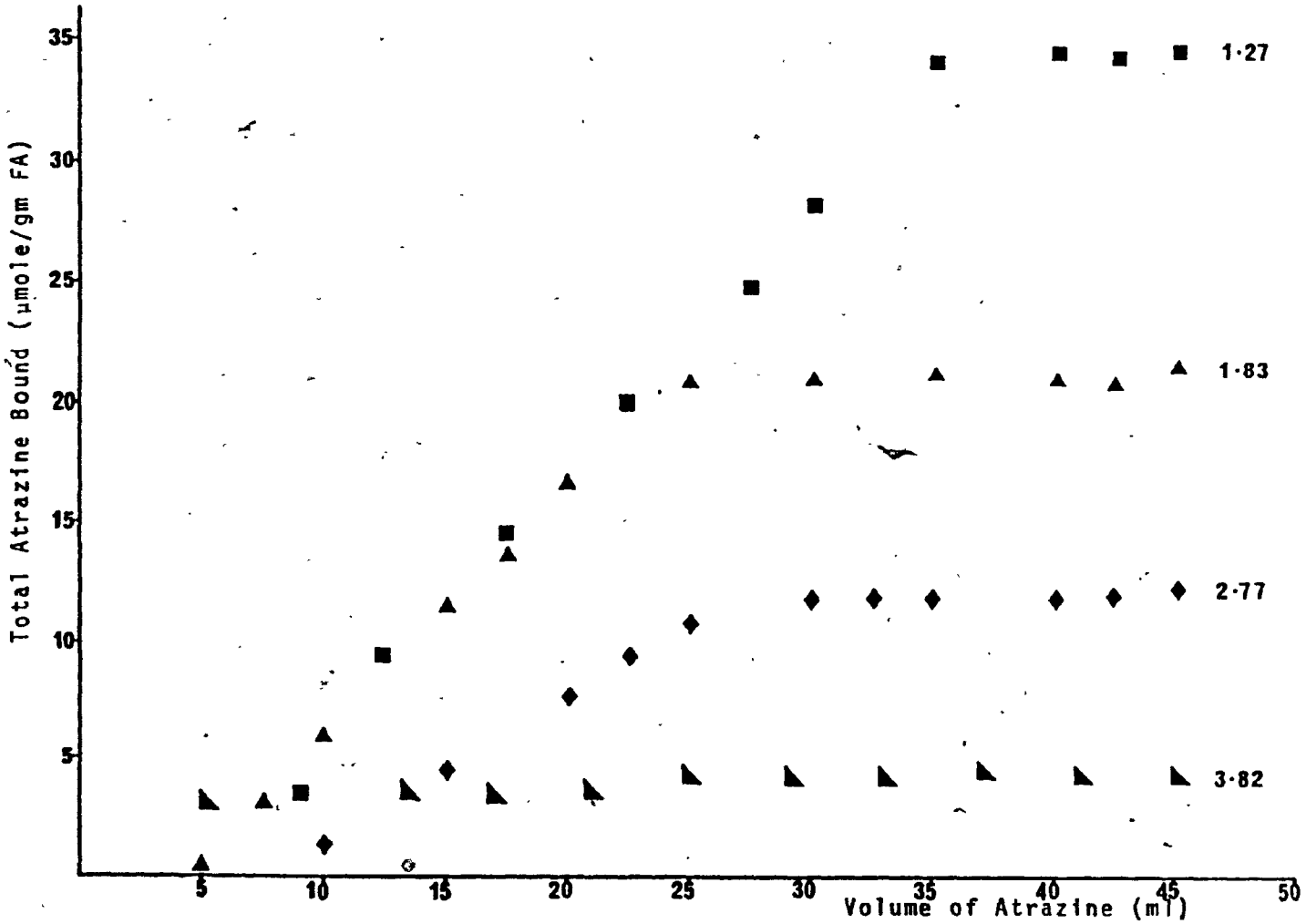


Figure (20): Total Atrazine bound as a function of volume of Atrazine titrant at various pH values in the presence of 0.100 M KCl. FA = 1.0000 gm/litre.

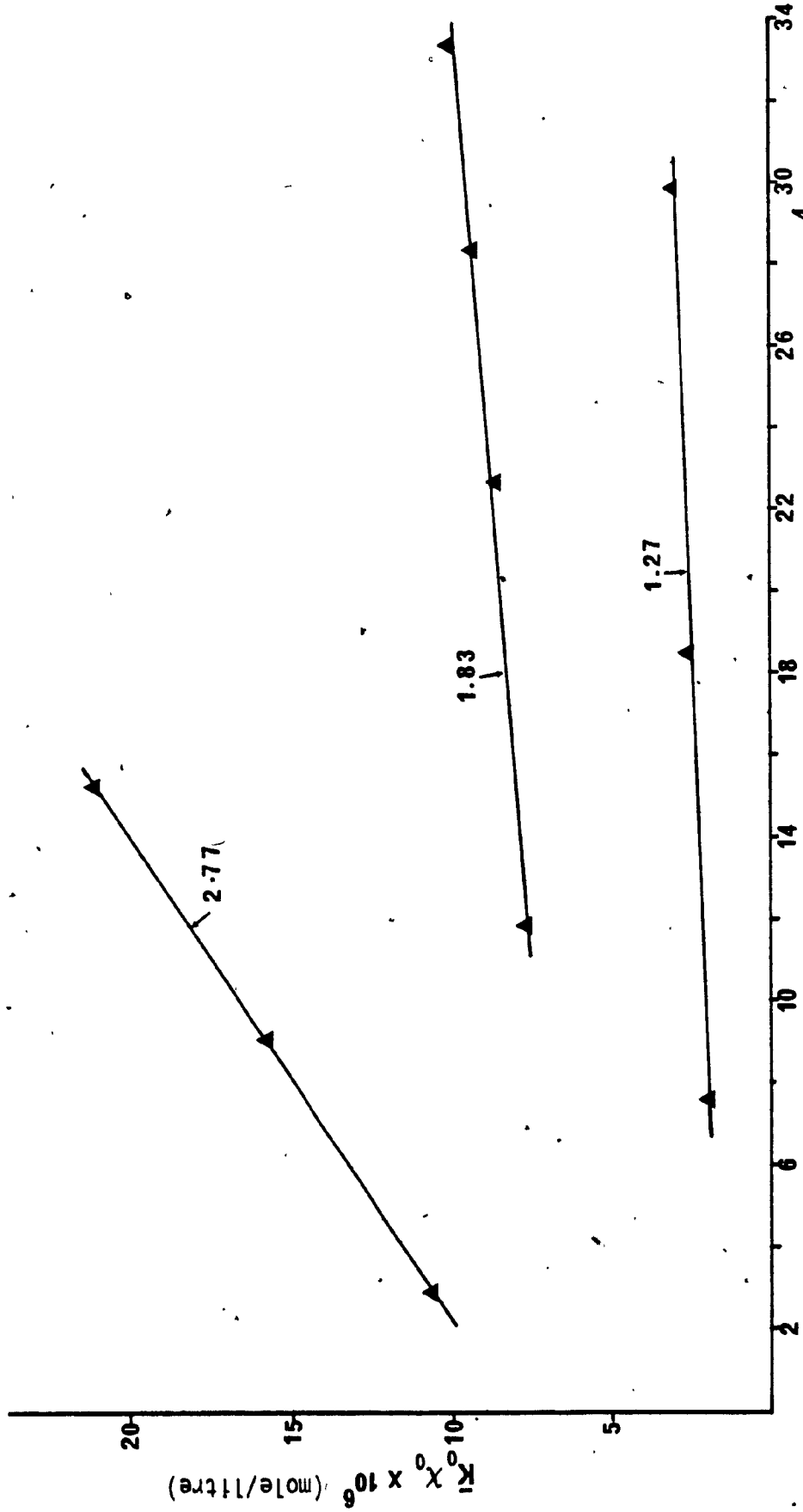


Figure (21): Calculation of $\partial(\bar{K}_0\chi_0)/\partial\chi_T$ for unprotonated Atrazine, from a plot of $\bar{K}_0\chi_0$ versus χ_T at various pH values. The experiments were done in 0.100 M KCl.

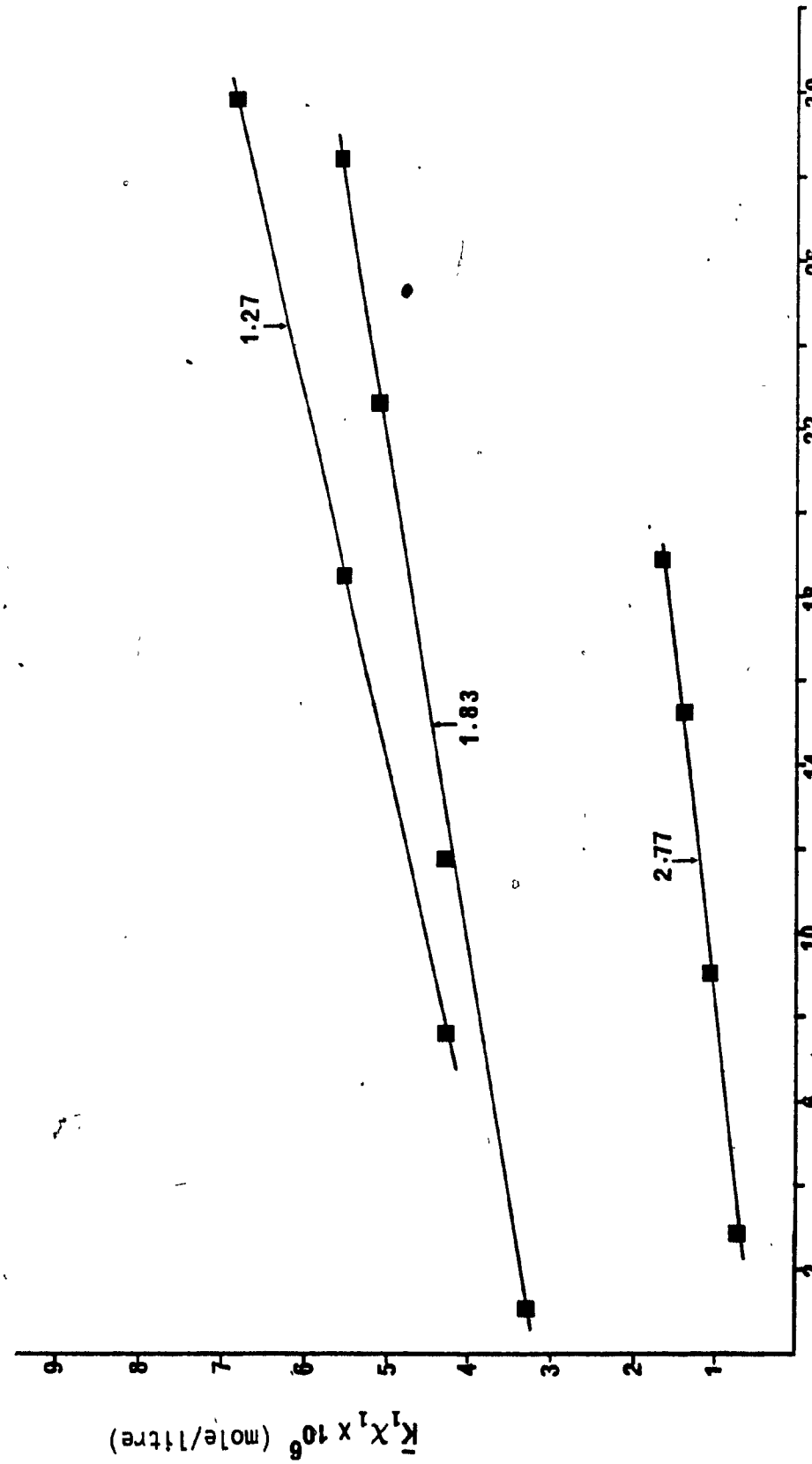


Figure (22): Calculation of $\partial(\bar{K}_1\chi_1)/\partial\chi_T$ for protonated Atrazine, from a plot of $\bar{K}_1\chi_1$ versus χ_T at various pH values. The experiments were done in 0.100 M KCl.

Table (13): Determination of the formation functions and free energies for complexed unprotonated and protonated Atrazine at various α_{1B} values in the presence of 0.100 M KCl.

Complexed Unprotonated Atrazine

pH	α_{1B}	$\frac{\partial(\bar{K}_o X_o)}{\partial X_T}$ (mole/l)	r	K_o (mole/l)	$1/K_o$ (l/mole)	$-(\Delta G^o + RT\ln\Gamma)$ (Kj/mole)
1.27	0.312	5.38×10^{-4}	0.999	1.73×10^{-3}	5.79×10^{2}	15.8
1.83	0.625	1.31×10^{-3}	0.999	2.10×10^{-3}	4.76×10^{2}	15.3
2.77	0.935	8.46×10^{-3}	0.999	9.04×10^{-3}	1.01×10^{2}	11.7

Complexed Protonated Atrazine

pH	α_{1B}	$\frac{\partial(\bar{K}_1 X_1)}{\partial X_T}$ (mole/l)	r	K_1 (mole/l)	$1/K_1$ (l/mole)	$-(\Delta G^o + RT\ln\Gamma)$ (Kj/mole)
1.27	0.312	1.19×10^{-3}	0.999	1.72×10^{-3}	5.81×10^{2}	15.8
1.83	0.625	7.84×10^{-4}	0.999	2.09×10^{-3}	4.78×10^{2}	15.3
2.77	0.935	5.86×10^{-4}	0.999	9.04×10^{-3}	1.11×10^{2}	11.7

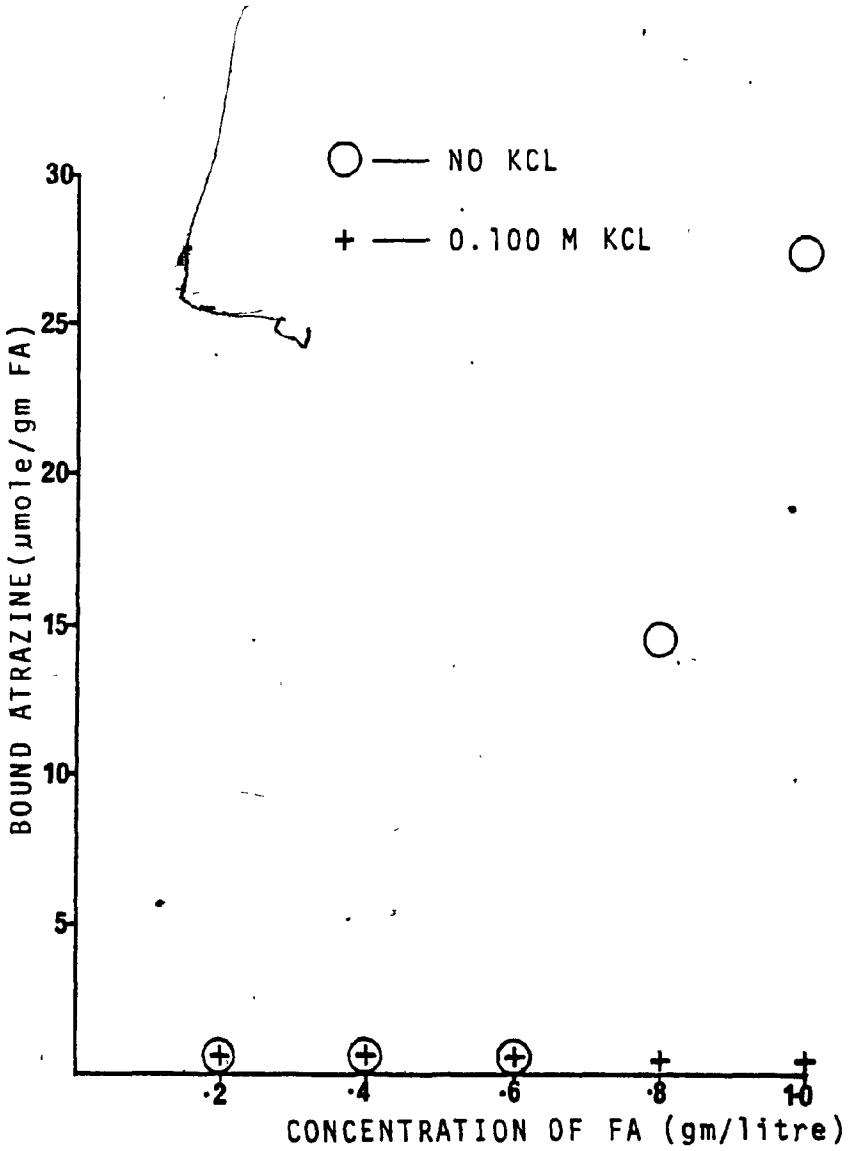


Figure (23); Binding Capacity of Atrazine as a function of FA concentration at pH 3.50.

litre. For FA concentrations of 0.8000 and 1.0000 gram per litre, the respective complexing capacities are 14.5 and 27.6 µmole per gram FA.

Appendix (IV) shows the titration graphs for varying concentrations of FA in the presence of 0.100 M KCl at pH 3.50. No binding of Atrazine was observed for the FA concentrations studied.

Figure (23) shows plots of the complexing capacity versus the concentration of FA. The circles show binding in the absence of KCl while

the pluses show binding in the presence of KCl.

4.0.6 ATRAZINE VARIATION IN THE PRESENCE OF CONSTANT COPPER (II) CONCENTRATION AND AT CONSTANT pH

For the experiments in Section 3.3.4e, copper (II) was added in amounts approximately equivalent to the Type A carboxylic sites (4.99 mmole/gm FA) and in amounts less than the Type 1 carboxylic sites (3.0 to 3.3 mmole/gm FA). Table (5) of Chapter 3 lists the total copper (II) concentrations added at each pH value. The experiments done at pH 1.19 and 2.38 had copper (II) concentrations less than the Type 1 sites (an average of 1.055 mmole/litre) while experiments done at pH 1.38, 2.14, 3.02, 3.96, 4.04 and 5.23 had copper (II) concentrations which were close to the Type A sites (an average of 4.744 mmole/litre). The equilibrium free copper (II) concentration for each experiment is given in column three of Table (5). The amount of copper (II) bound is given in column four of Table (5).

The Atrazine titration graph for each of the pH values in Table (5) is given in Appendix (V).

4.0.6a TREATMENT OF COPPER (II) RESULT

The weighted average stability constant, $\bar{K}_4$, and the differential stability constant, K_4, can be calculated for the data in Table (5). But before these calculations can be done, Gamble's (31) integral equation (4-19) has to be rearranged so as to obtain a form which is applicable to the experimental data present in Table (5). The rearrangment is as follows: the reaction of FA bidentate site (SH^-) with Cu^{2+} is given in reaction (4-17).

$$SH^- + Cu^{2+} \overset{\bar{K}_4}{\rightleftharpoons} SCu + H^+ \qquad (4\text{-}17)$$

The weighted average stability constant is,

$$\bar{K}_4 = \left[\frac{m_C a_H}{m_{SH} m_M}\right] \qquad (4\text{-}18)$$

where,

m_C – molarity of the complex

a_H – activity of the hydrogen ion concentration

m_{SH} – molarity of singly ionized chelation site

m_M – molarity of free metal ion in solution

The integral equation for the weighted average stability constant is,

$$\bar{K}_4 = -\left[\frac{1}{1-x_C-x_{SH_2}}\right] \int_0^{x_C} K_4 \, dx_C \qquad (4\text{-}19)$$

where,

$$x_C = m_C/C_S \qquad (4\text{-}20)$$

$$x_{SH} = m_{SH}/C_S \qquad (4\text{-}21)$$

$$x_{SH_2} = m_{SH_2}/C_5 \qquad (4\text{-}22)$$

where,

C_S – total chelating sites = 5.43 mmole/gm FA

m_{SH_2} – molarity of fully protonated chelation sites

For a constant amount of x_{SH_2}, equation (4-19) can be transformed into a differential equation (4-23).

$$K_4 = -\left(\frac{d[(1-x_C-x_{SH_2})\bar{K}_4]}{dx_C}\right) \qquad (4\text{-}23)$$

But, it can be shown that,

$$(1-x_C-x_{SH_2})\bar{K}_4 = x_C\left[\frac{a_H}{m_M}\right] \qquad (4\text{-}24)$$

Equation (4-23) will then become equation (4-25).

$$K_4 = -\left(\frac{d[x_C(a_H/m_M)]}{dx_C}\right) \qquad (4\text{-}25)$$

Hence, a plot of $x_C(a_H/m_M)$ versus x_C will give the differential stability constant K_4 as the slope.

The data in Table (5) were converted into the parameters in equation (4-25). These parameters are listed in Table (14). A program called POLYCU (see Section 4.1.2b for the testing of this program) was written to fit $x_C(a_H/m_{Cu^{2+}})$ against x_C to a fourth degree polynomial (Appendix (VI). K_4 and the free energy were calculated from the polynomial. The K_4 and free energy values for pH 1.19 and 2.38 were obtained by interpolating from the polynomial representing the other data in Table (14). Figure (24) represents a plot of $(1-x_C-x_{SH_2})\bar{K}$ versus x_C.

4.0.6b TREATMENT OF ATRAZINE RESULT

From the titration graphs in Appendix (V) the complexing capacities at pH 1.19, 1.38, 2.14 and 2.38 were 10.3, 15.1, 7.00, and 10.0 μmole per

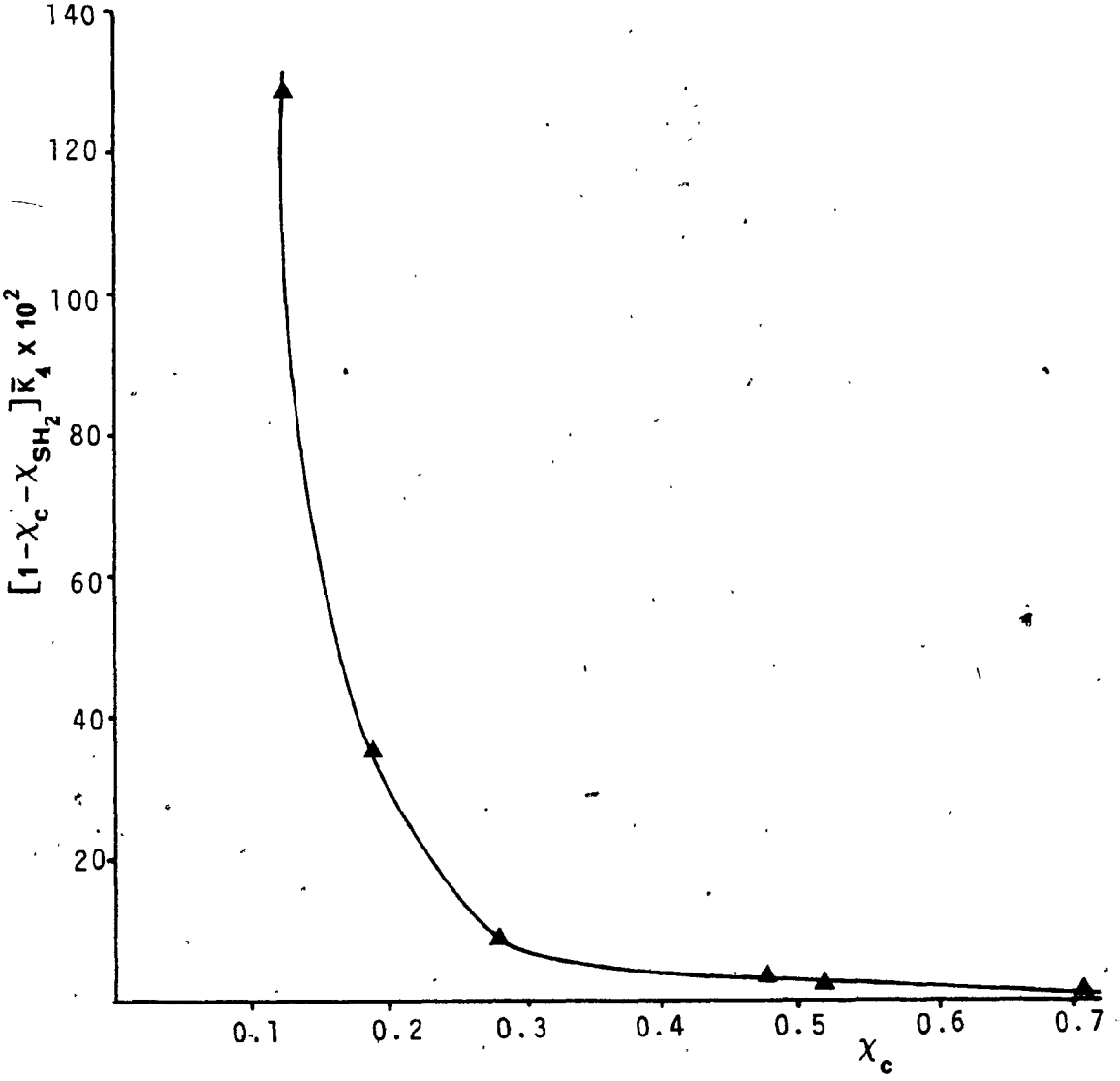


Figure (24): Calculation of K_4, the differential function for copper-fulvate complexes. FA = 1.000 gm/l.

Table (14): Determination of K_4 for Copper (II)-fulvate complexes at various pH values. FA = 1.000 gm/l.

χ_c	pH	a_H (mole/l)	$m_{Cu^{2+}} \times 10^4$ (mole/l)	$\chi_c(a_H/m_{Cu^{2+}})$	K_4	$-(\Delta G_4^o + RT\ln\Gamma_4)$ (Kj/mole)
0.0246	1.19	6.46×10^{-2}	9.40	1.69	*40.3	8.96
0.0810	2.38	6.17×10^{-3}	5.96	0.567	*26.0	7.89
0.124	1.38	4.17×10^{-2}	40.2	1.29	17.2	7.02
0.189	2.14	7.22×10^{-3}	38.7	0.353	8.00	5.13
0.278	3.02	9.55×10^{-4}	31.8	0.0834	1.20	0.454
0.479	3.96	1.10×10^{-4}	20.1	0.0262	1.00	---
0.517	4.04	9.12×10^{-5}	18.1	0.0260	0.170	---
0.707	5.23	5.89×10^{-6}	11.2	0.00373	---	---

$$\chi_c \frac{(a_H)}{(m_{Cu^{2+}})} = 5.02 - 48.0\chi_c + 1.65 \times 10^2\chi_c^2 - 2.41 \times 10^2\chi_c^3 + 1.26 \times 10^2\chi_c^4 \pm 0.137$$

* — these values were calculated from the 4th degree polynomial.

gram FA respectively. For pH values of 3.02, 3.96, 4.04 and 5.23 no binding of Atrazine was observed. Figure (17) shows a plot of the complexing capacity versus the pH (solid diamonds) for an average copper (II) concentration of 4.74×10^{-3} M.

K_0 and K_1 values were determined in the same way as was done in Section 4.0.3a for Atrazine variation at constant pH. Table (15) lists the values calculated from the titration graphs in Appendix (V).

4.0.7 COPPER (II) VARIATION AT CONSTANT pH IN THE PRESENCE OF A CONSTANT AMOUNT OF ATRAZINE

From the duplicate experiments in Section 3.3.4f, titration graphs are prepared which are similar to those in Section 4.0.3a. These graphs are shown in Appendix (VII). The complexing capacities for Graphs A and B

Table (15)[a]: Determination of the formation constants and free energies for complexed unprotonated and protonated Atrazine at various α_{1B} values in the presence of a constant amount of Copper (II).

Complexed Unprotonated Atrazine

pH	α_{1B}	$\frac{\partial(\bar{K}_o x_o)}{\partial x_T}$ (mole/l)	r	K_o (mole/l)	$1/K_o$ (l/mole)	$-(\Delta G^o + RT\ln\Gamma)$ (Kj/mole)
1.19	0.275[b]	1.07×10^{-3}	0.999	3.89×10^{-3}	257	13.4
1.38	0.370	3.65×10^{-3}	0.999	9.85×10^{-3}	102	11.2
2.14	0.772	6.83×10^{-3}	0.999	8.84×10^{-3}	113	11.5
2.38	0.855[b]	1.64×10^{-3}	0.999	1.92×10^{-3}	521	15.2

Complexed Protonated Atrazine

pH	α_{1B}	$\frac{\partial(\bar{K}_1 x_1)}{\partial x_T}$ (mole/l)	r	K_1 (mole/l)	$1/K_1$ (l/mole)	$-(\Delta G^o + RT\ln\Gamma)$ (Kj/mole)
1.19	0.725[b]	4.57×10^{-3}	0.999	3.89×10^{-3}	257	13.4
1.38	0.630	6.21×10^{-3}	0.999	9.86×10^{-3}	101	11.2
2.14	0.228	2.02×10^{-3}	0.999	8.85×10^{-3}	113	11.4
2.38	0.145[b]	2.76×10^{-3}	0.999	1.90×10^{-3}	527	15.2

a- no binding was observed at pH values of 3.02, 3.96, 4.04 and 5.23.

b- at these pH values a lower concentration of copper (II) was present in solution (see Table(5)).

are 2.97 and 2.71 mmole Cu^{2+} per gram FA respectively.

Using the equilibrium copper (II) concentrations before the equivalence point for graph A in Appendix (VII), the differential stability constants were calculated. Table (16) gives the values needed for the calculation of K_4 according to equation (4-25).

The program POLYCU was used to fit a polynomial to the data points $(\chi_C, \chi_C(a_H/m_{Cu^{2+}}))$ in Table (16). A fourth degree polynomial was the best fit to the data points. The first derivative of the polynomial gives the K_4 value at a particular χ_C value. Table (16) has the calculated values of K_4, $-(\Delta G_4^o + RT \ln \Gamma_4)$, and the fourth degree polynomial fit.

Similar calculations were repeated for graph B in Appendix (VII). The data were fitted best by a third degree polynomial: $\chi_C(a_H/m_{Cu^{2+}}) = 1.296 - 5.103\ \chi_C + 10.93\ \chi_C^2 - 7.734\ \chi_C^3 \pm 2.083 \times 10^{-2}$. For χ_C values of 0.0589, 0.146, 0.228, 0.309 and 0.473 the K_4 values calculated were 3.90, 2.41, 1.32, 0.561, 0.104 and 0.00, respectively. Figure (25) show plots of $(1-\chi_C-\chi_{SH_2})\bar{K}_4$ versus χ_C for both experiments. The solid triangles represent data points for titration graph A while the solid squares represent data points from titration graph B. Free energy values ranged from -3.36 to -0.443 when calculated from the differential constant.

Table (17) shows the initial and final Atrazine concentrations for the equilibrated FA solutions in graph A of Appendix (VII). The total copper (II) concentrations in the table refer to the six control solutions in graph A. The control solution with 80.5×10^{-2} mmole per litre was not included in graph A. Table (17) demonstrates that no Atrazine was bound to FA at pH 3.86 in the presence of varying amounts of copper (II). Similar results were obtained from graph B.

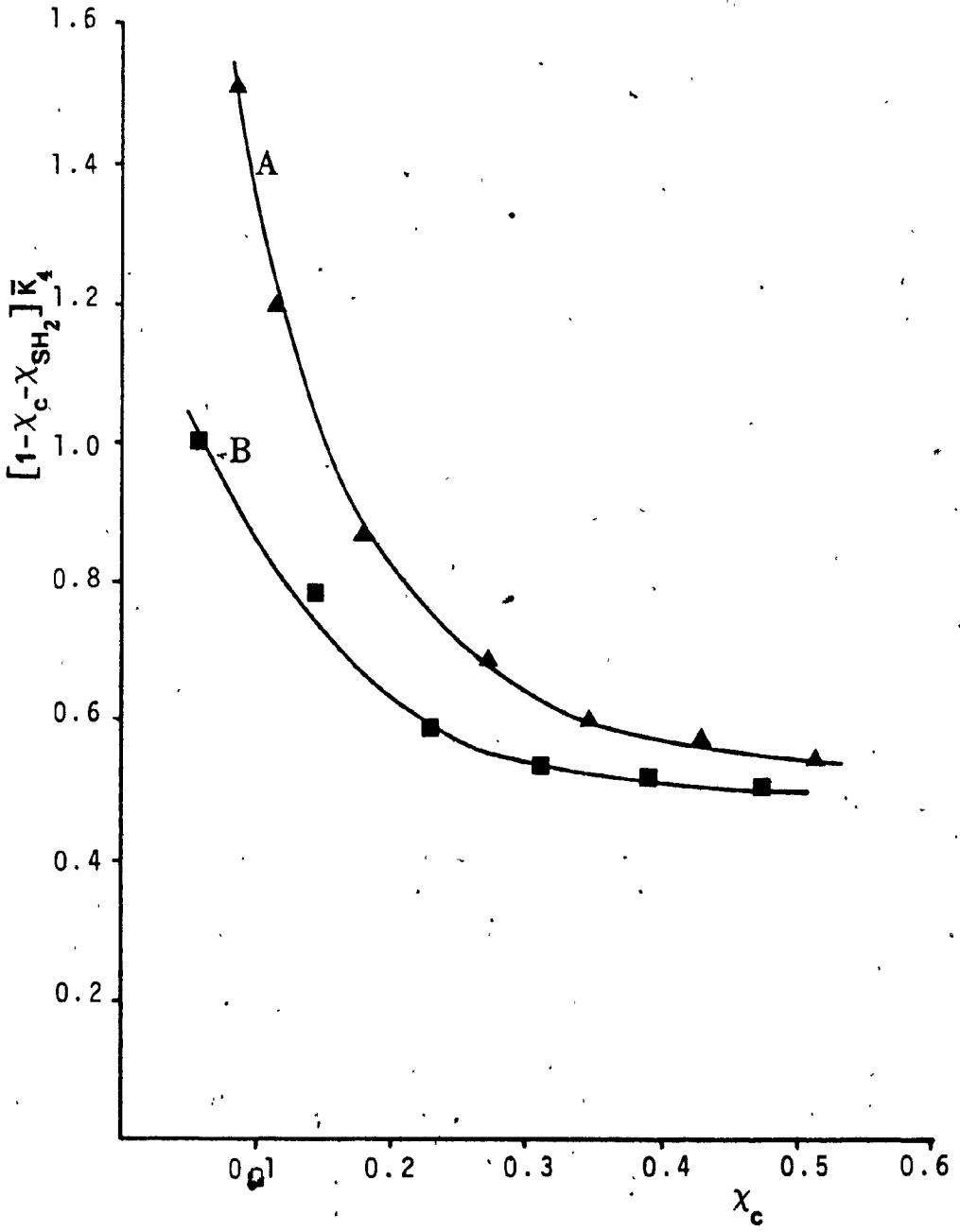


Figure (25): Calculation of K_4, the differential function for copper (II)-fulvate complexes at pH 3.86 and FA = 0.1000 gm/l.
A and B represent duplicate experiments.

Table (16) : Determination of K_4 for Copper (II)-fulvate complexes for $a_H = 1.39 \times 10^{-4}$ and FA = 0.1000 gm/l.

$m_{Cu^{2+}} \times 10^5$ (mole/l)	x_c	$x_c(a_H/m_{Cu^{2+}})$	K_4	$-(\Delta G_4^o + RT\ln\Gamma_4)$ (KJ/mole)
0.80	0.0866	1.509	10.8	5.87
1.34	0.115	1.200	7.97	5.12
2.90	0.182	0.875	3.51	3.10
5.50	0.271	0.687	1.04	0.0961
8.00	0.346	0.603	0.685	--
10.50	0.432	0.573	0.600	--
13.00	0.516	0.553	--	--

$$x_c \frac{(a_H)}{(m_{Cu^{2+}})} = 2.926 - 23.47x_c + 93.90x_c^2 - 171.5x_c^3 + 117.0x_c^4$$
$$\pm 3.021 \times 10^{-2}$$

4.0.8 pH VARIATION FOR CONSTANT ATRAZINE CONCENTRATION AND LOW IONIC STRENGTH

The filtrates for the experiments in Section 3.3.4g were not adjusted to pH 4 and higher so as to convert protonated Atrazine (< pH 4.0) to the unprotonated form. Figure (26) shows the equilibrium unprotonated Atrazine concentrations in the controls (triangles) and in the FA solutions (circles) as a function of the pH of the solutions. Hence, the amount of Atrazine bound at each pH can be obtained by subtracting the amount in the FA solution from that in the control solution. The bound Atrazine from Figure (26), therefore, only represents the unprotonated form. The bound protonated Atrazine could not be determined from these

Table(17): Equilibrium Atrazine concentrations for varying concentrations of Copper (II) in titration graph A in Appendix (VII)

#	Total Copper (II) Concentration (mMole/litre) x 10^2	Initial Atrazine Concentration (μMole/litre)	Final Atrazine Concentration (μMole/litre)
1	3.6	27.0	27.1
2	10.6	27.2	26.9
3	24.6	27.2	27.4
4	38.6	27.0	27.8
5	52.6	26.7	27.1
6	66.6	27.3	26.4
7	80.5	27.1	26.6
		AVE. 27.1 ± 0.17	27.0 ± 0.42

experiments.

Figure (27) represent plots for the amount of unprotonated Atrazine bound per gram of FA versus the pH of the solution. Triplicate experiments were done; two at the same Atrazine concentration and the other at a higher Atrazine concentration. What is clear from the graphs in Figure (27) is that the shapes are similar to the graph in Figure (17) which has no KCl, even though two different experimental approaches were taken.

The equilibrium functions derived in Chapter 2 cannot be applied to these experiments. Using the non state function, equation (2-26), gives both positive and negative values for K_0; a negative value for K_0 is not possible. Using equation (2-49) is also not possible, since that equation assumes χ_T is constant as pH varies. Also, above pH 4, the expression in equation (2-53) is always zero, since α_{1B} is always one (above pH 4).

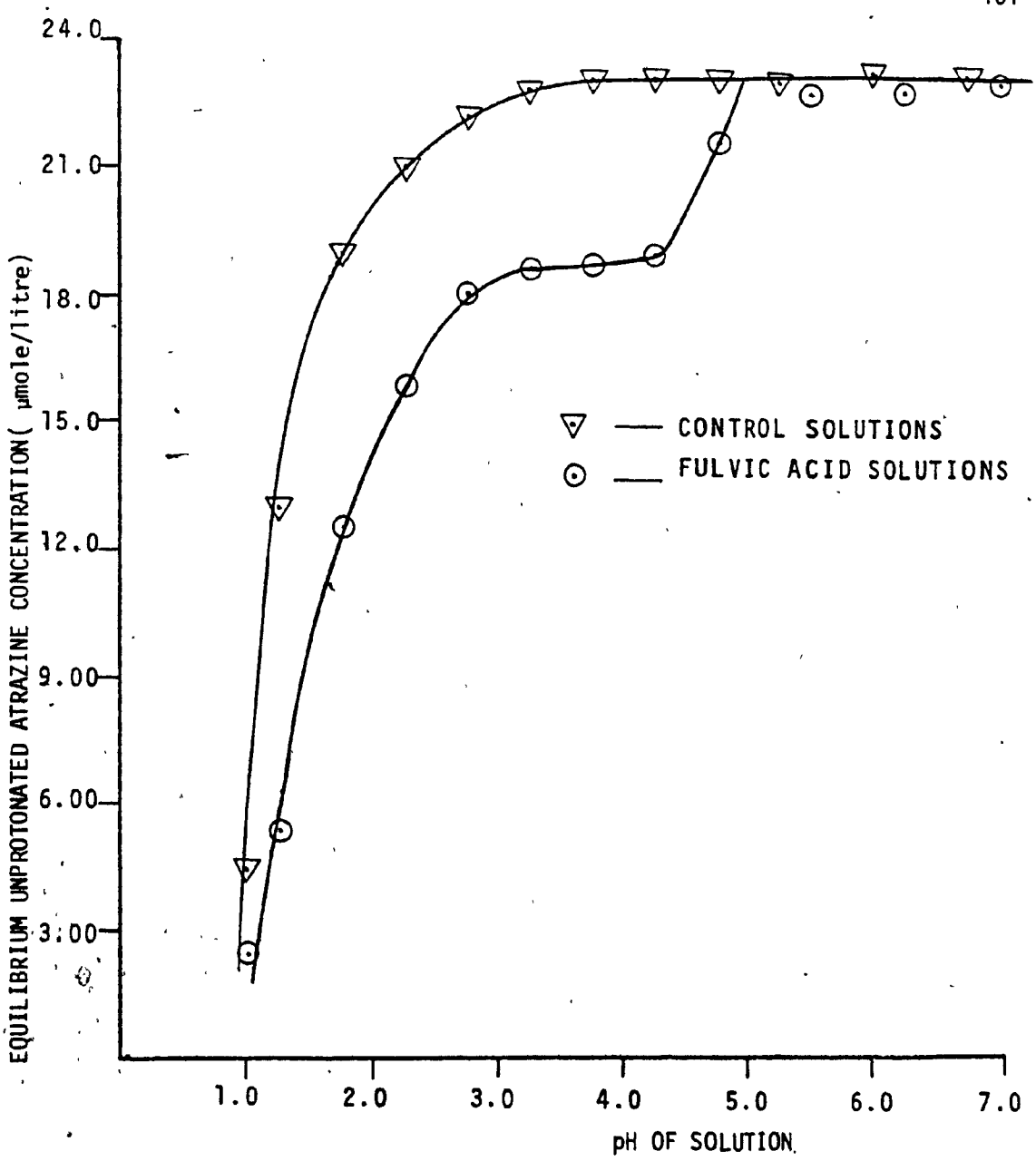
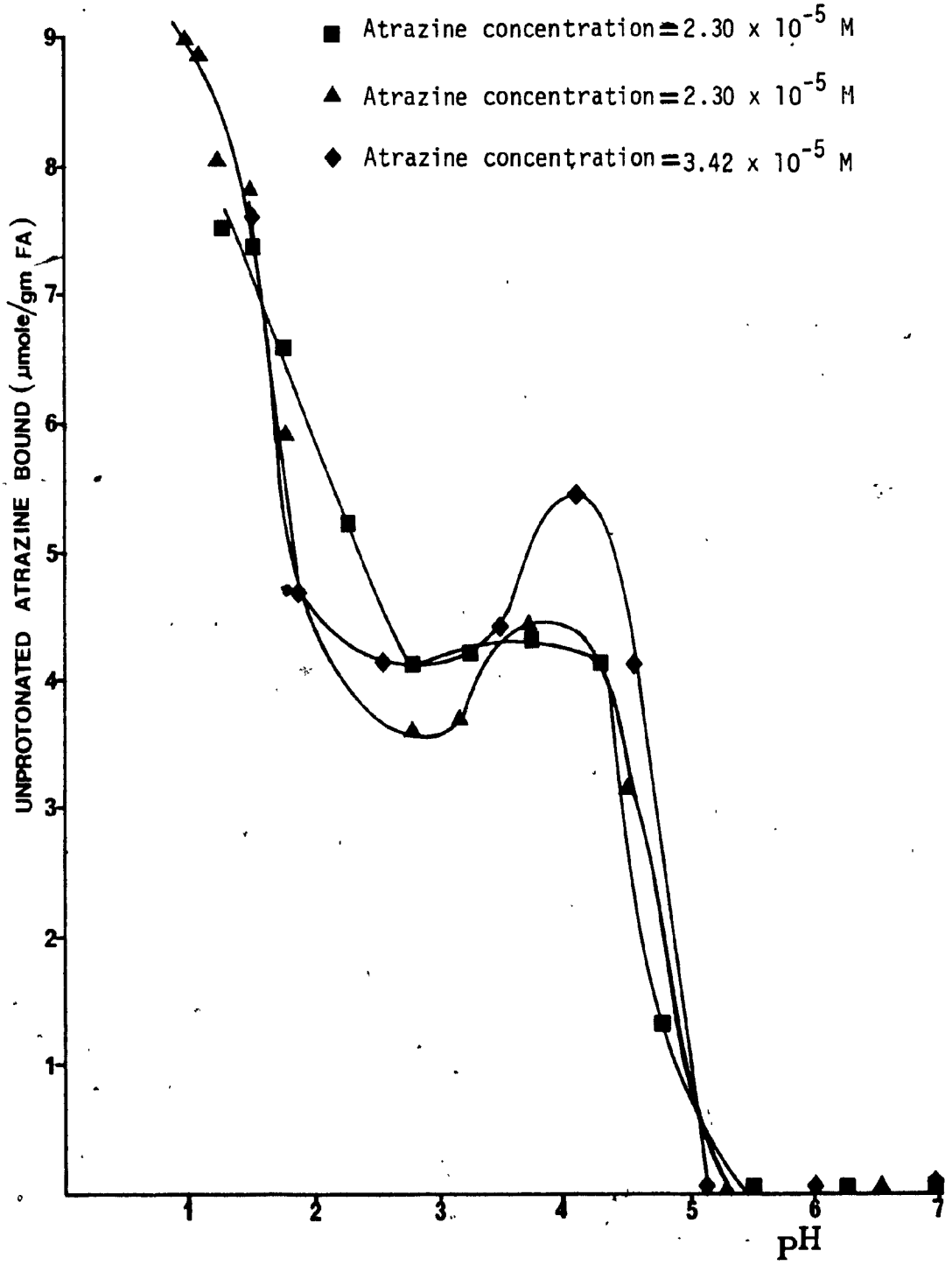


Figure (26): Equilibrium unprotonated Atrazine concentration as a function of pH. FA = 1.0000 gm/litre. Atrazine = 2.30×10^{-5} M. Total volume = 50.00 ml.



Figure(27): Bound unprotonated Atrazine as a function of pH for three independent experiments. FA=1.0000 gm/litre.

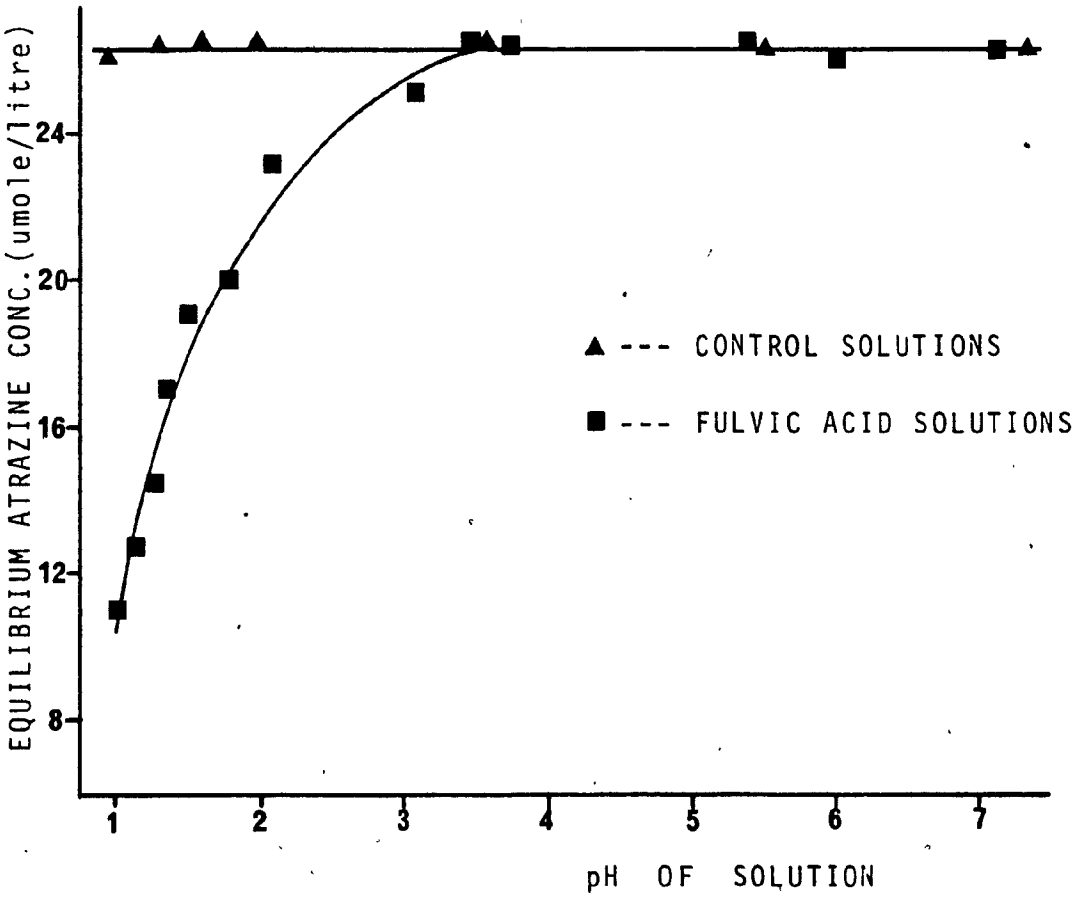


Figure (28): Equilibrium total Atrazine concentrations as a function of pH. FA = 1.0000 gm/litre. Concentration of KCl = 0.100 M. Atrazine = 2.46×10^{-5} M. Total volume = 50.00 ml.

4.0.9 pH VARIATION FOR CONSTANT ATRAZINE CONCENTRATION AND HIGH IONIC STRENGTH (0.100 M KCl)

For the experiments in Section 3.3.4h the equilibrium total Atrazine concentration was plotted against the pH of the respective solution (Figure (28)). The amount of Atrazine bound (both protonated and unprotonated) is obtained by subtracting the quantity in the FA solution from that in the control solution at the same pH values.

Figure (29) represent plots of the amount of total Atrazine bound

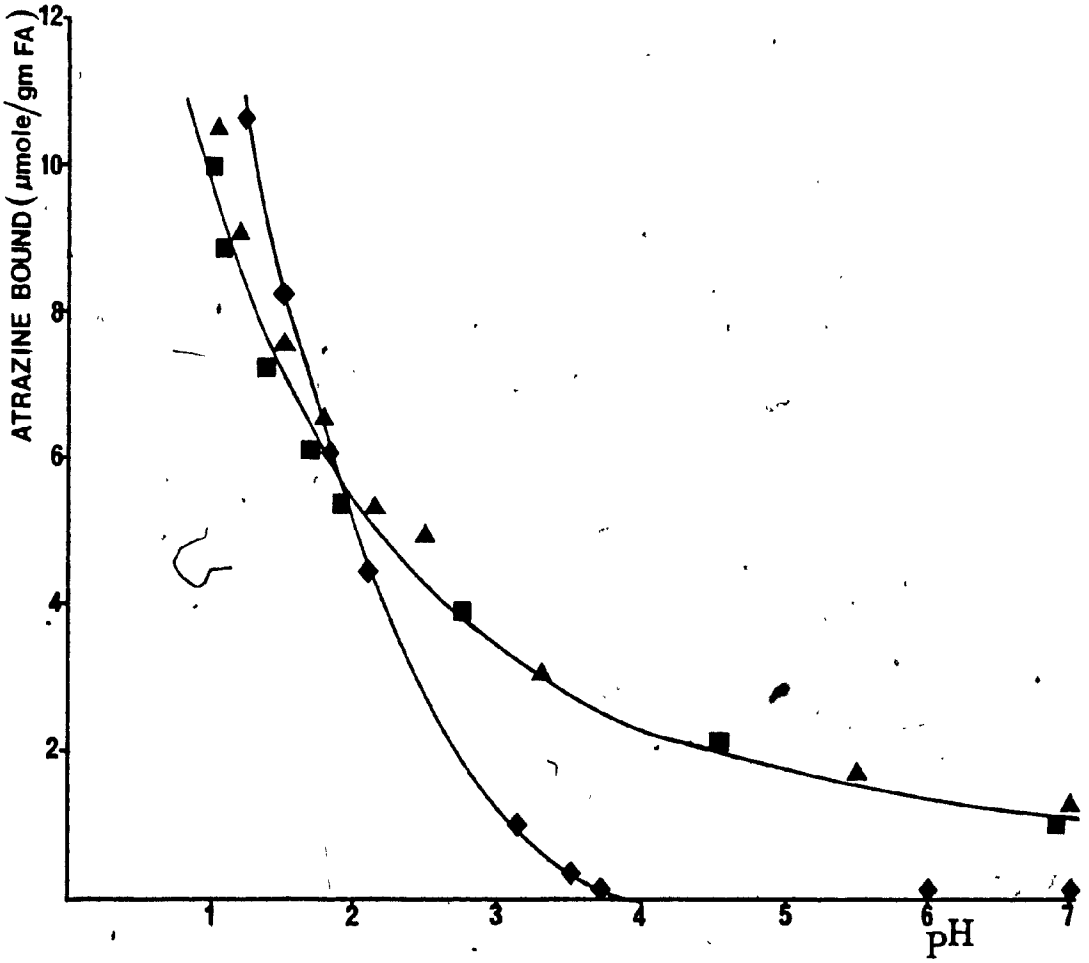


Figure (29): Total Atrazine bound as a function of pH in the presence of 0.100 M KCl for three independent experiments.

■ - Atrazine concentration 2.46×10^{-5} M

▲ - Atrazine concentration 2.46×10^{-5} M

◆ - Atrazine concentration 2.46×10^{-5} M

FA - 1.0000 gm/litre.

per gram of FA versus the pH of the solutions. The general trend in Figure (29) is consistant with that of Figure (17) for the KCl case.

4.1.0 DISCUSSION OF RESULTS

4.1.1 EVALUATION OF THE BATCH ULTRAFILTRATION METHOD

Grice and Hayes (3) have reported the use of a batch ultrafiltration method (BUM), which they called "pressure filtration". They said, "The amounts of herbicide bound by humic substances were estimated by measuring the radioactivity in solution before and after pressure filtering 5 ml of supernatent through a 25 millimetre diameter Diaflow Ultrafilter PM-10 membrane". It is important to note, however, that they did not test the method for membrane sorption and rejection problems.

Some of the YM-2 membranes used in this project were subjected to repeated methanol extraction. The extract for each membrane was tested for the presence of Atrazine by gas chromatography. No traces of Atrazine was found to be present in these extracts. Hence, the YM-2 membrane did not absorb any Atrazine.

Rejection of Atrazine in the FA solutions (if any occurs) by the YM-2 membranes are corrected for by subjecting control solutions to the same filtration process as the FA solutions. Therefore, Atrazine rejected in the FA solutions will also be rejected in the control solutions assuming FA does not play any part in the rejection process. This is the same technique used by Roy and Miles (60) to correct for membrane rejection of a solute. This is called a "point by point" correction technique for rejection of a solute by the membrane.

The reproducibility and reliability of the BUM was tested in one way by carrying out the duplicate experiments in Section 3.3.4f of Chapter 3. The results from these experiments were presented in Section 4.0.7 of Chapter 4. The average complexing capacity for the two experiments is

2.84 mmole Cu^{2+} per gram FA at a pH value of 3.86 in the absence of KCl. Langford et al. (61) and Lee (62) reported a binding capacity of 2.6 mmole Cu^{2+} per gram FA at a pH of 3.50 for a FA concentration of 0.100 gram per litre. According to Langford et al. the binding capacity is sensitive to pH, ionic strength and the concentration of FA. The higher the pH the higher will be the binding capacity. The higher binding capacity obtained in the present study for Cu^{2+} at pH 3.86 is, therefore, not surprising. Table(17A) shows a comparison for the amount of Cu^{2+} bound, x_C, and K_4 for varying amounts of total copper (II) added during a titration. The experimental values were obtained form Appendix (VII) (graph A) and Table (16) while the reference values were obtained from Lee (62). The K_4 values for the reference data were obtained by using the polynomial at the bottom of Table (16). This table demonstrates that for the same amount of total copper (II) added similar values for the amount of copper (II) bound, x_C, and K_4 are obtained. Hence, copper (II) binding results for the Armadale FA are comparable even though they are done by different experimental procedures.

The titration graphs introduced in Section 4.0.0 can also be plotted in a different way so as to obtain the complexing capacity. Shuman et al. (63) have plotted the uncomplexed sorbate concentration versus the total sorbate concentration in order to obtain the complexing capacity, C_L, for the sorbent. Tuschall et al. (64) and Greter et al. (65) have used differential pulse anodic stripping voltammetry techniques to determine the C_L for copper (II) complexing to organic matter. Figure (30) shows a plot of the equilibrium uncomplexed copper (II) versus the total copper added for the data in graph A of Appendix (VII). The C_L obtained from

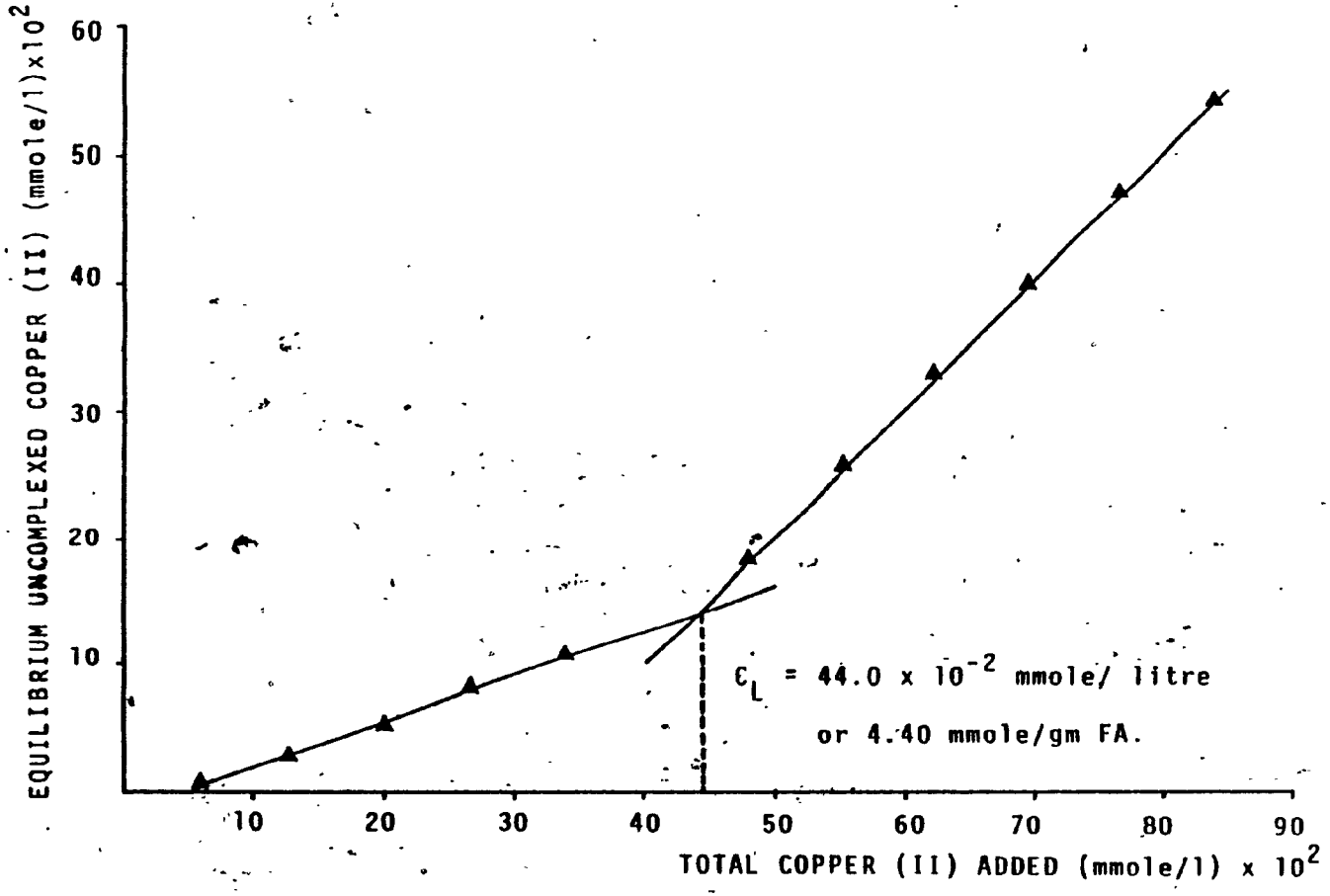
Table (17A): A comparison of χ_C and K_4 values from Table (16) with that of Reference (62). FA = 0.1000 gm/litre.

	Experimental; pH = 3.86			Reference (62); pH = 3.50		
Total Cu^{2+} Added (mmole/gm FA)	Bound Cu^{2+} (mole/litre) x 10^5	χ_C	K_4	Bound Cu^{2+} (mole/litre) x 10^5	χ_C	K_4*
0.550	4.70	0.0866	10.8	4.80	0.0884	10.6
0.758	6.24	0.115	7.97	6.00	0.111	8.96
1.28	9.90	0.182	3.51	11.4	0.210	2.39
2.00	14.7	0.271	1.04	14.4	0.265	1.12
2.68	18.8	0.364	0.685	18.4	0.339	0.700
3.40	23.5	0.432	0.600	19.8	0.365	--
4.10	28.0	0.516	--	20.1	0.370	--

* --- K_4 was calculated from the polynomial in Table (16).

Figure (30) for bound Cu^{2+} is 4.40×10^{-2} mmole per litre or 4.40 mmole per gram FA. This value is 48% higher than the binding capacity obtained from graph A of Appendix (VII) (2.97 mmole per gram FA). A closer examination of graph A in Appendix (VII) shows that C_L in Figure (30) includes the concentration from ab(14.3×10^{-2} mmole per litre) plus the true amount of copper (II) bound, bc(29.7×10^{-2} mmole per litre). Hence, the titration graph in Figure (30) overestimates the binding capacity for FA. It is, also, not possible to use Figure (30) for equilibrium calculations as was done with graph A in Appendix (VII), i.e., such plots are unreliable as has been shown by several authors (66,67,68,69).

Even though this method (BUM) has been shown to be reliable and reproducible it is very time consuming since it involves many steps before the final results can be obtained. The method also consumes a large quantity of FA which is an expensive material, i.e., to obtain enough data



Figure(30): BUM titration curve for the data in graph A of Appendix (VII).

pH = 3.86; FA = 0.1000 gm/litre.

points so as to construct a titration graph one has to use at least 0.7 gram of FA. A method which is less time consuming, uses less FA, and is more automated than the BUM is the continuous flow ultrafiltration method (CFUM). The possibility of replacing BUM with CFUM was tried. The result from CFUM are evaluated in Chapter 5.

4.1.2 INTERACTION OF ATRAZINE WITH FA TYPE A SITES

From the results in Section 4.0.1, Atrazine exists in the unprotonated and protonated forms at pH 4 and lower. Unprotonated Atrazine exists at pH 4 and higher. Protonated Atrazine exists at pH 0.1 and lower. However, between pH 3.1 and 4 it was difficult to experimentally observe any protonated Atrazine since the amount present was 3% or less.

From Section 4.0.2 it was shown that the Armadale FA8 used for the work in the project was similar to the FA1 batch used by Gamble (28,29) for acidometric titrations.

4.1.2a EXTENT OF BINDING

Figure (17) shows the extent of Atrazine binding to FA under various experimental conditions. The figure shows that binding is generally higher in the absence of both KCl and Cu^{2+}. Between KCl and Cu^{2+}, binding is higher in the presence of KCl than in the presence of Cu^{2+}. In the absence of both KCl and Cu^{2+} binding starts at about pH 5 and increases as pH decreases except for a minimum at about pH 2.8. In the presence of 0.100 M KCl, binding starts at about pH 4.6 and increases as pH decreases. In the presence of 4.74×10^{-3} M Cu^{2+}, binding starts at about pH 3.2 and increases as pH decreases.

From the results in Section 4.0.8 the extent of Atrazine binding

(Figure (27)) is about 2.5 to 3.5 times less than shown by the curve with the solid squares in Figure (17). The concentration of Atrazine used to equilibrate the samples for the curves in Figure (27) is about 3 times less, than that for the Atrazine stock solutions ($78.9 \pm 14 \times 10^{-6}$M) used to prepare the titration graphs which gave the curve in Figure (17) (the curve with the solid squares). Hence, the extent of binding increases as the concentration of Atrazine increases. However, once the equivalence point (or saturation point) is reached in a titration, binding becomes independent of the Atrazine concentration. The curve with the solid diamonds in Figure (27) was equilibrated with a higher concentration of Atrazine, hence, a larger amount of Atrazine is bound compared to the other curves in the same figure. Binding starts at about pH 5.3 and it increases as pH decreases. The binding trend is similar to that in Figure (17) for the case without KCl and Cu^{2+}. This similarity is not surprising since the only difference between the two experimental designs is the concentration of Atrazine used. However, the curves in Figure (27) are only for bound unprotonated Atrazine whereas the curve in Figure (17) is for bound unprotonated and protonated Atrazine.

A similar comparison can be made for the curve with 0.100 M KCl in Figure (17) and those in Figure (29). Again a smaller concentration (about 3 times less) of Atrazine was used to equilibrate the samples which gave the binding curve in Figure (29). Therefore, the 3 to 4 times increase in binding in Figure (17) is expected. It should be noted that the curve with the solid diamonds in Figure (29) was obtained from an experiment which used the FA1 fulvic acid whereas the curves with the solid squares and triangles were done with the FA8 fulvic acid (the same FA that was used to obtain the curve with 0.100 M KCl present in Figure (17)).

Binding beyond pH 4 for the curves with the solid triangles and squares in Figure (29) was unexpected. However, the binding trend is the same for both Figures (17) and (29), i.e., as pH decreases from about pH 4.5 the binding of Atrazine increases.

From the above discussion all binding of Atrazine to FA takes place below pH 5.4 except for the two curves in Figure (29). Since binding generally increases as pH decreases, then, one can associate the Type A carboxyl sites with the binding of Atrazine.

4.1.2b COMPLEXING WITH THE TYPE A SITES

The pK_A values for the Type A carboxyl groups will give an indication of the pH range at which FA becomes protonated. If this pH range is the same range at which Atrazine binds to FA, then, one can say that Atrazine binds by hydrogen bonds to the Type A sites. Gamble's (29) equation (1-7) in Chapter 1 was used to evaluate the dissociation constants K_A, for the Type A acidic groups. In order to calculate K_A, a plot of $(1-\alpha_A)\bar{R}_A$ versus α_A has to be made and the first derivative taken from the fitted curve. A polynomial regression program, called POLYAC, was written to fit all functions that needed a first derivative. The program POLYAC was tested to make sure it was carrying out the correct calculations. Table (18) compares the coefficients of a 4^{th} degree polynomial fit by POLYAC for values obtained from Reference (70). There is no significant difference between the values in the table. One can, therefore, conclude that POLYAC is acceptable.

Using the data in Table (9), $(1-\alpha_A)\bar{R}_A$ was calculated and tabulated in Table (19). The program POLYAC (Appendix (VI)) was then used to fit $(1-\alpha_A)\bar{R}_A$ versus α_A from Table (19) to a polynomial that give the smallest

Table (18): Comparison of coefficients of a fourth degree polynomial fit obtained for POLYAC with that of Reference (70).

COEFFICIENTS	POLYAC	REFERENCE (70)
A(0)	6.31569	6.316
A(1)	- 4.23011	- 4.230
A(2)	6.95477	6.955
A(3)	- 1.49302	- 1.493
A(4)	7.60754	7.608
	Variance of fit = 0.25713	Variance of fit = 0.257

variance of fit. The program takes the first derivative of the fitted polynomial at the experimental points and then evaluates K_A according to equation (1-7). Table (19) gives calculated K_A, pK_A, and the fitted equation for the data. The standard deviation of the equation is also given at the bottom of Table (19). The pK_A range for the Type A carboxylic acids is 1.74 to 4.08. Atrazine binds to FA at about pH 5.4 and lower. Therefore, hydrogen bonds could be responsible for Atrazine binding. Figure (11) also indicates that the Type A sites become protonated at pH 5.85 and lower. The figure further shows that there are roughly two kinds of protonation sites. The pH range of 3.4 to 5.85 represent one kind of sites and for pH values less than 3.4 a second kind of Type A sites exist. The latter sites are what Gamble (28,29) probably refers to as Type 1 sites, the former sites represent all the other Type A sites.

The amount of Type A sites which are responsible for binding Atrazine is rather small. Figure (31) shows a plot of the percentage of Type A sites occupied by Atrazine as a function of pH for the data in Figure (17).

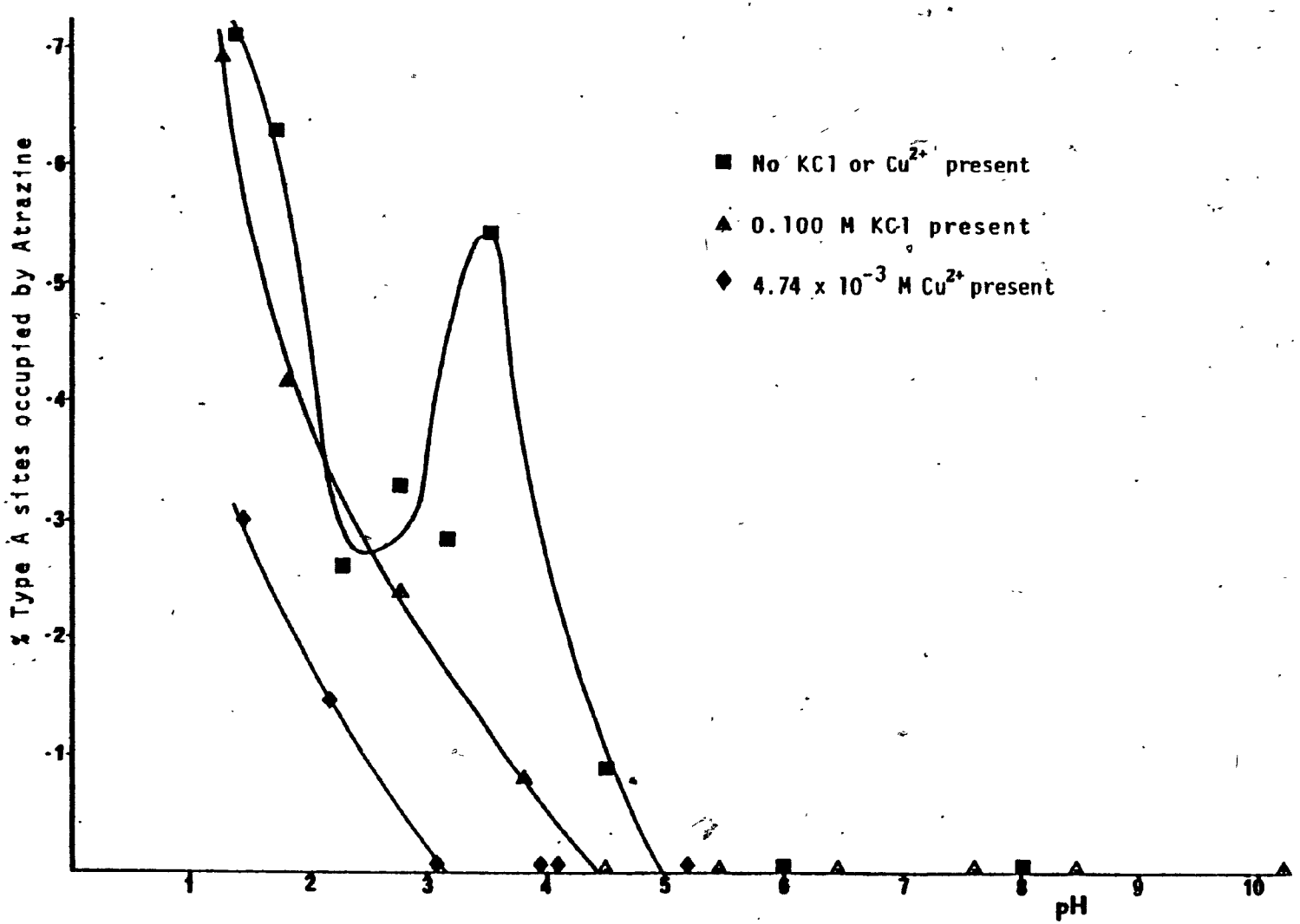
Table (19): Determination of pK_A for Type A carboxylic acid groups.

pH	α_A	$(1-\alpha_A)\bar{K}_A \times 10^4$ (moles/litre)	$K_A \times 10^3$ (moles/litre)	pK_A
2.99	0.408	4.122	18.18	1.74
3.31	0.420	2.051	9.87	2.01
3.35	0.430	1.877	5.40	2.27
3.70	0.496	0.988	0.799	3.10
4.01	0.565	0.551	0.488	3.31
4.10	0.588	0.462	0.404	3.39
4.43	0.659	0.245	0.206	3.69
4.63	0.708	0.167	0.123	3.91
4.73	0.733	0.135	0.098	4.01
4.91	0.782	0.097	0.082	4.08

$$(1-\alpha_A)\bar{K}_A \doteq 1.50215 \times 10^{-3} - 5.61167 \times 10^{-3}\alpha_A + 7.13522 \times 10^{-3}\alpha_A^2 - 3.06888 \times 10^{-3}\alpha_A^3 \pm 5.9648 \times 10^{-7}$$

A maximum of 0.7% of the Type A sites (4.99 mmole/gm FA) are involved in binding at a pH value of 1.36 for both the KCl and in the absence of KCl and Cu^{2+} cases. For the Cu^{2+} case, only about 0.3% of the Type A sites bind Atrazine for a pH value of 1.36. Hence, Atrazine binds to a small and specific set of Type A fulvic acid sites.

If a correlation is made between the complexing capacities and the protonation of the Type A sites for the case where KCl and Cu^{2+} are absent in Figure (17), a graph looking like Figure (32) results. The solid line represents the true experimental data while the dashed line in the figure is a linear regression least square fit to the data points. The equation for the least square fit is $C_L = -0.7205 + 36.107(1-\alpha_A)$; the correlation coefficient of the fit is 0.837. Two questions can be asked about the experimental



Figure(31):% Type A sites occupied by Atrazine as a function of pH for various experimental conditions.

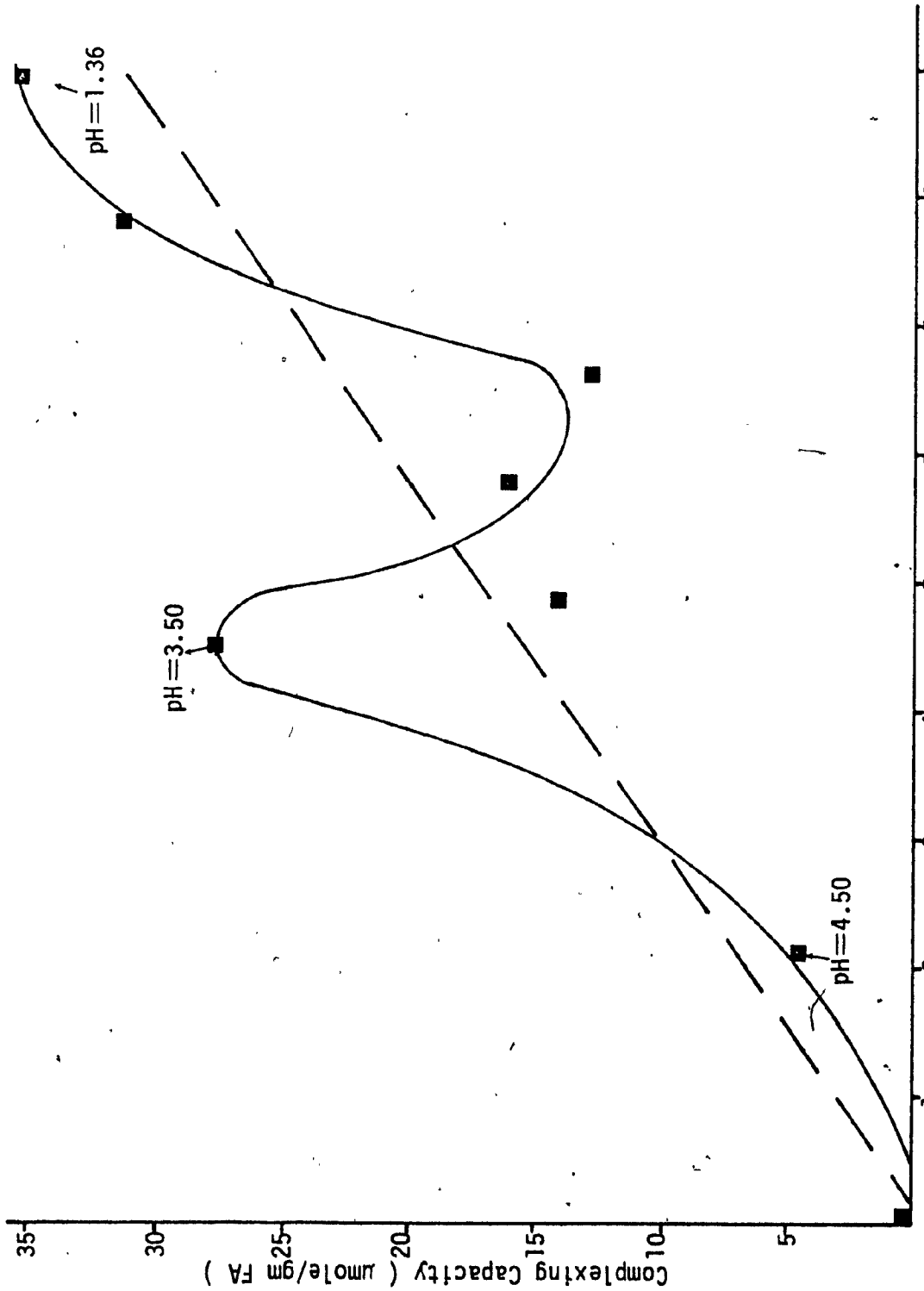
FA=1.0000 gm/litre.

points in Figure (32). Are the data all on a curve with a complicated shape as shown by the solid line ? Or are they simply scattered off the straight line ? The complicated shape curve can be justified if one considers Atrazine to be binding to two different kinds of Type A sites. Those Type A sites above $(1-\alpha_A)$ equals 0.48 (at and below pH 3.4) are the Gamble's Type I sites. The remainder of the Type A sites are binding Atrazine below $(1-\alpha_A)$ equals 0.48 (at and above pH 3.4). Therefore, the kinds of binding sites observed here are in the same pH regions as the two kinds of protonation sites observed in Figure (11). On the other hand, if a simple general trend is accepted for Atrazine binding to the Type A sites, then, the data points off the straight line in Figure (32) can be considered as due to experimental scatter.

The results from Figure (27) reinforce the complicated curve shape in Figure (32). If the percentage of Atrazine bound is plotted against the pH for the solid triangle case in Figure (27), a curve results which looks like that in Figure (33) (solid squares). A curve for the percentage of protonation of the Type A groups (the $(1-\alpha_A)$ curve in Figure (11)) as a function of pH is also given in Figure (33). The curves in Figure (33) are the same as the curve in Figure (32) except that the $(1-\alpha_A)$ axis is changed into a pH axis. The increased Atrazine binding from pH 3.4 and lower is related to the protonation of the Type 1 groups. The binding between pH 3.4 and 5.4 is related to the other Type A groups which are not included in the Type 1. Hence, the complicated curve shapes in Figures (32) and (33) do have chemical explanations.

4.1.2c EFFECT OF AGGREGATION ON BINDING

From Chapter 1 Section 1.2.1 it was shown that FA aggregates with



Figure(32) : A plot of complexing capacity as a function of protonation of Type A carboxyl groups for the results in Section 4.0.3.

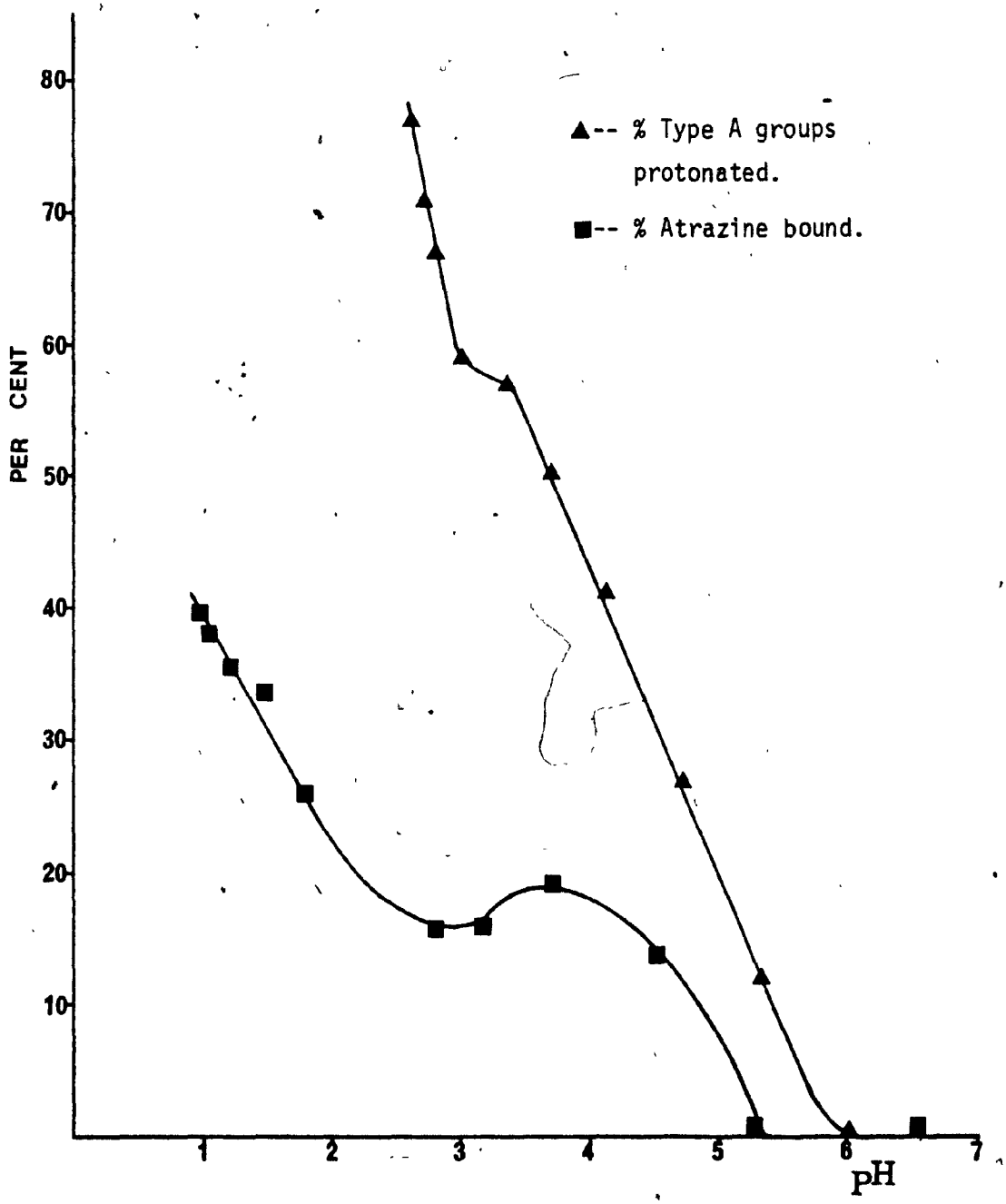


Figure (33): A comparison of the % Atrazine bound on the Type A carboxylic acid groups and the extent (%) of protonation of the Type A groups.

Atrazine concentration = 2.30×10^{-5} M

FA concentration = 1.0000 gm/litre

decreasing pH and in the presence of KCl and Cu^{2+} (32,33).

With decreasing pH, there is a small amount of FA aggregation (aggregation reaches a plateau - the solid circles in Figure (4)), hence, the protonated Type A sites are still available for hydrogen bonding. Since the larger FA particles were shown to be responsible for aggregating, hence, removing possible hydrogen bonding sites which binds Atrazine, then, one can predict that it was the smaller FA particles which are responsible for binding Atrazine. From Figure (31) it was shown that only a small amount (< 0.7%) of these small FA particles are responsible for binding to Atrazine in the absence of KCl and Cu^{2+}. The binding sites cover the whole spectrum of the Type A sites (both the Type 1 and the remaining Type A groups - see Figure (33)).

The presence of 0.100 M KCl in FA solutions causes two effects. First, the high ionic strength of the medium causes the small FA particles to aggregate extensively at pH 5 and lower. This aggregation no doubt involves hydrogen bonding (32,33). Therefore, there is a reduction of hydrogen bonding sites available for binding Atrazine in a high ionic strength medium at low pH values. The second effect is that K^+ in KCl makes the Type A carboxylic acid groups becomes more acidic, hence, causing them to dissociate at pH values less than 5.85 in Figure (11). The consequence of the increased acidity of the Type A groups (29,71) is that there will be a reduction of the amount of available protonated Type A sites. Hence, a reduction of Atrazine binding is expected. Work by Chen and Schnitzer (72,73) also support the aggregation of FA at low pH values in the presence of KCl.

The removal of protonated Type A sites by KCl caused a reduction in

binding of Atrazine to FA at the higher pH values in Figure (17). For the curve with no KCl or Cu^{2+}, Atrazine starts binding at about pH 5; in the presence of 0.100 M KCl, Atrazine starts binding at about pH 4.5; this shift in binding from pH 5 to pH 4.5 can be due to the Type A sites becoming more acidic, hence, sites are protonated at a lower pH in the presence of KCl. Atrazine binding due to sites other than the Type 1 sites are almost lost in the presence of KCl. This is indicated by the absence of the maximum at about pH 3.5 which is present for the case where KCl and Cu^{2+} are absent. However, at about pH 2.5 and lower binding in the presence of KCl is almost the same as binding in the absence of KCl and Cu^{2+}. This is expected, since H^+ competes effectively to protonate the Type A sites as pH decreases.

The effect of KCl on Atrazine binding as FA concentration is varied is shown in Figure (23). This figure illustrates that no Atrazine is bound to FA at pH 3.50 in the presence of 0.100 M KCl. However, in the absence of KCl binding is observed for FA concentrations of 0.800 and 1.0000 gram per litre. Therefore, FA aggregation and (or) increased acidity of the Type A groups in the presence of KCl caused a reduction of Atrazine binding.

When the curves in Figure (29) are compared with the KCl curve in Figure (17), one can see that the binding trends with pH are similar. Again, the results in Figure (29) can be explained in terms of FA aggregation and (or) increased acidity of the Type A groups, hence, causing a reduction of Atrazine binding between pH 2.5 and 5. The reduction in binding is more noticeable if one compares the curves in Figure (27) with that in Figure (29). The data for both of these figures were obtained

from experiments which used similar concentrations of Atrazine. It is obvious from both figures that the maxima at about pH 3.5 in Figure (27) is missing in Figure (29).

However, there are discrepancies among the KCl results obtained in Figures (17), (23) and (29). In Figure (17), Atrazine is bound at pH 4.5 and less. In Figure (23), no Atrazine was bound at pH 3.50 for the FA concentration of 1.0000 gm per litre, whereas a complexing capacity of 5.0 µmole/gm FA is observed in Figure (17) for the same experimental conditions. Also, two experimental results in Figure (29) show Atrazine binding beyond pH 4. The causes for the discrepancies among the three figures are unknown at present. Further investigations are needed in order to find the reasons for the inconsistant results. One possibility which can show Atrazine binding beyond pH 4 is hydrophobic interaction. From the work of Takagishi et al. (74,75,76,77) electrolytes such as LiCl, NaCl, KCl etc., cause the polyelectrolyte to attain a more compact conformation. The compact polymer, then, has clusters of nonpolar parts which can offer a very favourable environment for formation of hydrophobic bonds between the cosolute (Atrazine) and the polyelectrolyte (FA). The above phenomenon is also suggested by Kagawa et al. (78,79), Mittal (80), and Katachalsky (81). Work done by Ghosh and Schnitzer (82) also suggests that FA forms clusters of hydrophobic sites in the presence of NaCl. A number of authors (83,84,85,86,87,88) have suggested that FA binds organic compounds hydrophobically. But a recent study by Carter and Suffet (89) showed that the nonpolar pesticides Lindane and DDT do not bind significantly to the nonpolar clusters of FA. These authors further suggested that the hydrophobic character of FA depends on the clean up procedure used in preparing FA. This suggestion may have merit in the light of the present KCl results.

The controversy, therefore, continues as to the hydrophobic character of FA.

Atrazine binding in the presence of an average of 4.744 mmole/gm FA of Cu^{2+} is shown in Figure (17). Binding occurs at about pH 3.2 or less. From the work of Underdown et al. (32,33) it was shown that Cu^{2+} binds first to the Type 1 sites (about 3.0 to 3.3 mmole/gm FA) without much increase of FA aggregation. However, beyond this, copper (II) is used to connect (cross-link) aggregates which are already large, hence, causing extensive aggregation (Figure (5) Chapter 1). Cu^{2+} binding and hence aggregation completely blocks the Type A sites which are responsible for binding Atrazine between pH 3.2 and 5 as is shown in Figure (17). However, below pH 3.2, H^+ competes effectively against Cu^{2+} to protonate the Type A sites. Hence, the binding of Atrazine at pH 3.2 and lower. As pH decreases (below 3.2), Atrazine binding increases.

From the results presented here, one can say that FA binds by hydrogen bonding to Atrazine. Once the protonated Type A sites becomes deprotonated or are involved in hydrogen bonding through aggregation, then, there is a reduction in Atrazine binding. The possibility of protonated Atrazine binding ionically to the deprotonated Type A sites also exists. Ionic bonds between protonated Atrazine and FA can only take place at pH 4 and lower.

4.1.2d MECHANISMS FOR BINDING

From the results obtained in the present study, one can only speculate as to the binding processes involved. The mechanism by which s-triazines interact with humic substances has been quite controversal in the literature. This controversy can be expected since humic substances are mixtures

rather than pure compounds.

Table (20): Elemental composition (%) and major oxygen-containing functional groups (mmole per gram) in humic substances. (Taken from reference (17)).

Elemental Composition(%)	Soil Fulvic Acid	Soil Humic Acid	Soil Humin
C	42.5 - 50.9(49.5)*	53.8 - 60.4	55.4 - 56.3
H	3.3 - 5.9(4.60)*	3.7 - 5.8	5.5 - 6.0
N	0.7 - 2.8(0.58)*	1.6 - 4.1	4.6 - 5.1
S	0.1 - 1.7	0.4 - 1.1	0.7 - 0.8
O	44.8 - 47.3	31.9 - 36.8	31.8 - 33.8
Functional Groups(mmole/gm)			
Carboxyl	7.7 - 9.1(7.40)*	1.5 - 4.7	2.6 - 3.8
Phenolic OH	2.7 - 5.7	2.1 - 5.7	2.1 - 2.4
Alcoholic OH	3.4 - 4.9	0.2 - 3.5	---
Carbonyl	1.1 - 3.1	0.9 - 5.2	4.8 - 5.7
Total Acidity	11.8 - 14.2	5.7 - 10.2	5.0 - 5.9

* -- Numbers in parenthesis are values obtained for the FA used in this work.

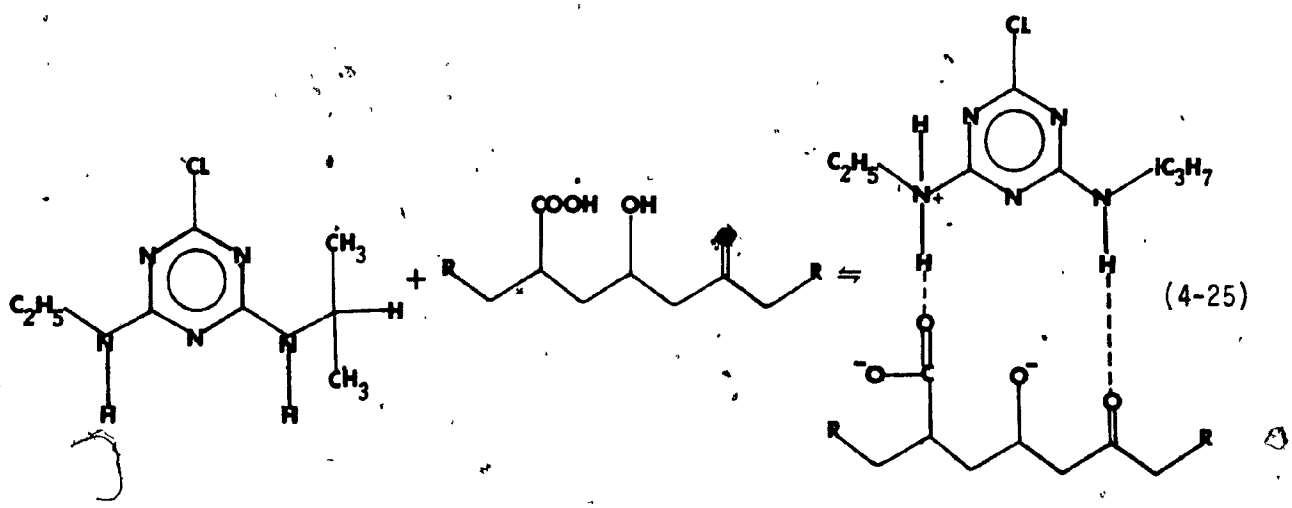
According to the literature (17), the three humic fractions (fulvic acid, humic acid, and humin) appear to be structurally similar. Table (20) shows the elemental composition and major oxygen-containing functional groups in humic substances. From this table it can be seen that they differ in elemental analysis and functional group content, with FA containing more oxygen but less carbon and nitrogen, and having a higher content of oxygen-containing functional groups (e.g., -COOH, -OH, -C=O) per unit

weight. FA has the lowest molecular weight of the three fractions. Weber and Wilson (90) also reported that the total acidity and carboxyl values are higher in FA than in HA irrespective of their source.

Weber et al. (91) and Dunigan and McIntosh (92) did binding studies between s-triazines and soil organic matter (Section 1.2.0 of Chapter 1). They found that the carboxylic groups in the humic materials were responsible for binding the s-triazines. Since from Table (20), FA has a higher range of total acidity (11.8 to 14.2 mmole per gram) it would be expected to complex more s-triazines than either HA (5.7 to 10.2 mmole acid groups per gram) or humin (5.0 to 5.9 mmole acid groups per gram). Also, the complexes which are formed will be more mobile in the FA fraction than in the other two fractions, i.e., the humic acids are soluble in dilute alkaline solution but are precipitated in acidic medium, fulvic acids are soluble in both acidic and basic media, and humins are insoluble in both acidic and basic media. So complexes which are formed between FA and s-triazines are more likely to mobilize from soils and enter our lakes and rivers. Complexes that are formed with HA will remain in the top soil in an acidic medium; however, in a basic medium, these complexes would be mobilized into the lakes and rivers. When complexes are formed with humin they will remain in the top soil as insoluble products.

Some ideas of the mechanisms of binding involved between s-triazines and humic substances can be obtained for the literature (91,92,93,94). It appears that hydrogen bonding and ion exchange are mainly involved in complex formation; however, the possibility of other mechanisms such as physical adsorption (van der Waals forces and hydrophobic bonding), charge transfer and chemisorption cannot be ruled out. Sullivan et al. (95) proposed from detailed IR studies that the amines on Atrazine form

hydrogen and ionic bonds with carbonyl and carboxyl groups on humic acid. The proton from the carboxyl group of humic acid (HA) was transferred to one of the amine groups so as to form an ionic bond. Reaction (4-25) shows the complex formed. Recent spectroscopic studies by Senesi and



ATRAZINE HUMIC ACID ATRAZINE-HUMIC ACID COMPLEX

Testini (96) suggest that hydrogen and ionic bonds are mainly responsible for s-triazines complexing to HA. Even when spectroscopic methods are used to characterize the humic acid-s-triazine binding processes, the results obtained are very doubtful (95,96). The reason for this difficulty is because only a small amount of complex is formed and, hence, cannot be detected (without complications) by present spectroscopic methods. Since FA has similar functional groups to HA (Table (20)) it would be expected that complexes with similar binding mechanisms will be formed.

From the work done in this project it can be said that only the Type A carboxyl groups of FA are responsible for binding Atrazine. The binding is mainly through hydrogen bonding and possibly weak ionic bonds. Depending on the pH range, different mechanisms are operative in the binding process. If

R-COOH represents a carboxylic acid group from the FA structure in Figure (3) of Chapter 1, then, one or more of the following mechanisms would apply in a particular pH region.

$$At + H_3O^+ \rightleftharpoons AtH^+ + H_2O \qquad (4\text{-}26)$$

$$R\text{-}COOH + H_2O \rightleftharpoons R\text{-}COO^- + H_3O^+ \qquad (4\text{-}27)$$

$$R\text{-}COO^- + AtH^+ \rightleftharpoons R\text{-}COO^-AtH^+ \qquad (4\text{-}28)$$

$$R\text{-}COOH + At \rightleftharpoons R\text{-}COO\text{-}H\text{---}At \qquad (4\text{-}29)$$

$$R\text{-}COO^-AtH^+ + H_3O^+ \rightleftharpoons R\text{-}COOH + AtH^+ + H_2O \qquad (4\text{-}30)$$

$$R\text{-}COO^-AtH^+ + M^{n+} \rightleftharpoons (R\text{-}COO^-)_nM + nAtH^+ \qquad (4\text{-}31)$$

$$R\text{-}COO\text{-}H\text{---}At + M^{n+} \rightleftharpoons (R\text{-}COO^-)_nM + nAt + nH^+ \qquad (4\text{-}32)$$

$$R\text{-}COOH + M^{n+} \rightleftharpoons (R\text{-}COO^-)_nM + nH^+ \qquad (4\text{-}33)$$

$$R\text{-}COO\text{-}H\text{---}At + H_3O^+ \rightleftharpoons RCOOH + AtH^+ + H_2O \qquad (4\text{-}34)$$

$$R\text{-}COOH + AtH^+ \rightleftharpoons R\text{-}COOH\text{---}AtH^+ \qquad (4\text{-}35)$$

$$R\text{-}COOH\text{---}AtH^+ + M^{n+} \rightleftharpoons (R\text{-}COO^-)_nM + AtH^+ + nH^+ \qquad (4\text{-}36)$$

where M^{n+} are cations other than H_3O^+, such as Na^+, K^+, and Cu^{2+} with

valence "n". Reactions with protonated Atrazine can only occur at about pH 4 and lower (see $(1-\alpha_{1B})$ curve in Figure (1)). Reactions with unprotonated Atrazine can take place at about pH 0.1 and higher (see α_{1B} curve in Figure (1)). The Type A groups in FA are all deprotonated at about pH 5.85 (see $(1-\alpha_A)$ curve in Figure (11)). From about pH 3.4 and lower, there is protonation of the Type 1 carboxylic sites; between pH 3.4 and 5.85 there is protonation of the rest of the Type A sites (see α_A curve in Figure (11)). Therefore at pH 4 and lower ionic bonds between protonated Atrazine and deprotonated Type A sites can occur (reaction (4-28)). Also hydrogen bonds between protonated Atrazine and protonated Type A sites can occur (reaction (4-35)). Reaction (4-29) shows the hydrogen bond formed between unprotonated Atrazine and a protonated Type A site. Many competitive reactions can take place for weak complexes, i.e., reaction (4-30) shows that the hydronium ion can replace protonated Atrazine to give a protonated Type A site; reaction (4-31) shows a metal ion replacing protonated Atrazine to give a metal-fulvate complex; reaction (4-32) shows a metal ion replacing the hydrogen-bonded unprotonated Atrazine to give a metal-fulvate complex; reaction (4-34) shows a hydronium ion replacing hydrogen-bonded unprotonated Atrazine to give a protonated Type A site; and reaction (4-36) shows a metal ion replacing hydrogen-bonded protonated Atrazine to give a metal-fulvate complex.

The curve without KCl and Cu^{2+} in Figure (17) shows the binding of unprotonated Atrazine from pH 5 and lower (reaction (4-29)) and also the binding of protonated Atrazine from pH 4 and lower (reactions (4-28) and (4-35)). The curve with 0.100 M KCl in the same figure represents the same reactions as above except that the reduced binding of Atrazine is due to aggregation of the FA particles and also increased acidity of the

Type A groups (reaction (4-27)). The curve with 4.74×10^{-3} M Cu^{2+} shows the same binding mechanisms as the other two, but this time Cu^{2+} competes effectively for the Type A sites above pH 3.2 according to reactions (4-31), (4-32) and (4-36); however, below pH 3.2 there is mutual competition for the Type A sites by Cu^{2+} (reaction (4-33)) and H_3O^+ (reverse of reaction (4-27)); once the Type A sites are protonated, binding by reactions (4-29) and (4-35) is possible; hence, the binding of Atrazine below pH 3.2 in the presence of Cu^{2+}.

For the experiments that produced the curves in Figure (27), only the equilibrated unprotonated Atrazine was determined. Hence, the Atrazine that is bound is in the unprotonated form (reaction (4-29)). The same binding mechanisms hold for the curves in Figure (29) as for the KCl curve in Figure (17). The binding mechanism above pH 4 in Figure (29) is not known; but as discussed before this binding could be due to hydrophobic interactions.

Most of the work discussed so far has shown that Atrazine binding is strictly pH dependent, i.e., in the absence of protonated Type A groups no binding is observed. Binding of other s-triazines is also pH dependent. Weber et al. (91) showed that four structurally related s-triazines were adsorbed to soil organic matter in the greatest amounts at pH levels in the vicinity of their respective pKa values. Table (21) shows the correspondence between pKa, pH at which maximum binding was observed, and the amount of herbicide bound. The results in Figures (27) and (29) for Atrazine are similar to those in Table (21). About the same experimental conditions as used in Table (21) were used for Atrazine. At a pH of about 1.6 (pKa for Atrazine is 1.62) in Figures (27) and (29) approximately 7 μmole per gram FA of Atrazine was bound. So, Atrazine binding is of

the same magnitude as for the other s-triazines. However, there were no maxima at pH 1.6 in either Figures (27) and (29). Instead binding increases continuously as pH decreases. This trend was attributed to increasing protonation of the Type 1 sites as pH decreases below 3.4. The binding of the s-triazines above pH 5 in Table (21) was due to the presence of humic acid and humin in the organic matter. The pKa for humic acid is 4 to 5.5 (97) compared to 1.74 to 4.08 (Table (19)) for the Armadale FA. Considering that s-triazines bind in the pKa range for carboxylic acid groups, then, the pH range for binding will be greater in soil organic matter than in fulvic acid which is only a component of soil organic matter.

Table (21)[a]: The pKa, the pH at which maximum binding is observed, and the amount of herbicide bound (Taken from reference (91)).

s-triazine	pKa	pH[b]	Amount Bound[c]
Propazine	1.85	1.9	3.5
Prometryne	4.05	4.3	8.3
Prometone	4.28	4.4	7.0
Hydroxypropazine	5.20	5.5	> 8

a --- 40 ml of 25 x 10^{-6} M herbicide was used to equilibrate 100 mg of organic matter (or about 2 gram per litre).

b --- pH value at which maximum binding was observed.

c --- in units of µmole per gram organic matter.

From the work of Weber et al. (91) it was also shown that as the pKa increases for methoxy-s-triazines the complexing capacities also increase. Table (22) shows the binding of four methoxy-s-triazines and

their respective pKa's. From the structures (98) of the methoxy-s-triazines in Table (22), it can be seen that as alkyl groups are substituted for hydrogen on the nitrogens in the 4 or 6 positions (Section 1.1.1) the basicity (pKa) increases. The implication here is that s-triazines act as Lewis bases and the protons on the carboxylic acid groups act as Lewis acids. In a similar fashion we can say that the protonated Type A sites in FA are Lewis acids and that Atrazine acts as a Lewis base. So in our titration graphs we are titrating the Type A sites with Atrazine. These titration graphs can only be done with very sensitive probes such as gas chromatography.

Table (22): The complexing capacities of four methoxy-s-triazines and their respective pKa values. (Taken form reference (91)).

methoxy-s-triazines	pKa	Complexing Capacity[a]
Simetone	4.15	6.2
Prometone	4.28	7.0
Trietatone	4.51	8.0
Tetraetatone	4.76	9.0

a --- in units of μmole per gram organic matter.

In a study done by Dunigan and McIntosh (92) it was found that Atrazine binds more to humic acid (2.22 μmole per gram at pH 6.8) than on nucleic acid (0.18 μmole per gram) or protein (0.28 μmole per gram). Nucleic acids and proteins contain functional groups which should be very reactive and binding of Atrazine, theoretically, should have been quite high. The low binding values found for these compounds were explained as probably due to the potentially reactive sites being involved in inter-

molecular hydrogen bonding.

The work of Armstrong et al. (99) showed that Atrazine hydrogen bonded to a protonated carboxyl resin called Bio-Rex 70. When the carboxylic acid groups were deprotonated the binding of Atrazine was reduced correspondingly.

One can summarize this section by saying that Atrazine only binds to the Type A carboxylic acid sites. The binding mechanism is mainly by hydrogen bonds. The Type A sites act as Lewis acids and the Atrazine ring nitrogen(s) act as Lewis bases. If the protons on the Type A sites are removed through dissociation, aggregation, or chelation, then, Atrazine binding is reduced correspondingly. There is also the possibility of weak ionic bonds being formed between protonated Atrazine and deprotonated Type A sites.

4.1.3 EQUILIBRIUM FUNCTIONS: COMPLEXING OF ATRAZINE AND CHELATION OF COPPER (II)

The weighted average differential functions for Atrazine, $1/\bar{K}_0$ and $1/\bar{K}_1$ obtained from equations (2-12) and (2-56) respectively, were calculated for the data in Tables (10) and (11) and listed in Table (23). Figure (34) shows a plot of total Atrazine added versus $1/\bar{K}_0$ (solid squares) and $1/\bar{K}_1$ (solid triangles). This plot indicates that both $1/\bar{K}_0$ and $1/\bar{K}_1$ are dependent on the total Atrazine added to the system. As the total Atrazine increases the weighted average functions also increases. This means that as the Atrazine concentration increases the complexes formed are stronger. At the higher total Atrazine concentrations the weighted average functions tend to approach a limiting value. This nonlinear relationship means that the weighted average functions are seeing different and stronger binding

Table (23): Determination of $1/\bar{K}_0$ and $1/\bar{K}_1$ for the data in Tables (10) and (11).

	Complexed Unprotonated Atrazine			Complexed Protonated Atrazine		
Total Atrazine added (μmole/gm FA)	$x_0 \times 10^4$	$1/\bar{K}_0$ (l/mole)	$-(\Delta G^o + RT\ln\Gamma)$ (Kj/mole)	$x_1 \times 10^4$	$1/\bar{K}_1$ (l/mole)	$-(\Delta G^o + RT\ln\Gamma)$ (Kj/mole)
11.67	5.27	336	14.1	9.36	334	14.1
14.82	7.06	390	14.4	12.54	388	14.4
17.97	8.84	431	14.7	15.75	432	14.7
21.12	10.64	465	14.9	18.92	464	14.9
24.27	12.42	491	15.0	22.10	490	15.0
30.58	16.00	533	15.2	28.50	532	15.2

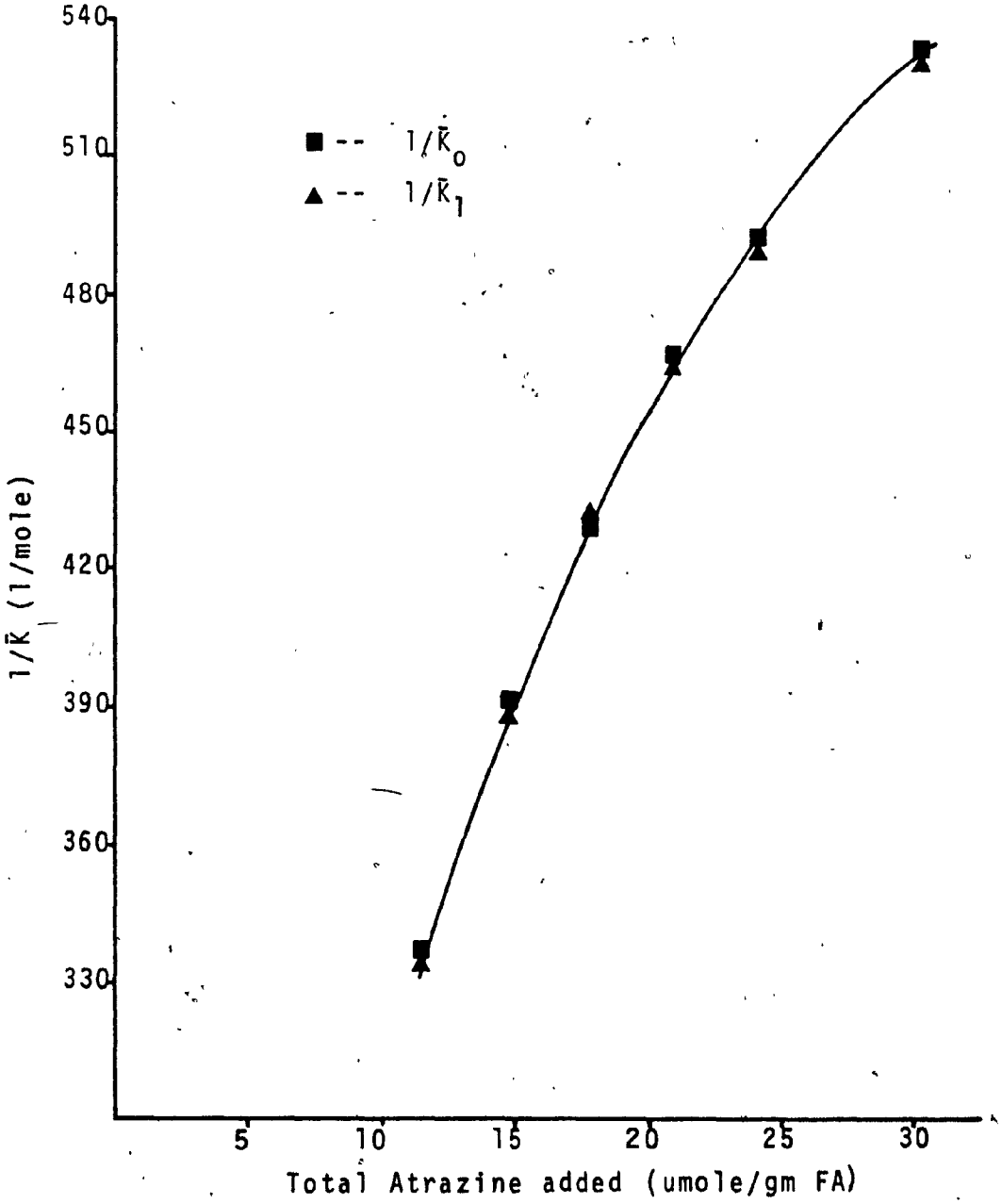


Figure (34): Variation of $1/\bar{K}_0$ and $1/\bar{K}_1$ as a function of total Atrazine added for data obtained from Tables (10) and (11).
pH = 1.36 and FA = 1.000 gm/litre.

sites as total Atrazine increases. Once all the sites are complexed, then, a plateau should, theoretically, be obtained in Figure (34). It is suggested here, that the plateau values for $1/\bar{K}_0$ and $1/\bar{K}_1$ are the differential equilibrium functions $1/K_0$ and $1/K_1$, respectively. Hence, the differential equilibrium functions are only giving the values for the strongest binding sites at a particular pH value, i.e., the value for both $1/K_0$ and $1/K_1$ for the data in Tables (10) and (11) is 746 litre per mole. In general, the 1/K values are always higher than the highest $1/\bar{K}$ values for the experiments done in this project.

The trend in Figure (34) indicates a binding mechanism similar to that of proteins (100,101,102). That is, as Atrazine is added to the system, Atrazine binding tends to unfold the aggregated FA molecules, hence, exposing protonated Type A carboxylic acid sites which, then, bind more Atrazine. The new sites exposed are stronger Type A sites which bind Atrazine even more strongly than did the initial sites, hence, the increased $1/\bar{K}$ values. Once all the binding sites are saturated with Atrazine molecules, binding stops and the equivalence point is obtained. The above explanation is quite reasonable since FA aggregates at high concentrations (31,32,33,37,82,103). FA behaves like spherical colloids at high concentrations ($\geq$ 1 gram per litre) and flexible linear colloids at low concentrations (37,82).

From the above discussion, then, the 1/K values represent the strongest binding sites at a particular pH value. It means that the differential function does not distinguish between the FA sites at a fixed pH as does the weighted average function ($1/\bar{K}$).

4.1.3a COMPLEXING OF UNPROTONATED ATRAZINE

From Tables (12) and (13) the differential equilibrium functions ($1/K_0$) are plotted against the pH for the binding of the unprotonated Atrazine case (Figure (35)). From Figure (35) it can be seen that the trend of the $1/K_0$ values with pH for the case with no KCl is similar to that in Figure (17) for the case with no KCl or Cu^{2+}. One can, then, draw similar conclusions form Figure (35) as were drawn from Figure (17). That is, from pH 5 and lower the protonated Type A carboxylic acid groups are responsible for binding the unprotonated Atrazine (reaction (4-29)). Below pH of about 2.3 binding is due to the Type 1 sites. Above pH 2.3 binding is due to the Type A sites which are not included in the Type 1 sites. The noticeable large maximum at about pH 3.5 is due to the inherent character of the differential equilibrium function. As discussed in Section 4.1.3, this function represents binding to the strongest sites at a particular pH value, hence, the high value for $1/K_0$ at pH 3.5.

The curve for the presence of 0.100 M KCl is similar to the curve in Figure (17) with 0.100 M KCl. The $1/K_0$ values increases as pH decreases from pH 4. The same explanation holds for Atrazine binding as in Figure (17). The presence of KCl causes the Type A groups to become more acidic, hence, the shifting of binding from pH 5 to pH 4 and lower. KCl also causes aggregation of the smaller FA particles, thus, making the protonated Type A sites less accessible to the unprotonated Atrazine. Hence, the reduction of binding between pH 2.2 and 5 as has been observed in the absence of KCl in Figure (35).

The differential functions for the complexes formed in the absence of KCl varied from 30.6 to 1.37×10^3 litre/mole. In the presence of KCl,

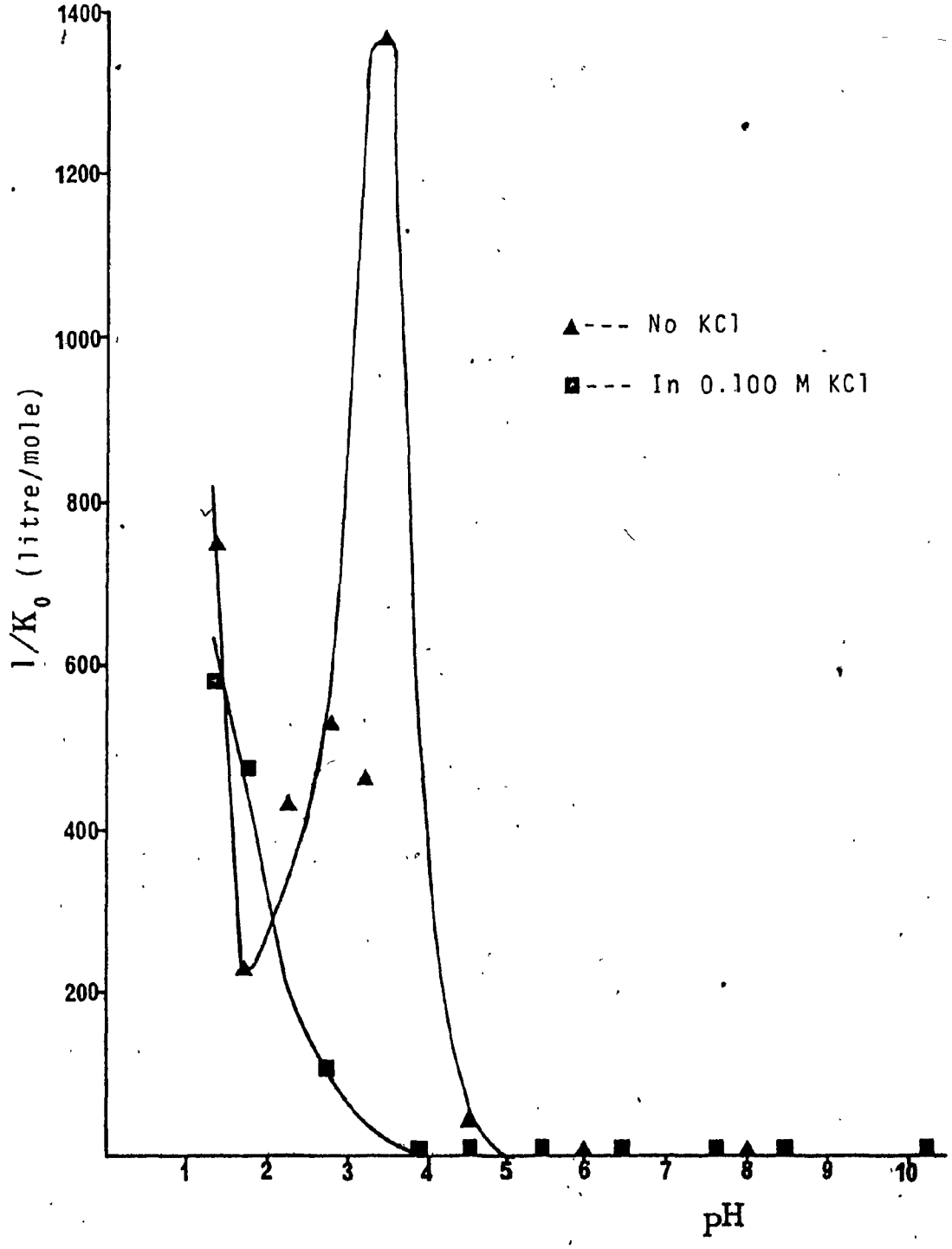


Figure (35): Unprotonated Atrazine differential equilibrium function as a function of pH at 25°C.

the differential functions varied from 101 to 571 litre/mole. From these values of $1/K_0$ it can be said that the complexes formed are weak ones.

4.1.3b COMPLEXING OF PROTONATED ATRAZINE

From Tables (12) and (13) the differential equilibria ($1/K_1$) are plotted against the pH for the binding of the protonated Atrazine case (Figure (36)). Figure (36) shows that the $1/K_1$ values are at pH 4 and lower. The larger $1/K_1$ values between pH 2.7 and 4 for the no KCl case are due to the binding of the protonated Atrazine to the protonated Type A sites (excluding the Type 1 sites) according to reactions (4-28) and (4-35). Below pH 2.7, protonated Atrazine binding is due to the Type 1 sites.

In the presence of 0.100 M KCl, protonated Atrazine binding is reduced between pH 2.7 and 4. This reduction in binding is again due to the increased acidity and aggregation of the Type A groups in the presence of KCl. Reactions (4-28) and (4-35) are also responsible for protonated Atrazine binding. Most of the binding, however, can be associated with reaction (4-35), i.e., since Type A sites become deprotonated in the presence of KCl, then, there should be more ionic bonds with protonated Atrazine (4-28). However, a reduction of binding is observed. Therefore, Atrazine binding to the Type A sites can, in general, be mainly associated to hydrogen bonding.

The range of $1/K_1$ values in the absence of KCl is 53.7 to 1.19×10^3 litre/mole. In the presence of KCl the range is 111 to 581 litre/mole. These $1/K_1$ values indicate that weak complexes are formed between protonated Type A groups.

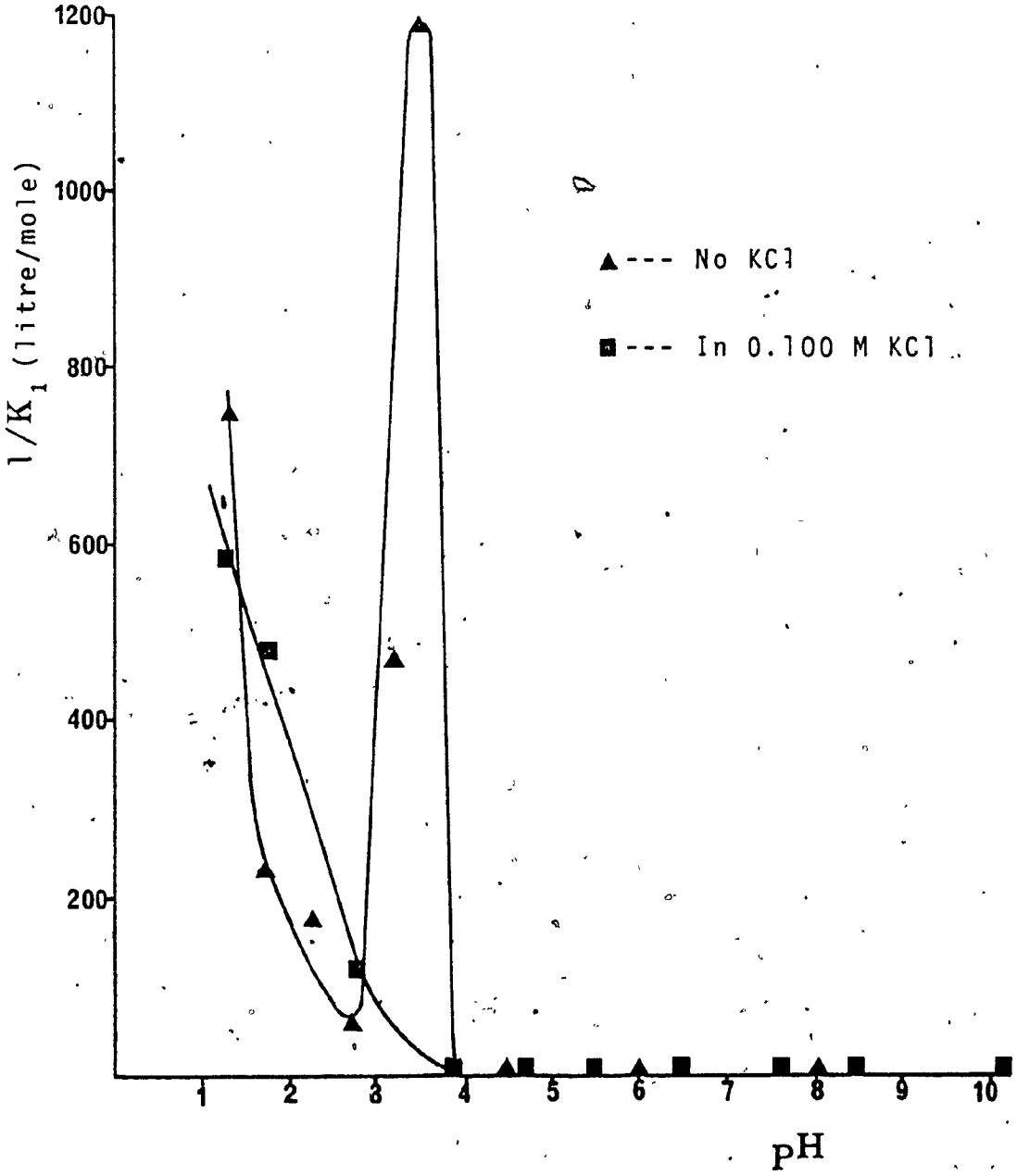


Figure (36): Protonated Atrazine differential equilibrium function as a function of pH at 25°C.

4.1.3c CHELATION OF COPPER (II)

Using the data in Tables (14) and (16) the values of K_4 are plotted against χ_c and given in Figure (37). From the figure it can be seen that for low copper (II) loading of the FA sites ($\chi_c < 0.3$) the differential equilibrium function, K_4, is much higher than at high loading. At high loading of copper (II) onto FA ($\chi_c > 0.5$), the K_4 values become ambiguous and even negative numbers can be obtained. This ambiguity could be due to a lack of sufficient data points. However, these results are consistant with those obtained by Langford et al. (61), Lee (62), Cheam (104), and Cheam and Gamble (105) for copper (II)-fulvic systems. The curves in Figure (37) indicate that copper (II) binds to the strongest FA sites first and the weakest sites last.

The curve with the solid triangles is for the data in Table (14) while the curve with the solid squares is for the data in Table (16). These curves cannot be compared quantitatively, since, different concentrations of FA were used in each case and, also, the curve with the solid squares was obtained for a single titration graph at a fixed pH value while the curve with the solid triangles was obtained from several pH values for a fixed amount of copper (II) and varying Atrazine concentrations. However, from the curve with the solid triangles, it can be seen that as the pH becomes lower (smaller χ_c) the K_4 values increase. This trend implies that at the lower pH values most of the strong carboxylic sites are deprotonated.

4.1.3d COMPLEXING OF ATRAZINE IN THE PRESENCE OF COPPER (II)

From the data in Table (15) the differential equilibrium functions are plotted against the pH and given in Figure (38). This figure shows

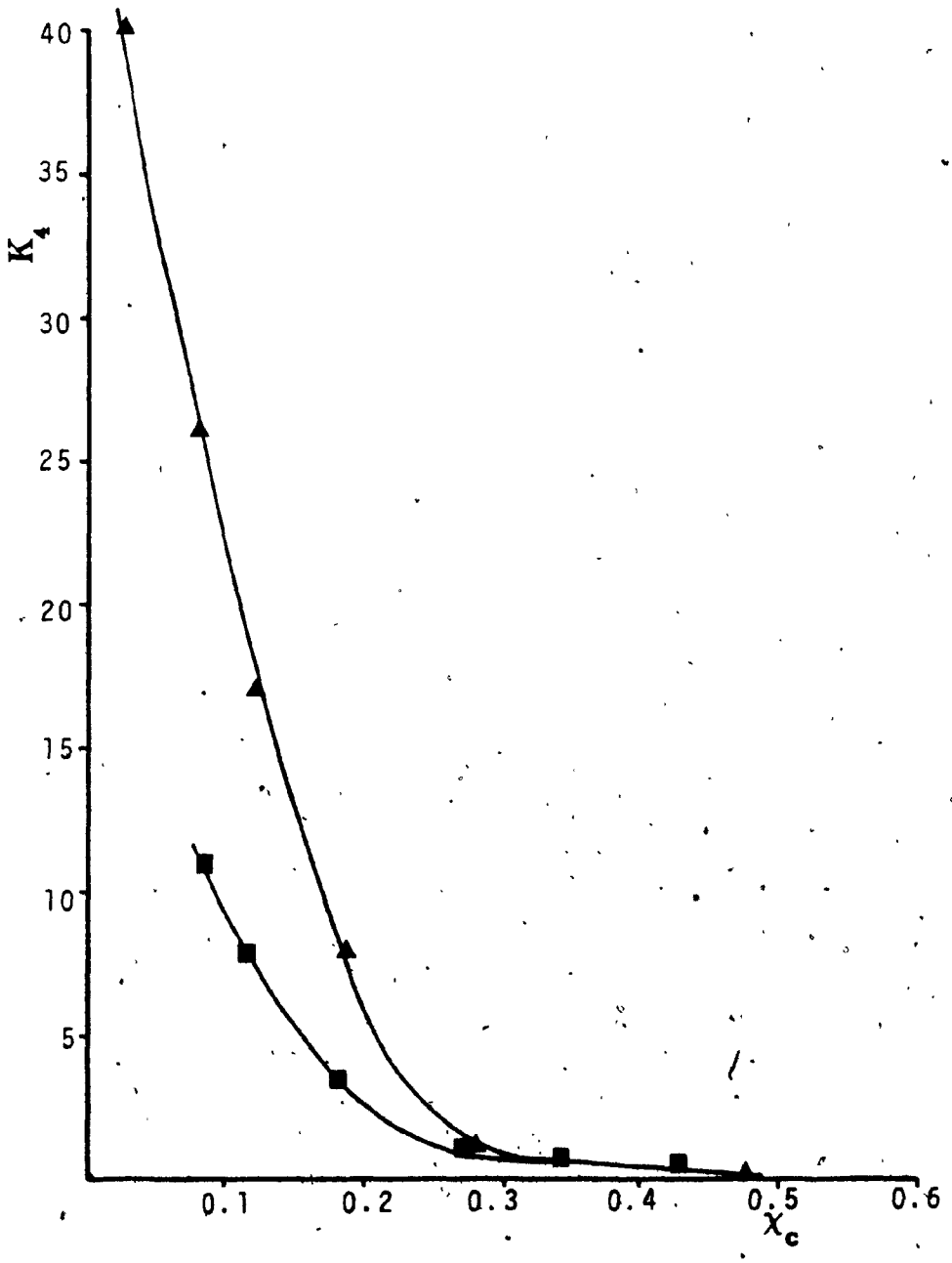


Figure (37): A plot of K_4, the differential equilibrium function for Cu(II)-fulvate complex.

▲ - 1.0000 gm FA/l in the presence of a fixed amount of Cu(II) at various pH values (Table (14)).

■ - 0.1000 gm FA/l titrated with Cu(II) at pH 3.86 (Table (16)).

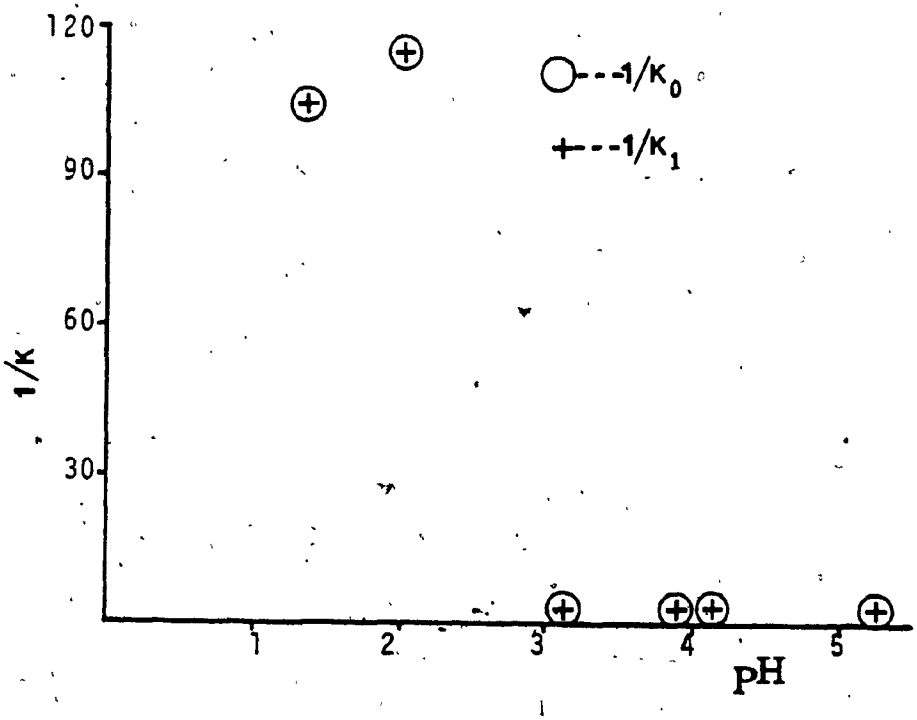


Figure (38): Atrazine differential equilibrium functions as a function of pH in the presence of 4.74×10^{-3} M Cu^{2+}.

that both the protonated ($1/K_1$) and unprotonated ($1/K_0$) functions have the same values at the same pH. At about pH 3 and higher no Atrazine binds to FA. From Figures (35) and (36) Atrazine does not bind from pH 4 and higher in the presence of KCl. It means, as discussed for Figure (17), that copper (II) is more effective than KCl in preventing Atrazine from binding to the FA Type A protonated sites. Copper (II) chelates with the sites that are responsible for binding Atrazine (31,32,33) whereas KCl decreases the binding of Atrazine by making the Type A sites more acidic and also aggregating the FA particles. The differential functions in the presence of KCl are higher than the differential functions in the presence of copper (II) for the same pH values. This fact is also demonstrated in Figure (17) for the complexing capacities. Hence, stronger complexes are

formed in the presence of KCl than in the presence of copper (II).

At about pH 2 and lower in Figure (38) it seems as though the strength of the Atrazine-FA complexes begin to decrease, hence, suggesting that the copper (II)-FA interactions in this pH region are becoming stronger. From the data in Tables (14) and (15), curves are drawn for $1/K_0$ and K_4 versus χ_c (Figure (39)). The curves in Figure (39) can only be compared for their trends since the dimensions for $1/K_0$ (litre/mole) and K_4 (unitless) are different. These curves, however, reinforce the predicted trend in Figure (38). Below χ_c of about 0.08, copper (II) binds stronger to the Type A sites than Atrazine, hence the increase in K_4 and the decrease in $1/K_0$ as χ_c decreases. Both $1/K_0$ and K_4 decrease as χ_c increases from about 0.08. These results imply that the amount of complexing sites for FA are highly dependent on the history of FA, i.e., an FA which has a high metal ion content will block the Atrazine binding sites - assuming that the metal ions bind stronger to the Type A sites than Atrazine. Chan et al. (106) showed that when Fe(III) or Al (III) are bound to FA, the complexing capacity for that FA is reduced. Gamble et al. (31) showed that as χ_c becomes very small, K_4 becomes strikingly large; e.g., for $\chi_c = 0.0184$, a value of $K_4 = 5.90 \times 10^4$ is obtained. It is, therefore, not difficult to appreciate what K_4 will be when χ_c approach a value of 10^{-4} which is close to the values (see χ_T, χ_0 and χ_1 in Table (11)) for Atrazine binding to the Type A sites. From Figure (39) it can be seen that at χ_c equal to about 0.08 and lower, Atrazine complexes are getting weaker and copper (II) chelates are getting stronger. Therefore, copper (II) will tend to replace all bound Atrazine on the strongest Type A sites as χ_c approach 10^{-4}. This postulate is true for experiments done at

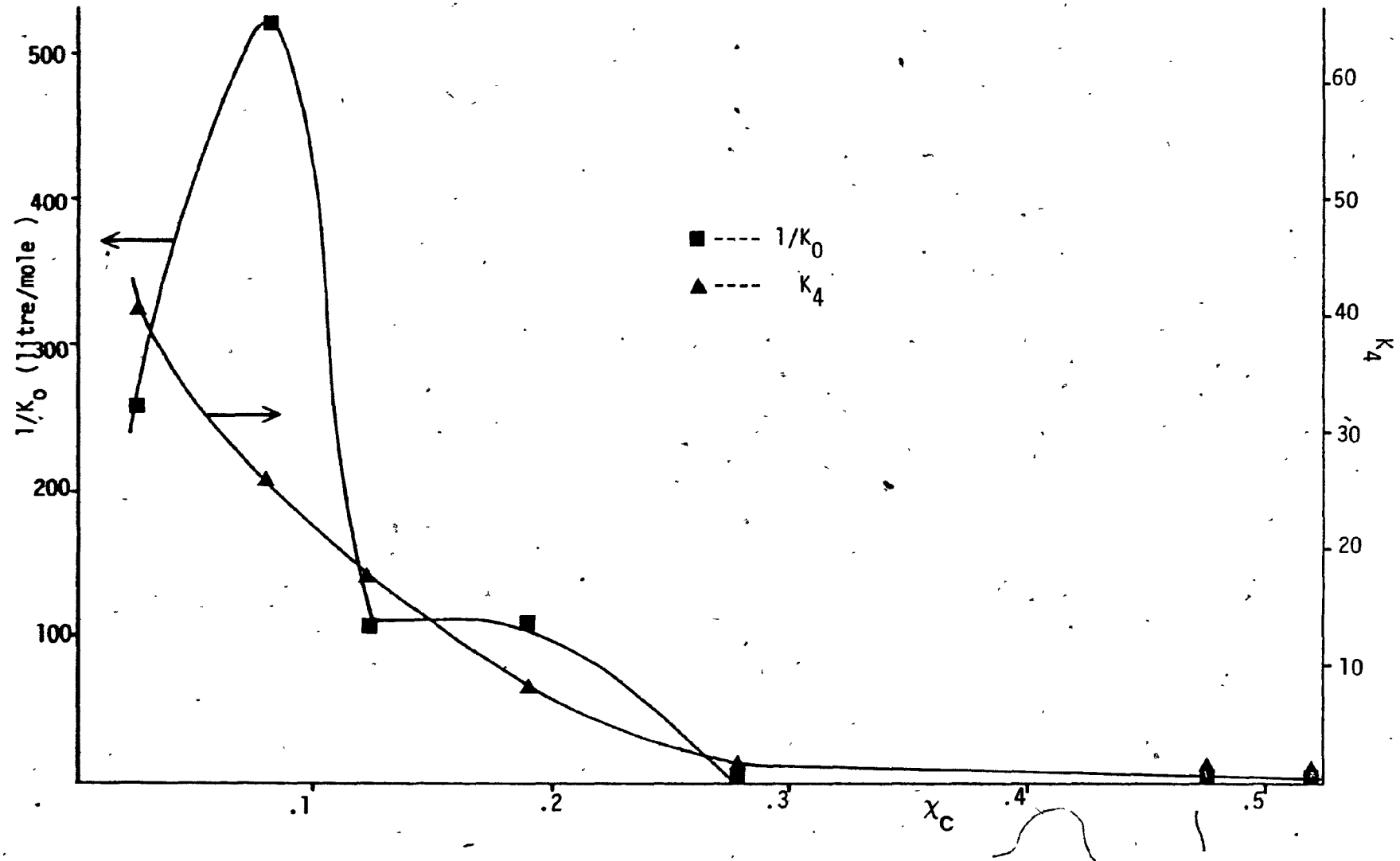


Figure (39): Comparison of the differential functions $1/K_0$ and K_4 as a function of χ_c for the data in Tables (14) and (15).

about pH 3.2 and higher (see Figures (17) and (38)). However, below pH 3.2, H^+ competes with copper (II) for the carboxylic acid sites, hence, the binding of Atrazine at these pH values. The competing reactions between Atrazine and copper (II) for the Type A sites are reactions (4-31), (4-32) and (4-36).

Figure (40) shows a comparison for the binding trends of copper (II) and Atrazine to FA. This figure exemplifies the reversal of binding at low and high fractions of bound species. The data for curve A was taken from Table (17) while the data for curve B was taken for Table (23). The explanations for the binding trends in these curves were given before (Sections 4.1.3 and 4.1.3c), i.e., the differential equilibrium function (K_4) increases as χ_c decreases for copper (II) while the weighted average differential function ($\bar{1}/\bar{K}_0$) increases as χ_0 increases for unprotonated Atrazine.

4.1.4 STANDARD GIBBS FREE ENERGY ESTIMATES AT 25 ± 1 °C.

The discussion in the previous sections has shown that the mechanisms most likely to be involved in the Atrazine binding to the Type A sites are (a) hydrogen bonding (b) ionic bonding and (c) hydrophobic bonding. The energy range for hydrogen bond formation is 9 to 42 Kj/mole. The distinction between ionic bonds and hydrogen bonds is sometimes arbitrary and the energies of ionic bonds may fall within the range for hydrogen bonds (107,108). The range of hydrophobic bond energies is from 4.18 to 8.36 Kj/mole (108,109).

Table (24) shows a summary of the ranges of standard Gibbs free energies for three of the experimental conditions studied in this project. These values show that only hydrogen and ionic bonds are responsible for

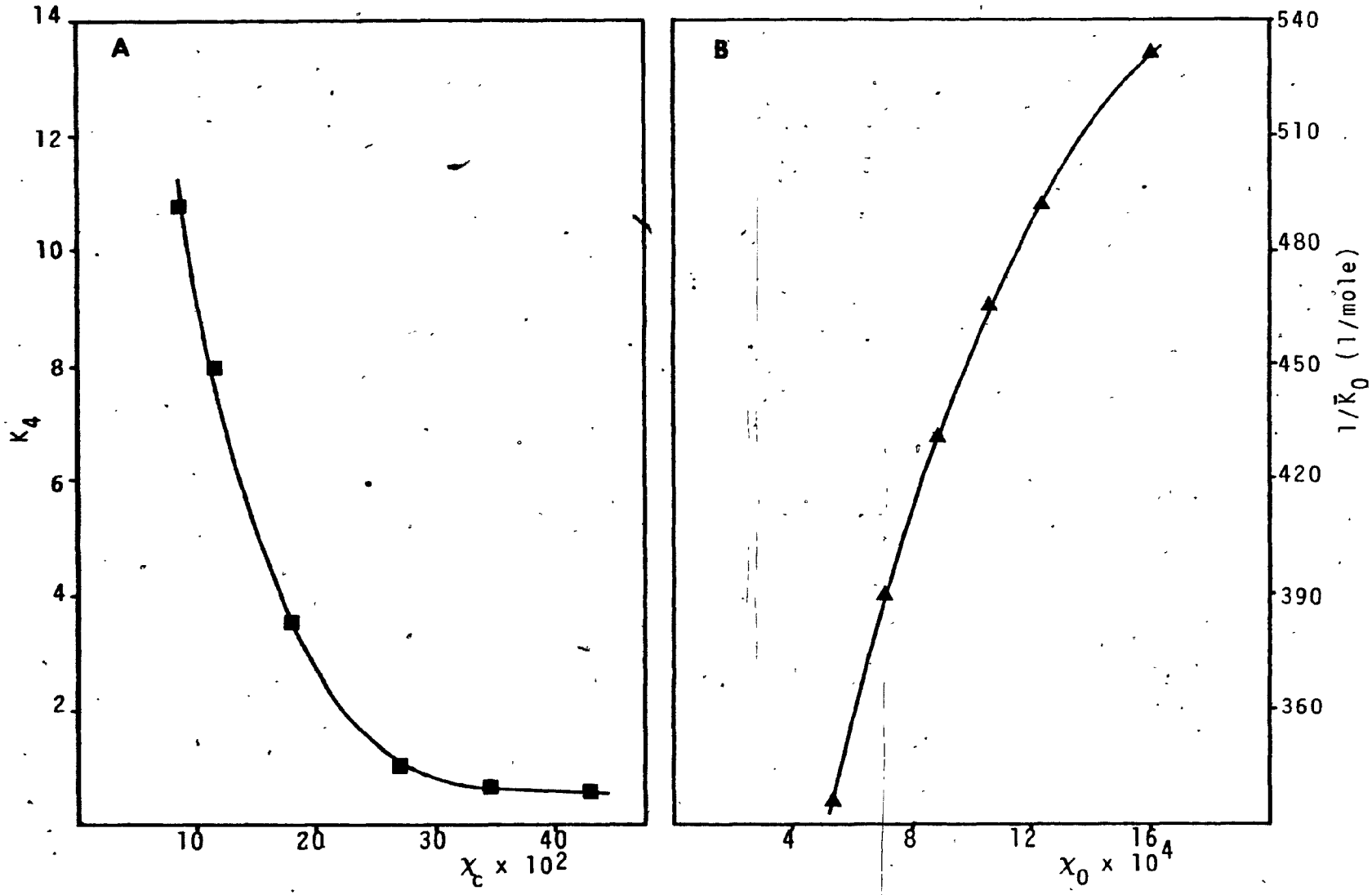


Figure (40): Comparison of (A) the differential K_4 as a function of χ_c (fraction of copper (II) bound at pH = 3.86) and (B) the weighted average $1/\bar{K}_0$ as a function of χ_0 (fraction of unprotonated Atrazine bound at pH = 1.36).

Table (24): Estimates of the standard Gibbs free energies at 25 ± 1 ^{o}C for the interactions between Atrazine and fulvic acid under various experimental conditions.

Experimental Conditions	Range of 1/K (litre/mole)	Range of $-(\Delta G^{o} + RT\ln\Gamma)$ (Kj/mole)
No metal ion (Table (12))	30.6 to 1.37×10^{3}	8.48 to 16.4
KCl (0.100 M) (Table (13))	101 to 581	11.7 to 15.8
Cu^{2+} (4.74×10^{-3}M) (Table (15))	101 to 113	11.2 to 11.5

binding Atrazine to the Type A sites. From a previous discussion it was shown that Atrazine binds mainly by hydrogen bonding and very little, if any, by ionic bonds. According to Vickerstaff (107), one hydrogen bond between Atrazine and organic matter is about 16.3 Kj/mole. The energy data in Table (24), therefore, reflects a single hydrogen bond between Atrazine and fulvic acid. Therefore, only one of the nitrogens in Atrazine acts as a Lewis base to the protonated Type A sites. Organic chemists (13,45) seem to think that the nitrogen in the 5-position of Atrazine is responsible for the hydrogen bond formation.

The work of Bailey et al. (11) shows that Atrazine has a driving force of 17 Kj/mole for protonated montmorillorite clay and 10.5 Kj/mole for sodium montmorillorite clay. The removal of protons from the clay causes a simultaneous weaking of the driving force for Atrazine binding. By analogy, the introduction of KCl and Cu^{2+} to FA also causes a reduction

in the driving force of binding between Atrazine and FA (comparing only the highest free energy values in Table (24)). From Table (24) this reduction of the driving force is small in the case of KCl, e.g., comparing only the highest free energy values, the energy difference is 0.6 Kj/mole. In the presence of KCl it was shown that Atrazine binding decreased because of increased acidity of the Type A groups and also because of aggregation of the FA particles. It was also shown by Gamble (110) and Gamble et al. (111) that K^+ ion binds with a driving force of about 17.8 Kj/mole to FA. Whether or not the K^+ ions in KCl took part in any binding with FA is still subject to speculation. In the presence of Cu^{2+}, the reduction of the driving force is about 4.9 Kj/mole. It was shown that Cu^{2+} does bind to FA, hence, the reduction in the Atrazine driving force for binding. For a lower concentration of copper (II) present (1.055×10^{-3} M Cu^{2+}) the driving force for Atrazine binding increases to about 13.4 Kj/mole. Hence, Atrazine binding shows a copper (II) concentration dependence, i.e., the higher the copper (II) concentration present the smaller the driving force for Atrazine binding.

In summary the driving force for Atrazine binding depends on the ionic strength of the system. Copper (II) chelates with the Type A sites which are responsible for binding Atrazine. This chelation causes a weakening of the hydrogen bond formation between Atrazine and FA. Hydrogen bond formation between Atrazine and FA is pH dependent. From about pH 5 and lower hydrogen bond formation generally increases as pH decreases.

4.1.5 SOME PRACTICAL IMPLICATIONS OF BOUND ATRAZINE

A number of authors (112,113,114,115,116,117) have stated that Atrazine is hydrolyzed to hydroxyatrazine in acidic media. Since hydroxy-

atrazine is a nonphytotoxic compound it means that the prevention of Atrazine hydrolysis is critical.

The studies by Armstrong et al. (112) indicate that when carboxylic acid groups hydrogen bond to Atrazine, hydroxyatrazine is formed as a catalyzed product. Russell et al. (113) has shown that Atrazine was hydrolyzed by montmorillonite clay in acidic media. Khan et al. (114,115, 116,117) studied the hydrolysis of Atrazine in the presence of 1 gram per litre of FA and found that as pH increases the half life of Atrazine increases. At pH 2.8 the half life was 24.4 days and at pH 7.0 it was 56.3 days. Therefore, Atrazine is also hydrolyzed more in a FA medium which is acidic. All of the above studies suggest that Atrazine hydrolysis is through a hydrogen bonding mechanism.

The present work also reinforces the findings of Khan et al. (116,117). As pH decreases from about 5, the binding of Atrazine through hydrogen bonding also increases. With increased hydrogen bonding there is increased hydrolysis of Atrazine. At high ionic strengths and in the presence of metal ions which binds to the Type A sites, it was shown that reduced binding was observed and hence reduced hydrolysis of Atrazine is predicted. The binding of Atrazine to FA, therefore, has an economical impact. For Atrazine to be effective as a weedicide it has to be sprayed on soils which are low in organic matter. Another possibility is that Atrazine can be sprayed on soils which are high in organic matter but the ionic strength or the metal ion content must be high in those soils. A dangerous and costly possibility is the spraying of high concentrations of Atrazine to soils which are rich in organic matter. The last possibility can cause increased pollution of lakes and rivers through flooding of sprayed fields.

According to Reuter et al. (118) FA concentrations in natural waters range from 1 to 100 milligram per litre. Using this concentration range one can predict the degree of complexation of Atrazine to the Type A sites of FA. Assuming that unprotonated Atrazine exists in the environment at a concentration of 1.86×10^{-6} mole per litre for a pH value of 3.21 (assume an acidic environment) and, that, $1/K_0 = 1/\bar{K}_0 = 468$ litre per mole (see Table (12)), then, the fraction of Atrazine-FA complex formed can be calculated from equation (2-12). C is the concentration of Type A sites (4.99 mmole per gram FA). Figure (41) shows a plot of % Atrazine complexed as a function of micromole Type A sites per litre of solution. This figure indicates that Atrazine binding is quite dependent on the concentrations of fulvic acid. A FA concentration of 10 mg per litre is representative of streams and lakes. This amount of FA corresponds to 2.5 % of Atrazine complexed. Similar calculations can be done with other weighted average and differential functions.

Figure (41) is a critically important type of correlation that is totally lacking in the existing literature. The experimental results are described directly and stoichiometrically in terms of those particular functional groups that are responsible for the complexing. The existing literature descriptions of pesticides/herbicides binding to masses of polydisperse polyelectrolyte are chemically blind, "black box", empirical descriptions which represent nothing except the particular experiments out of which they have come. Because they lack generality, they lack the capacity for predictive calculations. The fundamental importance of Figure (41) is that it represents a big step towards the removal of that practical difficulty.

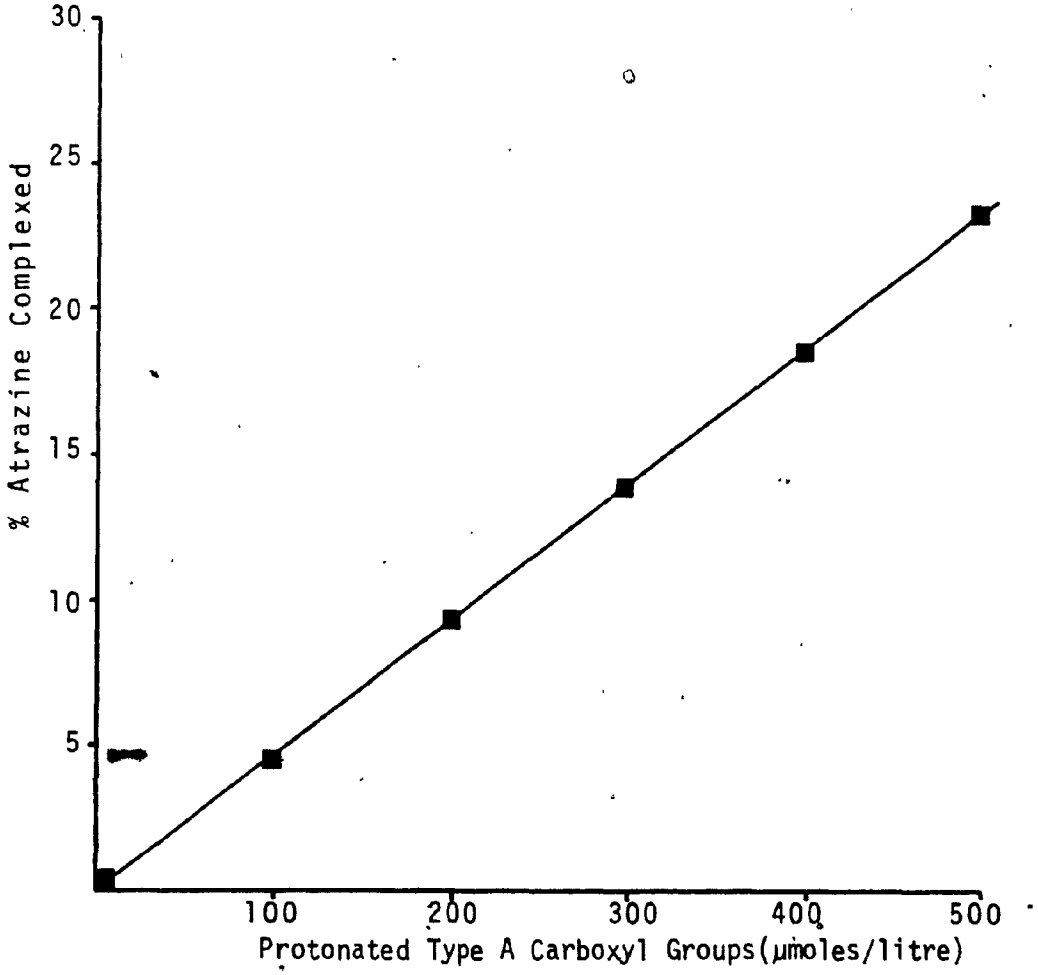


Figure (41): Percent unprotonated Atrazine complexed as a function of the concentration of protonated Type A carboxyl groups. Total unprotonated Atrazine concentration is 1.86×10^{-6} mole per litre.

CHAPTER 5

EVALUATION OF THE CONTINUOUS FLOW ULTRAFILTRATION METHOD

5.0.0 INTRODUCTION

As discussed in Chapter 4 the Batch Ultrafiltration Method (BUM) was costly since it utilized about 0.7 gram of FA to produce one titration graph. FA is an expensive material and, hence, a method which uses a small amount of it would be preferred over the BUM. Also the BUM involves many steps before the final results are obtained and, hence, it is time consuming. The continuous Flow Ultrafiltration Method (CFUM) used by Grice et al. (43), Crawford et al. (119) and Blatt et al. (120) for binding studies offered an alternative possibility which is cheaper, more automated and less time consuming.

5.1.0 EXPERIMENTAL

5.1.1 APPARATUS

Figure (42) shows the CFUM apparatus which was used to study the binding of Atrazine onto FA. It consisted of an Amicon Ultrafiltration cell (Model # 8010) which was connected to a polyethylene reservoir (made by the author to withstand high pressures) with a 250-ml sorbate capacity. The cell has a pressure valve which was used to remove trapped air in the system. An Amicon UM2 membrane was assembled as directed in the operation manual (54). Stirring was carried out magnetically. An air gap of 4 cm was left between the cell and the magnetic stirrer so as to minimize heat transfer to the cell contents. The helium gas (oxygen-free) was used to pressurize the sorbate through the ultrafiltration cell.

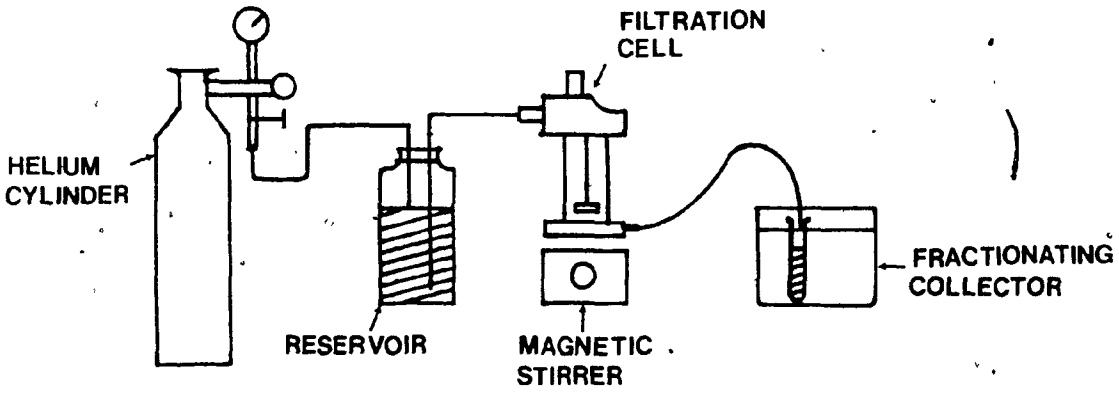


Figure (42): Continuous flow ultrafiltration apparatus.

5.1.2 SORPTION STUDIES

A typical sorption experiment was as follows. The cell was filled to capacity (13.0 ml) by pouring the 0.7692 gm FA/100 ml solution through a fill port at the top of the cell. Atrazine stock solution (Section 3.2.6a) was added to the reservoir which was, then, sealed properly to prevent helium gas leakage. Before the experiment commenced air was removed from the cell by means of a pressure relief valve which was at the same position as the fill port at the top of the cell. Atrazine solution was then passed through the cell system at a helium pressure of 40 lb/in^2. The eluate samples were collected by means of the Braun fractionating collector. A flow rate of 7.0 ml/hour was maintained. Preliminary studies have indicated that 25 fractions of eluate containing 8.0 ml/fraction, was enough volume to saturate the quantity of FA in the cell. Hence, a typical sorption run took about 28 hours. The dashed line before DF in Figure (43) represents a typical sorption curve for Atrazine onto FA and the membrane. The solid line before DF represents the sorption curve for Atrazine onto the UM2 membrane; this curve was determined by placing 13.0 ml of H_2O in the cell instead of the FA stock solution; it corrects

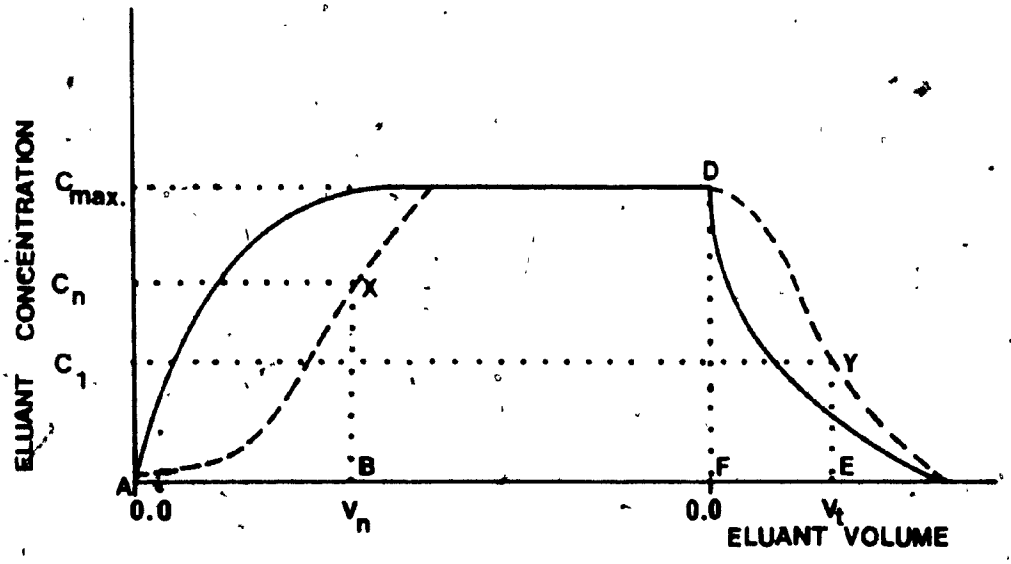


Figure (43): Typical sorption (before line DF) and desorption (after line DF) curves for Atrazine in the absence of FA (solid line) and in the presence of FA (dashed line).

for any sorption due to the membrane. Grice et al. (43) refer to these curves as "Wash in" curves.

5.1.3 DESORPTION STUDIES

The reservoir and its connections which contained the Atrazine stock solution in the sorption study was replaced by another reservoir and its connections which contained nanopure water. Air in the system was again removed as discussed before. The water was passed through the cell with helium at a pressure of 40 lb/in^2. Fractions were collected as before for the sorption studies. Again, about 25 fractions were collected with each fraction having a volume of 8.0 ml. The dashed line after DF in Figure (43) represents a typical desorption curve for Atrazine bound onto FA and the membrane. The solid line after DF in Figure (43) represents the desorption

curve for Atrazine bound onto the membrane in the presence of water in the cell; this curve corrects for desorption due to the membrane.

5.1.4 DETERMINATION OF ATRAZINE BY GC

The volume of each fraction in a Continuous Flow experiment was determined by weighing.

Each fraction was evaporated to dryness on a rotary evaporator. The residue was, then, taken up in 3.00 ml of pesticide grade methanol and analysed for Atrazine by GC according to the procedure described in Section 3.3.3a, i.e., a calibration curve was prepared for each experiment and the corresponding free Atrazine concentration was determined for each fraction. The results for these experiments are given in Section 5.2.0.

5.2.0 RESULTS AND DISCUSSION

5.2.1 RESULTS

Appendix (VIII) gives the sorption and desorption curves for the binding of Atrazine onto FA at pH values between 2.10 and 5.93. The curves plotted with the solid squares are the sorption curves while the curves plotted with the solid triangles are the desorption curves. Only a sorption curve was done for E in Appendix (VIII). Curves O and P in Appendix (VIII) represent duplicate experiments which determine the extent of Atrazine-UM2 membrane interactions.

From the sorption and desorption curves in Appendix (VIII), the equilibrium Atrazine concentration, the amount of Atrazine sorbed, the amount of Atrazine desorbed and the binding capacity for a particular pH value can be determined. In order to perform these calculations the following equations were used. According to Grice et al. (43) and Crawford et al. (119) the

amount of Atrazine bound can be calculated from the diafiltration profiles in Figure (43) and Appendix (VIII). For the sorption profile in Figure (43) the amount of Atrazine bound, L_b, is given by equation (5-1):

$$L_b = V_{out}C_{max} - \int_0^{V_n} C_n dV_n - VC_n \qquad (5\text{-}1)$$

where,

V_{out} - total volume of effluent collected.

C_{max} - influent concentration of Atrazine from the reservoir.

C_n - effluent Atrazine concentration in each fraction.

V_n - total volume up to fraction n.

V - volume of ultrafiltration cell which was 13.0 millilitres.

For the desorption profile in Figure (43) the amount of Atrazine sorbed, L_d, after removal of the n^{th} fraction, is given by equation (5-2):

$$L_d = (L_{tb} + VC_{max}) - \int_0^{V_t} C_1 dV_t - VC_1 \qquad (5\text{-}2)$$

where,

L_{tb} - total amount of Atrazine sorbed.

C_1 - the concentration of free ligand inside the cell at the end of collecting fraction n.

V_t - total volume up to fraction t.

The other parameters in equation (5-2) have the same meaning as in equation (5-1). The integral in both of these equations can be evaluated by taking the area under their respective sorption profile. The total amount of Atrazine desorbed, L_{td}, which was sorbed in the same experiment is given in equation (5-3) (i.e., when VC_1 and L_d in equation (5-2) are equal to zero):

$$L_{td} = \int_0^{V_t} C_1 dV_t - VC_{max} \qquad (5\text{-}3)$$

From Appendix (VIII) the values of V_{out}, C_n, C_1, and M_{out} (values for the integrals in equations (5-1), (5-2) and (5-3)) have been calculated and entered into Table 25 of Appendix (IX). The total amount of Atrazine sorbed (L_{tb}) and (L_{td}) was calculated according to equations (5-1) and (5-3) and entered into Table (26) for various pH values. It should be noted that for experiments O and P in Table (26), only, Atrazine diafiltration profiles were done (no FA present in the cell), hence, the amount bound could only be expressed in units of μmole.

5.2.2 DISCUSSION OF RESULTS

From Appendix (VIII), the diafiltration profiles experimentally obtained are similar to those theoretically expected (Figure (43)). From Table (26) the following can be deduced:

(a) the pH changes during a diafiltration profile;

(b) the total amount of Atrazine sorbed, L_{tb}, is less than the total amount of Atrazine desorbed, L_{td}, in 81% of the experiments;

(c) for two experiments with the same experimental conditions (e.g., pH, FA concentration etc.), the amounts sorbed and desorbed are significantly different.

Table (26): Total Atrazine sorbed and desorbed at various pH values using the CFUM.

Appendix (IX)	pH		Amount Sorbed, L_{tb}	Amount Desorbed, L_{td}	Excess Desorbed
	Before	After	(μmole/gmFA)	(μmole/gmFA)	(μmole/gmFA)
A	2.10	2.60	22.0	14.2	--
B	2.10	2.30	19.9	34.4	14.5
C	2.28	--	5.52	8.29	2.77
D	2.30	2.50	6.01	8.67	2.66
E	2.35	--	8.51	--	--
F	2.50	--	10.4	30.8	20.4
G	2.50	2.72	36.9	57.6	20.7
H	2.60	2.75	7.47	16.6	9.13
I	2.90	3.06	0.110	18.3	18.2
J	2.93	3.12	6.01	22.7	16.7
K	3.25	3.10	31.0	76.0	45.0
L	3.67	3.55	4.10	51.1	47.0
M	4.05	3.88	11.0	47.3	36.3
N	4.32	4.25	-2.20	51.1	53.4
O*	5.92	--	0.680	0.513	--
P*	5.93	--	-3.00×10^{-3}	1.74	1.74

* - Obtained from diafiltration profiles for Atrazine only.

The quantities are in units of micromoles.

From the above deductions it can be said that the CFUM cannot be used to study the binding of Atrazine onto FA.

The inconsistant results obtained in Appendix (VIII) and Table (26) are not surprising. Blatt et al. (120) and others (121,122,123) found that experimental nonreproducibility could be caused by membrane rejection of the sorbate, membrane interaction with the sorbate, fluctuation of the cell volume, void volume and fraction volume. Preliminary experimentation had ruled out problems due to membrane interaction, fraction volume (determined by weighing), and the cell volume. Blatt et al. proposed that membrane rejection could be experimentally obtained for wash-in curves by equation (5-4):

$$\ln\left(\frac{C_{max}}{C_{max} - C_n}\right) = \left(\frac{V_{out} - V'}{\bar{V}_0}\right) \qquad (5\text{-}4)$$

where,

V' - the apparent void volume of the system.

$\bar{V}_0$ - the average sample volume in the cell during the run.

For wash-in curves, membranes rejection could be obtained from equation (5-5):

$$\ln\left(\frac{C_{max}}{C_1}\right) = \left(\frac{V_{out} - V'}{\bar{V}_0}\right) \qquad (5\text{-}5)$$

By plotting $\ln(C_{max}/(C_{max} - C_n))$ and $\ln(C_{max}/C_1)$ versus V_{out}, $\bar{V}_0$ and V'

can be obtained from the slope and intercept of the plots, respectively. If $\bar{V}_0$ is greater than the cell volume (13.0 ml)), then, the membrane is rejecting the Atrazine. The data from Tables (25-B) and (25-O) in Appendix (IX) were fitted to equations (5-4) and (5-5). Figure (44) shows the graphs for the wash-in (sorption) data while Figure (45) shows the graphs for the wash-out (desorption) data. Only the linear sections in Figure (44) were used to determine $\bar{V}_0$ and V'. For Figure (45), only, the curve with the solid squares could be used to determine $\bar{V}_0$ and V'. Table (27) list these values. The void volumes in Table (27) are either negative or small compared to the fraction volume (an average of 7.50 millilitres) and the volume of the cell; hence, V' does not seem to contribute any error to the CFUM. The calculated volumes of the cell, $\bar{V}_0$, are significantly different from the true volume of the cell (13.0 millilitres), thus, indicating that there is rejection of Atrazine by the UM-2 membrane. Blatt et al. (120) suggested that the rejection of a membrane can be corrected for by introducing the reflection coefficient, σ, into equations (5-4) and (5-5).

$$\sigma = 1 - (C_n/C_n') \qquad (5\text{-}6)$$

When C_n equals C_n', it means that the membrane is not rejecting the solute. When C_n' is greater than C_n it means that the membrane is rejecting the solute. For the wash-in curve, equation (5-7) corrects for solute rejection while for the wash-out curve equation (5-8) corrects for rejection (120).

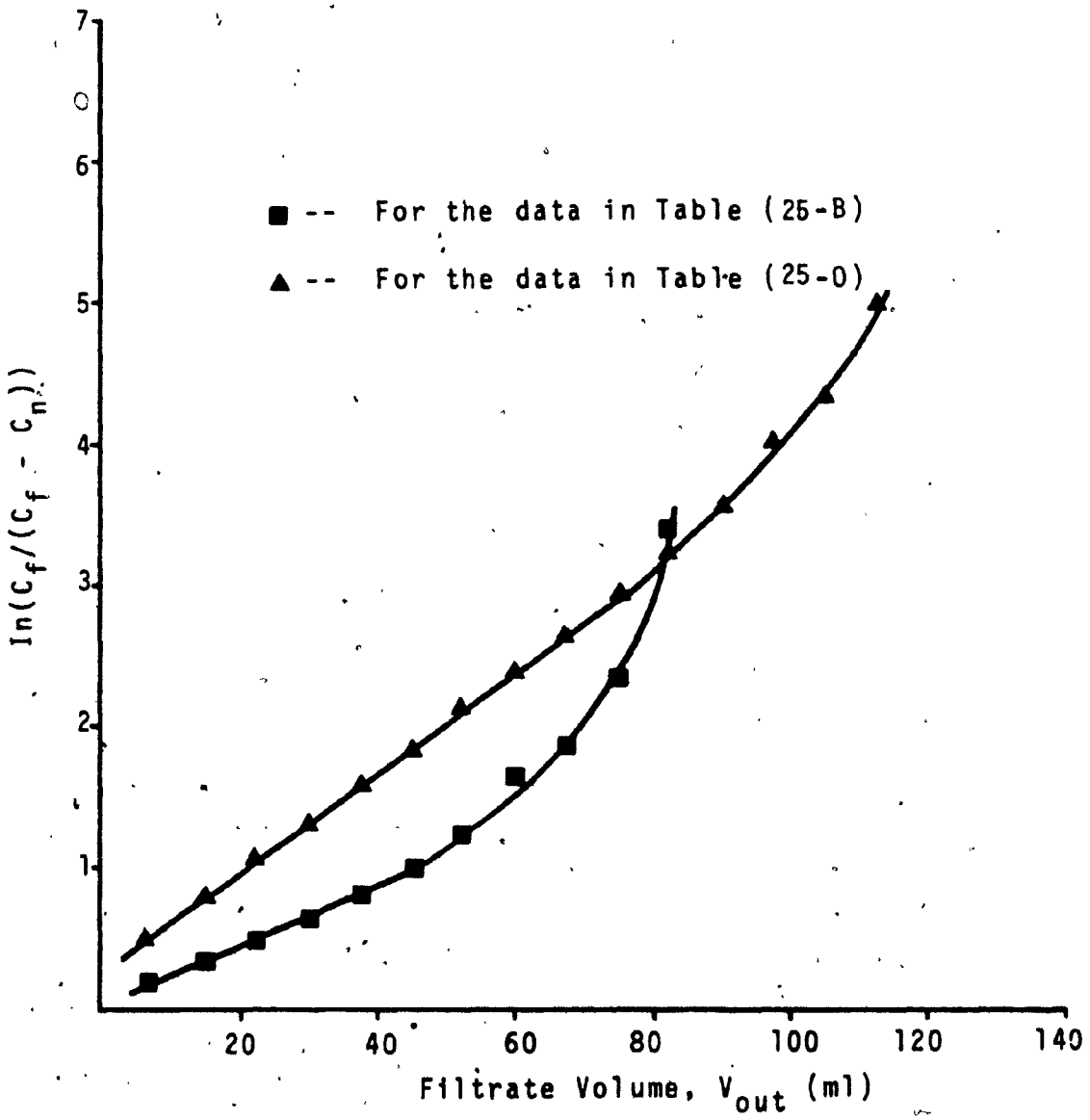


Figure (44): Diafiltration sorption curve for Atrazine through UM-2 membranes at 40 psi.

Table (27): Determination of V' and $\bar{V}_0$ from the data in Tables (25-B) and (25-0) in Appendix (IX).

	Table (25-B)		Table (25,0)	
Experiment	V'(ml)	$\bar{V}_0$(ml)	V(ml)	$\bar{V}_0$(ml)
Sorption	0.03	47.5	-6.50	28.3
Desorption	--	--	-2.00	20.8

$$\ln\left(\frac{C_{max}}{C_{max} - C_n}\right) = \left(\frac{V_{out} - V'}{\bar{V}_0}\right)\frac{(1-\sigma)}{1} \qquad (5\text{-}7)$$

$$\ln\left(\frac{C_{max}}{C_1}\right) = \left(\frac{V_{out} - V'}{\bar{V}_0}\right)\frac{(1-\sigma)}{1} \qquad (5\text{-}8)$$

In future research, corrections should be made for membrane rejection. Roy and Miles (60) suggested that point by point correction could be made for membrane rejection. This method involves running a diafiltration profile for the Atrazine alone. For every fraction collected in the presence of FA the amount of Atrazine rejected is deducted. This is exactly the same technique which is used in the BUM, i.e., controls are done simultaneously with the FA solutions, so that if there is any rejection by the membrane it will be corrected for by the controls. However, it must be rememered that the BUM used YM-2 rather than UM-2 membranes.

Figure (45) shows that there are linear regions for both curves. These results are different from those of Blatt et al. (120) who obtained one line for his plots. However, Roy and Miles (60) obtain similar plots to that in Figure (45) for the binding of nucleosides onto polynucleotides.

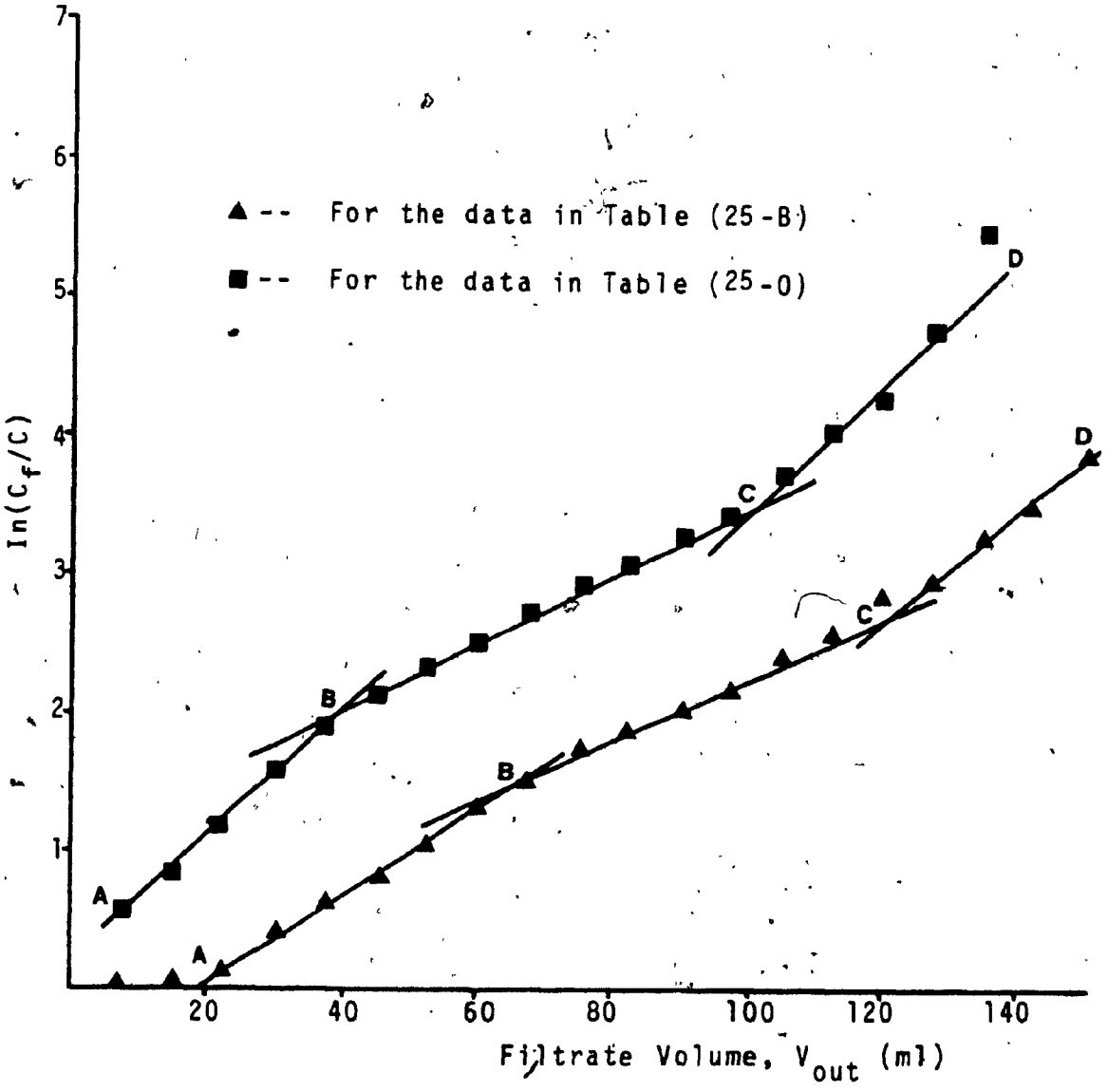


Figure (45): Diafiltration desorption curve for Atrazine through UM-2 membrane at 40 psi.

The linear region between AB was described as the washing out of the excess Atrazine in the cell; the BC region represents the dissociation of the complex formed between Atrazine and FA; CD represents elution of the dissociated ligand. The difference between the points B and C represents the total amount of Atrazine bound. For the curve with the solid

triangles in Figure (45) the Atrazine bound is 0.627 μmole while that with the solid squares gives 0.474 μmole of Atrazine bound. Since the solid squares curve is for Atrazine alone in the cell, it is expected to bind less. The determination of binding data by plots similar to Figure (45) needs more investigation.

From the literature survey it was found that the CFUM method is susceptible to a lot of experimental difficulties. For binding of micromole quantities, the errors incurred by these difficulties are very significant. In the BUM, one has greater control of experimental parameters (pH; correction for rejection of the membrane; cell volume is not significant; the fraction volume was always constant since it was collected manually; temperature variation was not significant since a sample takes only about an hour to filter). If the CFUM can be perfected, the data obtained from it can be treated in the same way as the data obtained from BUM.

CONCLUSIONS

The work presented in this thesis has examined the interaction between Atrazine and a well characterized fulvic acid which was obtained from Armadale, Prince Edward Island. It is now possible to predict the conditions under which Atrazine will bind to fulvic acid.

Of the two methods used to do binding studies, the BUM gave results which were more accurate. The CFUM is susceptible to difficulties which produce non-reproducible results. Using the BUM, one could control more readily experimental parameters which were difficult to handle in the CFUM. However, the BUM used about seven times more fulvic acid to produce the same result as the CFUM. The BUM is also more time consuming and more mechanical.

Atrazine can exist in two forms depending on the pH of the system. From about pH 0.1 and higher unprotonated Atrazine exists in aqueous solution. Protonated Atrazine exists in aqueous solution from about pH 4 and lower.

The fulvic acid used here had identical functional groups to that characterized by Gamble (28,29,30). There was 5.08 mmole Type A carboxylic acid groups per gram of FA and 2.33 mmole Type B groups per gram of FA. Protonation of the Type A carboxylic acid groups start at about pH 5.85. The Type 1 groups are the strongest carboxylic acids in the Type A groups. Protonation of the Type 1 groups starts at about pH 3.4.

Atrazine only interacted with the protonated Type A carboxylic acid groups. Unprotonated Atrazine interacted from about pH 5 and lower whereas protonated Atrazine interacted from about pH 4 and lower.

In the absence of KCl, Cu^{2+} and aggregation, the Atrazine binding

trend with pH shows that two kinds of Type A sites are responsible for binding Atrazine. From pH 3.4 and lower there is a positive correlation between the protonated Type 1 sites and bound Atrazine whereas between pH 3.4 and 5 there is a positive correlation between the Type A sites which are not included in the Type 1 sites and bound Atrazine. The maximum complexing capacity observed is about 0.7 mole % of the total Type A carboxylic acid groups. The differential equilibrium functions (1/K) range in values from 30.6 to 1.37×10^3 litre per mole. The standard Gibbs free energies range in values from 8.48 to 16.4 Kj/mole. This is the magnitude expected for weak physical forces such as hydrogen bonding.

In the presence of 0.100 M KCl, hydrogen bonded aggregation of the fulvic acid becomes important for more than about 3 mmoles per gram of the protonated Type A carboxyl groups. This reduces the number of protonated carboxyl groups available to the Atrazine. Atrazine binding starts at about pH 4.5 and it increases as pH decreases. The maximum binding capacity is about 0.7 mole % to the Type A sites. The equilibrium differential functions range in values from 101 to 581 litre per mole. The standard Gibbs free energies range in values from 11.7 to 15.8 Kj/mole. These thermodynamic values are essentially the same as those for the cases where there are no KCl, Cu^{2+}, and aggregation. Binding is therefore by hydrogen bonding between the protonated Type A carboxylic acid groups and the lone pair of electrons on the nitrogen in the 5-position in the Atrazine ring.

Cu(II) chelation makes the carboxyl groups unavailable to Atrazine by at least two processes: (a) by blocking carboxyl groups, especially the Type 1, that are ortho to phenolic groups, Cu(II) chelation reduces the

Atrazine complexing capacity, (b) by causing aggregation with carboxyls other than the Type 1 groups. Atrazine binding is lost above pH 3.2. Cu(II) chelation reduces both the Atrazine complexing capacities and the estimated free energies. The maximum complexing capacity is about 0.3% which is less than half of the previous two cases. The 1/K values range from 101 to 113 litre per mole. The Gibbs free energy values range from 11.2 to 11.5 Kj/mole.

Protonated Type A carboxylic acid groups act as Lewis acids whereas the lone pair of electrons in the 5-position of the Atrazine ring acts as a Lewis base. Once the protonated Type A groups become deprotonated or are used up through aggregation among the FA particles or are used for chelation, then, a reduction of Atrazine binding is observed. Chelation of the protonated Type A sites is more effective in reducing Atrazine binding to FA than the presence of high ionic strength.

In the absence of metal ions or aggregation, exactly the same protonated Type A carboxyl groups are responsible for Atrazine hydrolysis to hydroxyatrazine. There must, therefore, be a direct correlation between the hydrolysis rate constant, and the molarity of complexed Atrazine.

The differential equilibrium functions can be used to predict the concentration of the complex formed once the FA and Atrazine concentrations are known.

Synonymous trends are obtained for K_4 for decreasing χ_c and for decreasing pH values. As pH decreases for the same concentration of copper(II) (1.06×10^{-3} M or 4.74×10^{-3} M) the values of K_4 increase (see Table (14)). K_4 also increases as χ_c decreases. The maximum value obtained for K_4 is 40.3 which gives a free energy of 8.96 Kj/mole.

CLAIMS TO ORIGINAL RESEARCH

1) A batch ultrafiltration method (BUM) has been developed which can be used to obtain titration graphs for the weak complexes formed between Atrazine and the protonated Type A carboxylic acid groups.

2) Atrazine only complexes with the protonated Type A carboxylic acid groups.

3) Chelation, high ionic strength and aggregation of the FA particles reduces the binding of Atrazine to the protonated Type A carboxylic acid groups.

4) Differential equilibrium functions (1/K) are obtained which can be used for predictive calculations under various experimental conditions.

5) Atrazine binds by hydrogen bonding to the protonated Type A carboxylic acid groups.

SUGGESTIONS FOR FUTURE RESEARCH

The present study is a preliminary investigation of the interaction of Atrazine with fulvic acid under various experimental conditions. Further studies are required so as to have a complete understanding of the chemistry of FA towards pesticides/herbicides. It is suggested that the following be done:

1) More research be done on the CFUM so as to have a method which is cheaper and less time consuming.

2) Similar work as was done with Atrazine should be done with other s-triazines so as to see if the protonated Type A sites behave as Lewis acids.

3) Further work is needed for Atrazine binding in the presence of KCl. This work should be done above pH 4 so as to check for hydrophobic interactions.

4) Some Rayleigh light scattering experiments should be done in order to see if FA unfolds as total Atrazine concentrations increase.

5) At low pH studies (pH < 4) the presence of the hydrolyzed product, hydroxyatrazine, should be analyzed for. This would indicate if hydrolysis is through a hydrogen bonding mechanism or not.

6) A fulvic acid from a location other than Armadale, Prince Edward Island should be used for binding studies. In this way a comparison can be made between the two results so as to see if the same conclusions can be drawn.

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APPENDIX (I)

Fitted titration graphs for FA at different pH values. The number at the bottom right hand corner of each page represents the pH at which the experiment was done.

FA - 1.000 gm/litre

b - intercept of a line

m - slope of a line

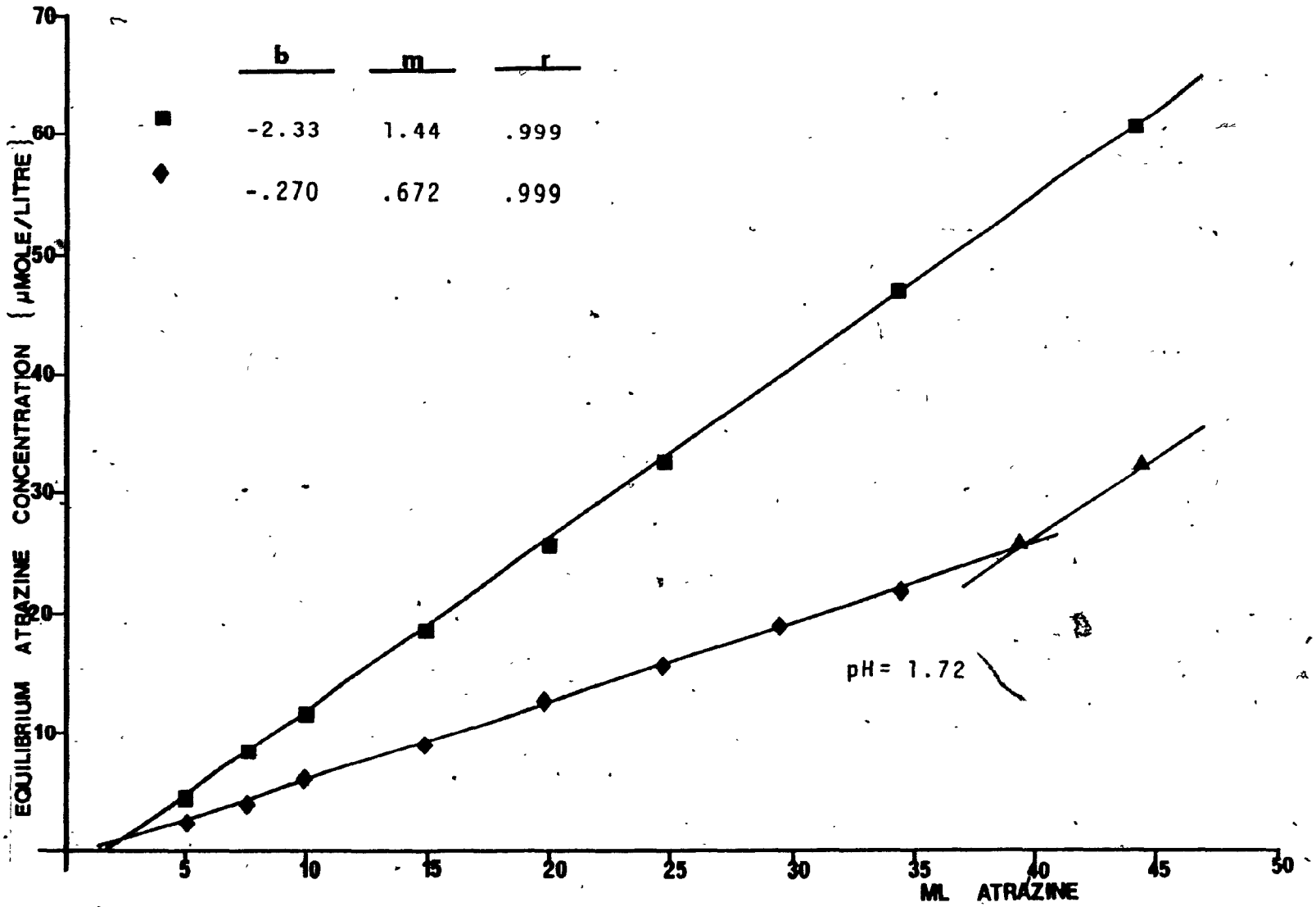
r - correlation factor of a line

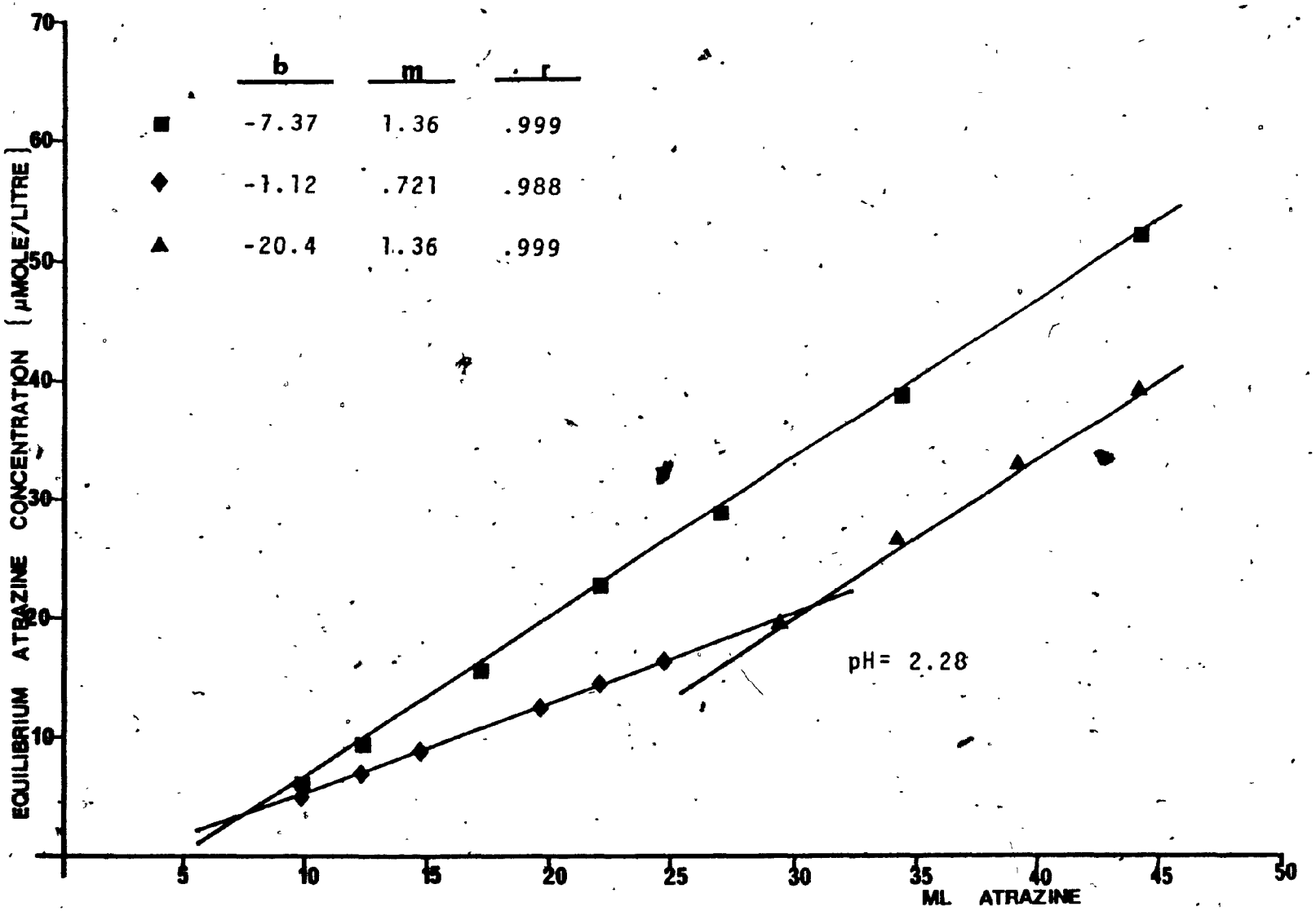
■ - Atrazine control solutions

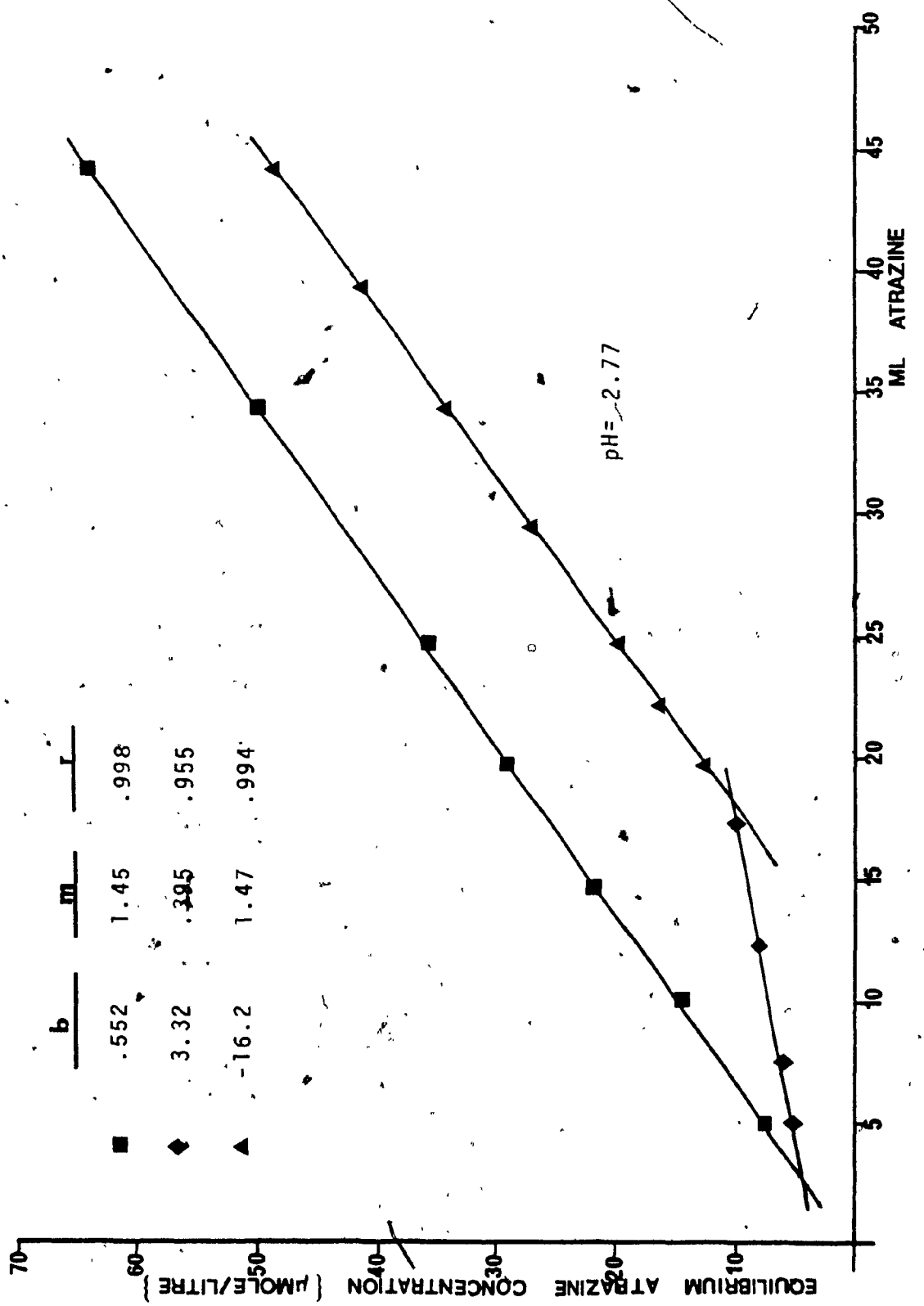
◆ - Atrazine solutions before the equivalence point

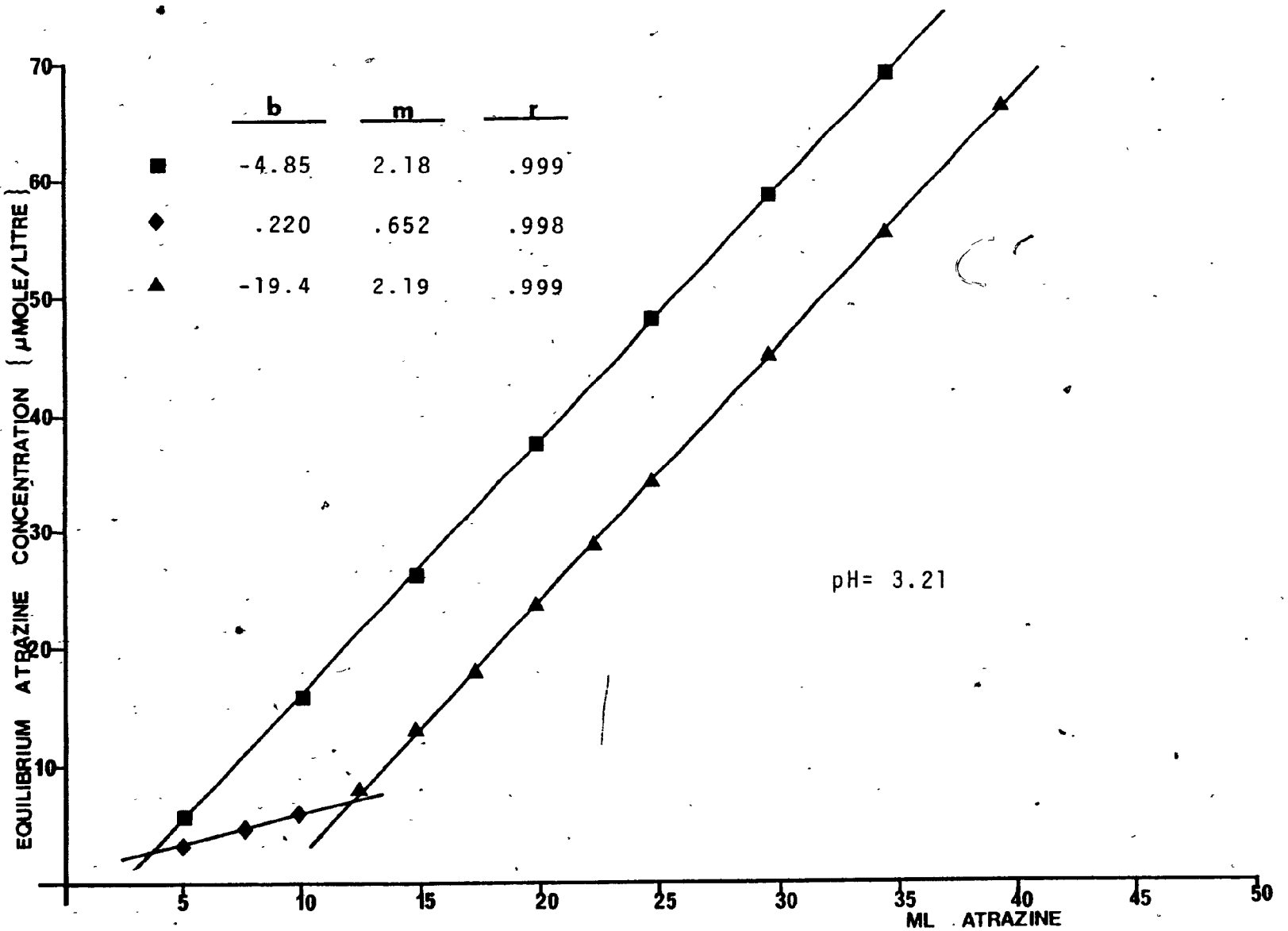
▲ - Atrazine solutions after the equivalence point

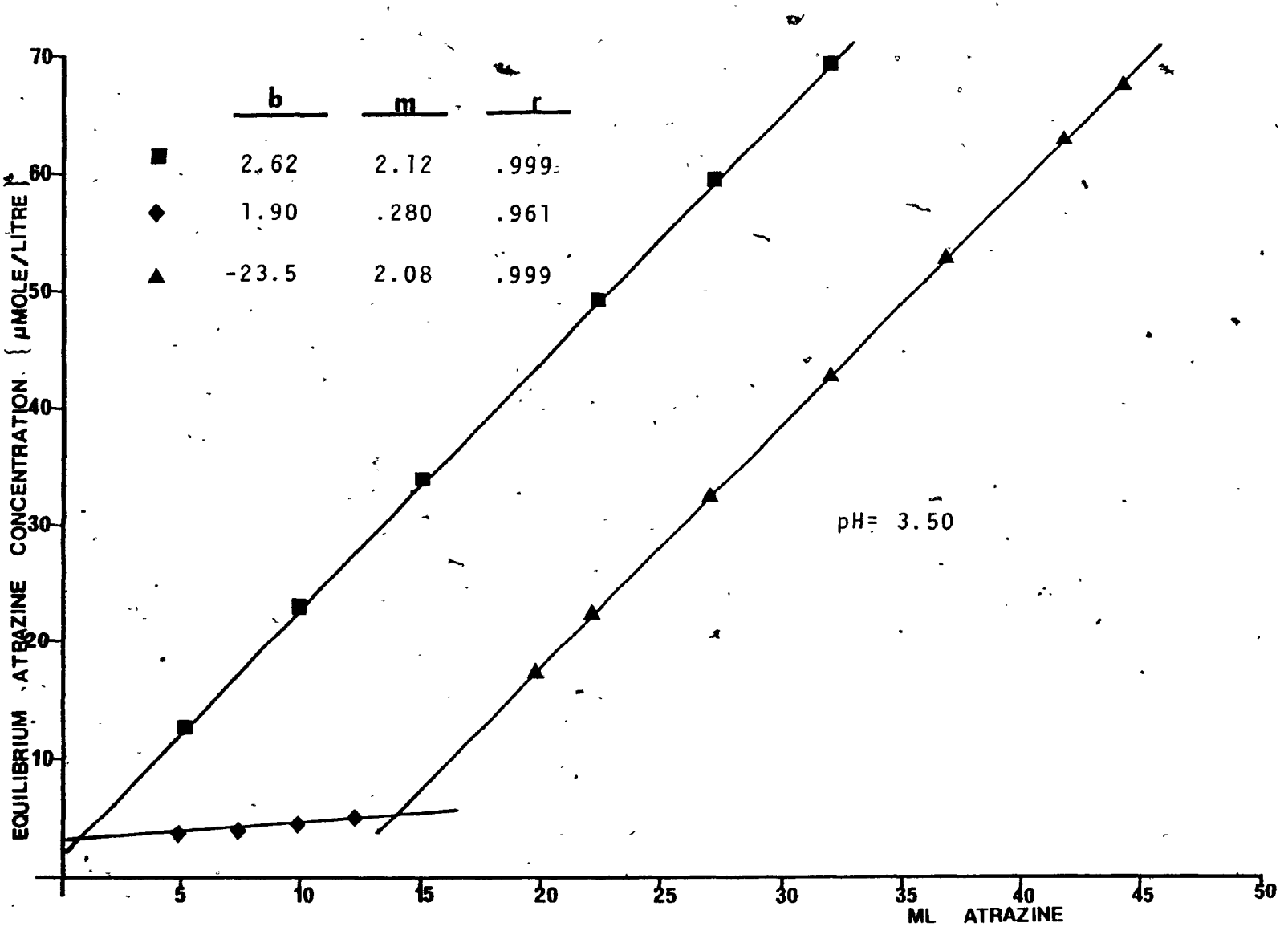
Volume of solution = 50.00 ml

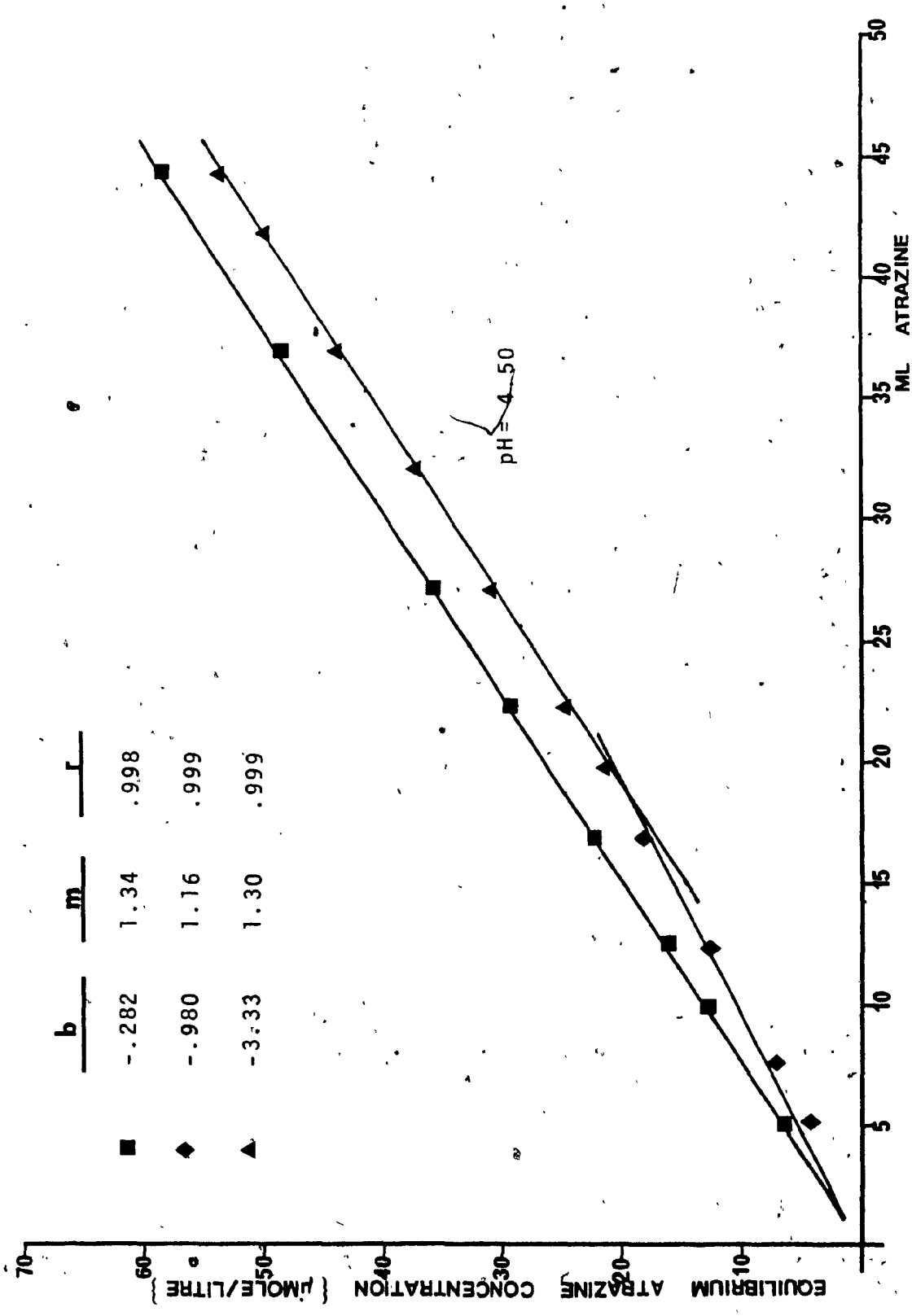

b
m
r
■ -2.33 1.44 .999
◆ -.270 .672 .999
pH= 1.72
EQUILIBRIUM ATRAZINE CONCENTRATION (μMOLE/LITRE)
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50

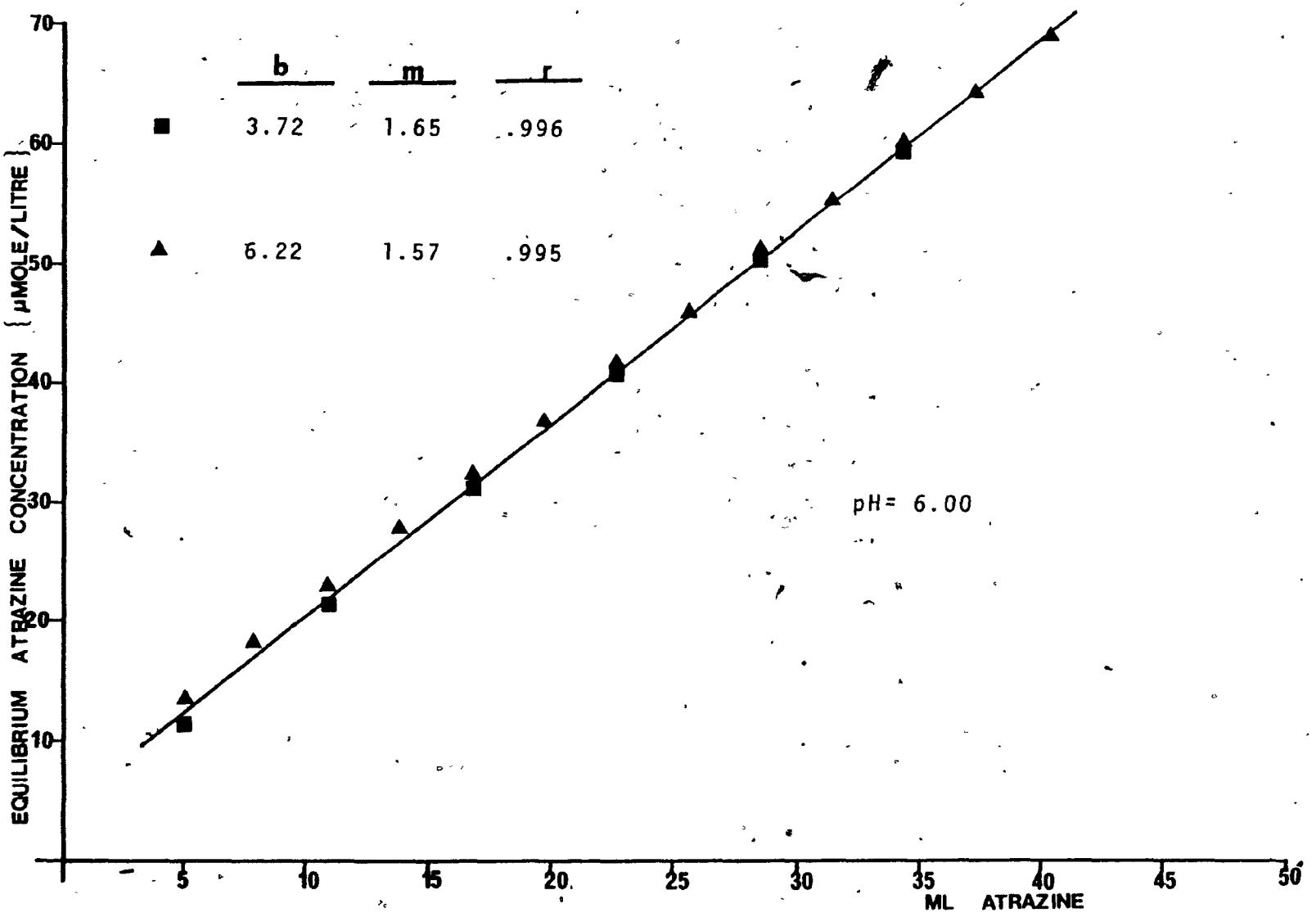

b
m
r
■ -7.37 1.36 .999
◆ -1.12 .721 .988
▲ -20.4 1.36 .999
pH= 2.28
EQUILIBRIUM ATRAZINE CONCENTRATION {µMOLE/LITRE}
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50

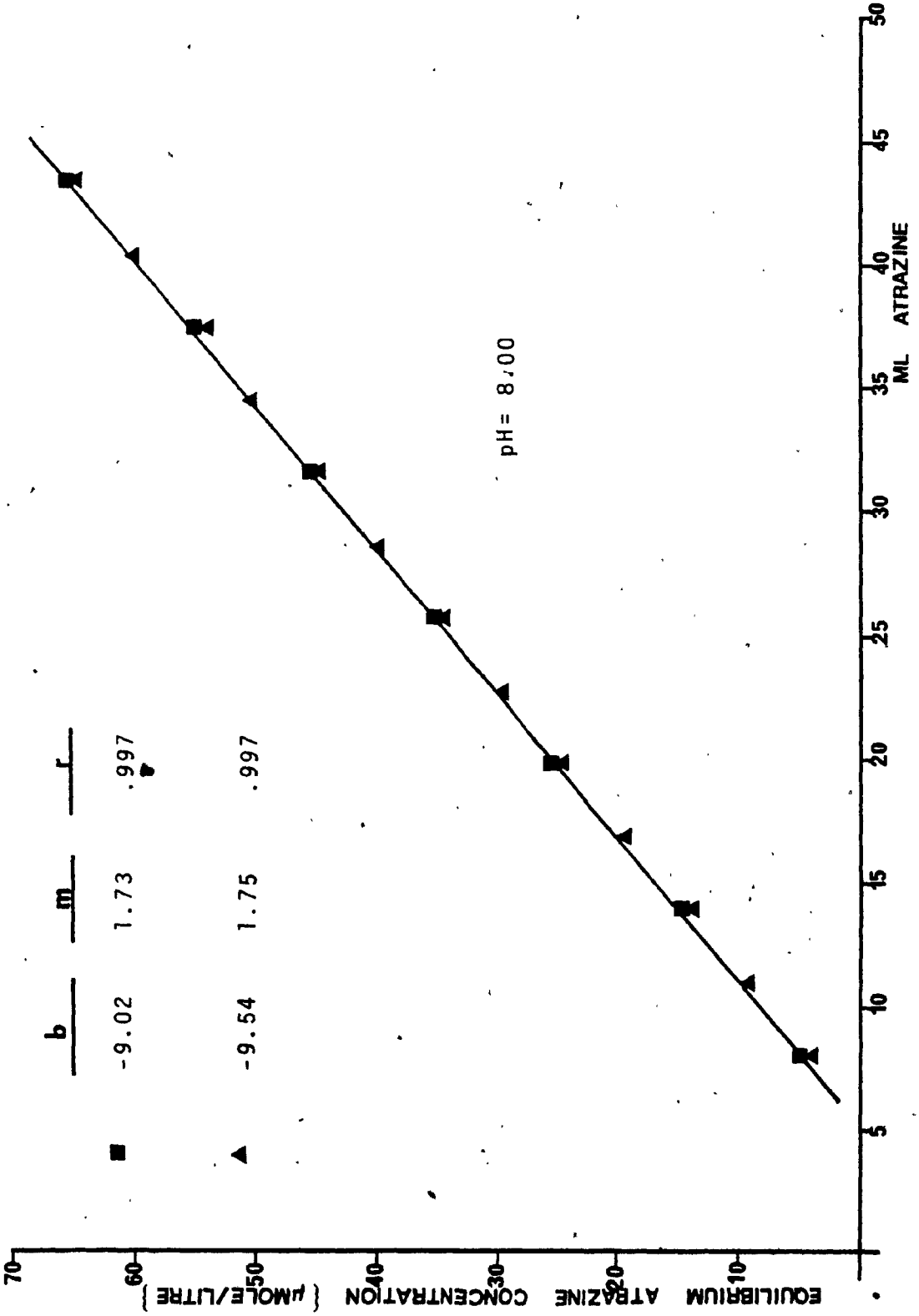

EQUILIBRIUM ATRAZINE CONCENTRATION (μMOLE/LITRE)
ML ATRAZINE
pH=2.77
b m r
.552 1.45 .998
3.32 .395 .955
-16.2 1.47 .994


b
m
r
■ -4.85 2.18 .999
◆ .220 .652 .998
▲ -19.4 2.19 .999
pH= 3.21
EQUILIBRIUM ATRAZINE CONCENTRATION {µMOLE/LITRE}
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50


b
m
r
2.62
2.12
.999
1.90
.280
.961
-23.5
2.08
.999
pH= 3.50
EQUILIBRIUM ATRAZINE CONCENTRATION (μMOLE/LITRE)
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50


EQUILIBRIUM ATRAZINE CONCENTRATION { μMOLE/LITRE }
ML ATRAZINE
pH = 4.50
b m r
■ -.282 1.34 .998
◆ -.980 1.16 .999
▲ -3.33 1.30 .999


b
m
r
3.72
1.65
.996
6.22
1.57
.995
pH= 6.00
EQUILIBRIUM ATRAZINE CONCENTRATION {µMOLE/LITRE}
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50


EQUILIBRIUM ATRAZINE CONCENTRATION (μMOLE/LITRE)
ML ATRAZINE
pH= 8.00
b m r
-9.02 1.73 .997
-9.54 1.75 .997

APPENDIX (II)

Titration graphs for FA at different pH values in the presence of 0.100 M KCl. The pH of each experiment is indicated at the bottom right hand corner of each graph.

FA - 1.000 gm/litre

b - intercept of a line

m - slope of a line

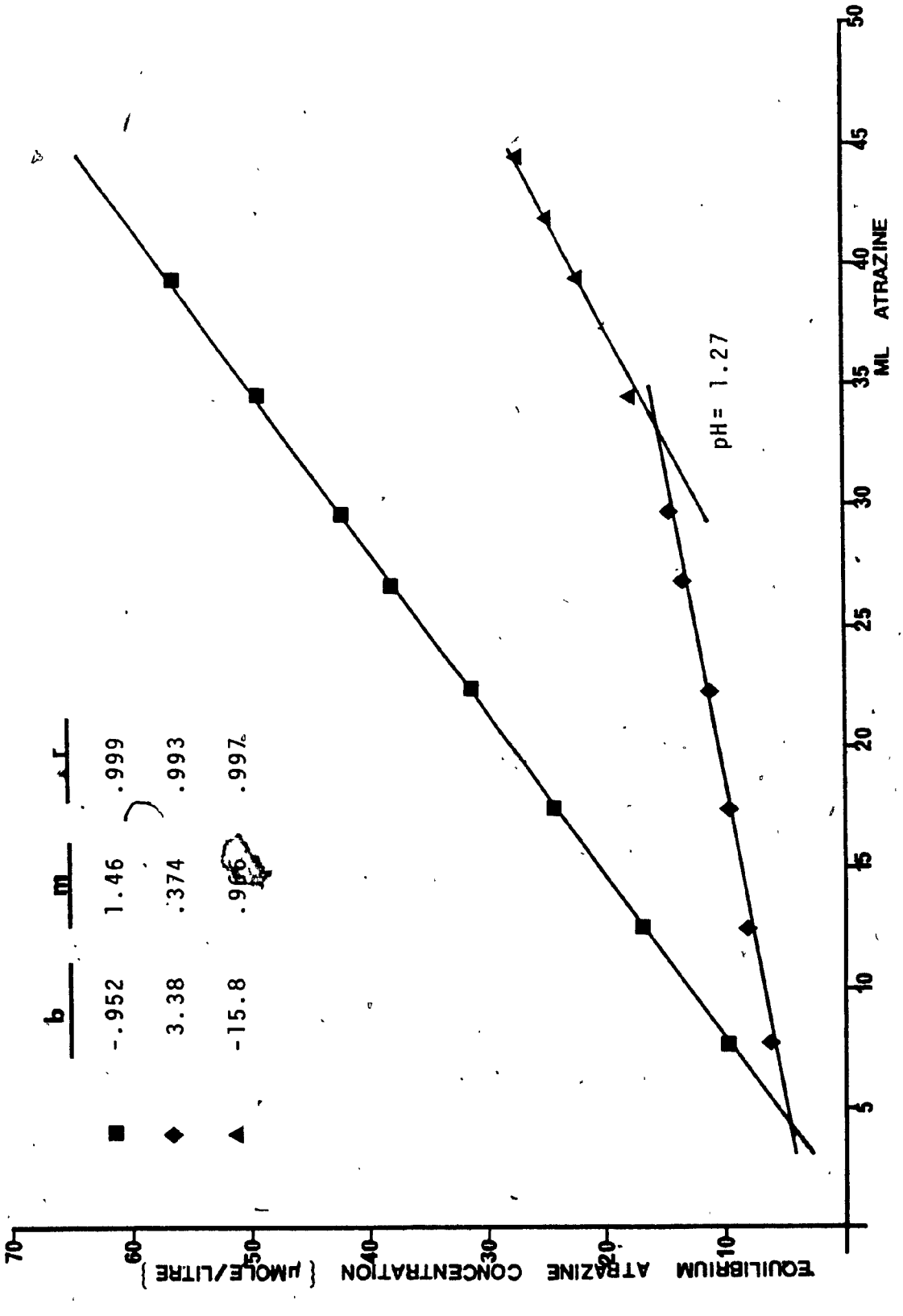
r - correlation factor of a line

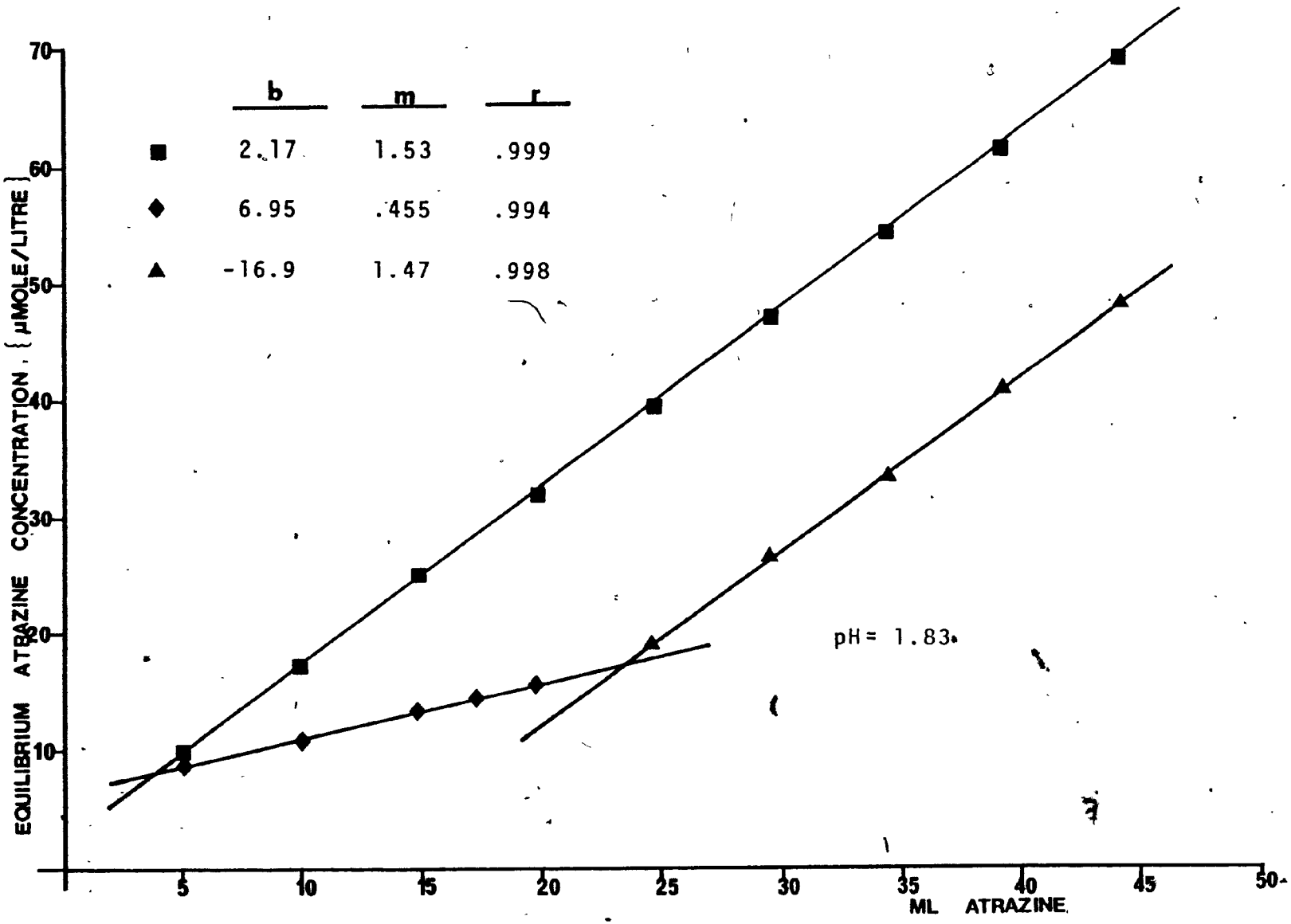
■ - Atrazine control solutions

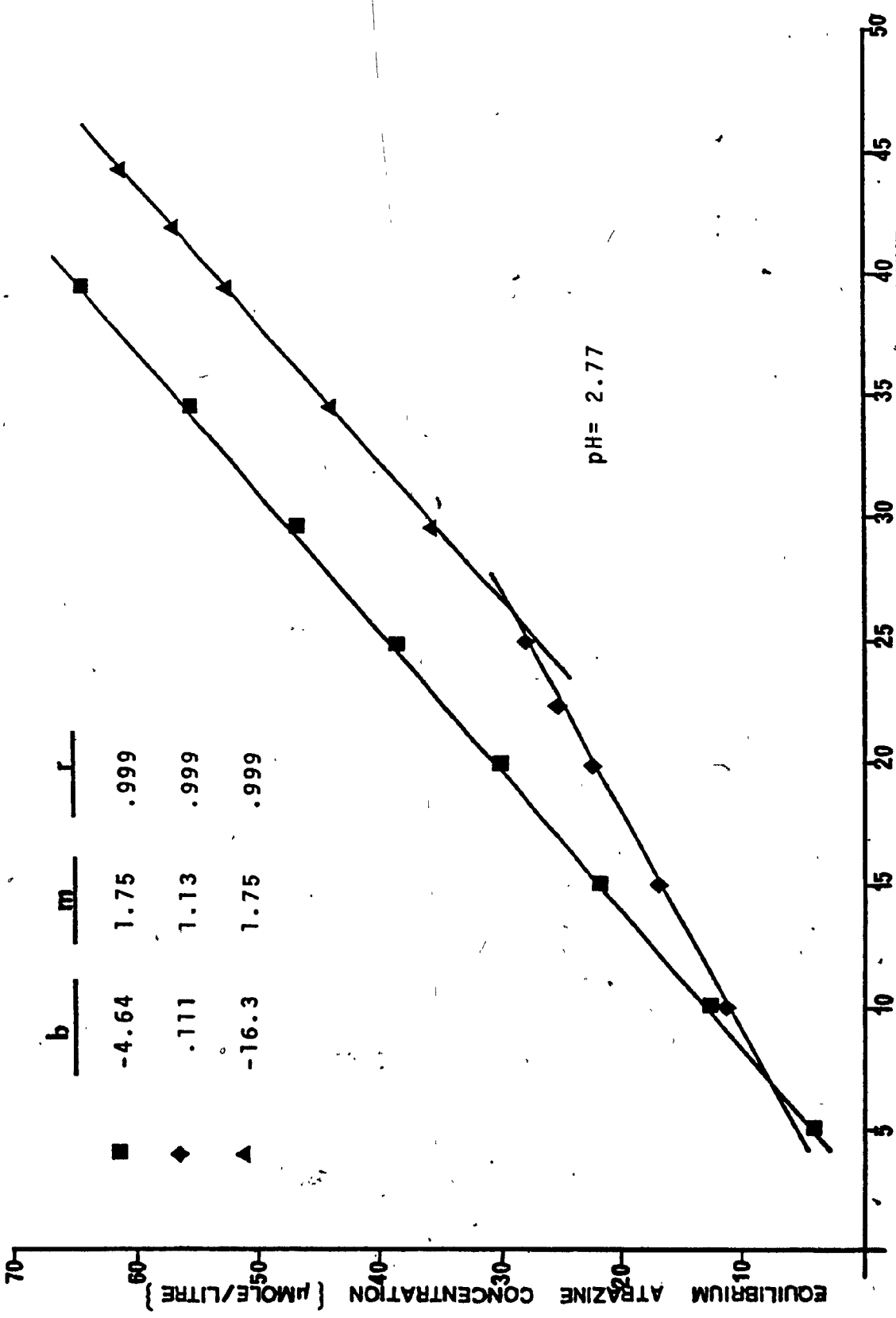
◆ - Atrazine solutions before the equivalence point

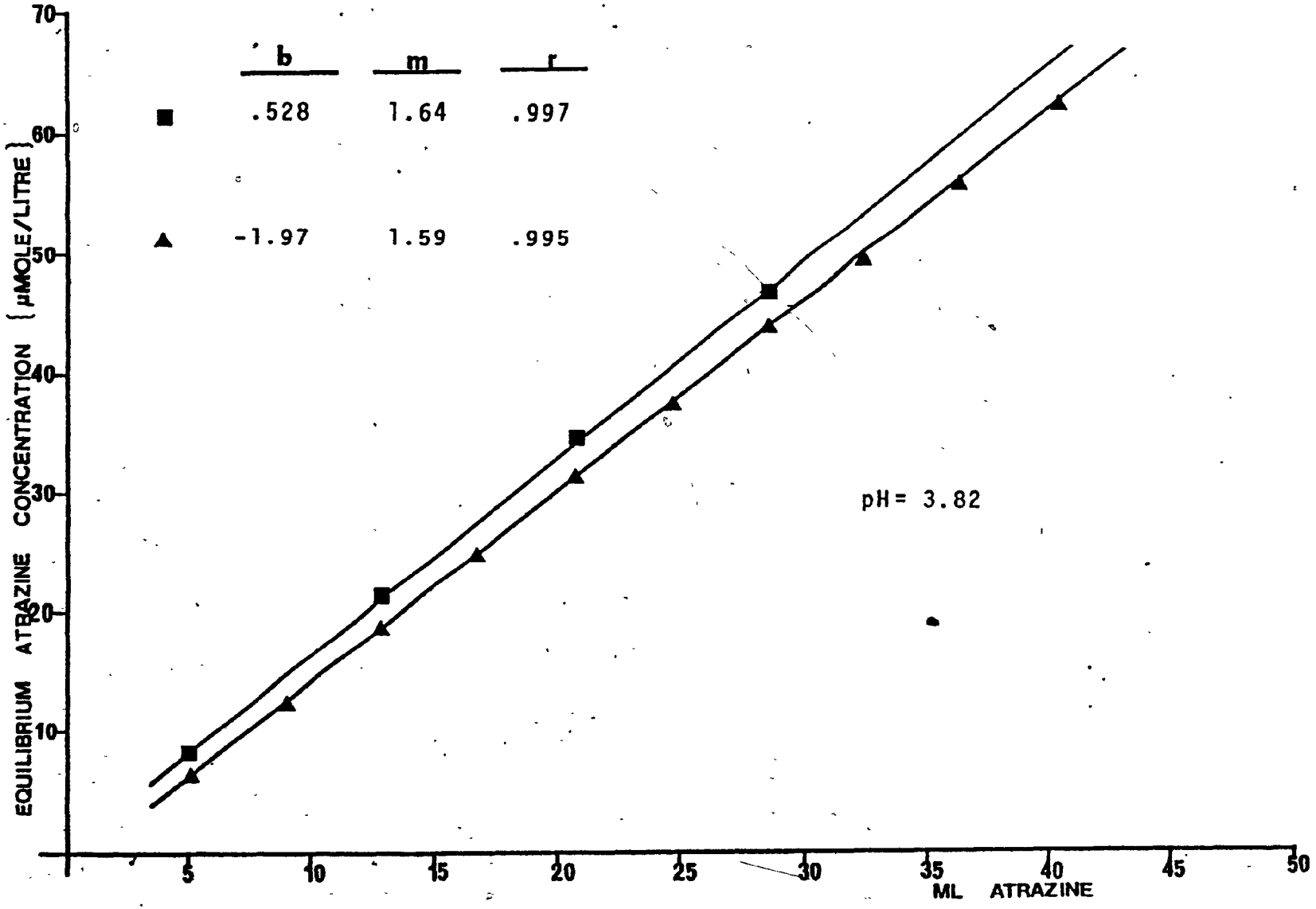
▲ - Atrazine solutions after the equivalence point

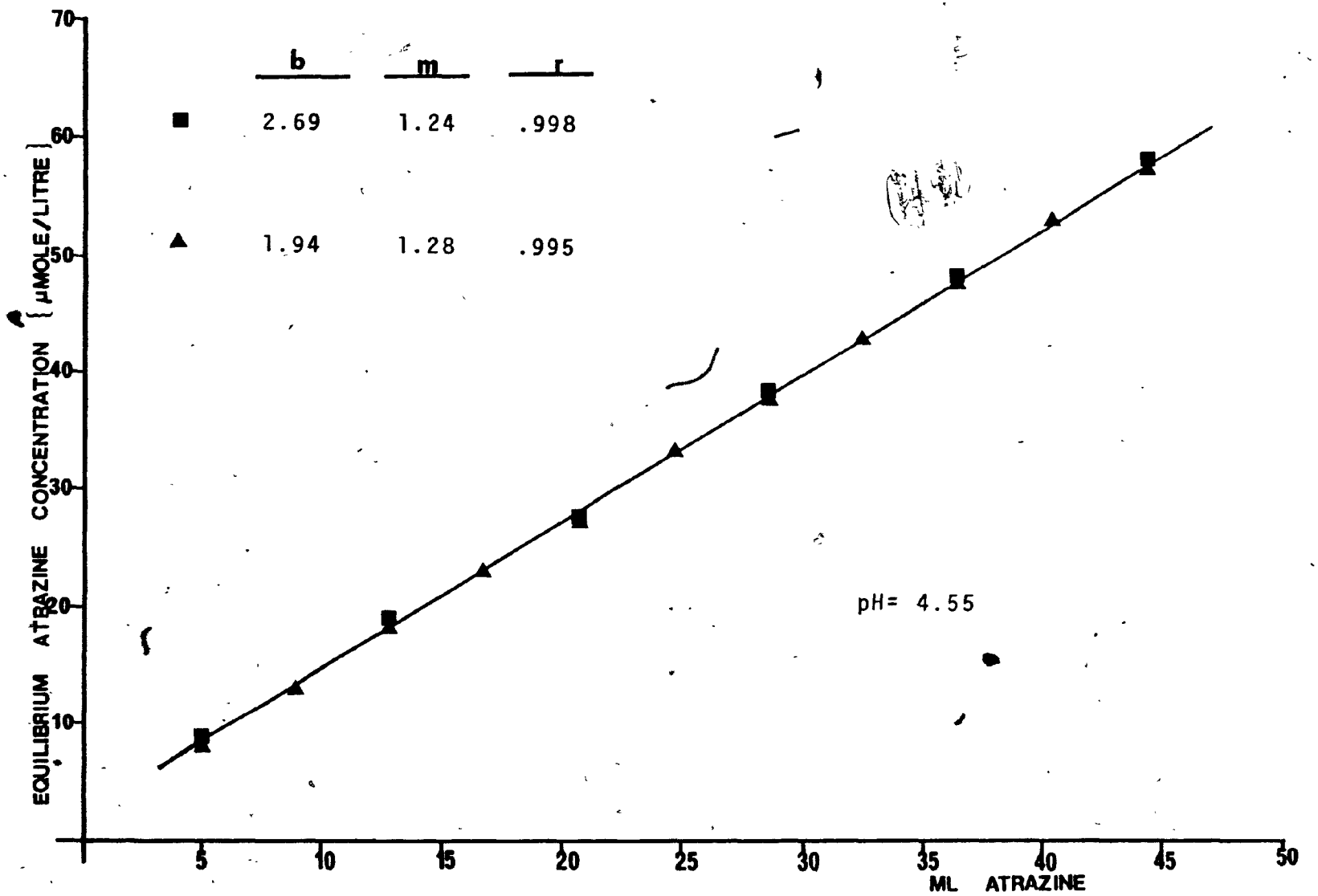
Volume of solution = 50.00 ml

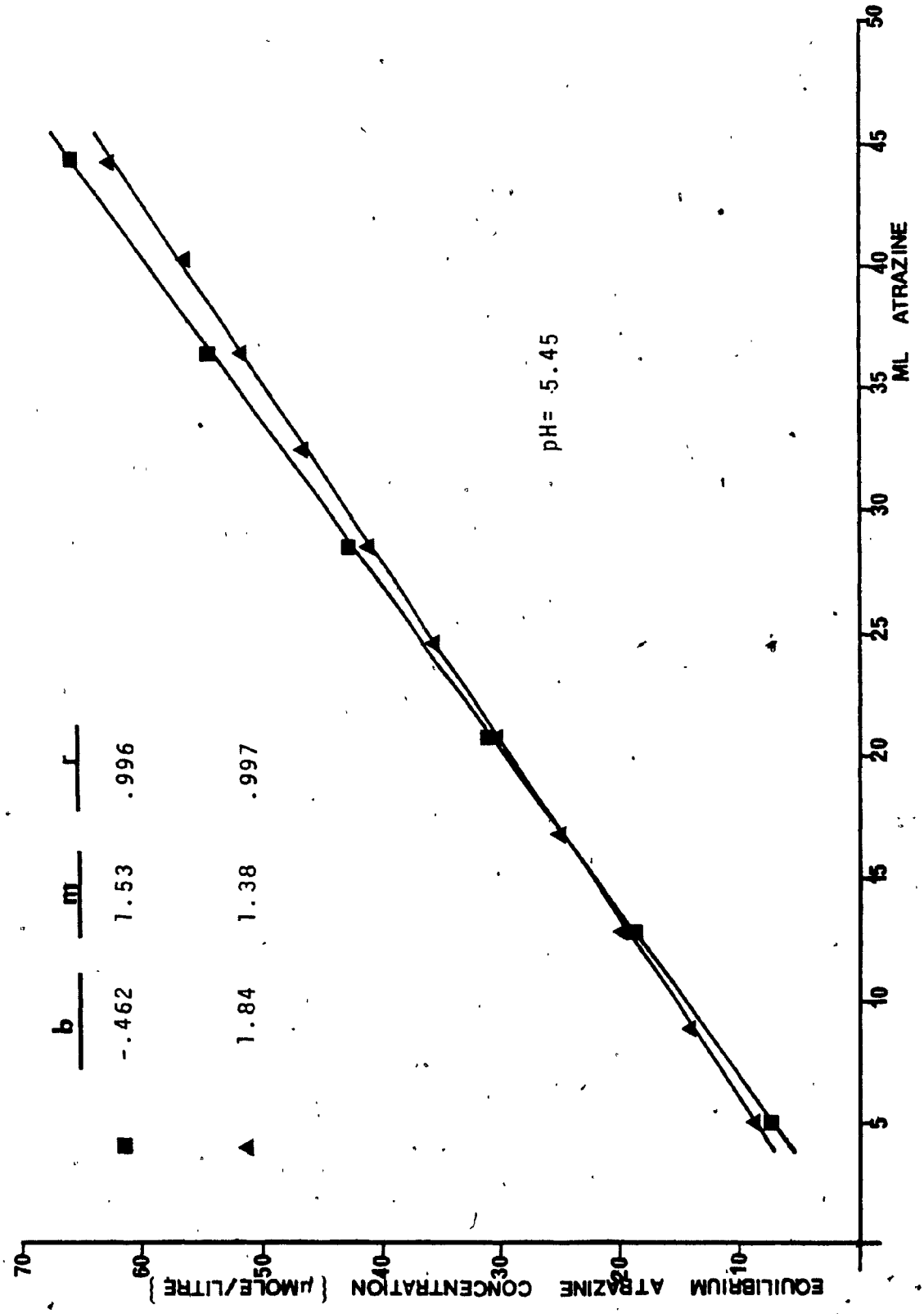

b
m
r
-.952
1.46
.999
3.38
.374
.993
-15.8
.966
.997
pH = 1.27
EQUILIBRIUM ATRAZINE CONCENTRATION {μMOLE/LITRE}
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50

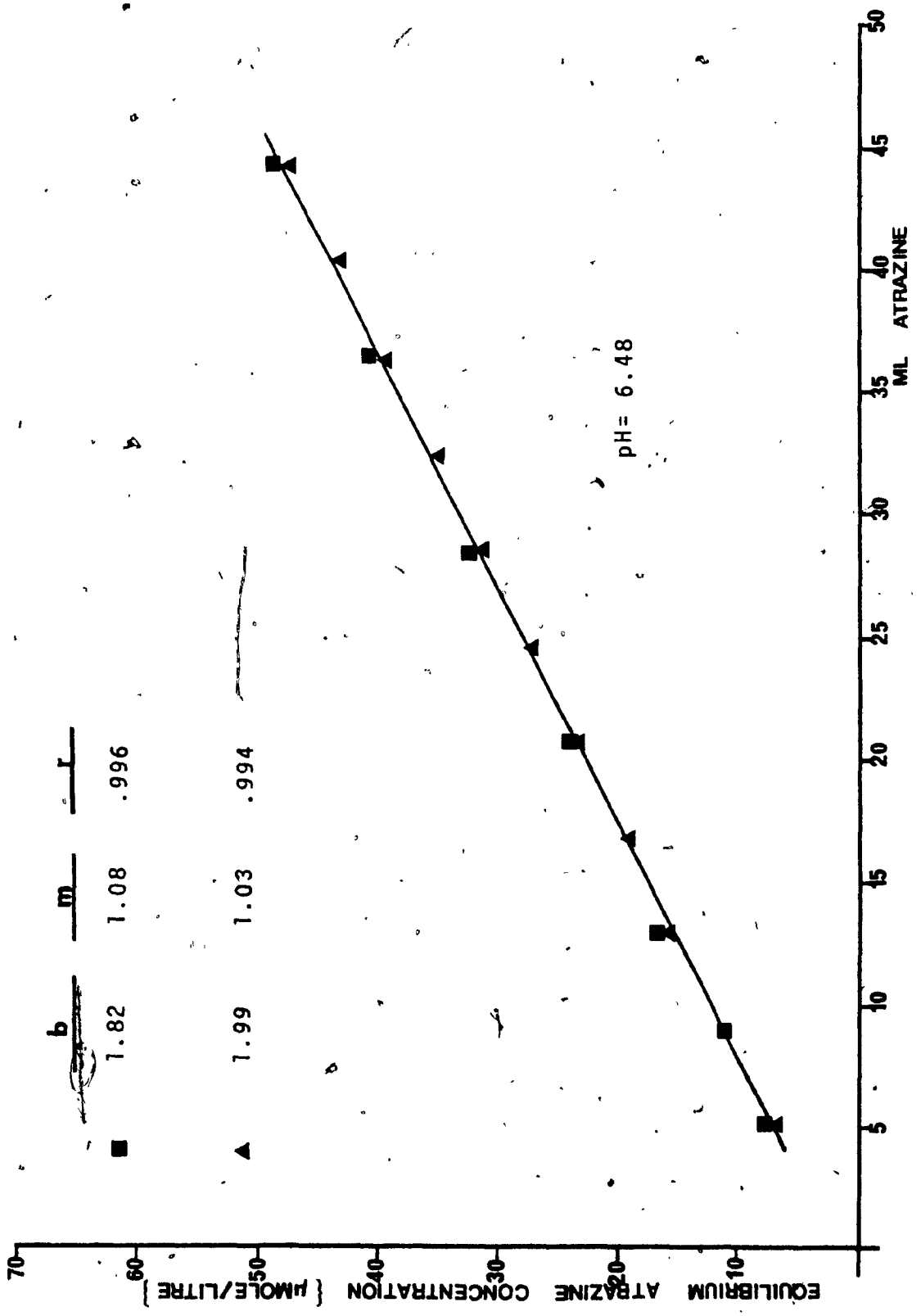

b
m
r
■ 2.17 1.53 .999
◆ 6.95 .455 .994
▲ -16.9 1.47 .998
pH = 1.83
EQUILIBRIUM ATRAZINE CONCENTRATION (µMOLE/LITRE)
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
ML ATRAZINE

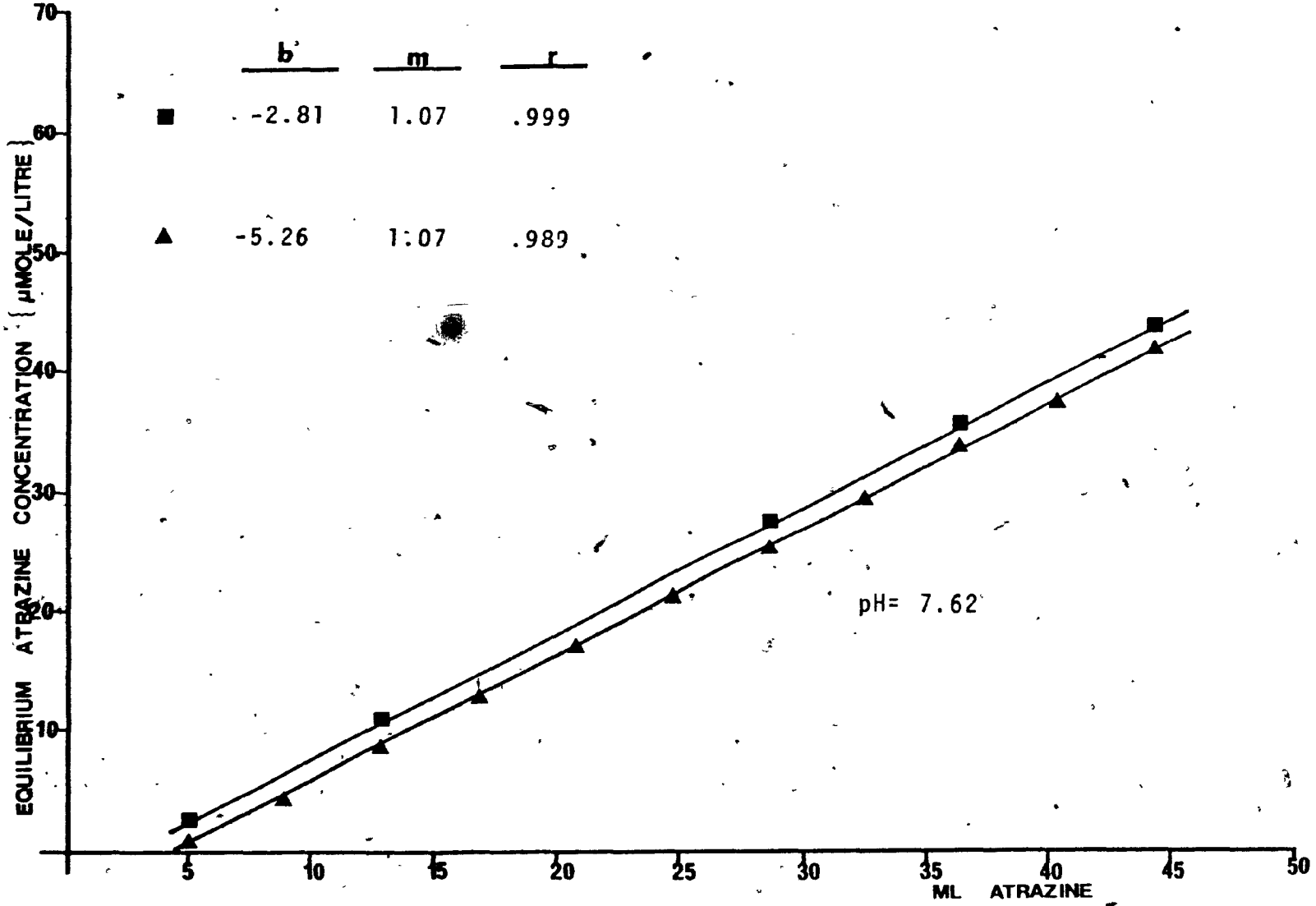

EQUILIBRIUM ATRAZINE CONCENTRATION {μMOLE/LITRE}
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
ML ATRAZINE
pH= 2.77
b
m
r
-4.64
1.75
.999
.111
1.13
.999
-16.3
1.75
.999

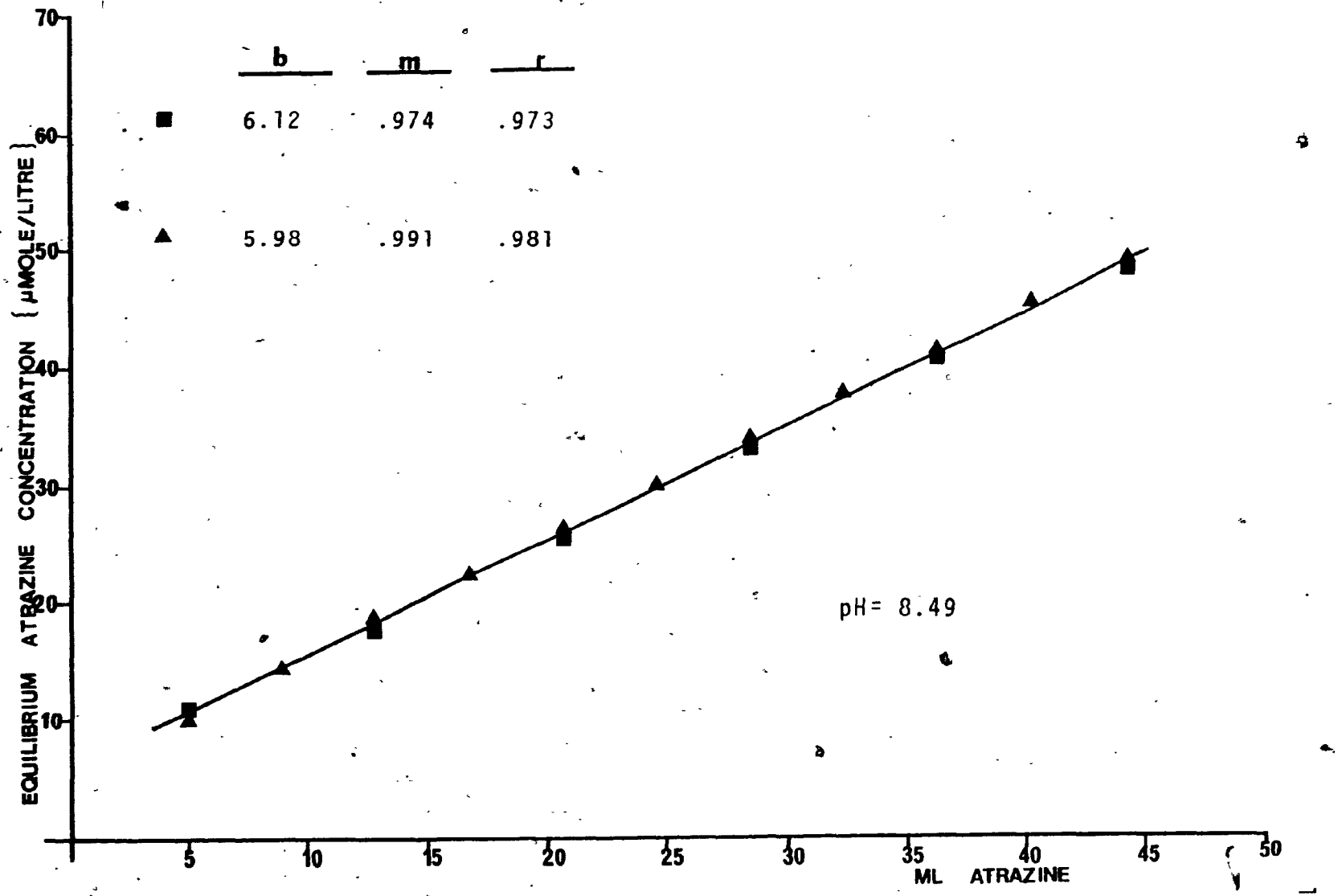

b
m
r
■ .528 1.64 .997
▲ -1.97 1.59 .995
pH= 3.82
EQUILIBRIUM ATRAZINE CONCENTRATION {µMOLE/LITRE}
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
ML ATRAZINE

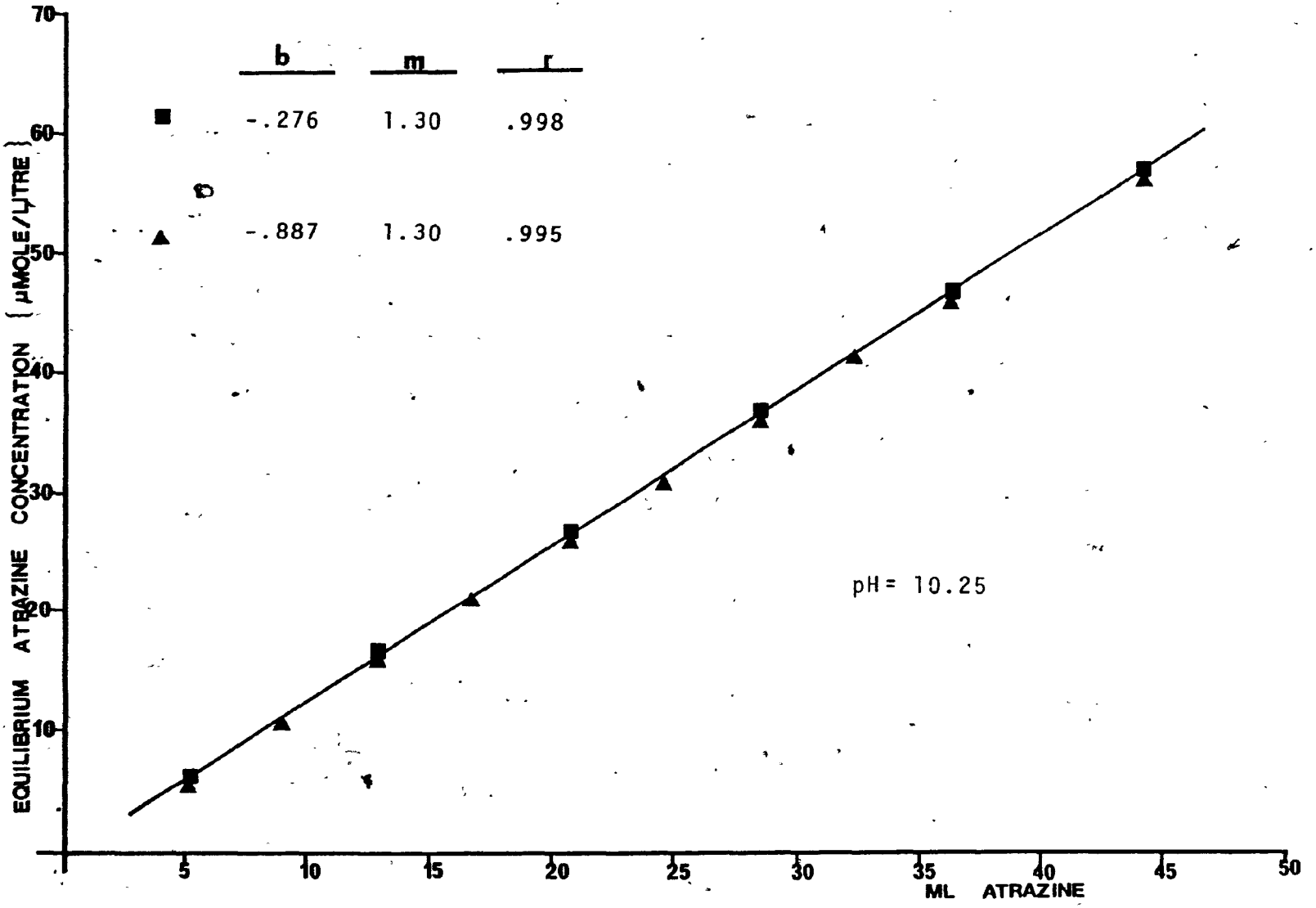

b
m
r
2.69
1.24
.998
1.94
1.28
.995
pH= 4.55
EQUILIBRIUM ATRAZINE CONCENTRATION {µMOLE/LITRE}
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50


EQUILIBRIUM ATRAZINE CONCENTRATION (μMOLE/LITRE)
ML ATRAZINE
pH= 5.45
b m r
■ -.462 1.53 .996
▲ 1.84 1.38 .997


EQUILIBRIUM ATRAZINE CONCENTRATION {μMOLE/LITRE}
ML ATRAZINE
pH= 6.48
b m r
1.82 1.08 .996
1.99 1.03 .994


b
m
r
■ -2.81 1.07 .999
▲ -5.26 1:07 .989
pH= 7.62
EQUILIBRIUM ATRAZINE CONCENTRATION (μMOLE/LITRE)
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50


b
m
r
6.12
.974
.973
5.98
.991
.981
pH= 8.49
EQUILIBRIUM ATRAZINE CONCENTRATION {µMOLE/LITRE}
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50


b
m
r
■ -.276 1.30 .998
▲ -.887 1.30 .995
pH = 10.25
EQUILIBRIUM ATRAZINE CONCENTRATION {µMOLE/LITRE}
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
ML ATRAZINE

APPENDIX (III)

Titration graphs for varying FA concentrations at a pH value of 3.50 and at low ionic strength.

b - intercept of a line

m - slope of a line

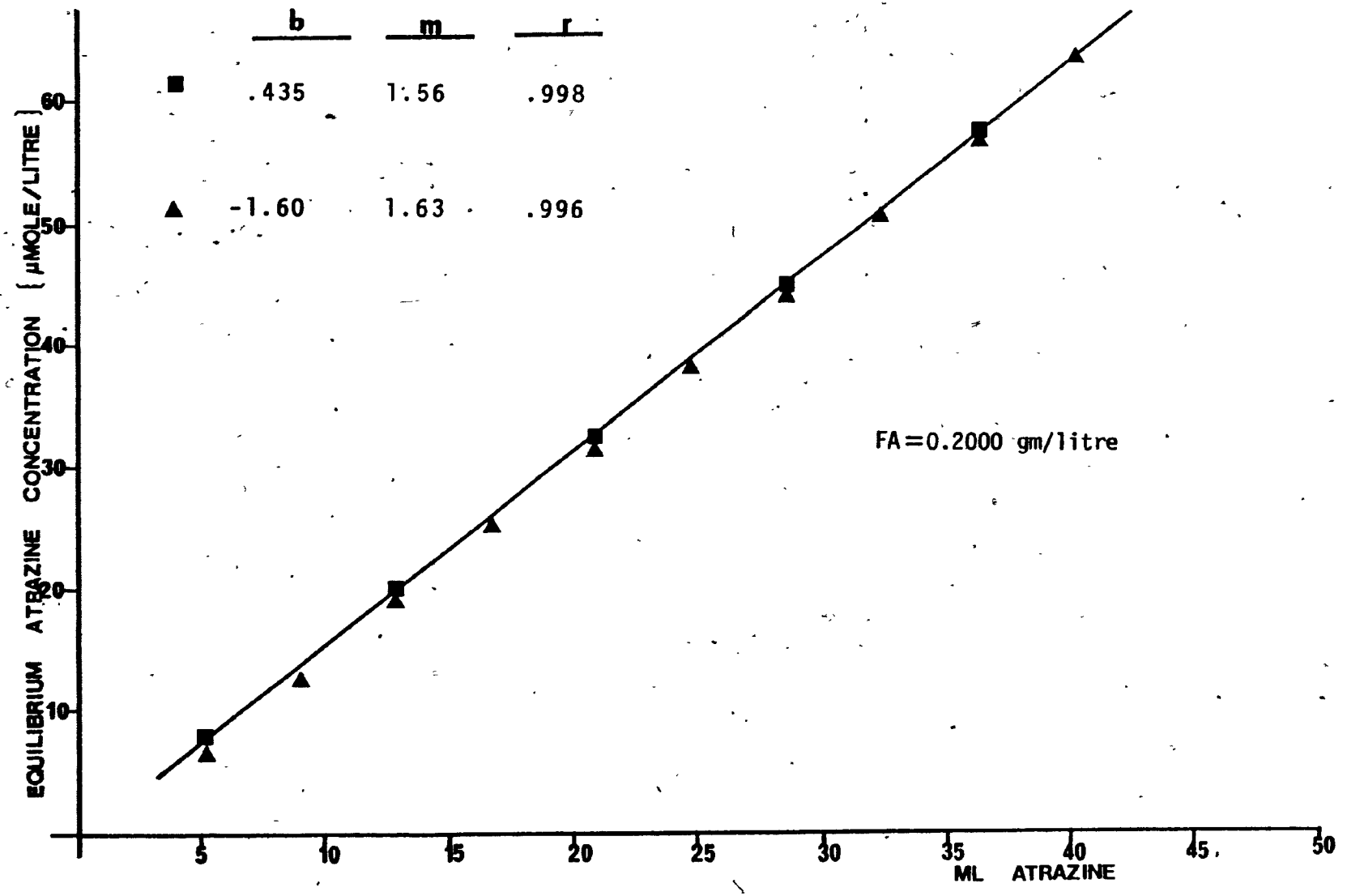
r - correlation factor of a line

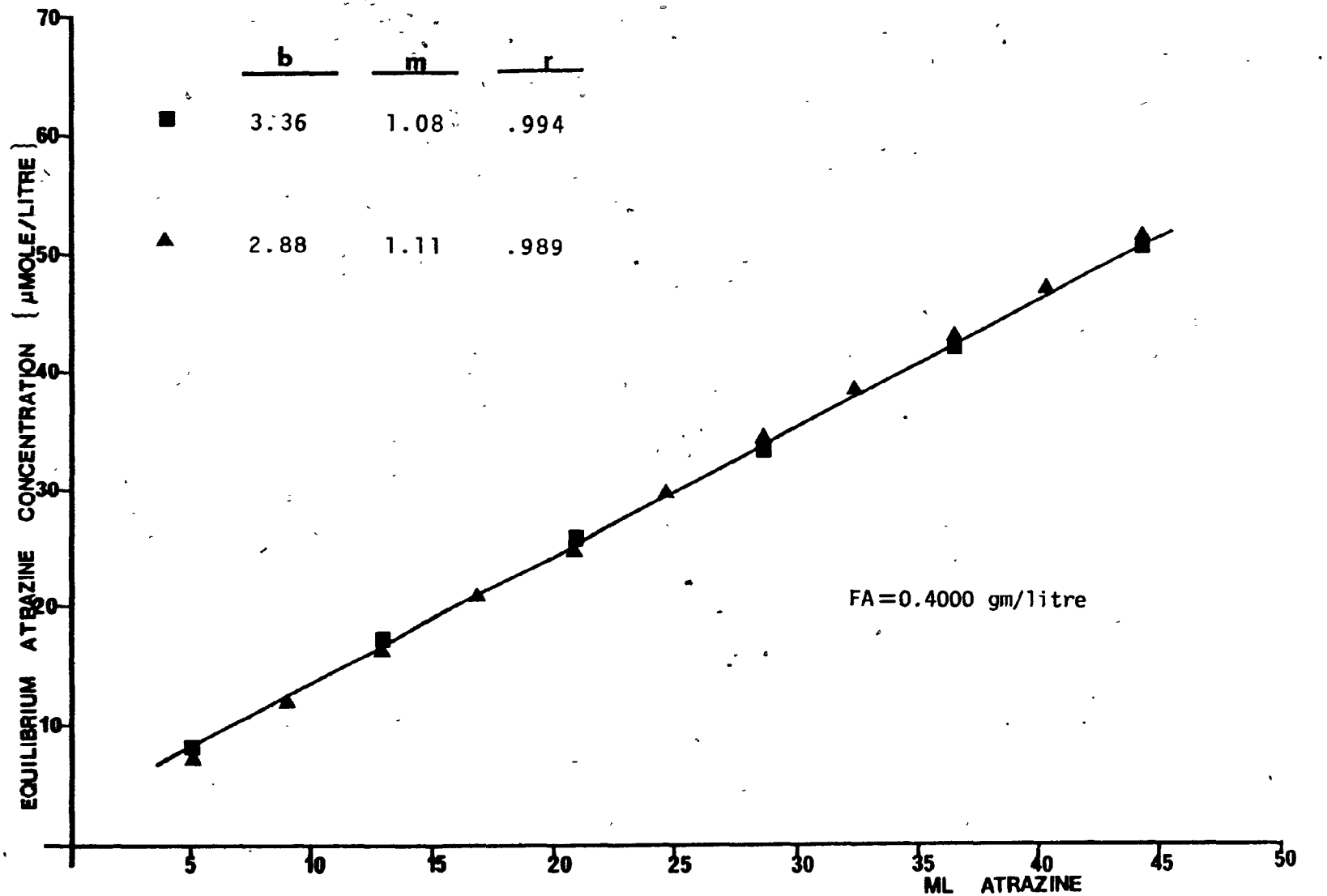
■ - Atrazine control solutions

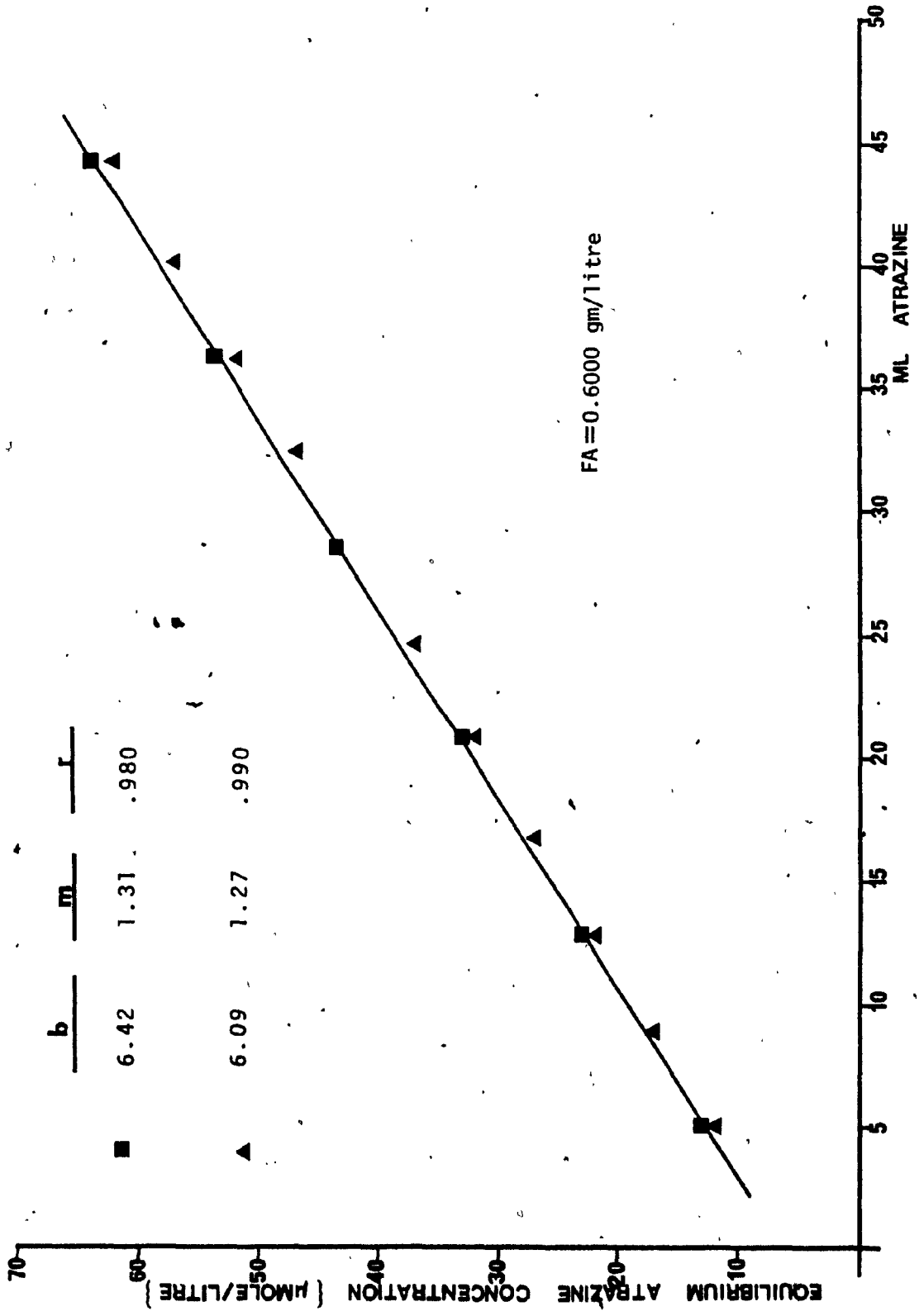
◆ - Atrazine solutions before the equivalence point

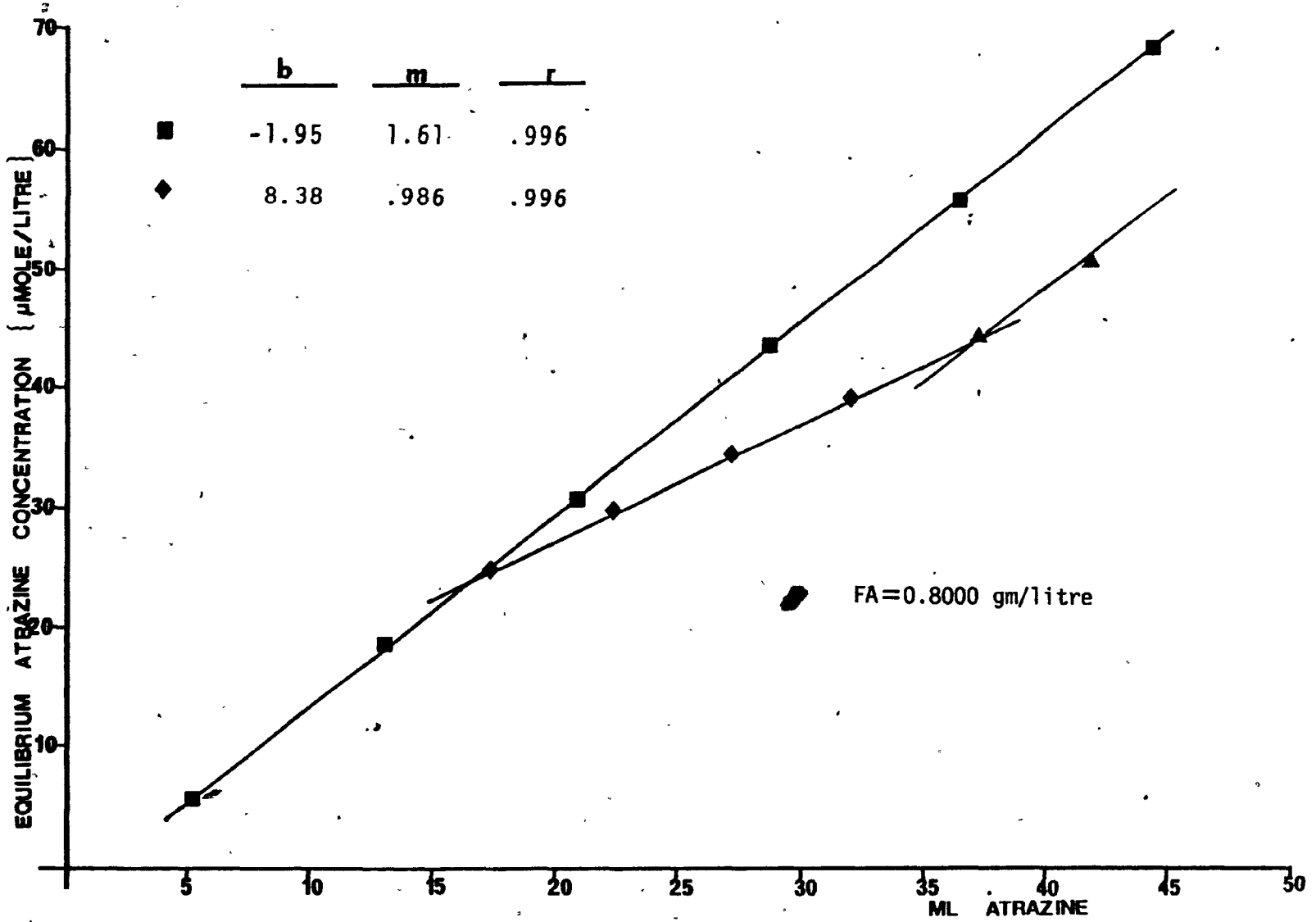
▲ - Atrazine solutions after the equivalence point

Volume of solution = 50.00 ml


b
m
r
■ .435 1.56 .998
▲ -1.60 1.63 .996
FA=0.2000 gm/litre
EQUILIBRIUM ATRAZINE CONCENTRATION (μMOLE/LITRE)
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
ML ATRAZINE


b
m
r
3.36
1.08
.994
2.88
1.11
.989
FA=0.4000 gm/litre
EQUILIBRIUM ATRAZINE CONCENTRATION (µMOLE/LITRE)
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50


EQUILIBRIUM ATRAZINE CONCENTRATION (μMOLE/LITRE)
ML ATRAZINE
FA=0.6000 gm/litre
b m r
6.42 1.31 .980
6.09 1.27 .990
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50


b
m
r
■ -1.95 1.61 .996
◆ 8.38 .986 .996
FA=0.8000 gm/litre
EQUILIBRIUM ATRAZINE CONCENTRATION (µMOLE/LITRE)
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
ML ATRAZINE

APPENDIX (IV)

Titration graphs for varying FA concentrations at a pH value of 3.50 and 0.100 M KCl.

b - intercept of a line

m - slope of a line

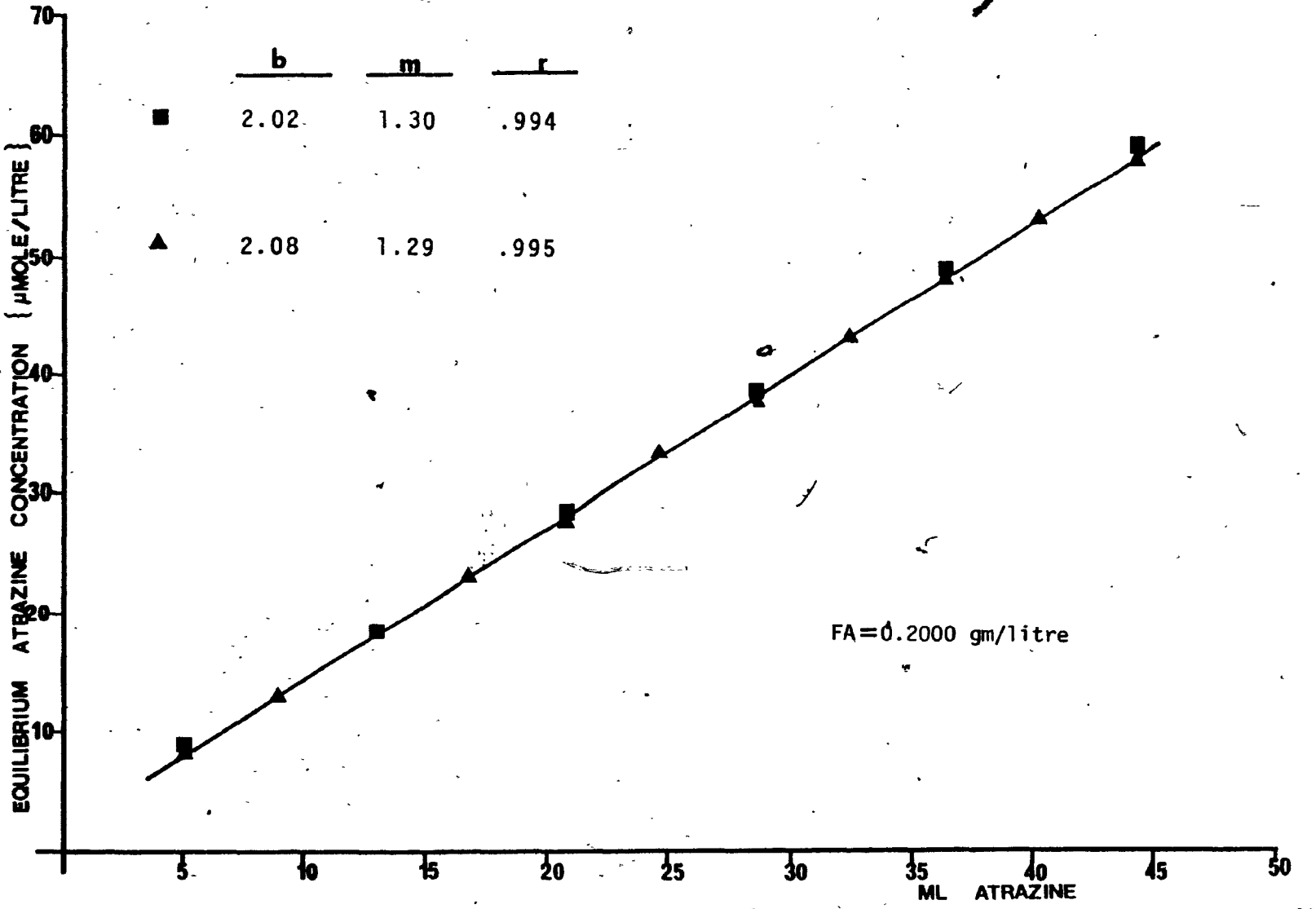
r - correlation factor of a line

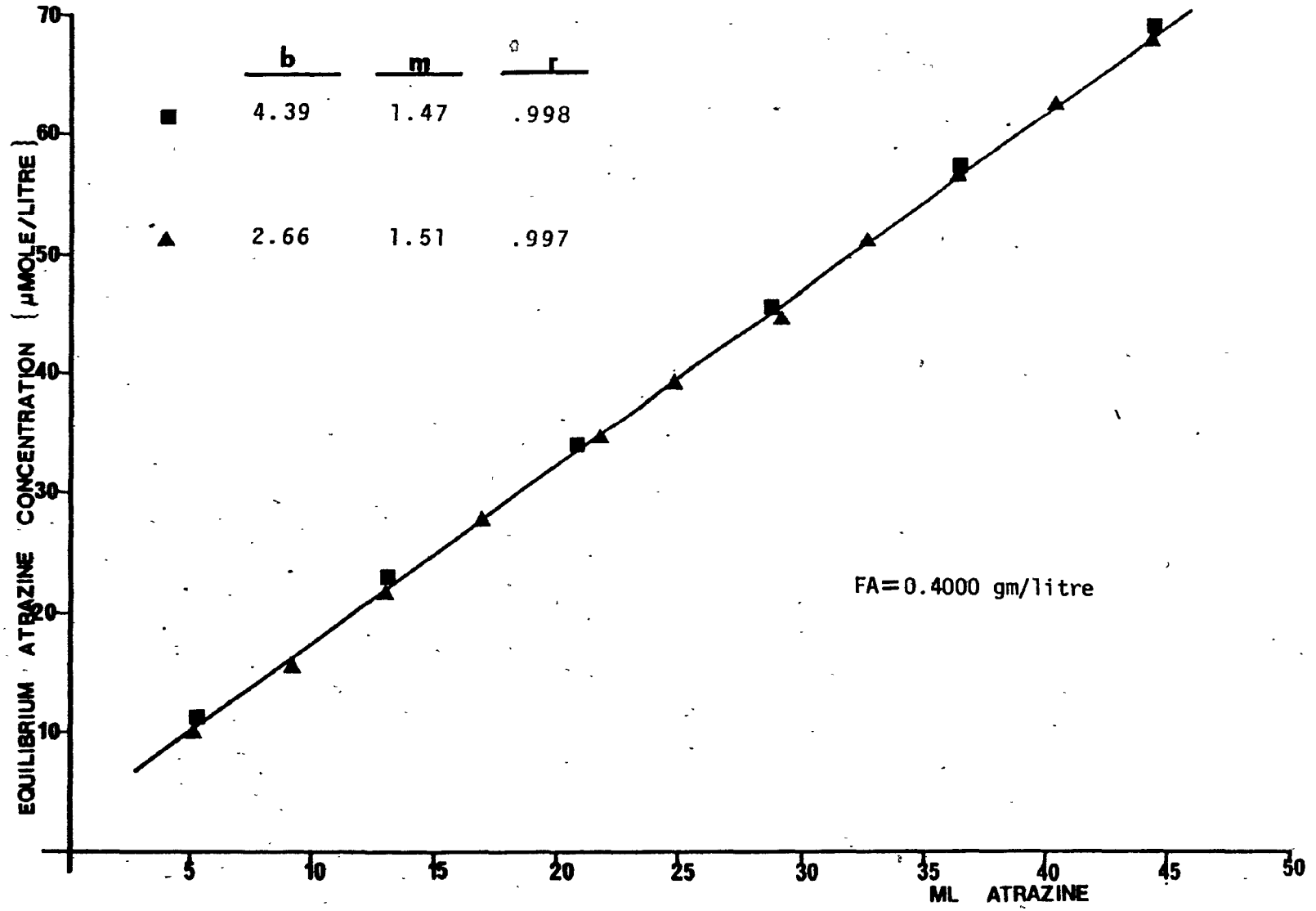
■ - Atrazine control solutions

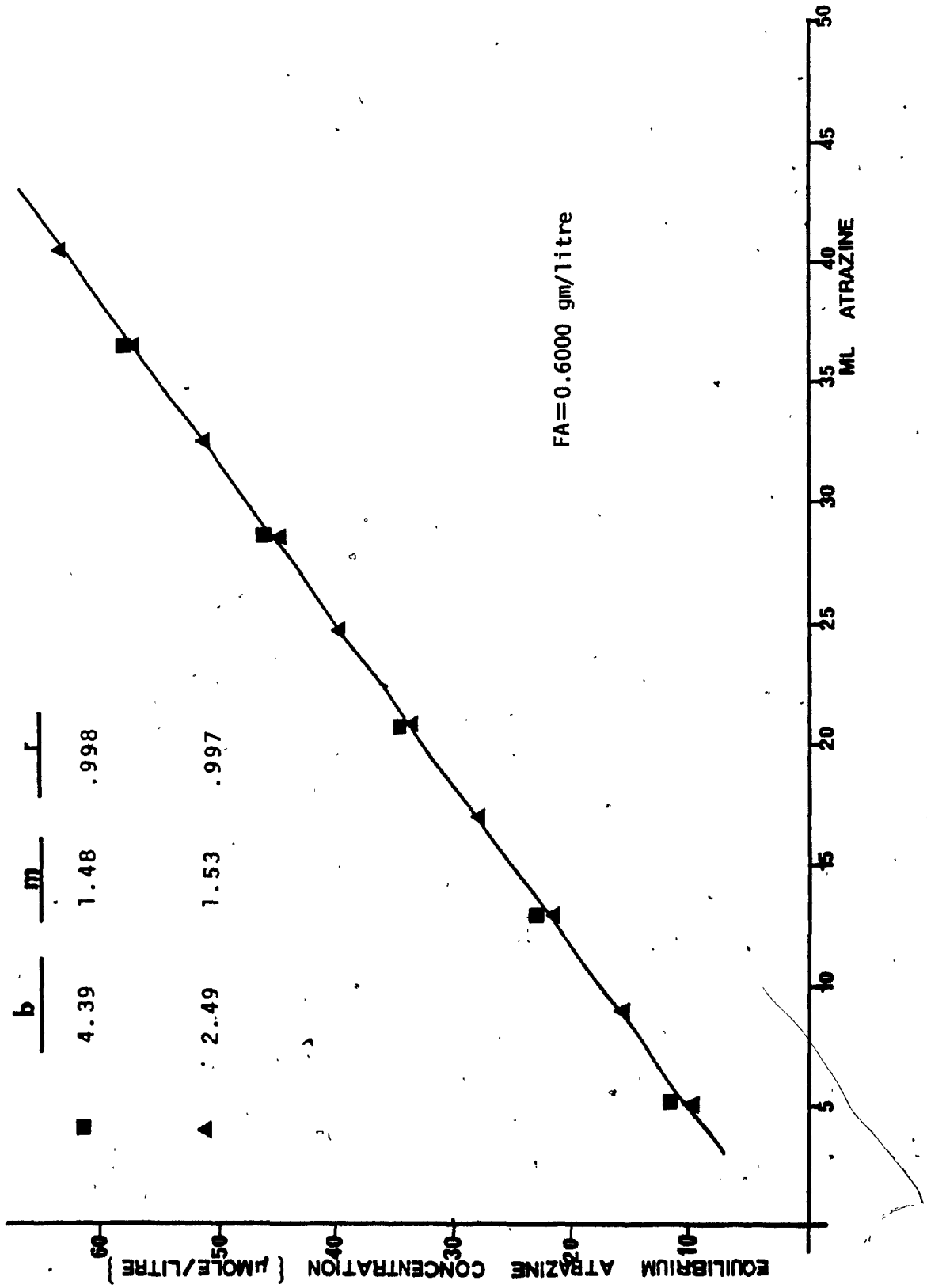
◆ - Atrazine solutions before the equivalence point

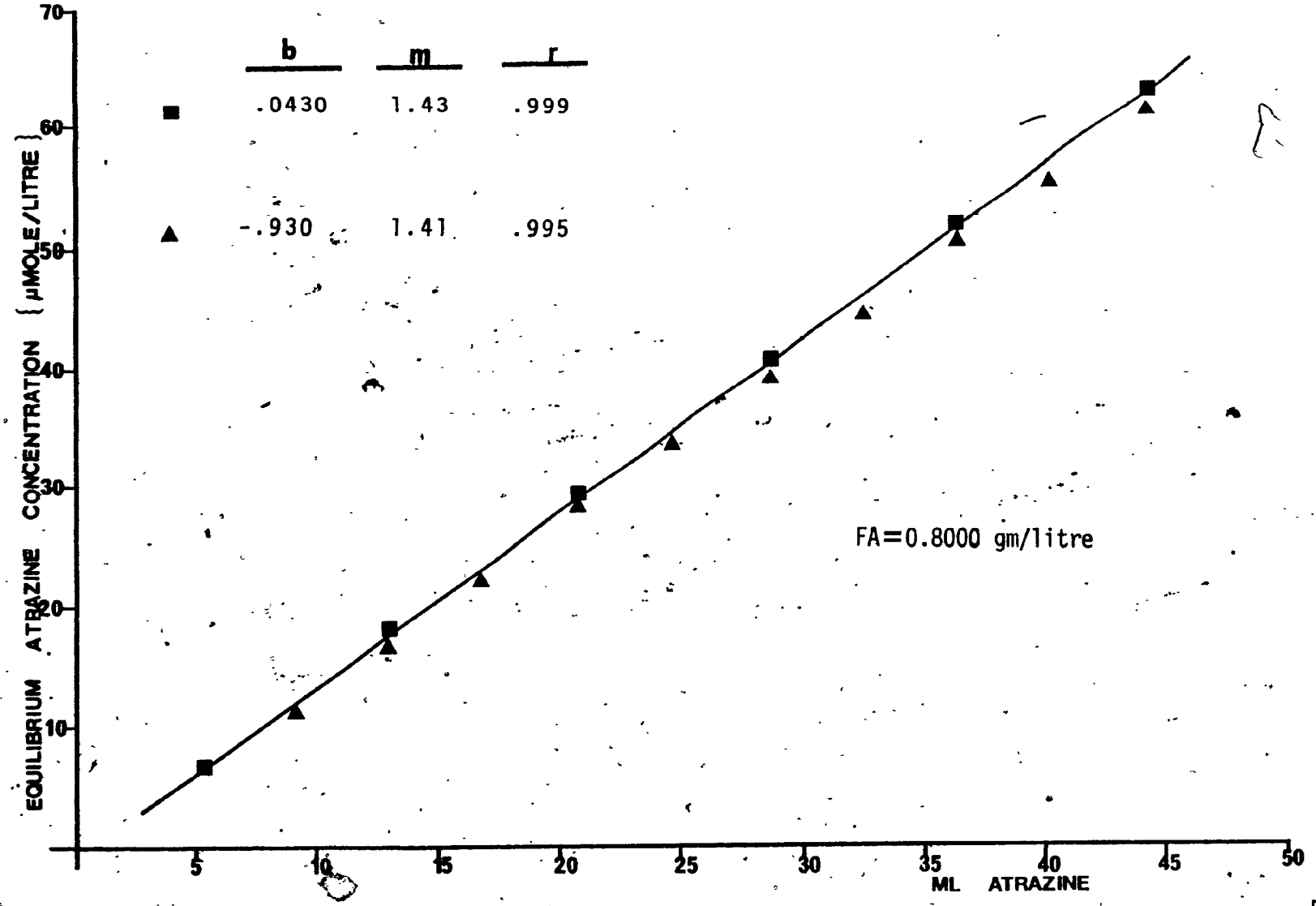
▲ - Atrazine solutions after the equivalence point

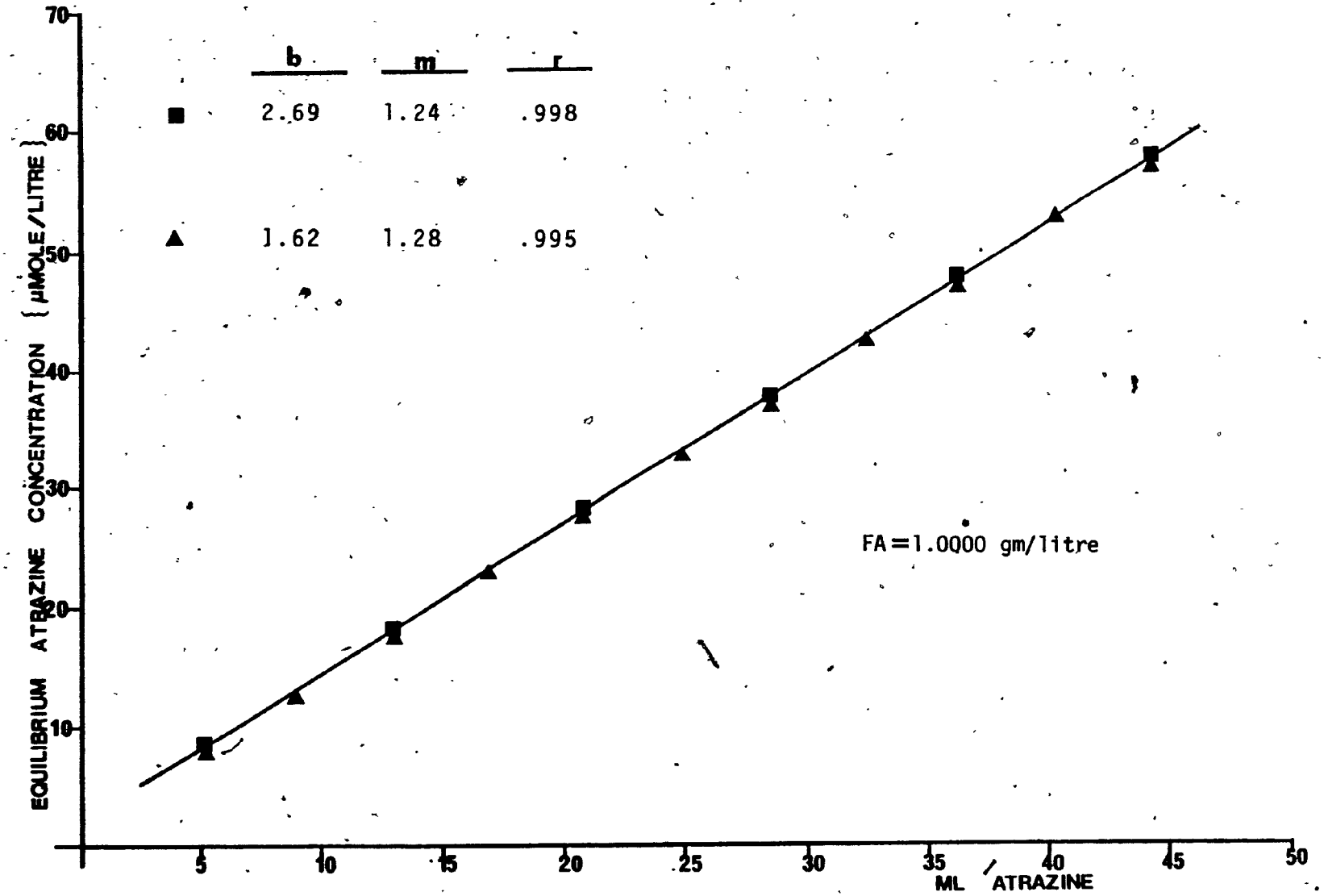
Volume of solution = 50.00 ml


b
m
r
2.02
1.30
.994
2.08
1.29
.995
FA=0.2000 gm/litre
EQUILIBRIUM ATRAZINE CONCENTRATION {µMOLE/LITRE}
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50


b
m
r
4.39
1.47
.998
2.66
1.51
.997
FA=0.4000 gm/litre
EQUILIBRIUM ATRAZINE CONCENTRATION (µMOLE/LITRE)
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50


EQUILIBRIUM ATRAZINE CONCENTRATION { μMOLE/LITRE }
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
ML ATRAZINE
FA=0.6000 gm/litre
b m r
■ 4.39 1.48 .998
▲ 2.49 1.53 .997


b
m
r
■ .0430 1.43 .999
▲ -.930 1.41 .995
FA=0.8000 gm/litre
EQUILIBRIUM ATRAZINE CONCENTRATION (μMOLE/LITRE)
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
ML ATRAZINE


b
m
r
■ 2.69 1.24 .998
▲ 1.62 1.28 .995
FA=1.0000 gm/litre
EQUILIBRIUM ATRAZINE CONCENTRATION {µMOLE/LITRE}
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50

APPENDIX (V)

Titration graphs for FA at different pH values in the presence of copper (II).

FA - 1.000 gm/litre

b - intercept of a line

m - slope of a line

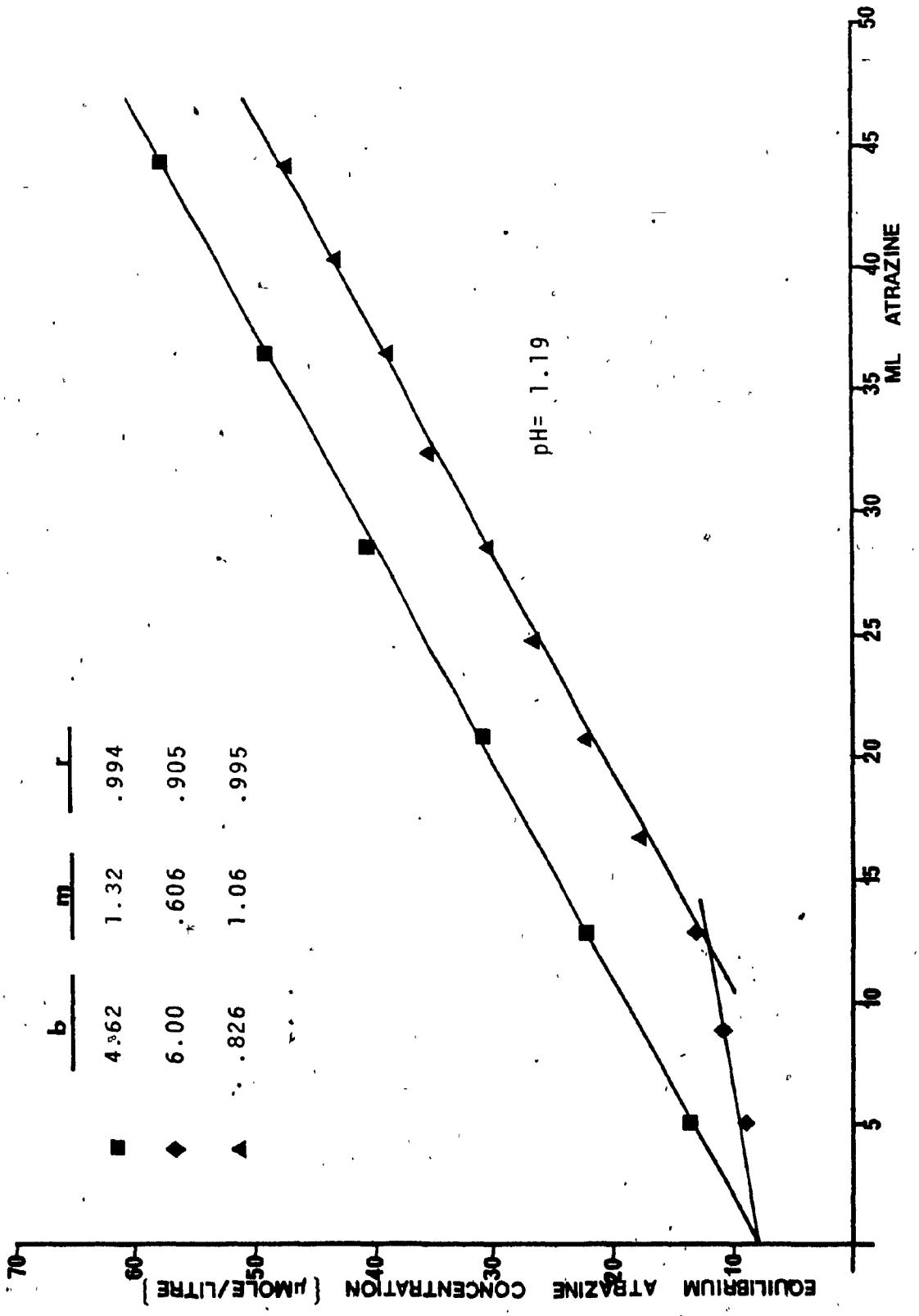
r - correlation factor of a line

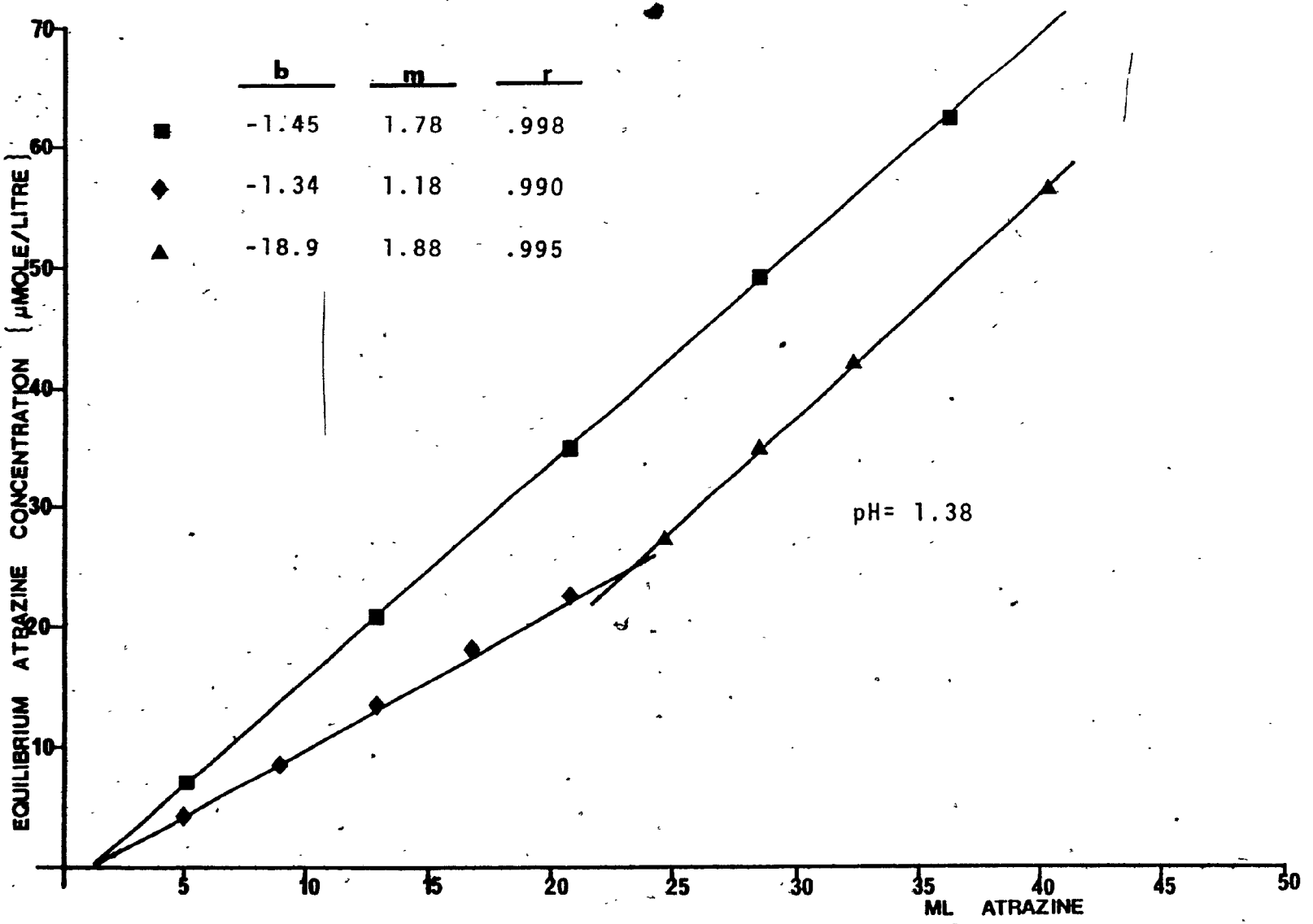
■ - Atrazine control solutions

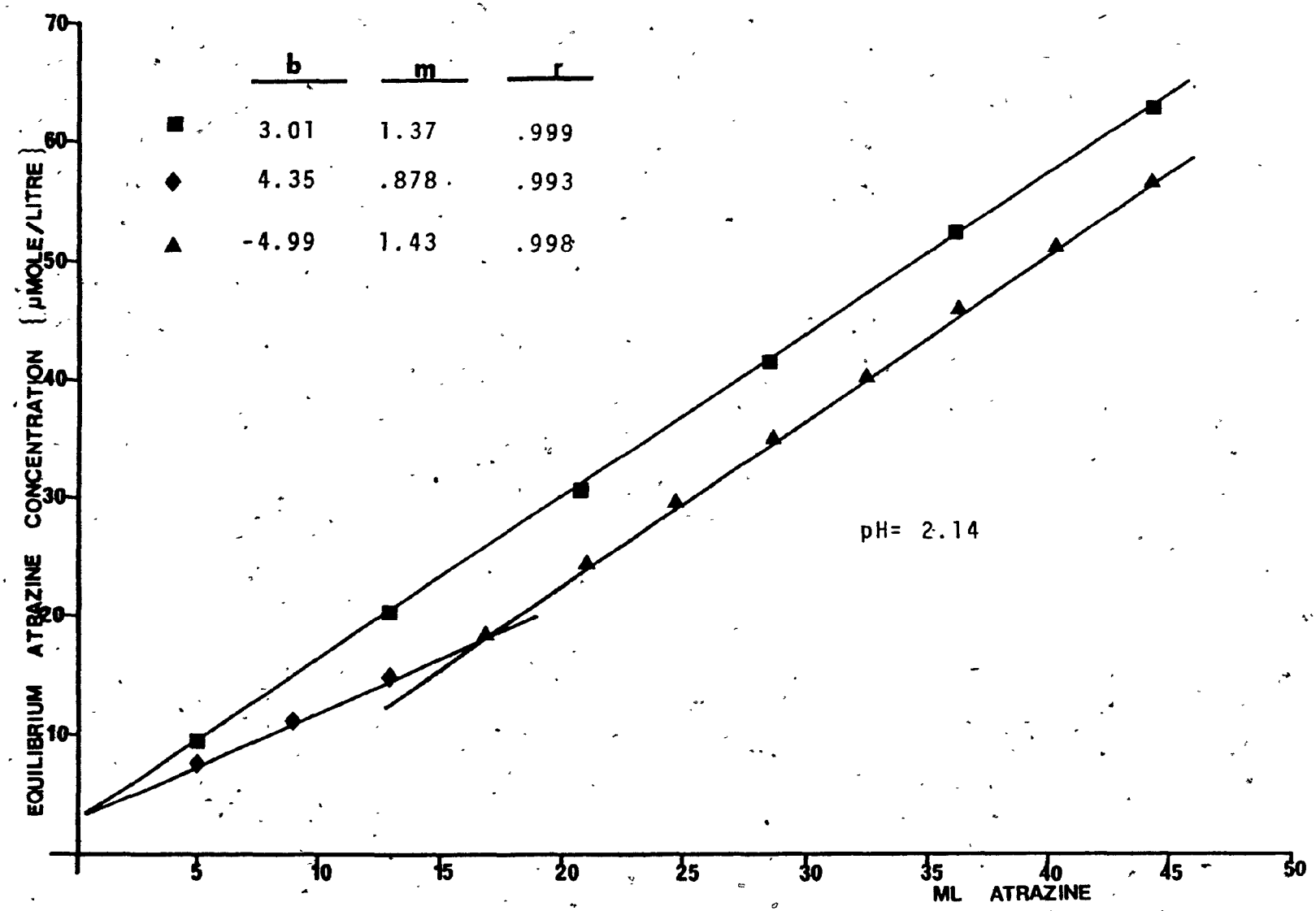
◆- Atrazine solutions before the equivalence point

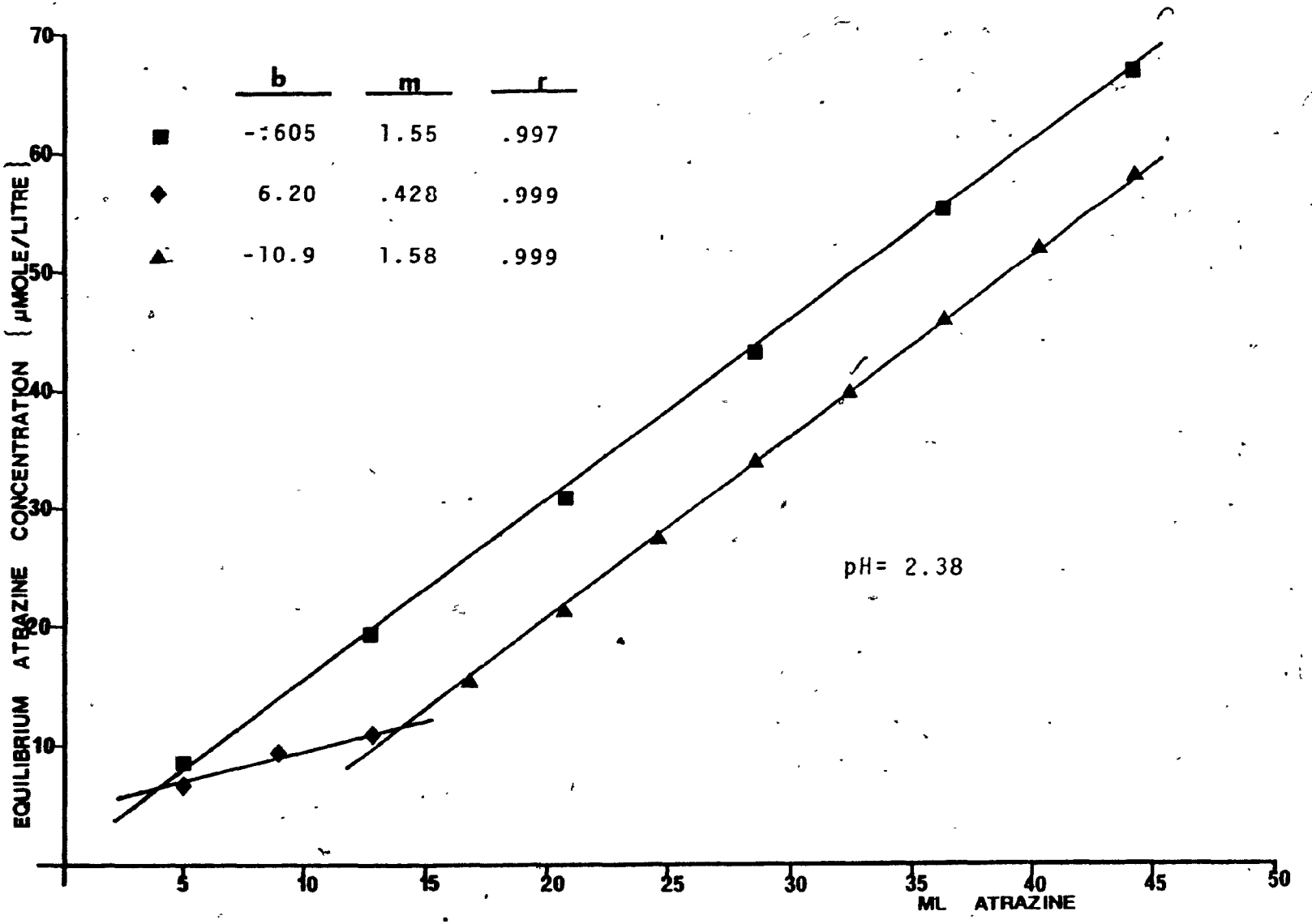
▲- Atrazine solutions after the equivalence point

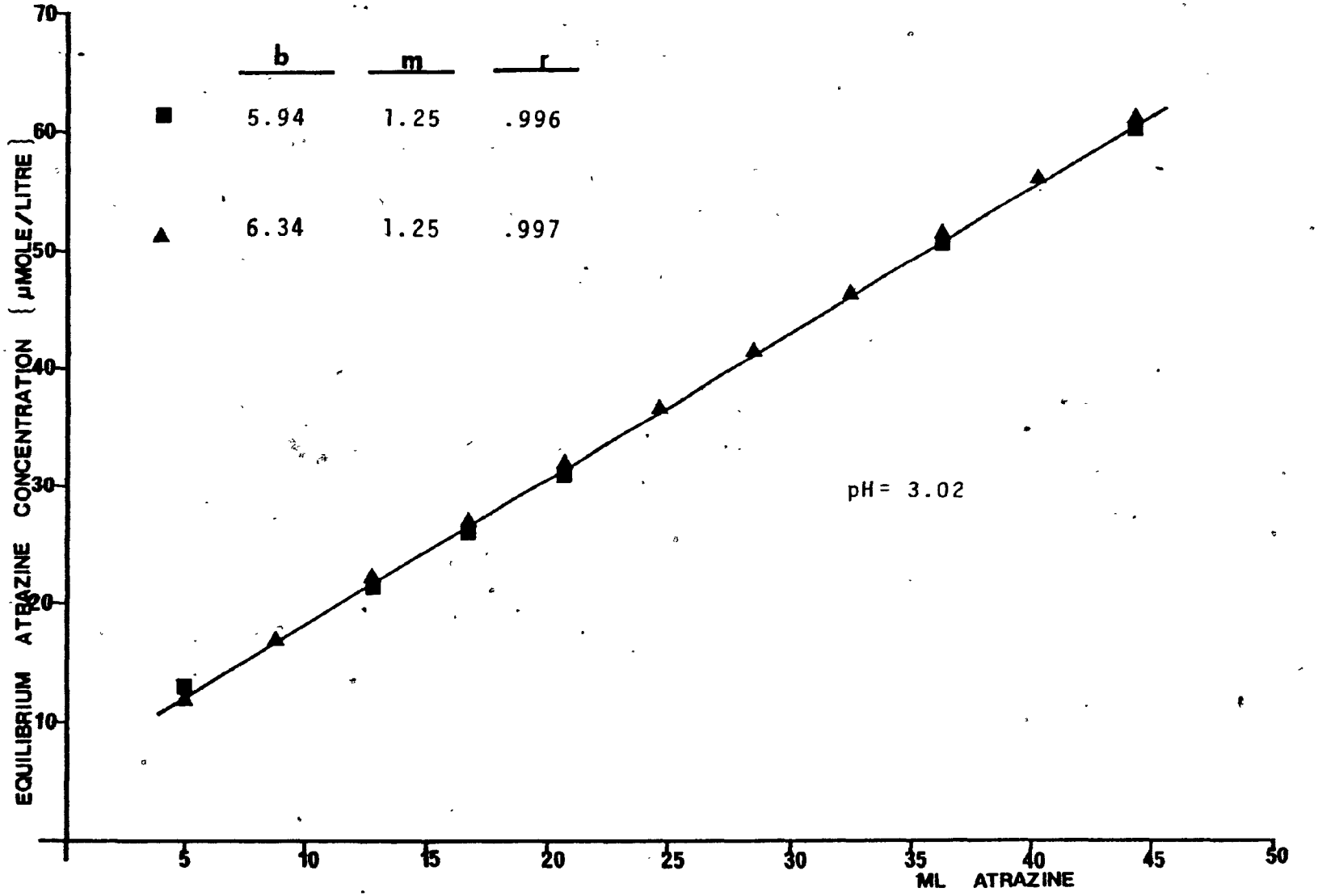
Table (5) gives the initial and final copper (II) concentrations at each pH value.

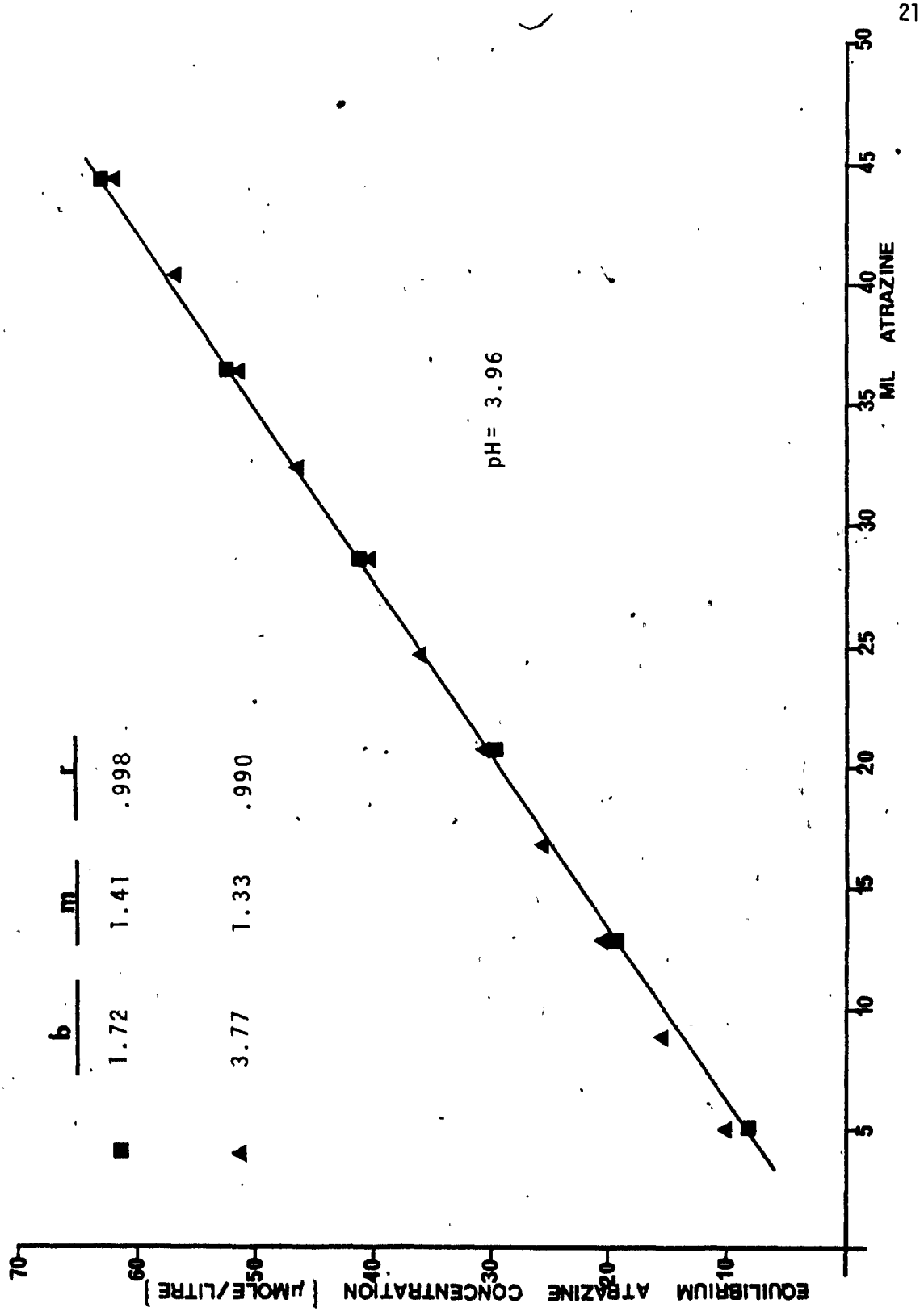

EQUILIBRIUM ATRAZINE CONCENTRATION {μMOLE/LITRE}
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
ML ATRAZINE
pH= 1.19
b m r
4.62 1.32 .994
6.00 .606 .905
.826 1.06 .995

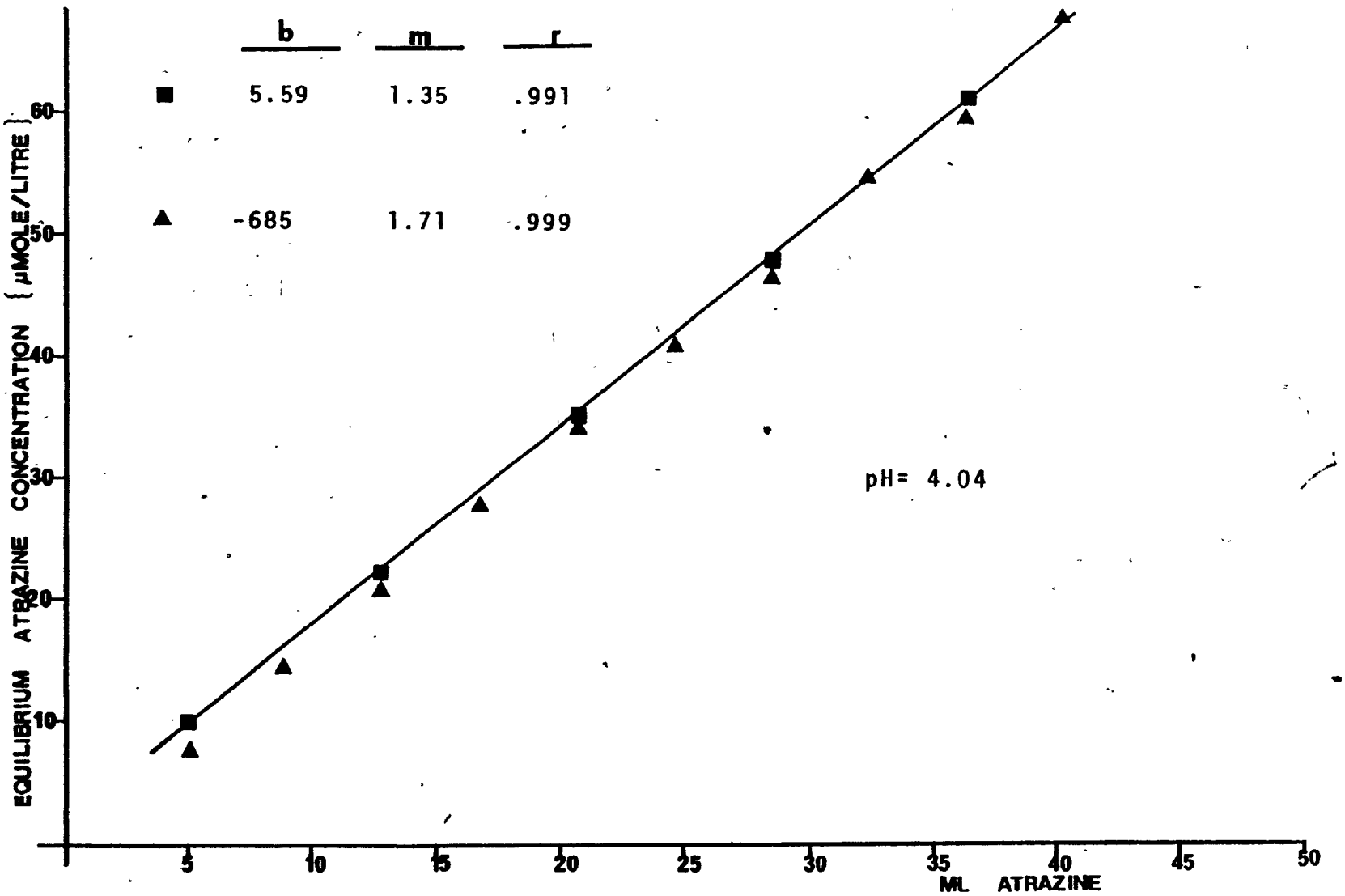

b
m
r
-1.45
1.78
.998
-1.34
1.18
.990
-18.9
1.88
.995
pH= 1.38
EQUILIBRIUM ATRAZINE CONCENTRATION (μMOLE/LITRE)
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50

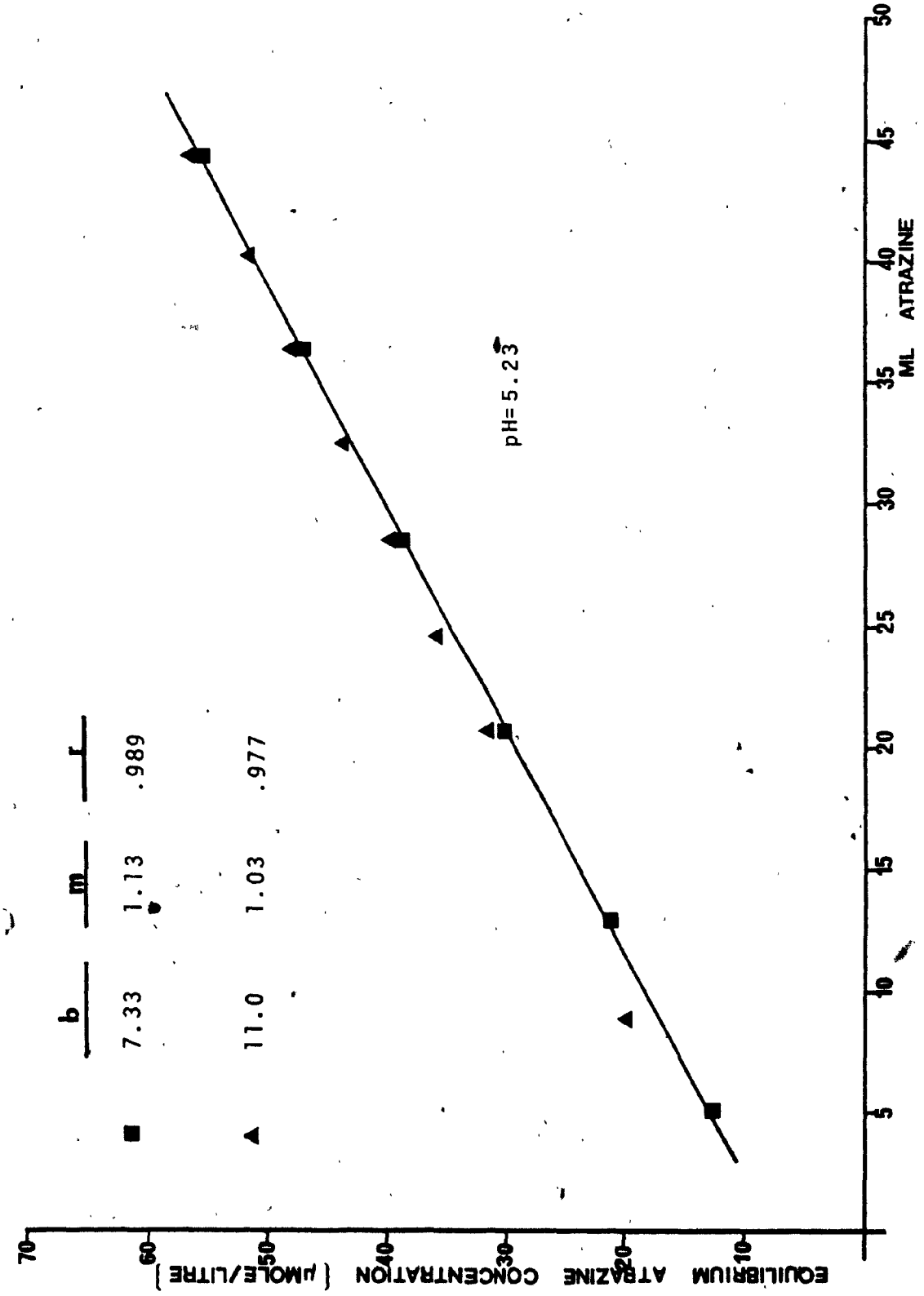

b
m
r
3.01
1.37
.999
4.35
.878
.993
-4.99
1.43
.998
pH= 2.14
EQUILIBRIUM ATRAZINE CONCENTRATION (µMOLE/LITRE)
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50


b
m
r
■ -.605 1.55 .997
◆ 6.20 .428 .999
▲ -10.9 1.58 .999
pH= 2.38
EQUILIBRIUM ATRAZINE CONCENTRATION (μMOLE/LITRE)
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
ML ATRAZINE


b
m
r
5.94
1.25
.996
6.34
1.25
.997
pH = 3.02
EQUILIBRIUM ATRAZINE CONCENTRATION {µMOLE/LITRE}
ML ATRAZINE
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50


EQUILIBRIUM ATRAZINE CONCENTRATION {μMOLE/LITRE}
ML ATRAZINE
pH= 3.96
b m r
1.72 1.41 .998
3.77 1.33 .990


b
m
r
■ 5.59 1.35 .991
▲ -685 1.71 .999
pH= 4.04
EQUILIBRIUM ATRAZINE CONCENTRATION (µMOLE/LITRE)
10
20
30
40
50
60
5
10
15
20
25
30
35
40
45
50
ML ATRAZINE


EQUILIBRIUM ATRAZINE CONCENTRATION (μMOLE/LITRE)
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
50
ML ATRAZINE
pH= 5.23
b m r
7.33 1.13 .989
11.0 1.03 .977

APPENDIX (VI)

Computer programs used for calculations in the thesis

(1) POLYCU

(2) POLYAC

(1) POLYCU

```
 1 C STABCON --MOHAMMED--  SUBMITTED FROM JEF.
 2       PROGRAM POLYFIT(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
 3       COMMON SIZE(100)
 4       COMMON/VC01B/LP
 5       INTEGER MORDER,IDERSW,IZ,IP,IR
 6       INTEGER N,M,L(50),LP,NN,NM,NK,IK
 7       REAL ALPHA(50),BETA(50),ACOEF(50),FAD(2)
 8       REAL X(50),Y(50),W(50),D(50),F(50),C(50)
 9       REAL K(50),G(50),AMB(50),INC(50),FIC(50),DX(50)
10       REAL A(50),B(50),C1(50),Z(50),FAC,SUM,VAR,DIFF
11       REAL H(50),AH,KIB,PH,KOI(50),FX(50),IT
12       REAL XT(50),AA(50),KBAR(50),DELTAG(50)
13       EQUIVALENCE (M,MORDER),(D(50),ACOEF(50))
14       DATA SAME/9999./,NE/5/
15 C
16 C     READ NUMBER OF DATA POINTS NN,N,DEGREE OF POLY.,M
17 C     DEGREE+1,NM
18 C
19       READ*,NN
20       READ*,N
21 C
22 C     POLYNOMIALS OF ONE TO ND ARE FITTED
23 C
24       READ*,ND
25 C
26 C     READ IN X AND Y VALUE AND ASSIGN UNIT WEIGHT
27 C
28       ABC=1.0000
29       IDERSW=1
30       DO 10 IM=1,NN
31          READ(5,22) X(IM)
32 10    CONTINUE
33       DO 12 IN=1,NN
34          READ(5,44) Y(IN)
35 12    CONTINUE
36       DO 6 I=1,NN
37          W(I)=ABC
38 6     CONTINUE
39       NK=1
40       DO 129 IK=1,ND
41       M=IK
42       NM=NK+IK
43 6
44 C     CALL POLYNOMIAL FIT DATA
45 C
46       CALL VC01A (X,Y,W,Z,N,A,B,C,G,H,L,M)
47 C
48 C     FIND THE VARIANCE OF THE POLYNOMIAL FIT
49 C
50       SUM=0.0000
```

```
        51        DO 1 IT=1,NN
        52        DIFF=Y(IT)-Z(IT)
        53        SUM=SUM+DIFF*DIFF
        54 1      CONTINUE
        55        VAR=SUM/(N-M-1)
        56        WRITE(6,101) VAR
        57 101    FORMAT(///'THE VARIANCE OF THE FIT IS',E13.6)
1 FTN 5.1+552          84/03/08. 18.32.37 PAGE     2
     PROGRAM POLYFIT  74/835  OPT=0

        58        WRITE(6,80)
        59 C
        60 C      CALCULATES THE COEFICIENTS OF THE POLYNOMIAL
        61 C
        62 80     FORMAT(///'                D(ID)          '//)
        63        DO 13 ID=1,NM
        64        CALL PE08A (A,B,C,D,M)
        65            WRITE(6,66) D(ID)
        66 13           CONTINUE
        67        WRITE(6,61)
        68 C
        69 C      EVALUATES THE FUNCTION AND THE FIRST DERIVATIVE OF
        70 C      THE FUNCTION
        71 C
        72 61     FORMAT(///'                    F(X)          F(XX)      '//)
        73        DO 30 IS=1,NN
        74        CALL PE09A (MORDER,ALPHA,BETA,ACOEF,X(IS),FAD,IDERSW)
        75        F(IS)=FAD(1)
        76        DX(IS)=FAD(2)
        77        WRITE(6,81) F(IS),DX(IS)
        78 30     CONTINUE
        79 C
        80 C      CALCULATES DIFFERENTIAL STABILITY CONSTANT
        81 C
        82        WRITE(6,115)
        83 115    FORMAT(///'          KOI(MOLES/L)       '//)
        84        DO 90 IR=1,NN
        85        KOI(IR)=-DX(IR)
        86        WRITE(6,62) KOI(IR)
        87 90     CONTINUE
        88 C
        89 C      CALCULATES THE FREE ENERGY
        90 C
        91        WRITE(6,112)
        92 112    FORMAT(///'              DELTAG(KJOULES/M)     '//)
        93        DO 99 IY=1,NN
        94        IF(KOI(IY).LE.0.0000)GO TO 120
        95        DELTAG(IY)=-5.68526*ALOG10(KOI(IY))
        96 120    CONTINUE
```

```
         97          WRITE(6,91) DELTAG(IY)
         98 99       CONTINUE
         99 22       FORMAT(E12.4)
        100 44       FORMAT(E12.4)
        101 66       FORMAT(10X,E12.6)
        102 81       FORMAT(10X,E12.4,5X,E12.4)
        103 62       FORMAT(10X,E12.4)
        104 91       FORMAT(10X,E12.4)
        105 C
        106 C        PLOTS THE CALCULATED Y VALUE AGAINST THE X VALUE
        107 C
        108          CALL MODE(3,7.25,SAME,SAME)
        109          CALL MODE(7,SAME,7.,SAME)
        110          CALL SCAN(X,KOI,-NE,440)
        111          CALL DRAW(X,KOI,NE,441)
        112          CALL AXES(16.2,'CHI AXIS(MOLE/G)',11.0,'KOI(MOLE/G)')
        113          CALL DRAW(0.,0.,1,9000)
        114 129      CONTINUE
1 FTN 5.1+552            84/03/08. 18.32.37 PAGE     3
     PROGRAM POLYFIT  74/835  OPT=0

        115          CALL DRAW(0,0,0,9999)
        116          CALL EXIT
        117          RETURN
        118          END
```

(2) POLYAC

```
 1 C STABCON --MOHAMMED--  SUBMITTED FROM JEF.
 2       PROGRAM POLYFIT(INPUT,OUTPUT,TAPE5=INPUT,TAPE6=OUTPUT)
 3       COMMON SIZE(100)
 4       COMMON/VC01B/LP
 5       INTEGER MORDER,IDERSW,IZ,IP,IR
 6       INTEGER N,M,L(50),LP,NN,NM
 7       REAL ALPHA(50),BETA(50),ACOEF(50),FAD(2)
 8       REAL X(50),Y(50),W(50),D(50),F(50),C(50)
 9       REAL K(50),G(50),AMB(50),INC(50),FIC(50),DX(50)
10       REAL A(50),B(50),C1(50),Z(50),FAC,SUM,VAR,DIFF
11       REAL H(50),AH,KIB,PH,KOI(50),FX(50),IT
12       REAL XT(50),AA(50),KBAR(50),DELTAG(50)
13       EQUIVALENCE (M,MORDER),(D(50),ACOEF(50))
14       DATA SAME/9999./,NE/7/
15 C
16 C     READ NUMBER OF DATA POINTS NN,N,DEGREE OF POLY.,M
17 C     DEGREE+1,NM
18 C
19       READ*,NN
20       READ*,NM
21       READ*,N
22       READ*,M
23 C
24 C     READ IN X AND Y VALUE AND ASSIGN UNIT WEIGHT
25 C
26       ABC=1.0000
27       IDERSW=1
28       DO 10 IM=1,NN
29          READ(5,22) X(IM)
30 10    CONTINUE
31       DO 12 IN=1,NN
32          READ(5,44) Y(IN)
33 12    CONTINUE
34       DO 6 I=1,NN
35          W(I)=ABC
36 6     CONTINUE
37 C
38 C     CALL POLYNOMIAL TO FIT DATA
39 C
40       CALL VC01A (X,Y,W,Z,N,A,B,C,G,H,L,M)
41 C
42 C     FIND THE VARIANCE OF THE POLYNOMIAL FIT
43 C
```

```
      SUM=0.0000
      DO 1 IT=1,NN
      DIFF=Y(IT)-Z(IT)
      SUM=SUM+DIFF*DIFF
1     CONTINUE
      VAR=SUM/(N-M-1)
      WRITE(6,101) VAR
101   FORMAT(///'THE VARIANCE OF THE FIT IS',E13.6)
      WRITE(6,80)
C
C     CALCULATES THE COEFICIENTS OF THE POLYNOMIAL
C
80    FORMAT(///'                    D(ID)          '//)
      DO 13 ID=1,NM
1 FTN 5.1+552        84/03/06. 17.59.39 PAGE     2
      PROGRAM POLYFIT  74/835  OPT=0

      CALL PE08A (A,B,C,D,M)
          WRITE(6,66) D(ID)
13          CONTINUE
      WRITE(6,61)
C
C     EVALUATES THE FUNCTION AND THE FIRST DERIVATIVE OF
C     THE FUNCTION
C
61    FORMAT(///'                    F(X)           F(XX)      '//)
      DO 30 IS=1,NN
      CALL PE09A (MORDER,ALPHA,BETA,ACOEF,X(IS),FAD,IDERSW)
      F(IS)=FAD(1)
      DX(IS)=FAD(2)
      WRITE(6,81) F(IS),DX(IS)
30    CONTINUE
C
C     CALCULATES DIFFERENTIAL INSTABILITY CONSTANT
C
      WRITE(6,115)
115   FORMAT(///'              KOI(MOLES/L)       '//)
      DO 90 IR=1,NN
      KOI(IR)=-DX(IR)
      WRITE(6,62) KOI(IR)
90    CONTINUE
C
C     CALCULATES THE DIFFERENTIAL STABILITY
C
      WRITE(6,111)
111   FORMAT(///'                 KBAR(L/MOLES)         '//)
      DO 88 IA=1,NN
      IF(KOI(IA).LE.0.0000)GO TO 108
      KBAR(IA)=1.0000/KOI(IA)
108   CONTINUE
      WRITE(6,89) KBAR(IA)
88    CONTINUE
```

```
 93 C
 94 C      CALCULATES THE FREE ENERGY
 95 C
 96        WRITE(6,112)
 97 112    FORMAT(///'              DELTAG(KJOULES/M)     '//)
 98        DO 99 IY=1,NN
 99        IF(KBAR(IY).LE.0.0000)GO TO 120
100        DELTAG(IY)=-5.68526*ALOG10(KBAR(IY))
101 120    CONTINUE
102        WRITE(6,91) DELTAG(IY)
103 99     CONTINUE
104 22     FORMAT(E12.4)
105 44     FORMAT(E12.4)
106 31     FORMAT(E12.4)
107 36     FORMAT(E12.4)
108 66     FORMAT(10X,E12.6)
109 81     FORMAT(10X,E12.4,5X,E12.4)
110 62     FORMAT(10X,E12.4)
111 89     FORMAT(10X,E12.4)
112 91     FORMAT(10X,E12.4)
113 C
114 C      PLOTS THE CALCULATED Y VALUE AGAINST THE X VALUE
1 FTN 5.1+552          84/03/06. 17.59.39 PAGE     3
     PROGRAM POLYFIT  74/835  OPT=0

115 C
116        CALL MODE(3,7.25,SAME,SAME)
117        CALL MODE(7,SAME,7.,SAME)
118        CALL SCAN(X,KOI,-NE,440)
119        CALL DRAW(X,KOI,NE,441)
120        CALL AXES(9.3,'ALFA AXIS',11.5,'KOI(L/MOLE)')
121        CALL DRAW(0.,0.,1,9000)
122        CALL DRAW(0,0,0,9999)
123        CALL EXIT
124        RETURN
125        END
```

APPENDIX (VII)

Titration graph for FA at a pH value of 3.86 in the presence of Atrazine.

FA - 0.1000 gm/litre

b - intercept of a line

m - slope of a line

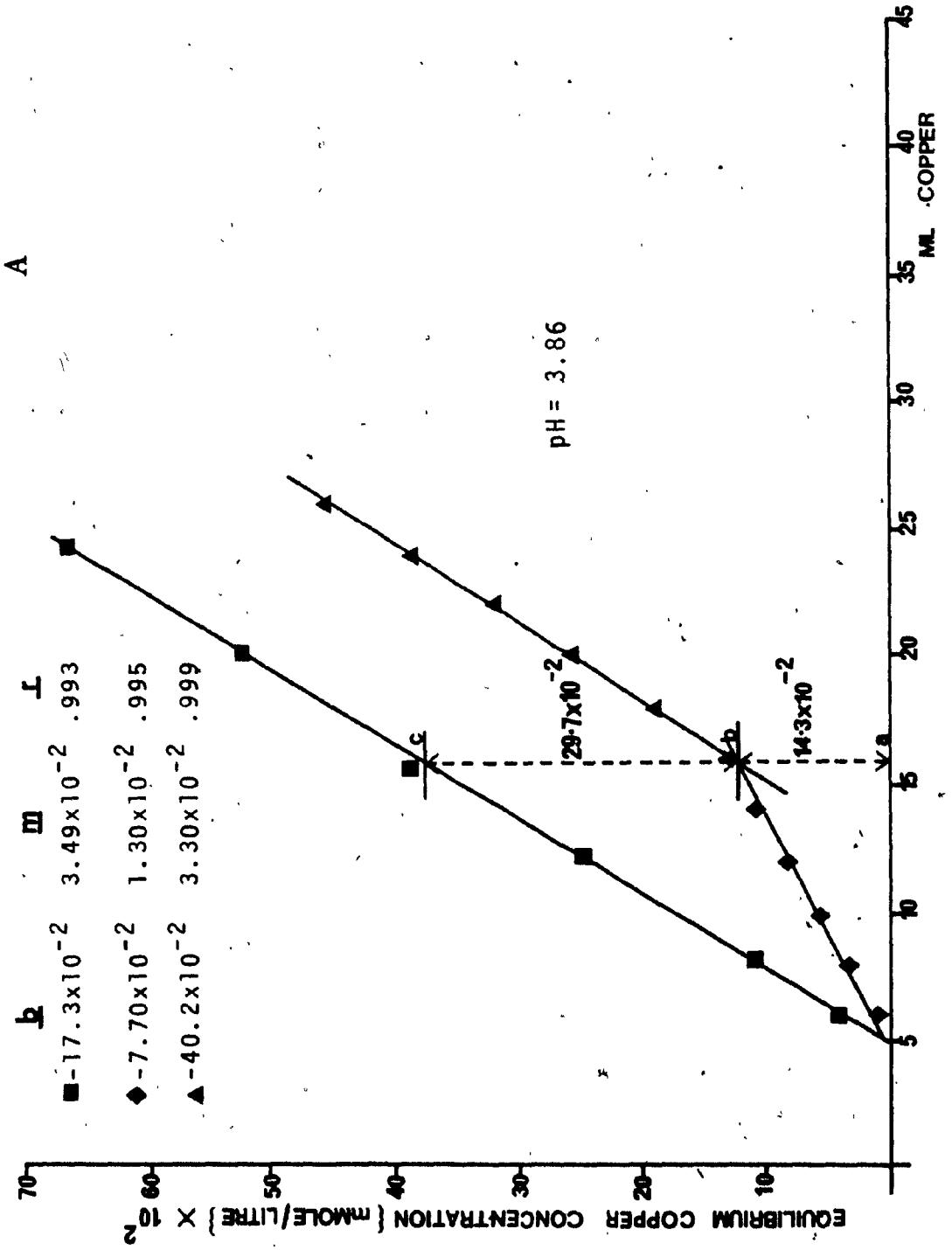
r - correlation factor of a line

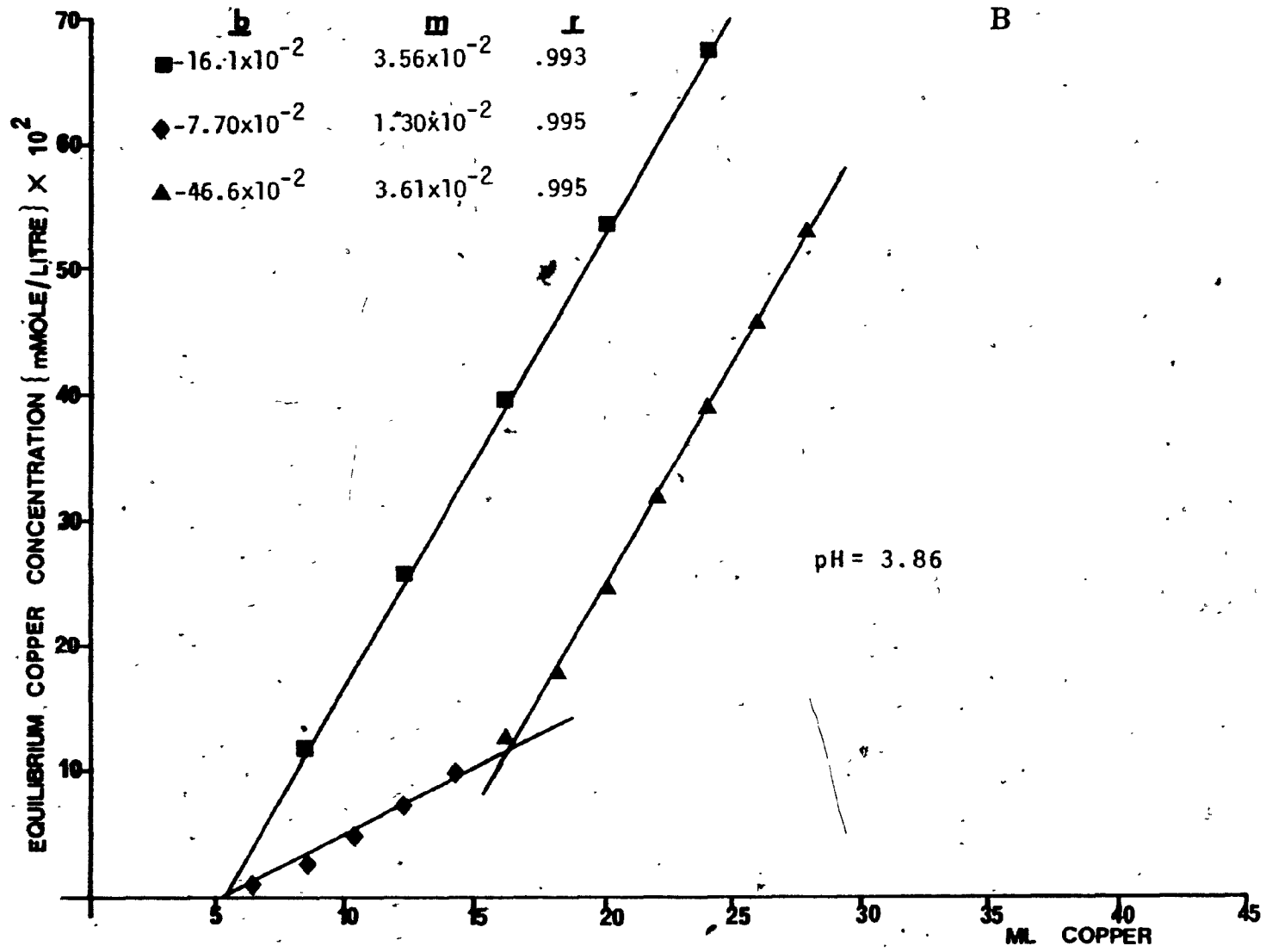
■ - Atrazine control solutions

◆ - Atrazine solutions before the equivalence point

▲ - Atrazine solutions after the equivalence point

Volume of solution = 50.00 ml


A
pH = 3.86
b
m
r
■ -17.3x10⁻² 3.49x10⁻² .993
◆ -7.70x10⁻² 1.30x10⁻² .995
▲ -40.2x10⁻² 3.30x10⁻² .999
29·7x10⁻²
14·3x10⁻²
a
b
c
EQUILIBRIUM COPPER CONCENTRATION {mMOLE/LITRE} X 10²
ML. COPPER
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45


B
b
m
r
■ -16.1x10^-2
3.56x10^-2
.993
◆ -7.70x10^-2
1.30x10^-2
.995
▲ -46.6x10^-2
3.61x10^-2
.995
pH = 3.86
EQUILIBRIUM COPPER CONCENTRATION {mMOLE/LITRE} X 10^2
70
60
50
40
30
20
10
5
10
15
20
25
30
35
40
45
ML COPPER

APPENDIX (VIII)

Sorption and desorption curves for Atrazine at different pH values.

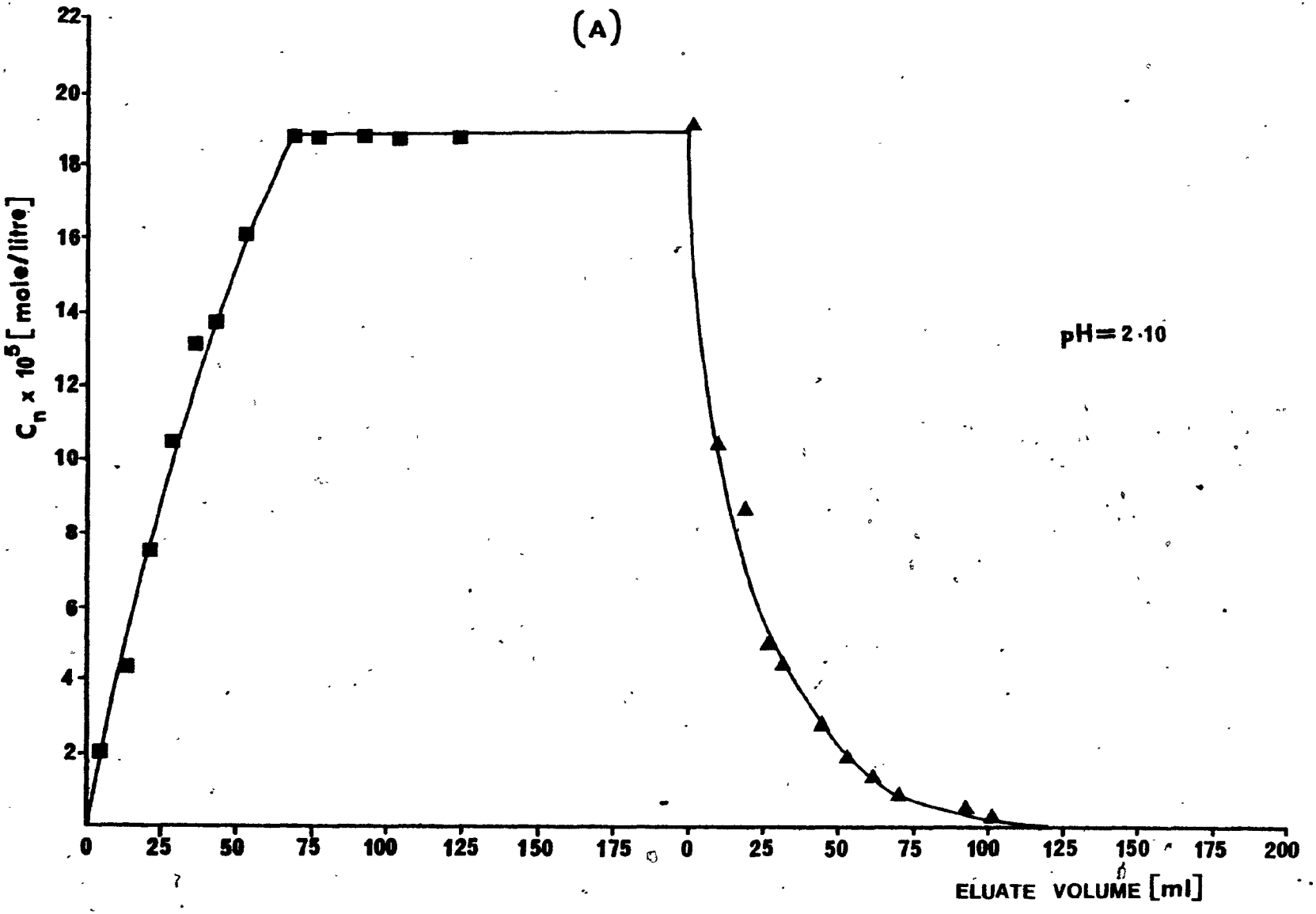
Volume of filtration cell = 13.00 ml

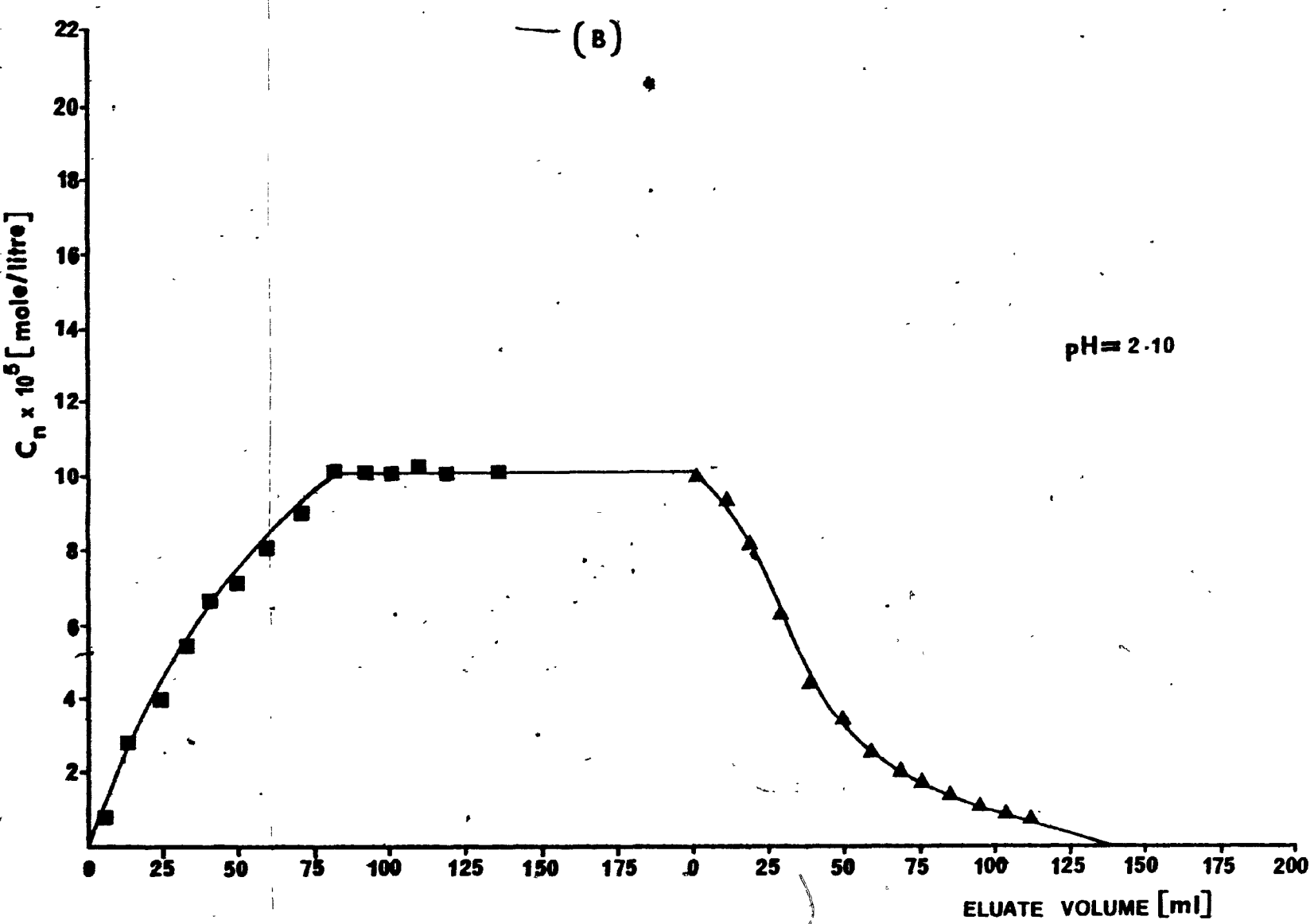
FA - 0.10000 gm per 13.00 ml

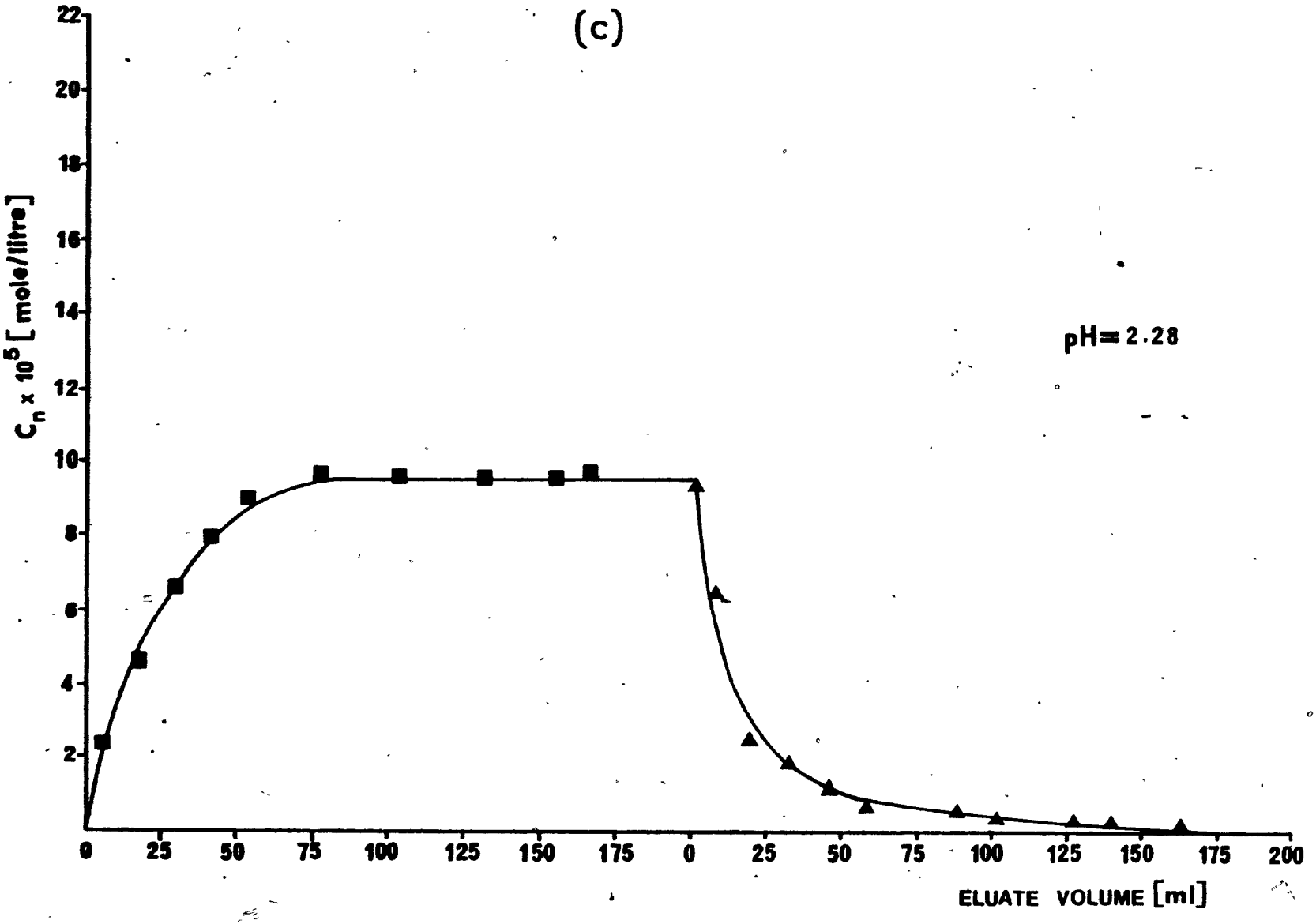
■ - sorption curves

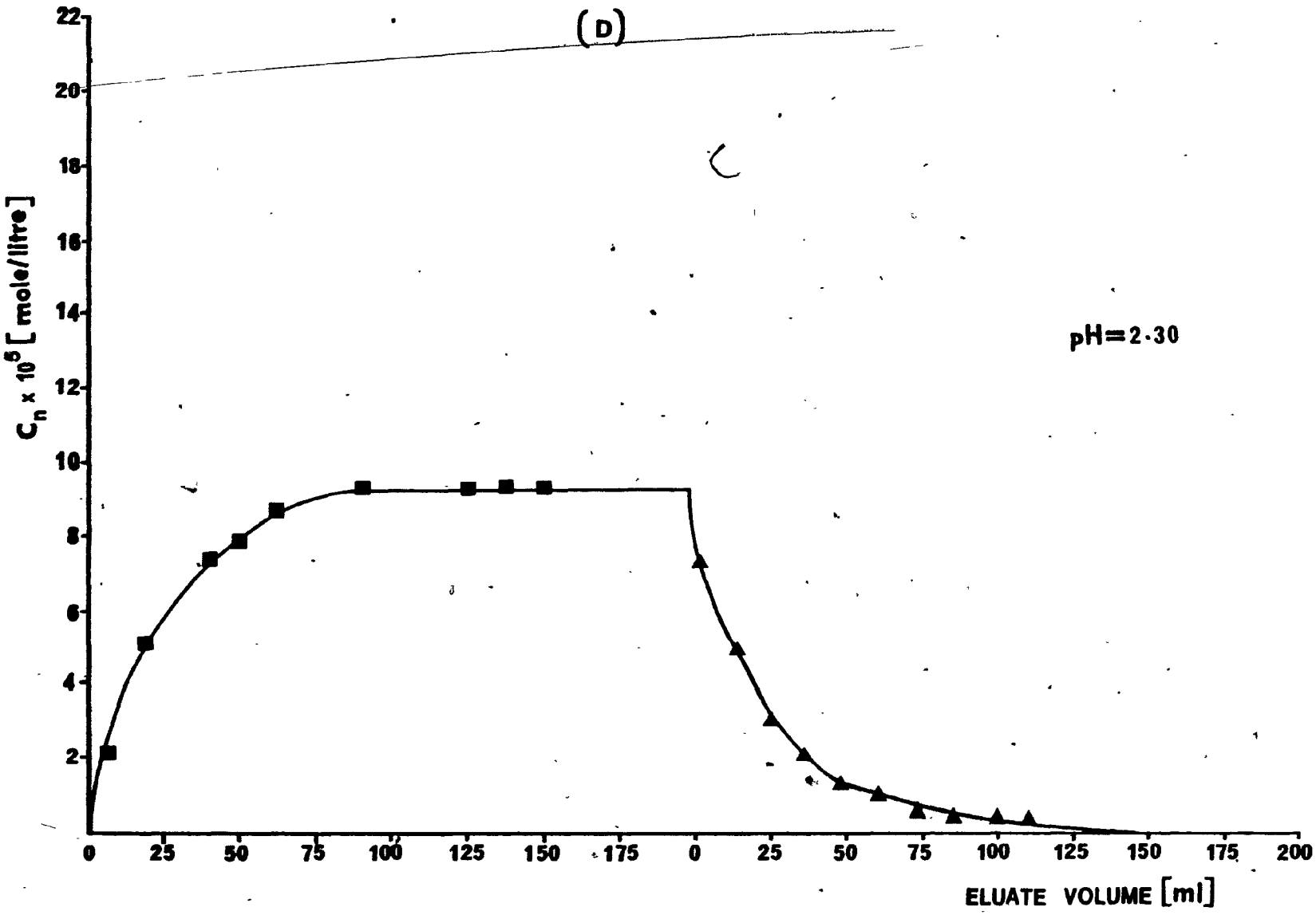
▲ - desorption curves

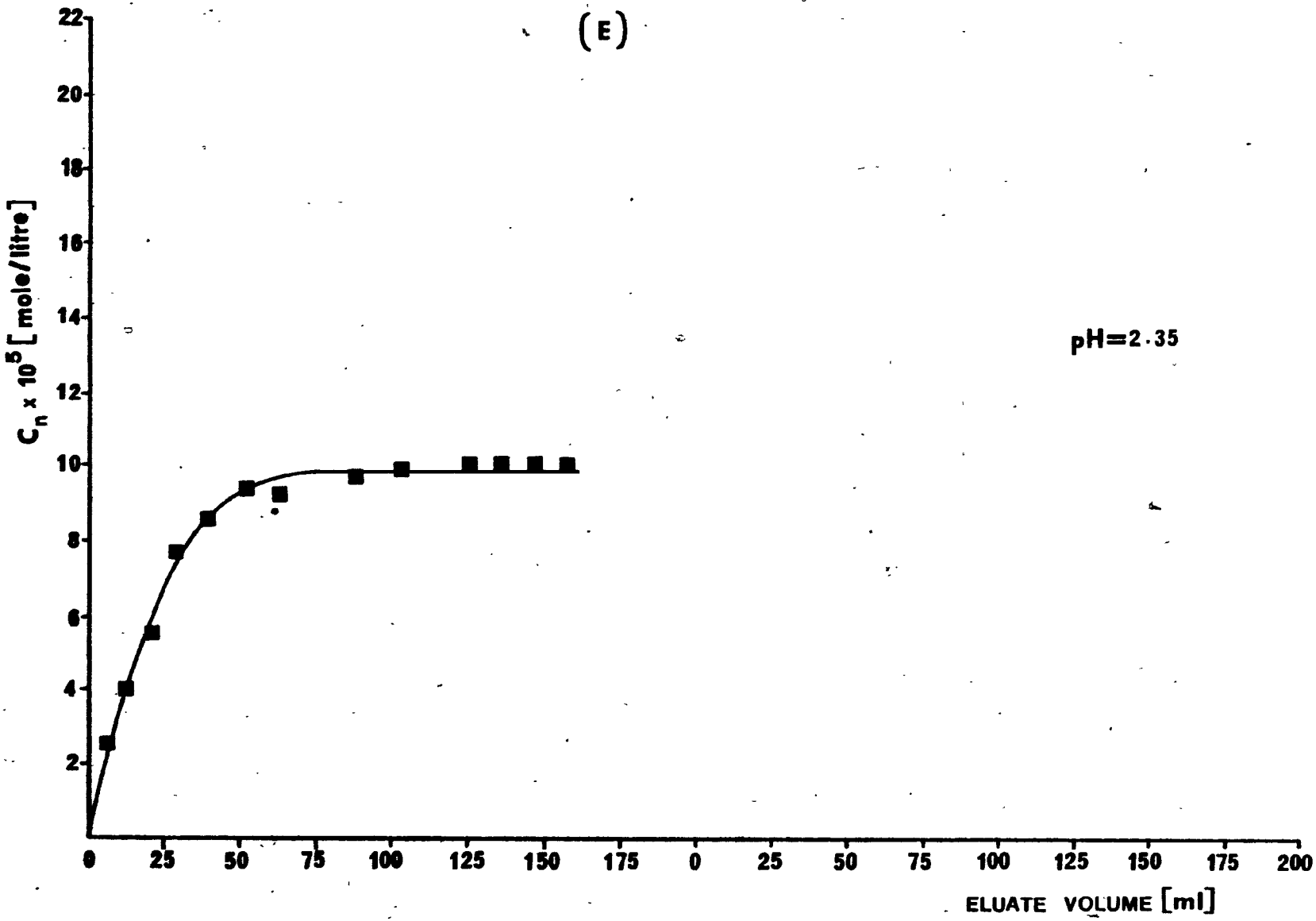
O,P - experiments which determine the Atrazine-UM2 interaction

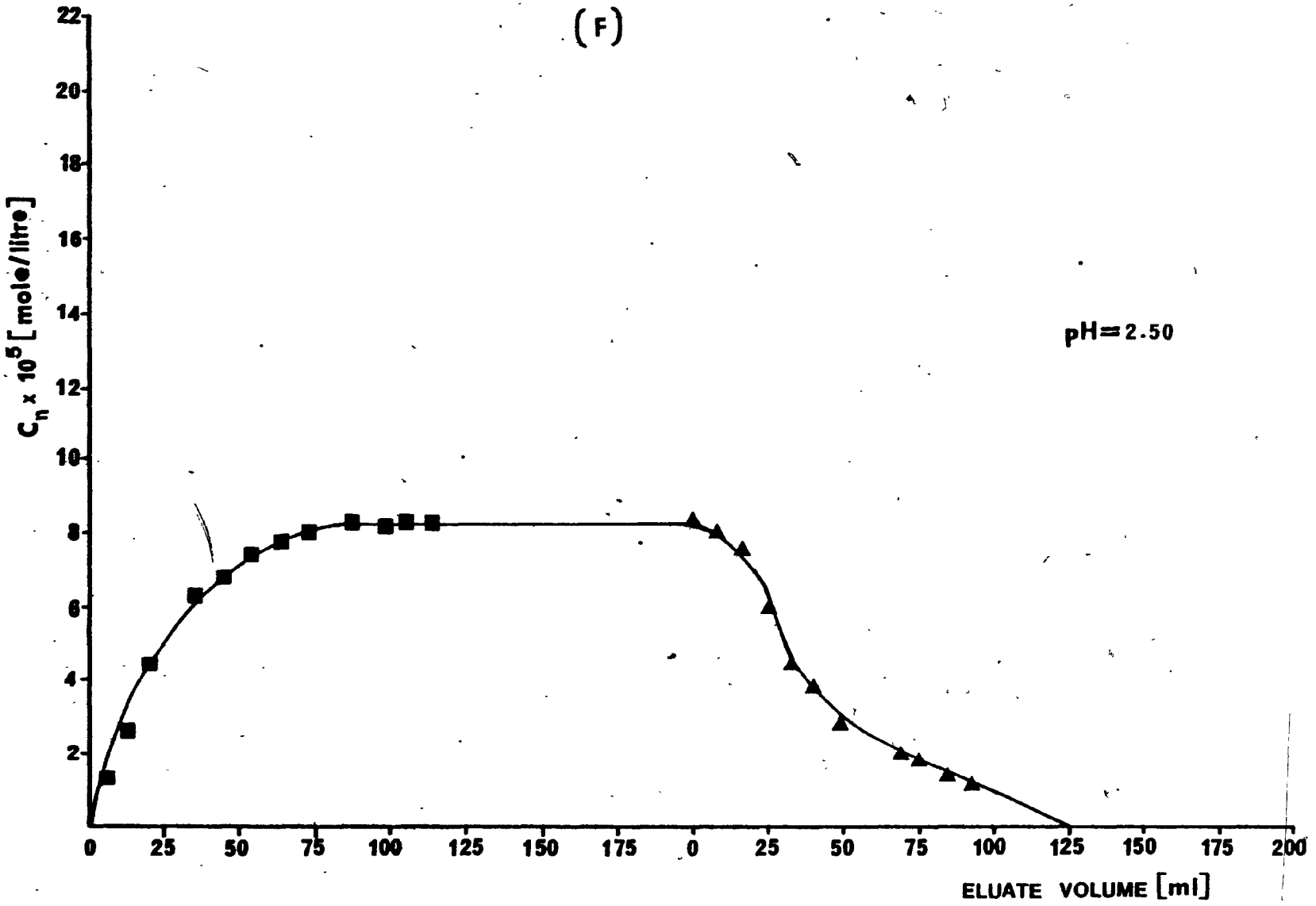

(A)
pH = 2·10
$C_n \times 10^5$ [mole/litre]
ELUATE VOLUME [ml]
22
20
18
16
14
12
10
8
6
4
2
0
25
50
75
100
125
150
175
0
25
50
75
100
125
150
175
200

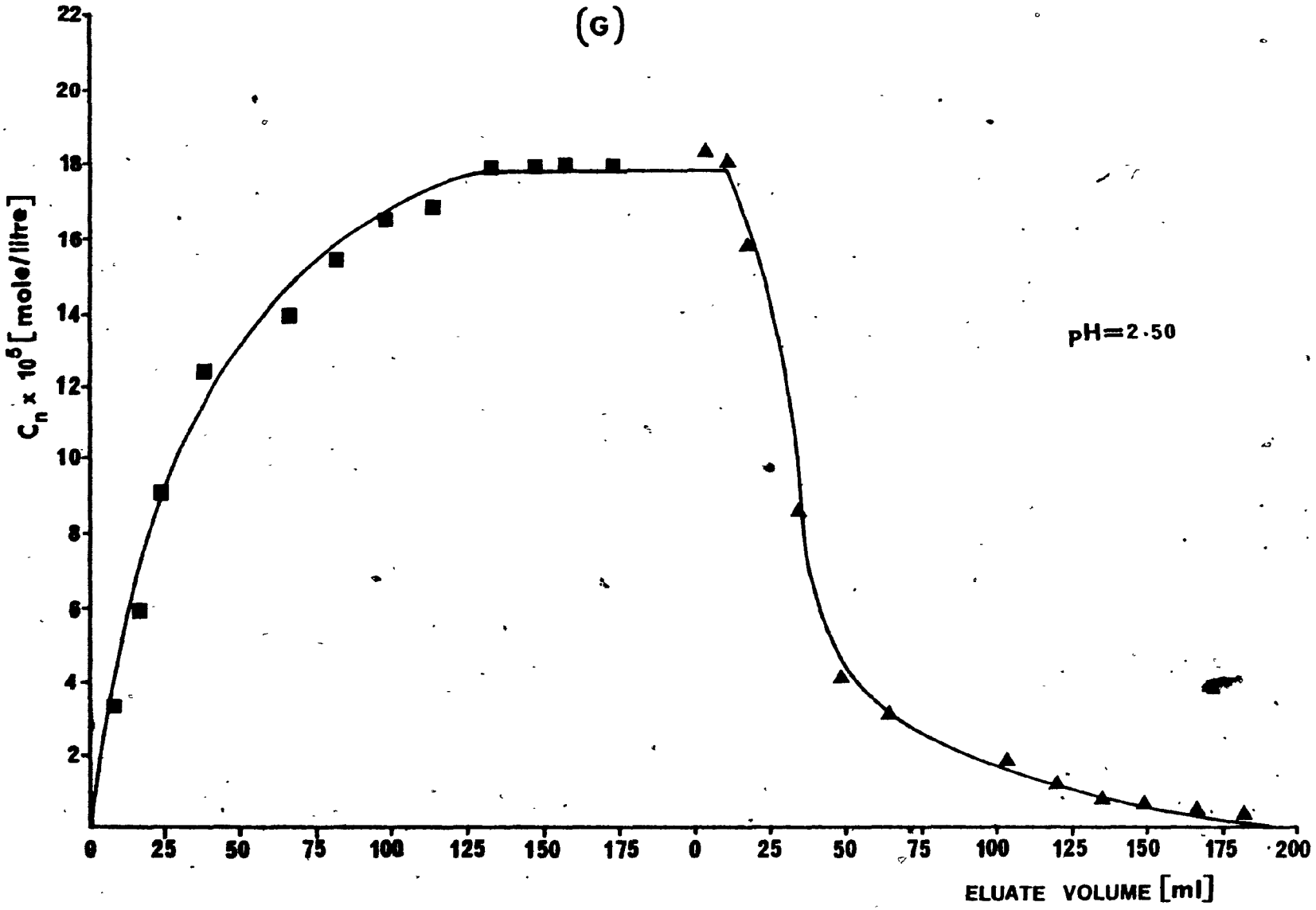

(B)
pH= 2·10
$C_n \times 10^5$ [mole/litre]
22
20
18
16
14
12
10
8
6
4
2
0 25 50 75 100 125 150 175
0 25 50 75 100 125 150 175 200
ELUATE VOLUME [ml]

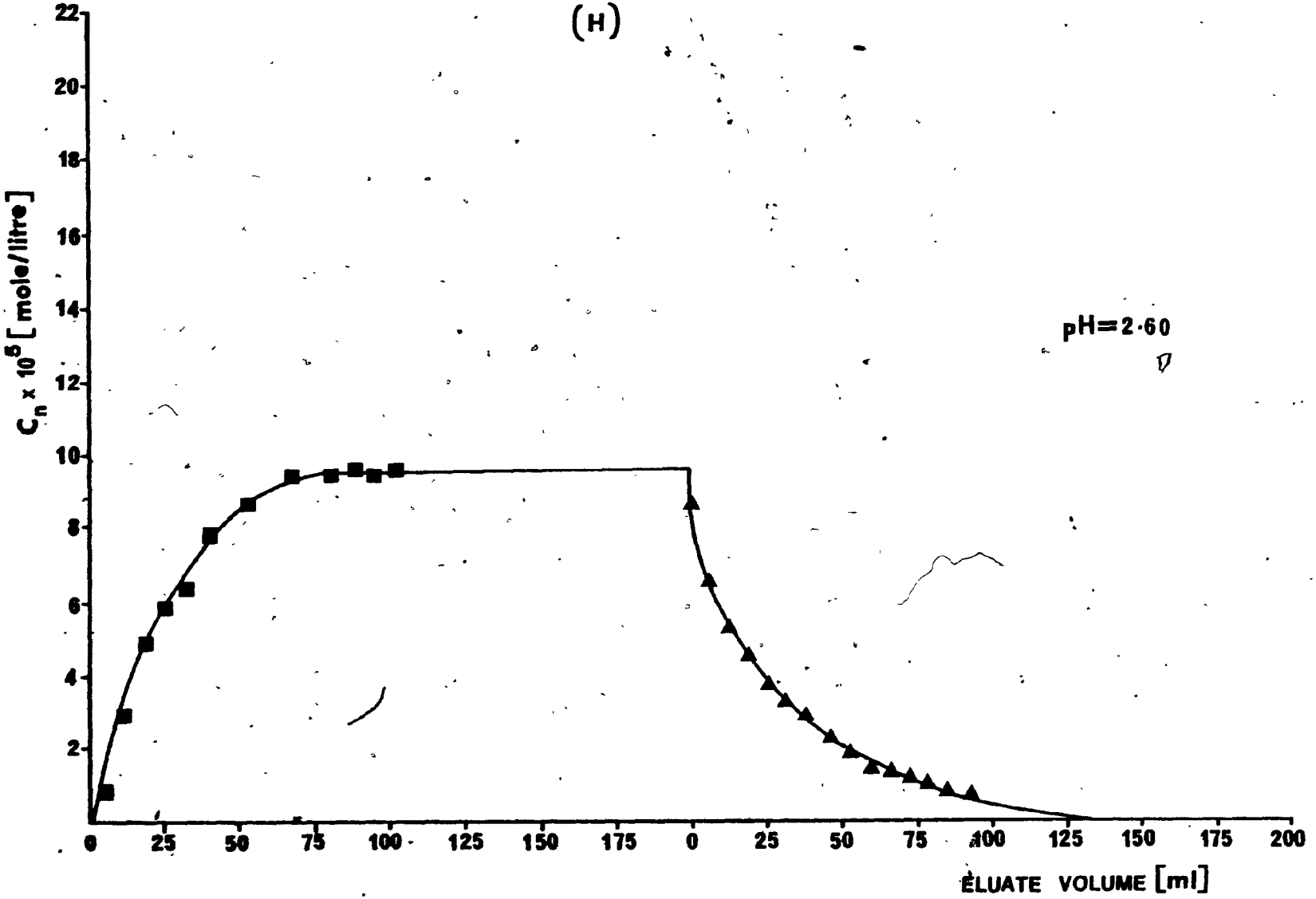

(c)
pH= 2.28
$C_n \times 10^5$ [mole/litre]
22
20
18
16
14
12
10
8
6
4
2
0 25 50 75 100 125 150 175 0 25 50 75 100 125 150 175 200
ELUATE VOLUME [ml]

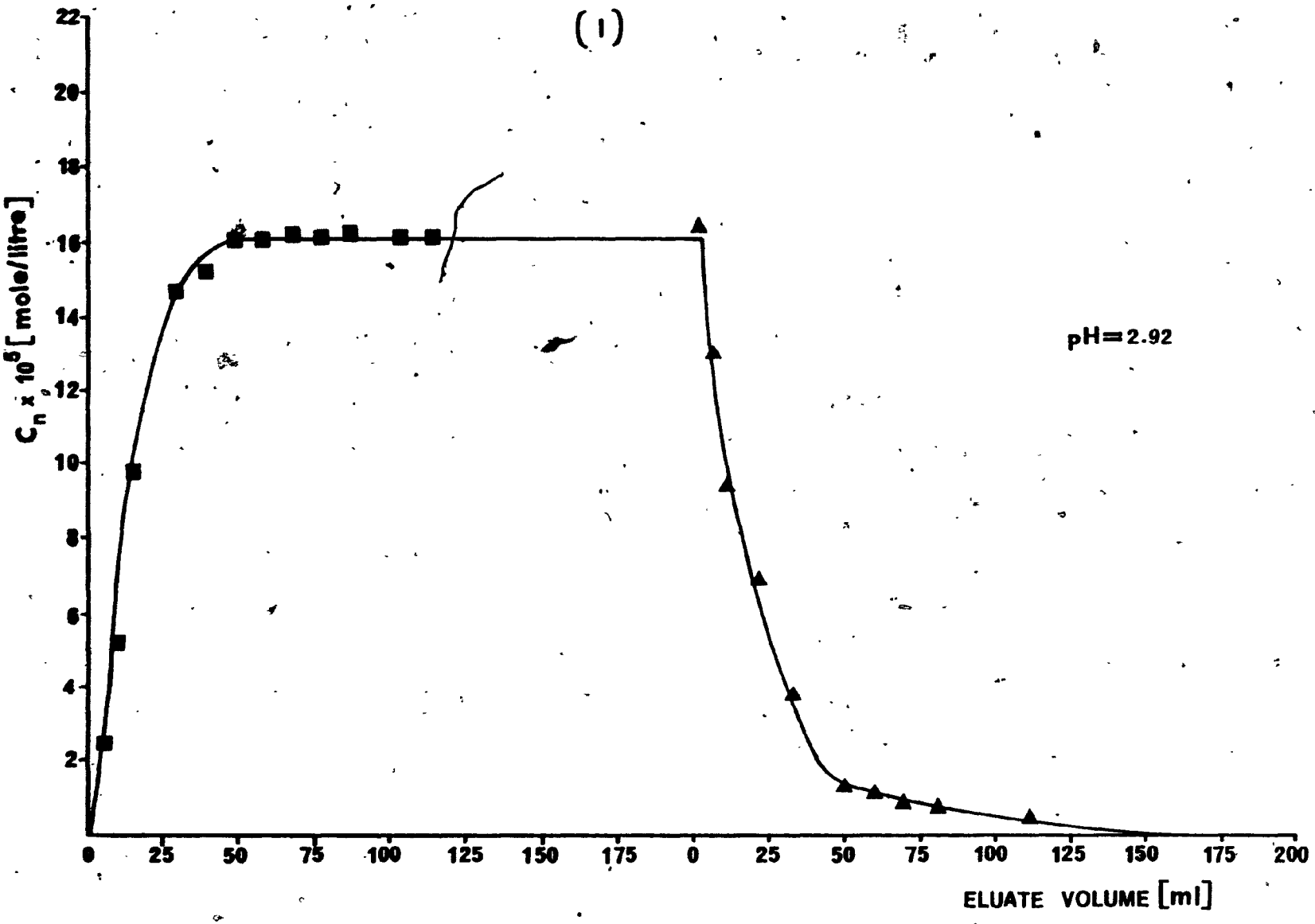

(D)
pH=2·30
$C_n \times 10^5$ [mole/litre]
22
20
18
16
14
12
10
8
6
4
2
0 25 50 75 100 125 150 175 0 25 50 75 100 125 150 175 200
ELUATE VOLUME [ml]

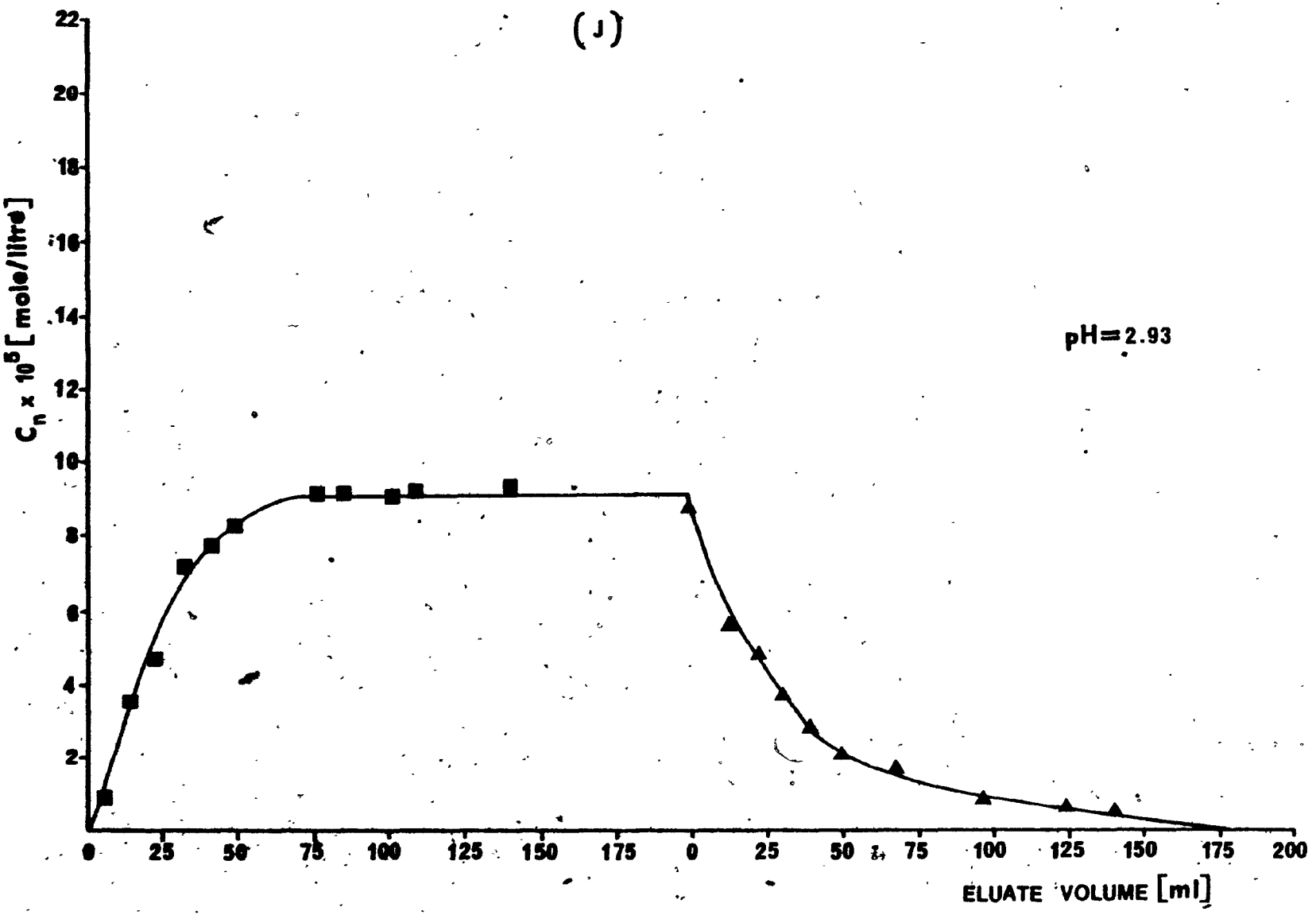

(E)
pH=2.35
$C_n \times 10^5$ [mole/litre]
22
20
18
16
14
12
10
8
6
4
2
0
25
50
75
100
125
150
175
0
25
50
75
100
125
150
175
200
ELUATE VOLUME [ml]

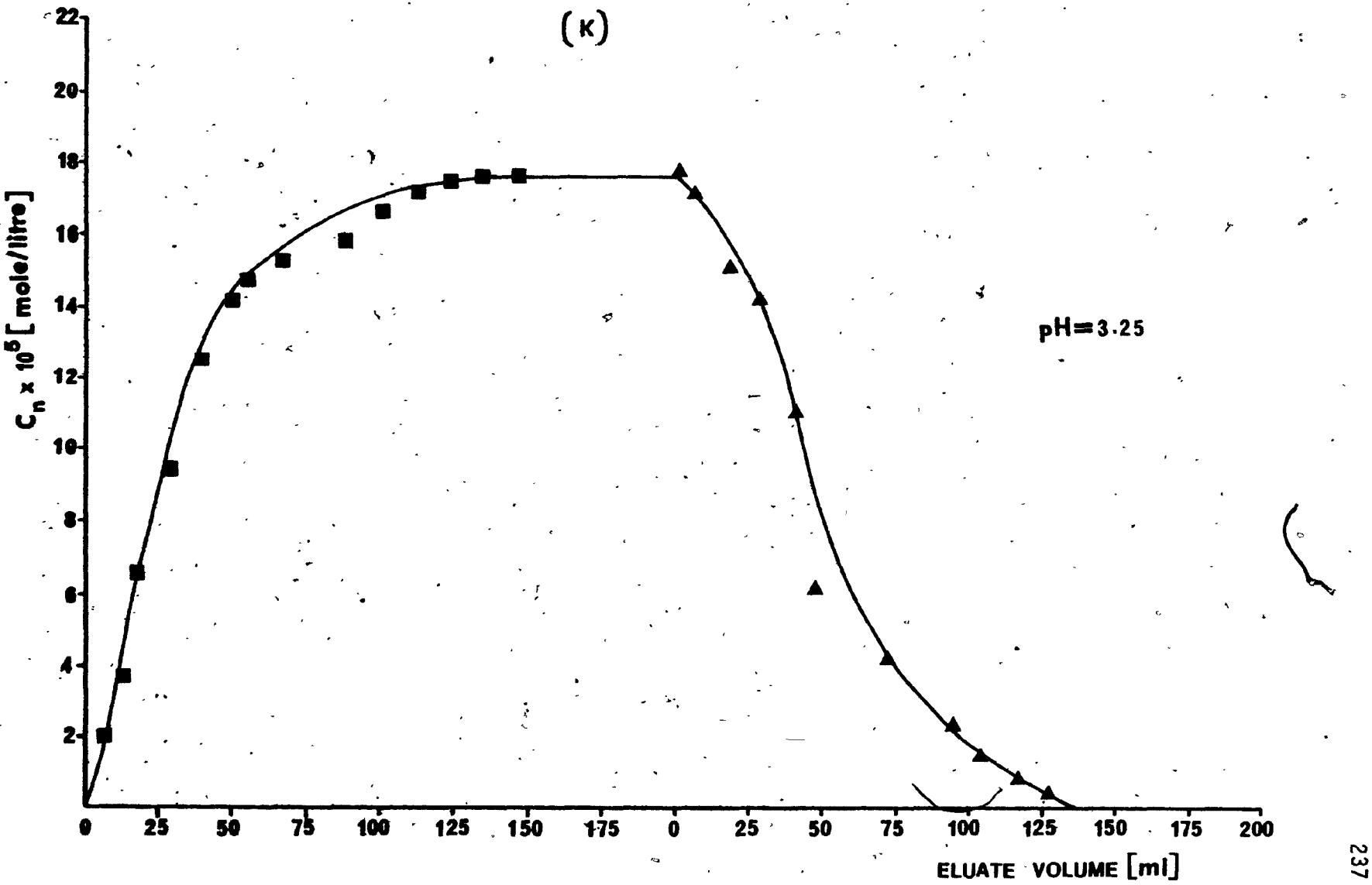

(F)
pH=2.50
$C_n \times 10^5$ [mole/litre]
22
20
18
16
14
12
10
8
6
4
2
0 25 50 75 100 125 150 175 0 25 50 75 100 125 150 175 200
ELUATE VOLUME [ml]

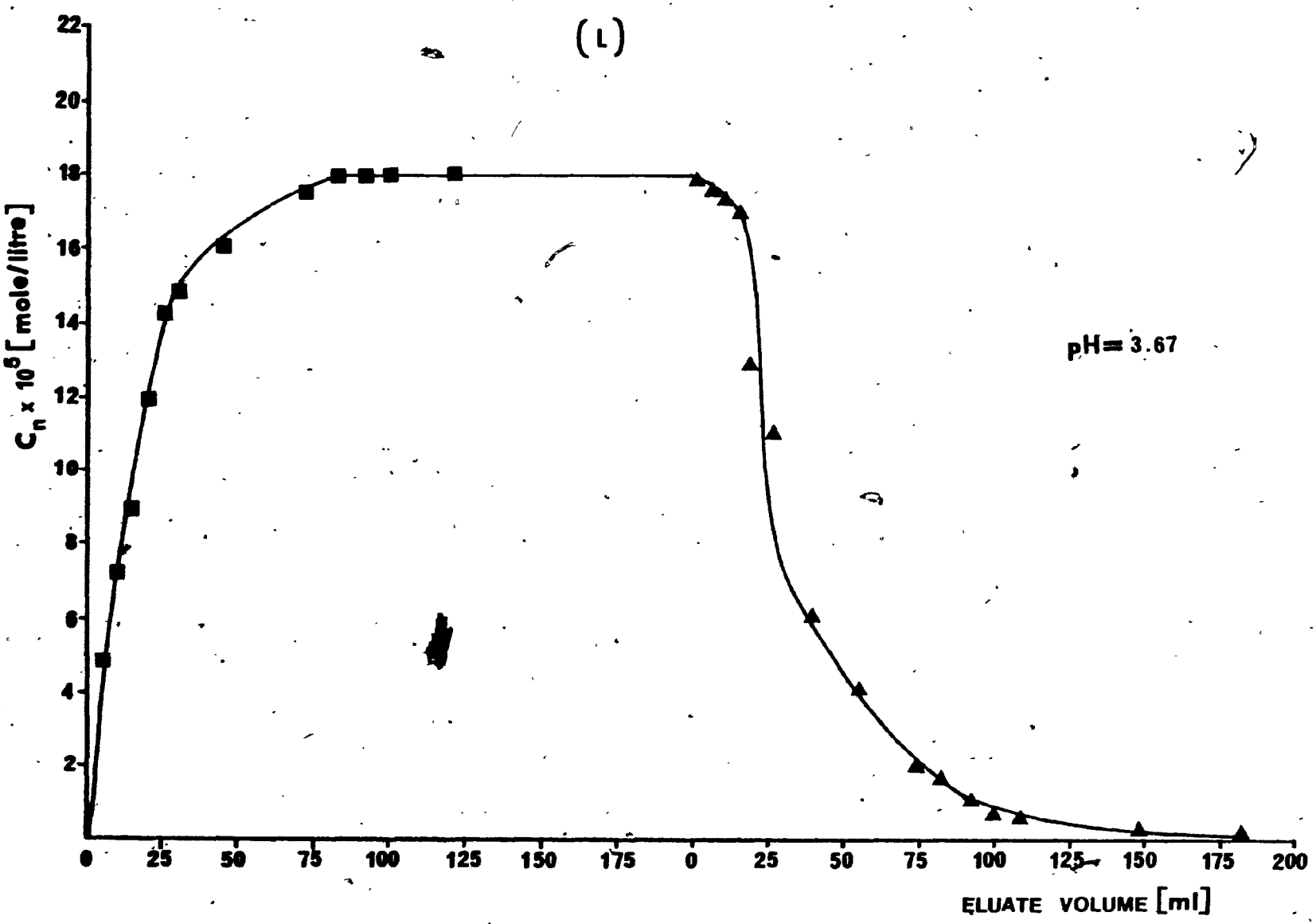

(G)
pH=2·50
$C_n \times 10^5$ [mole/litre]
22
20
18
16
14
12
10
8
6
4
2
0 25 50 75 100 125 150 175 0 25 50 75 100 125 150 175 200
ELUATE VOLUME [ml]

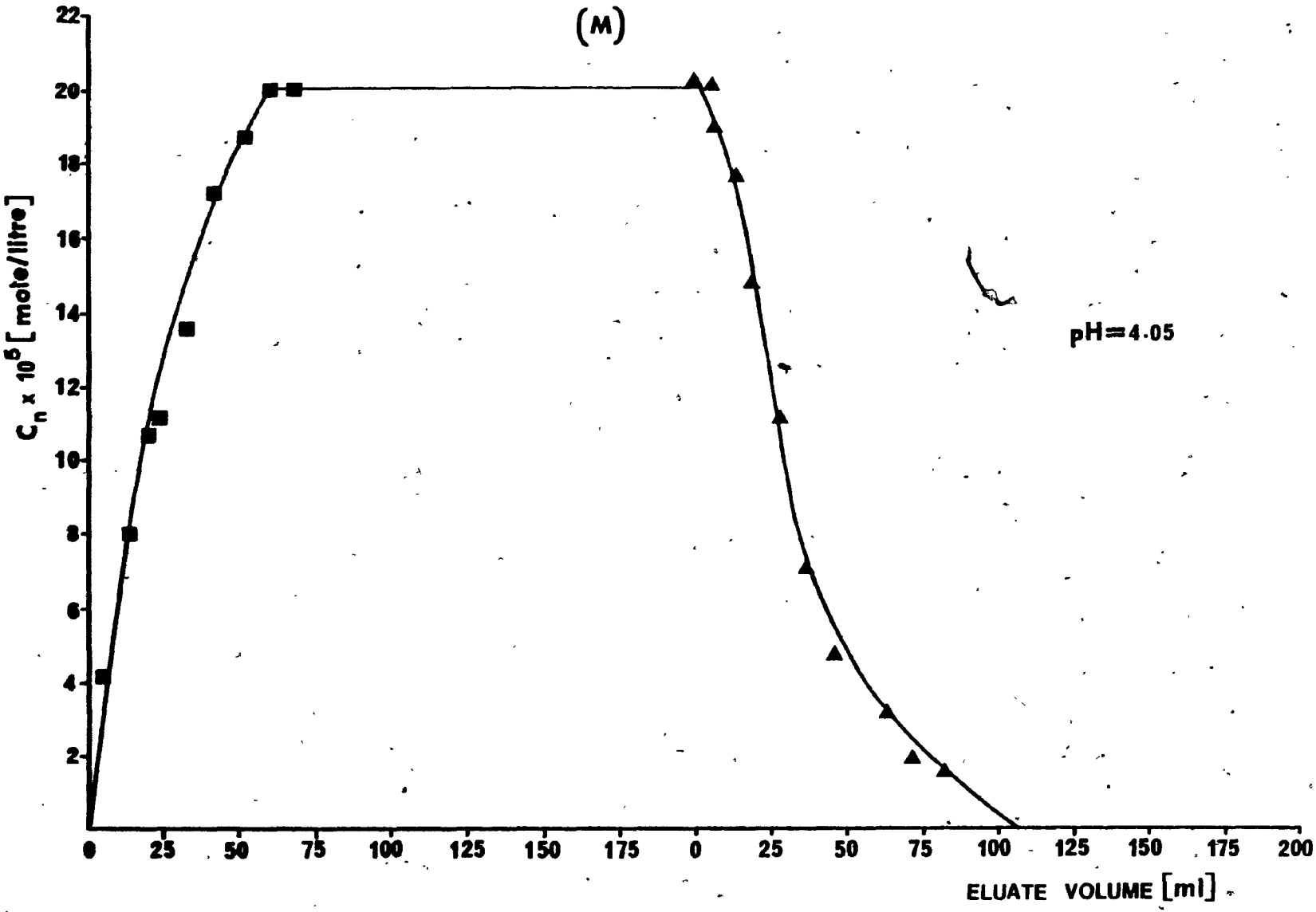

(H)
pH=2·60
$C_n \times 10^5$ [mole/litre]
22
20
18
16
14
12
10
8
6
4
2
0 25 50 75 100 125 150 175 0 25 50 75 100 125 150 175 200
ELUATE VOLUME [ml]

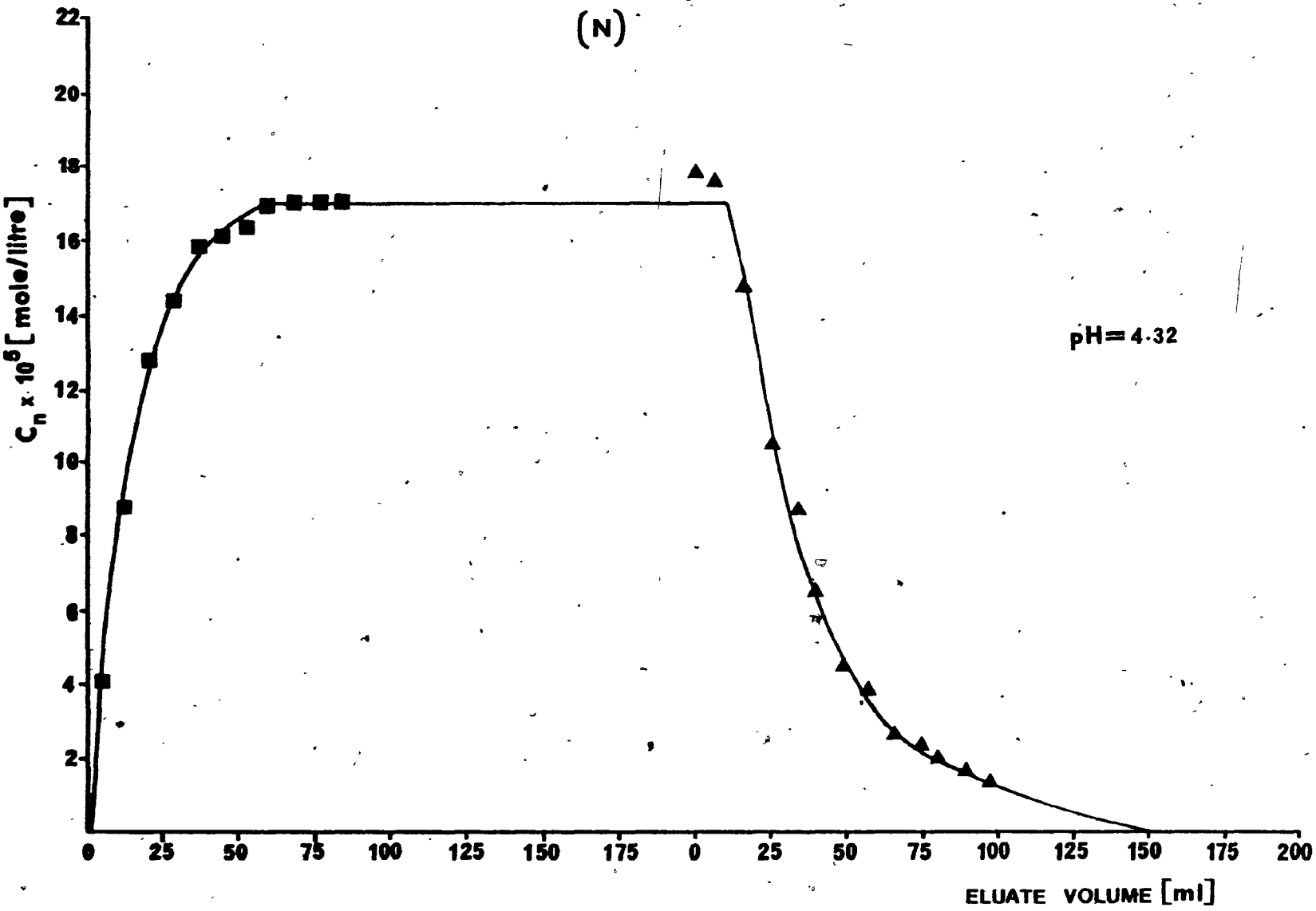

(1)
$C_n \times 10^5$ [mole/litre]
pH=2.92
ELUATE VOLUME [ml]
0
25
50
75
100
125
150
175
200
2
4
6
8
10
12
14
16
18
20
22

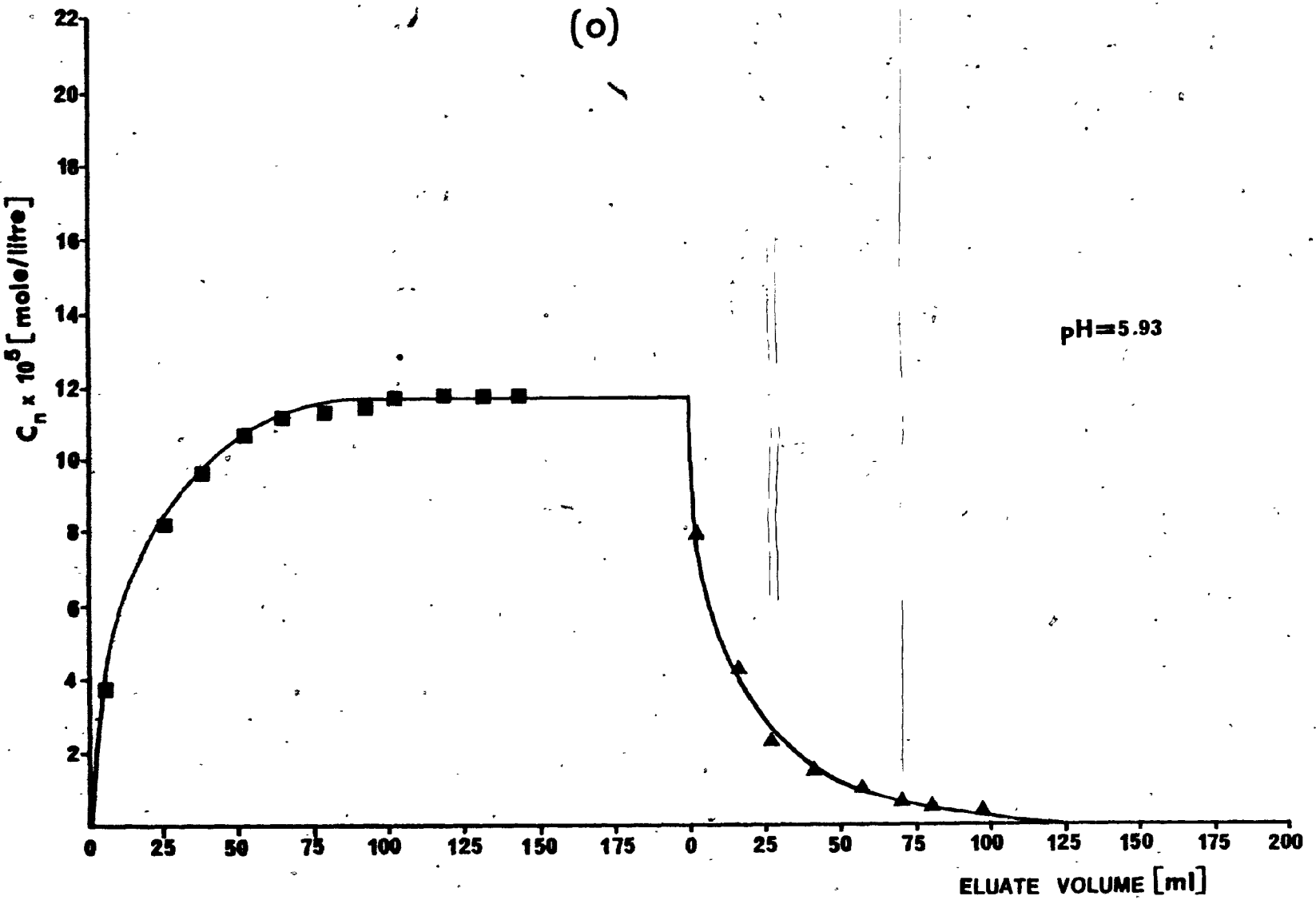

(J)
pH=2.93
$C_n \times 10^5$ [mole/litre]
22
20
18
16
14
12
10
8
6
4
2
0
25
50
75
100
125
150
175
0
25
50
75
100
125
150
175
200
ELUATE VOLUME [ml]

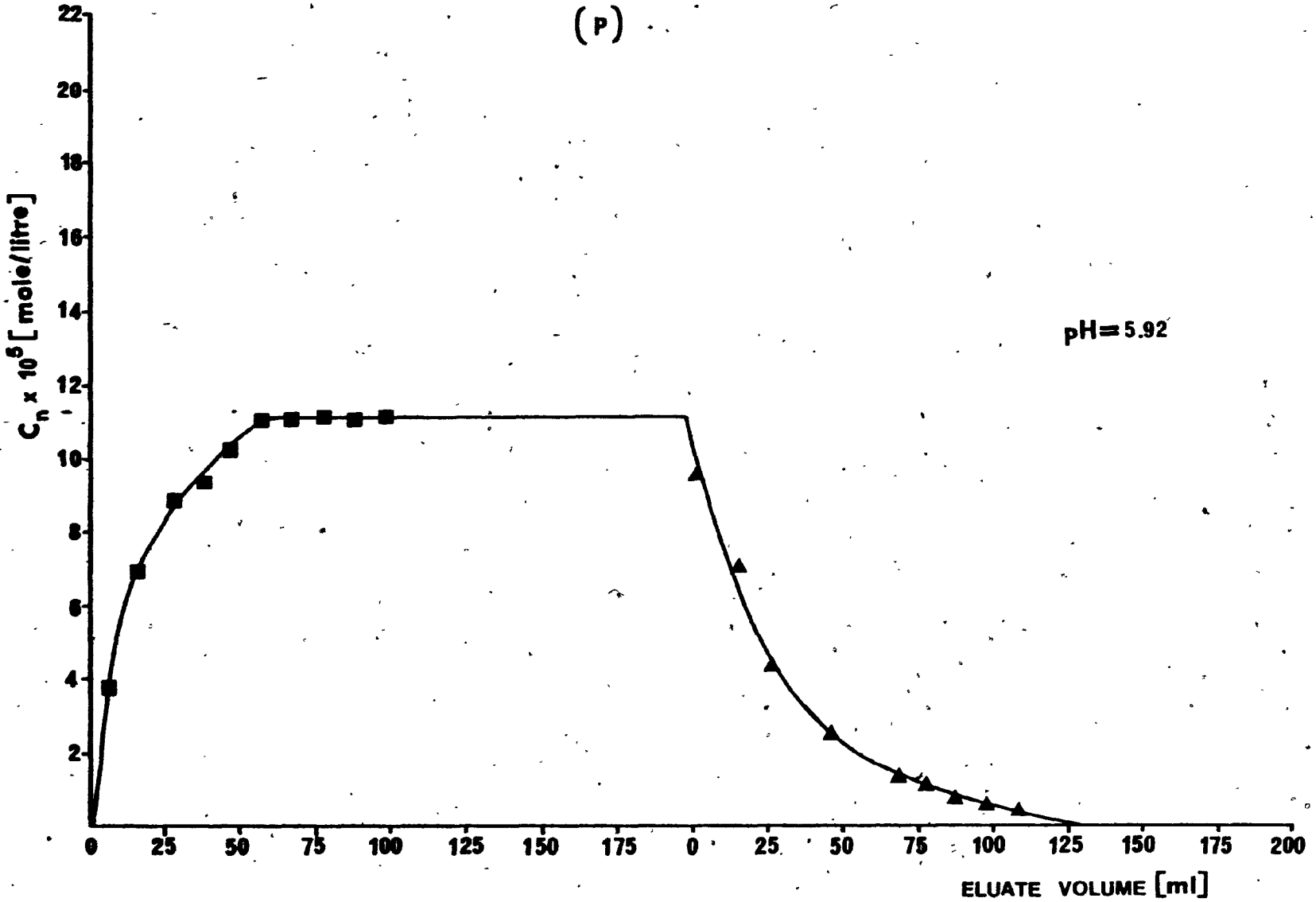

(K)
pH=3.25
$C_n \times 10^5$ [mole/litre]
22
20
18
16
14
12
10
8
6
4
2
0 25 50 75 100 125 150 175 0 25 50 75 100 125 150 175 200
ELUATE VOLUME [ml]


(L)
$C_n \times 10^6$ [mole/litre]
22
20
18
16
14
12
10
8
6
4
2
pH= 3.67
0 25 50 75 100 125 150 175 0 25 50 75 100 125 150 175 200
ELUATE VOLUME [ml]


(M)
$C_n \times 10^5$ [mole/litre]
pH=4.05
ELUATE VOLUME [ml]
0
25
50
75
100
125
150
175
200
2
4
6
8
10
12
14
16
18
20
22


(N)
pH = 4·32
$C_n \times 10^6$ [mole/litre]
22
20
18
16
14
12
10
8
6
4
2
0 25 50 75 100 125 150 175 0 25 50 75 100 125 150 175 200
ELUATE VOLUME [ml]


(o)
pH=5.93
$C_n \times 10^5$ [mole/litre]
22
20
18
16
14
12
10
8
6
4
2
0 25 50 75 100 125 150 175 0 25 50 75 100 125 150 175 200
ELUATE VOLUME [ml]


(P)
pH=5.92
$C_n \times 10^5$ [mole/litre]
22
20
18
16
14
12
10
8
6
4
2
0
25
50
75
100
125
150
175
0
25
50
75
100
125
150
175
200
ELUATE VOLUME [ml]

APPENDIX (IX)

Sorption and desorption data from Appendix (VIII).

Table (25-A): Sorption and desorption values for the evaluation of the amount of Atrazine bound to FA at pH 2.10.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	2.60	1.95	7.50	12.00	9.00
15.00	5.78	6.28	15.00	9.38	16.04
22.50	8.60	12.74	22.50	7.40	21.59
30.00	11.00	20.98	30.00	5.90	26.02
37.50	13.20	30.88	37.50	4.60	29.46
45.00	15.10	42.21	45.00	3.62	32.18
52.50	16.58	54.64	52.50	2.78	34.26
60.00	17.80	68.00	60.00	2.00	35.76
67.50	18.78	82.08	67.50	1.38	36.80
75.00	19.10	96.40	75.00	0.92	37.49
			82.50	0.70	38.02
			90.00	0.44	38.35
			97.50	0.36	38.62
			105.00	0.22	38.78
			112.50	0.18	38.92
			120.00	0.15	39.03
			127.50	0.00	39.03
Sorbed = 22.0 μmole/gm FA			Desorbed = 14.2 μmole/gm FA		

Table (25-B): Sorption and desorption values for the evaluation of the amount of Atrazine bound to FA at pH 2.10.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	1.94	1.46	7.50	10.20	7.65
15.00	3.10	3.78	15.00	9.56	14.82
22.50	4.08	6.84	22.50	8.30	21.04
30.00	4.90	10.52	30.00	6.92	26.23
37.50	5.80	14.87	37.50	5.50	30.36
45.00	6.60	19.82	45.00	4.52	33.75
52.50	7.38	25.36	52.50	3.60	36.45
60.00	8.40	31.66	60.00	2.82	38.56
67.50	8.78	38.24	67.50	2.30	40.29
75.00	9.42	45.31	75.00	1.88	41.70
82.50	10.05	52.85	82.50	1.60	42.90
90.00	10.40	60.65	90.00	1.38	43.94
			97.50	1.18	44.82
			105.00	0.94	45.52
			112.50	0.79	46.11
			120.00	0.60	46.56
			127.50	0.55	46.97
			135.00	0.40	47.27
			142.50	0.32	47.51
			150.00	0.22	47.68
			157.50	0.18	47.82
			165.00	0.15	47.93
			172.50	0.00	47.93
Sorbed = 19.9 μmole/gm FA			Desorbed = 34.4 μmole/gm FA		

Table (25-C): Sorption and desorption values for the evaluation of the amount of Atrazine bound to FA at pH 2.28.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	2.88	2.16	7.50	8.30	6.22
15.00	4.40	5.46	15.00	4.42	9.54
22.50	5.71	9.74	22.50	3.18	11.92
30.00	6.90	14.92	30.00	2.42	13.74
37.50	7.70	20.50	37.50	1.90	15.16
45.00	8.32	26.74	45.00	1.60	16.36
52.50	8.94	33.44	52.50	1.35	17.37
60.00	9.46	40.54	60.00	1.10	17.38
67.50	9.80	47.89	67.50	0.90	18.06
			75.00	0.78	18.64
			82.50	0.62	19.11
			90.00	0.55	19.52
			97.50	0.40	19.82
			105.00	0.38	20.11
			112.50	0.24	20.92
			120.00	0.22	20.46
			127.50	0.20	20.61
			135.00	0.18	20.74
			142.50	0.16	20.86
			150.00	0.14	20.96
			157.50	0.05	21.00
			165.00	0.05	21.03
			172.50	0.00	21.03
Sorbed = 5.52 μmole/gm FA			Desorbed = 8.29 μmole/gm FA		

Table (25-D): Sorption and desorption values for the evaluation of the amount of Atrazine bound to FA at pH 2.30.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	2.82	2.12	7.50	6.70	5.02
15.00	4.50	5.50	15.00	4.98	8.76
22.50	5.70	9.78	22.50	3.80	11.61
30.00	6.58	14.72	30.00	2.98	13.84
37.50	7.38	20.26	37.50	2.28	15.55
45.00	7.98	26.24	45.00	1.80	16.90
52.50	8.42	32.56	52.50	1.40	17.95
60.00	8.80	39.16	60.00	1.02	18.71
67.50	9.10	45.99	67.50	0.81	19.32
75.00	9.28	52.95	75.00	0.62	19.78
82.50	9.42	60.02	82.50	0.58	20.22
90.00	9.50	67.14	90.00	0.42	20.54
			97.50	0.30	20.76
			105.00	0.12	20.85
			112.50	0.10	20.92
			120.00	0.08	20.98
			127.50	0.05	21.02
			135.00	0.00	21.02
Sorbed = 6.01 μmole/gm FA			Desorbed = 8.67 μmole/gm FA		

Table (25-E): Sorption values for the evaluation of the amount of Atrazine bound to FA at pH 2.35.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	3.18	2.38			
15.00	4.84	6.01			
22.50	6.10	10.58			
30.00	7.02	15.84			
37.50	7.78	21.68			
45.00	8.38	27.96			
52.50	8.81	34.56			
60.00	9.22	41.48			
67.50	9.58	48.66			
75.00	9.80	56.01			
82.50	10.00	63.51			
90.00	10.16	71.13			
97.50	10.30	78.86			
105.00	10.34	86.62			
Sorbed = 8.51 μmole/gm FA					

Table (25-F): Sorption and desorption values for the evaluation of the amount of Atrazine bound to FA at pH 2.50.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	2.42	1.82	7.50	8.40	6.30
15.00	3.95	4.78	15.00	8.10	12.38
22.50	5.00	8.53	22.50	7.56	18.05
30.00	5.83	12.90	30.00	6.38	22.84
37.50	6.50	17.78	37.50	4.75	26.40
45.00	7.07	23.08	45.00	3.78	29.24
52.50	7.50	28.71	52.50	3.00	31.49
60.00	7.88	34.62	60.00	2.55	33.40
67.50	8.18	40.76	67.50	2.10	34.98
75.00	8.39	47.05	75.00	1.80	36.33
82.50	8.46	50.40	82.50	1.58	37.52
90.00	8.75	56.96	90.00	1.36	38.54
			97.50	1.20	39.44
			105.00	1.05	40.23
			112.50	0.90	40.09
			120.00	0.80	40.69
			127.50	0.66	41.18
			135.00	0.58	41.62
			142.50	0.40	41.92
			150.00	0.26	42.12
			157.50	0.10	42.20
Sorbed = 10.4 μmole/gm FA			Desorbed = 30.8 μmole/gm FA		

Table (25-G): Sorption and desorption values for the evaluation of the amount of Atrazine bound to FA at pH 2.50.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	3.78	2.84	7.50	18.50	13.88
15.00	7.00	8.09	15.00	18.45	27.72
22.50	9.00	14.84	22.50	15.50	39.34
30.00	10.32	22.58	30.00	11.32	47.83
37.50	11.39	31.12	37.50	8.10	53.91
45.00	12.32	40.36	45.00	6.20	58.56
52.50	13.10	50.18	52.50	4.98	62.30
60.00	13.75	60.49	60.00	4.00	65.30
67.50	14.38	71.28	67.50	3.30	67.78
75.00	15.10	82.61	75.00	2.78	69.86
82.50	15.72	94.40	82.50	2.39	71.65
90.00	16.20	106.55	90.00	2.00	73.15
97.50	16.66	119.04	97.50	1.71	74.43
105.00	17.20	131.94	105.00	1.46	75.52
112.50	17.38	144.98	112.50	1.23	76.44
120.00	17.60	158.18	120.00	1.04	77.22
127.50	17.85	171.57	127.50	0.92	77.91
135.00	18.14	185.18	135.00	0.80	78.51
142.50	18.20	198.83	142.50	0.71	79.04
150.00	18.20	212.48	150.00	0.62	79.51
			157.50	0.50	79.88
			165.00	0.42	80.20
			172.50	0.37	80.48
			180.00	0.30	80.71
			187.50	0.28	80.92
			195.00	0.20	81.07
			202.50	0.18	81.21
			210.00	0.10	81.28
			217.50	0.00	81.28
Sorbed = 36.9 µmole/gm FA			Desorbed = 57.6 µmole/gm FA		

Table (25-H): Sorption and desorption values for the evaluation of the amount of Atrazine bound to FA at pH 2.60.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_q \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	2.08	1.56	7.50	7.38	5.54
15.00	4.00	4.56	15.00	5.64	9.77
22.50	5.60	8.76	22.50	4.52	13.16
30.00	6.70	13.78	30.00	3.70	15.94
37.50	7.55	19.44	37.50	3.10	18.26
45.00	8.20	25.59	45.00	2.56	20.18
52.50	8.68	32.10	52.50	2.10	21.76
60.00	9.10	38.92	60.00	1.78	23.10
67.50	9.39	45.96	67.50	1.48	24.21
75.00	9.60	53.16	75.00	1.23	25.13
82.50	9.78	60.50	82.50	1.19	26.02
			90.00	0.99	26.76
			97.50	0.85	27.40
			105.00	0.70	27.92
			112.50	0.60	28.37
			120.00	0.48	28.73
			127.50	0.37	29.00
			135.00	0.25	29.19
			142.50	0.17	29.32
			150.00	0.00	29.32
Sorbed = 7.47 μmole/gm FA			Desorbed = 16.6 μmole/gm FA		

Table (25-I): Sorption and desorption values for the evaluation of the amount of Atrazine bound to FA at pH 2.92.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	3.65	2.74	7.50	14.50	10.95
15.00	9.00	9.49	15.00	9.58	19.14
22.50	12.62	18.96	22.50	6.95	23.35
30.00	14.80	30.06	30.00	5.10	27.18
37.50	15.42	41.62	37.50	5.65	31.42
45.00	15.83	53.49	45.00	2.65	33.41
52.50	16.20	65.64	52.50	1.94	34.86
60.00	16.42	77.96	60.00	1.40	35.91
67.50	16.54	90.36	67.50	1.00	36.66
75.00	16.60	102.81	75.00	0.80	37.26
			82.50	0.70	37.79
			90.00	0.58	38.22
			97.50	0.45	38.56
			105.00	0.40	38.86
			112.50	0.37	39.14
			120.00	0.30	39.36
			127.50	0.24	39.54
			135.00	0.20	39.69
			142.50	0.20	39.84
			150.00	0.00	39.84
Sorbed = 0.110 μmole/gm FA			Desorbed = 18.3 μmole/gm FA		

Table (25-J): Sorption and desorption values for the evaluation of the amount of Atrazine bound to FA at pH 2.93.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	2.20	1.65	7.50	7.52	5.64
15.00	3.90	4.58	15.00	6.00	10.14
22.50	5.37	8.61	22.50	4.92	13.83
30.00	6.44	13.44	30.00	4.08	16.89
37.50	7.40	18.99	37.50	3.37	19.42
45.00	9.10	25.06	45.00	2.80	21.52
52.50	8.63	31.53	52.50	2.40	23.32
60.00	9.00	38.28	60.00	2.10	24.90
67.50	9.28	45.24	67.50	1.80	26.25
75.00	9.37	52.27	75.00	1.60	27.45
82.50	9.40	59.32	82.50	1.45	28.54
			90.00	1.30	29.52
			97.50	1.18	30.40
			105.00	1.02	31.16
			112.50	0.90	31.84
			120.00	0.80	32.44
			127.50	0.70	32.96
			135.00	0.58	33.40
			142.50	0.45	33.74
			150.00	0.40	34.04
			157.50	0.30	34.26
			165.00	0.25	34.45
			172.50	0.20	34.60
			180.00	0.18	34.74
			187.50	0.15	34.85
			195.00	0.12	34.94
			202.50	0.00	34.94
Sorbed = 6.01 µmole/gm FA			Desorbed = 22.7 µmole/gm FA		

Table (25-K): Sorption and desorption values for the evaluation of the amount of Atrazine bound to FA at pH 3.25.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	2.70	2.02	7.50	17.80	13.35
15.00	5.70	6.30	15.00	17.00	26.10
22.50	8.00	12.30	22.50	15.80	37.95
30.00	10.02	19.82	30.00	14.45	48.78
37.50	11.80	28.67	37.50	12.97	58.51
45.00	13.30	38.64	45.00	11.30	66.99
52.50	14.58	49.58	52.50	9.50	74.12
60.00	15.20	60.98	60.00	7.72	79.91
67.50	15.68	72.74	67.50	6.17	84.54
75.00	16.08	84.80	75.00	4.72	88.08
82.50	16.40	97.10	82.50	3.75	90.89
90.00	16.70	109.62	90.00	3.05	93.18
97.50	16.95	122.33	97.50	2.44	95.01
105.00	17.20	135.23	105.00	1.97	96.49
112.50	17.39	148.27	112.50	1.50	97.62
120.00	17.57	161.45	120.00	1.05	98.41
127.50	17.70	174.72	127.50	0.68	98.92
135.00	17.80	188.07	135.00	0.37	99.20
142.50	17.90	201.50	142.50	0.16	99.32
150.00	17.95	214.96	150.00	0.00	99.32
Sorbed = 31.0 µmole/gm FA			Desorbed = 76.0 µmole/gm FA		

Table (25-L): Sorption and desorption values for the evaluation of the amount of Atrazine bound to FA at pH 3.76.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	6.58	4.94	7.50	18.20	13.65
15.00	10.90	13.12	15.00	17.78	26.98
22.50	13.20	23.02	22.50	14.20	37.63
30.00	14.62	33.98	30.00	11.00	45.88
37.50	15.55	45.64	37.50	8.20	52.03
45.00	16.23	57.81	45.00	6.56	56.95
52.50	16.80	70.41	52.50	5.28	60.91
60.00	17.25	83.35	60.00	4.20	64.06
67.50	17.61	96.56	67.50	3.37	66.59
75.00	17.94	110.02	75.00	2.55	68.50
82.50	18.20	123.67	82.50	1.98	69.99
90.00	18.35	137.43	90.00	1.55	71.15
97.50	18.38	151.22	97.50	1.20	72.05
			105.00	0.98	72.78
			112.50	0.70	73.30
			120.00	0.50	73.68
			127.50	0.38	73.97
			135.00	0.30	74.20
			142.50	0.22	74.36
			150.00	0.20	74.51
			157.50	0.18	74.64
			165.00	0.15	74.75
			172.50	0.15	74.86
			180.00	0.14	74.96
			187.50	0.00	74.96
Sorbed = 4.10 µmole/gm FA			Desorbed = 51.1 µmole/gm FA		

Table (25-M): Sorption and desorption values for the evaluation of the amount of Atrazine bound to FA at pH 4.05.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	6.20	4.65	7.50	20.55	15.41
15.00	9.50	11.78	15.00	18.98	29.64
22.50	12.00	20.78	22.50	14.92	40.83
30.00	14.00	31.28	30.00	12.00	49.83
37.50	16.16	43.40	37.50	7.90	55.76
45.00	17.75	56.71	45.00	6.15	60.37
52.50	18.83	70.83	52.50	4.83	63.99
60.00	19.70	85.61	60.00	3.84	66.87
67.50	20.55	101.02	67.50	2.98	69.11
			75.00	2.30	70.84
			82.50	1.70	72.12
			90.00	1.20	73.02
			97.50	0.80	73.62
			105.00	0.40	73.92
			112.50	0.10	74.00
Sorbed = 11.0 μmole/gm FA			Desorbed = 47.3 μmole/gm FA		

Table (25-N): Sorption and desorption values for the evaluation of the amount of Atrazine bound to FA at pH 4.32.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	7.40	5.55	7.50	18.00	13.50
15.00	11.40	14.10	15.00	16.00	25.50
22.50	13.50	24.22	22.50	13.10	35.32
30.00	14.79	35.31	30.00	10.74	43.38
37.50	15.58	46.99	37.50	8.70	49.91
45.00	16.18	59.12	45.00	6.60	54.86
52.50	16.63	71.59	52.50	5.00	58.61
60.00	16.97	84.32	60.00	4.05	61.65
67.50	17.20	97.22	67.50	3.28	64.11
75.00	17.42	110.28	75.00	2.70	66.14
			82.50	2.27	67.84
			90.00	1.90	69.26
			97.50	1.60	70.46
			105.00	1.30	71.44
			112.50	1.05	72.23
			120.00	0.82	72.84
			127.50	0.60	73.29
			135.00	0.40	73.59
			142.50	0.20	73.74
			150.00	0.00	73.74
Sorbed = -2.28 µmole/gm FA			Desorbed = 51.1 µmole/gm FA		

Table (25-O): Sorption and desorption values for the evaluation of the amount of Atrazine bound at pH 5.92.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	4.83	3.62	7.50	7.20	5.40
15.00	6.70	8.64	15.00	5.30	9.38
22.50	7.95	14.60	22.50	3.68	12.14
30.00	8.88	21.26	30.00	2.58	14.08
37.50	9.70	28.54	37.50	1.84	15.46
45.00	10.23	36.21	45.00	1.46	16.56
52.50	10.70	44.24	52.50	1.18	17.44
60.00	11.05	52.53	60.00	0.97	18.17
67.50	11.30	61.01	67.50	0.80	18.77
75.00	11.55	61.67	75.00	0.65	19.26
82.50	11.70	78.44	82.50	0.55	19.67
90.00	11.82	87.31	90.00	0.46	20.02
97.50	11.96	96.28	97.50	0.40	20.32
105.00	12.02	105.30	105.00	0.30	20.54
112.50	12.10	114.38	112.50	0.22	20.71
120.00	12.18	123.52	120.00	0.17	20.84
			127.50	0.10	20.92
			135.00	0.05	20.96
			142.50	0.00	20.96
Sorbed = 0.680 µmole			Desorbed = 0.513 µmole		

Table (25-P): Sorption and desorption values for the evaluation of the amount of Atrazine bound at pH 5.93.

SORPTION			DESORPTION		
V_{out} (ml)	$C_n \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)	V_{out} (ml)	$C_1 \times 10^5$ (mole/l)	$M_{out} \times 10^7$ (mole)
7.50	5.00	3.75	7.50	8.60	6.45
15.00	6.85	8.89	15.00	6.60	11.40
22.50	8.20	15.04	22.50	5.40	15.45
30.00	9.00	21.79	30.00	4.20	18.60
37.50	9.80	29.14	37.50	3.60	21.30
45.00	10.40	36.94	45.00	3.00	23.55
52.50	10.90	45.11	52.50	2.50	25.43
60.00	11.30	53.95	62.50	1.80	26.78
67.50	11.40	62.14	72.50	1.50	28.58
			82.50	1.20	29.78
			92.50	0.90	30.68
			102.50	0.65	31.33
			112.50	0.55	31.88
			122.50	0.24	32.12
			127.50	0.00	32.21
Sorbed = -3.00×10^{-3} µmole			Desorbed = 1.74 µmole		