4.1.5. Humic Acid Paraquat Titrations.

Exactly the same procedure used for copper was employed for the titrations of humic acid with paraquat. Paraquat stock solution were prepared as described below.

After the equilibration period, the pH of the suspensions was measured. This was followed by ultrafiltration on a YM2 1000 molecular weight cut-off membrane purchased from Amicon. 5.00 mLs filtrates were collected for each sample and control at 60 psi. Filtrates were diluted with acetate buffer pH 4.5 if necessary and analyzed for paraquat by UV at 254 nm on a Perkin Elmer UV-Vis Spectrophometer Model 552, or by HPLC with UV detection at 254 nm.

4.1.6. Humic Acid Magnesium Titrations.

The same procedure as described above was followed for the titrations of humic acid with magnesium. Magnesium stock solution were prepared as described below.

After the equilibration period, the pH of the suspensions was measured. This was followed by ultrafiltration on a YM2 1000 molecular weight cut-off membrane purchased from Amicon. 5.00 mLs filtrates were collected for each sample and control at 60 psi. Filtrates were diluted with 1% HCL, if necessary, and analyzed for magnesium by flame atomic absorption of an Perkin Elmer Model 305. The magnesium line at 312 nm was used for analysis.

4.1.7. Humic Acid Calcium Titrations.

The same procedure described above was used in the titration of humic acid with calcium. Calcium stock solution were prepared as described below.

After the equilibration period, the pH of the suspensions was measured. This was followed by ultrafiltration on a YM2 1000 molecular weight cut-off membrane purchased from Amicon. 5.00 mLs filtrates were collected for each sample and control at 60 psi. Filtrates were diluted with 1% HNO_3 if necessary and were analyzed by flame atomic absorption of a Perkin Elmer Model 305 at 212 nm.

4.1.8. Titrations of Humic Acid with more than one cation.

Titrations of humic acid with one cation in the presence of various concentration levels of a second cation were carried out exactly as described above. The total volume was still kept at 50.00 mLs by reducing the amount of water added to accommodate for the addition of the constant concentration cation. These titrations included: constant copper-paraquat titrant, constant paraquat-copper titrant, constant magnesium-paraquat titrant, constant paraquat-magnesium titrant, constant calcium-paraquat titrant, constant paraquat-calcium titrant, constant magnesium-copper titrant, constant copper-magnesium titrant, constant calcium-copper titrant, constant copper-magnesium titrant, constant calcium-magnesium titrant and constant magnesium-calcium

titrant. All titrations were performed at pH values of 3.00 and 5.00. Quantities for a typical experiment are shown in Table 3.

Titrations of humic acid with increasing concentrations of calcium, magnesium and paraquat; copper and paraquat were also carried out by adding appropriate aliquots of each cation. The final volume of 50.00 mLs was reached with water. A typical example is shown in Table 4.

For all the experiments at pH 5.00, humic acid was introduced into the sample container from a stock solution prepared as described below.

Table 3

Paraquat-Humic Acid Titration

Constant Copper pH 3.00

weight	mLs H_2O*	mLs MV^{+2}*	mLs Cu^{+2}*
0.00998	48.90	0.10	1.00
0.10770	48.80	0.20	1.00
0.01048	48.70	0.30	1.00
0.01019	48.60	0.40	1.00
0.01036	48.50	0.50	1.00
0.01000	48.40	0.60	1.00
0.01020	48.30	0.70	1.00
0.01365	48.20	0.80	1.00
0.01030	48.10	0.90	1.00
0.01200	48.00	1.00	1.00
0.01120	47.90	1.10	1.00

* Previously adjusted to pH 3.00

Copper stock solution 1.60×10^{-3} M

Paraquat stock solution 1.838×10^{-3}

Table 4

Multiple Cation Titration of Humic Acid

pH 5.00

mLs HA	mLs H_2O	mLs Ca	mLs Mg	mLs MV
2.00	47.40	0.200	0.200	0.200
2.00	46.80	0.400	0.400	0.400
2.00	46.20	0.600	0.600	0.600
2.00	45.60	0.800	0.800	0.800
2.00	45.00	1.000	1.000	1.000
2.00	44.40	1.200	1.200	1.200
2.00	43.80	1.400	1.400	1.400
2.00	43.20	1.600	1.600	1.600
2.00	42.60	1.800	1.800	1.800
2.00	42.00	2.000	2.000	2.000

4.1.5. Stock Solutions.

4.1.5.1. Sodium Hydroxide Solutions.

A 5 mL aliquot of 50% NaOH was diluted to 250 mls with previously boiled double deionized water. This gave an approximately 0.1 M NaOH solution. The final concentration was determined by standardization with potassium acid phthalate (KHP) to a phenolphtalein end point.

Sodium Hydroxide standard solution in background NaCl electrolyte was prepared exactly as above, but instead of water to dilute, 0.1 M NaCl solution was used.

4.1.5.2. Phosphoric Acid Standard Solution.

Ten mL of 85% Orthophosphoric acid, analytical reagent from Fisher Scientific, were diluted to 250 mLs with double deionized water. The approximate concentration was 1×10^{-3} M. This solution was standardized with standard 0.1 M NaOH solution. The end point was determined by the Gran's function method.

4.1.5.6. Copper Stock Solutions.

Copper stock solutions were prepared by dissolving an accurately known weight of 99% pure copper wire (approximately one gram) from Fisher Scientific, in 1:1 $HNO_3:H_2O$. Dissolution was enhanced by gently heating. Once the copper wire was totally dissolved, the solution was transferred quantitatively ot a 1 litre volumetric flask and diluted to the mark. This gave a copper concentration of about 1.6×10^{-2} Molar. This solution was further diluted to 1.6×10^{-3} M.

4.1.5.7. Magnesium Stock Solutions.

Approximately two grams of $MgCl_2.6H_2O$ were dissolved in double deionized water and diluted to one litre. The resulting solution was standardized by titrimetry with EDTA. Substock solutions were prepared from this solution ranging from 1×10^{-3} M to 1×10^{-1} M.

4.1.5.8. Calcium Stock Solutions.

Approximately two grams of calcium carbonate were accurately

weighed and carefully dissolved in dilute HCl. Dilution to one litre was carried out with double deionized water. The resulting solution was standardized with EDTA. Substock solutions were prepared from this solution by diluting appropriately with double deionized water. Concentrations ranged from 1×10^{-3} to 1×10^{-1} Molar.

4.1.5.9. Paraquat Stock Solutions.

About 0.8 grams of paraquat dichloride, 98% pure, from Chem. Service were dried in an oven at 100° C, cooled to room temperature, weighed and dissolved in double deionized water, followed by dilution to one litre. This gave a stock solution of approximately 8.00×10^{-3} Molar.

4.1.5.10. Copper Standard Solutions.

Copper standard solutions for atomic absorption were prepared by dissolving pure copper wire in 1:1 HNO_3 to give a 1000 ppm stock solution. This solution was further diluted to give standard solutions to cover the range from zero to 0.5 ppm Copper.

4.1.5.11. Magnesium Standard Solutions.

Magnesium metal was carefully dissolved in dilute HCl an diluted to give a 1000 ppm solution. Aliquots of this solution were diluted to cover the concentration range from 1 to 5 ppm magnesium.

4.1.5.12. Calcium Standard Solutions.

Calcium carbonate was carefully dissolved in dilute HCl and diluted to give a stock solution of 1000 ppm. Aliquots of this solution were diluted to cover the concentration range from 0 to 5 ppm calcium.

4.1.5.13. Paraquat Standard Solutions.

Standards for UV analysis were made by diluting paraquat stock solutions with acetate buffer pH 4.5. The concentration range covered was from 1.7×10^{-7} M to 2.0×10^{-5} M. Standards for HPLC analysis were obtained by diluting paraquat stock solution in double deionized water.

4.1.5.14. Laurentide Humic Acid Stock Solution (pH 5.00).

0.5000 grams of humic acid were suspended in 20 mls of double deionized water to which 0.1 M NaOH was added dropwise to increase the pH of the suspension to 5.00. The suspension was stirred constantly. Sodium hydroxide was added until no more changes in pH were observed. The suspension was quantitatively transferred to a 100 mL volumetric flask and diluted to the mark with water at pH 5.00.

4.1.6. HPLC Conditions for Paraquat Analysis.

Reverse Phase HPLC and UV spectrophotometry were used to detect paraquat in filtrates as well. A C_{18} (25cm x 2mm$^{\phi}$)column

from Chromatographic Science was used for HPLC. The mobile phase used was previously reported by Gill et al.(49) , and consisted of .2 grams of sodium heptanesulfonate mixed with 13.50 mLs of 85% orthophosphoric acid and 0.3 mLs of diethlyamine, dissolved in 1 litre of 25% v/v methanol:water. Flow rate was kept at 2 mLs per minute and, the pressure at 3000 psi. A sample chromatogram is shown in Appendix 5.

Chapter 5

5.1. Results and Discussion.

5.1.1. Titration of LHA with standard base (NaOH).

Titration curves for Laurentide Humic acid were obtained in the following way: electrode standardization was done by titration of a 1.00 x 10^{-3} molar orthophosphoric acid solution. The potentials recorded were plotted against volume of base added. The resulting calibration curve was fitted to polynomials at each decade by means of a Fortran routine provided by Dr. D. S. Gamble. Electrode potential readings for the sample were easily converted to hydrogen ion molarities. Equation (76) on Page (39) was used to determine the amount of acid remaining in the gel phase. Both quantities, hydrogen ion molarity, and moles of acid in the gel, phase were plotted against mLs of standard base added. Figures 3 and 4 show titration curves of Laurentide humic acid (LHA) in the absence and presence of background

electrolyte. The carboxyl content was determined by the use of Gran's function. The end point for the titration was calculated by graphical and analytical methods. The Gran's function was fitted to a polynomial of second degree and the end point was determined by iterative calculations. The Gran's function used was of the form $Y = V[H^+]$, as shown in figures 5 and 6. The number of moles of carboxyl groups per gram obtained represents an operationally defined quantity; that is, it is the quantity resulting from the vanishing of the Gran's functions. As has been mentioned by Perdue(64), the quantity of carboxyl groups determined depends on the method used. The assumption of the present method, is that at pH values higher than 7, all of the carboxyl groups are titrated. Extrapolation of the Gran's function to that region, should give an estimate of the carboxyl content. The carboxyl content determined in this way in the presence of 0,1 M NaCl was found to be 2.50 millimoles per gram. The same value was found in the absence of background electrolyte NaCl.

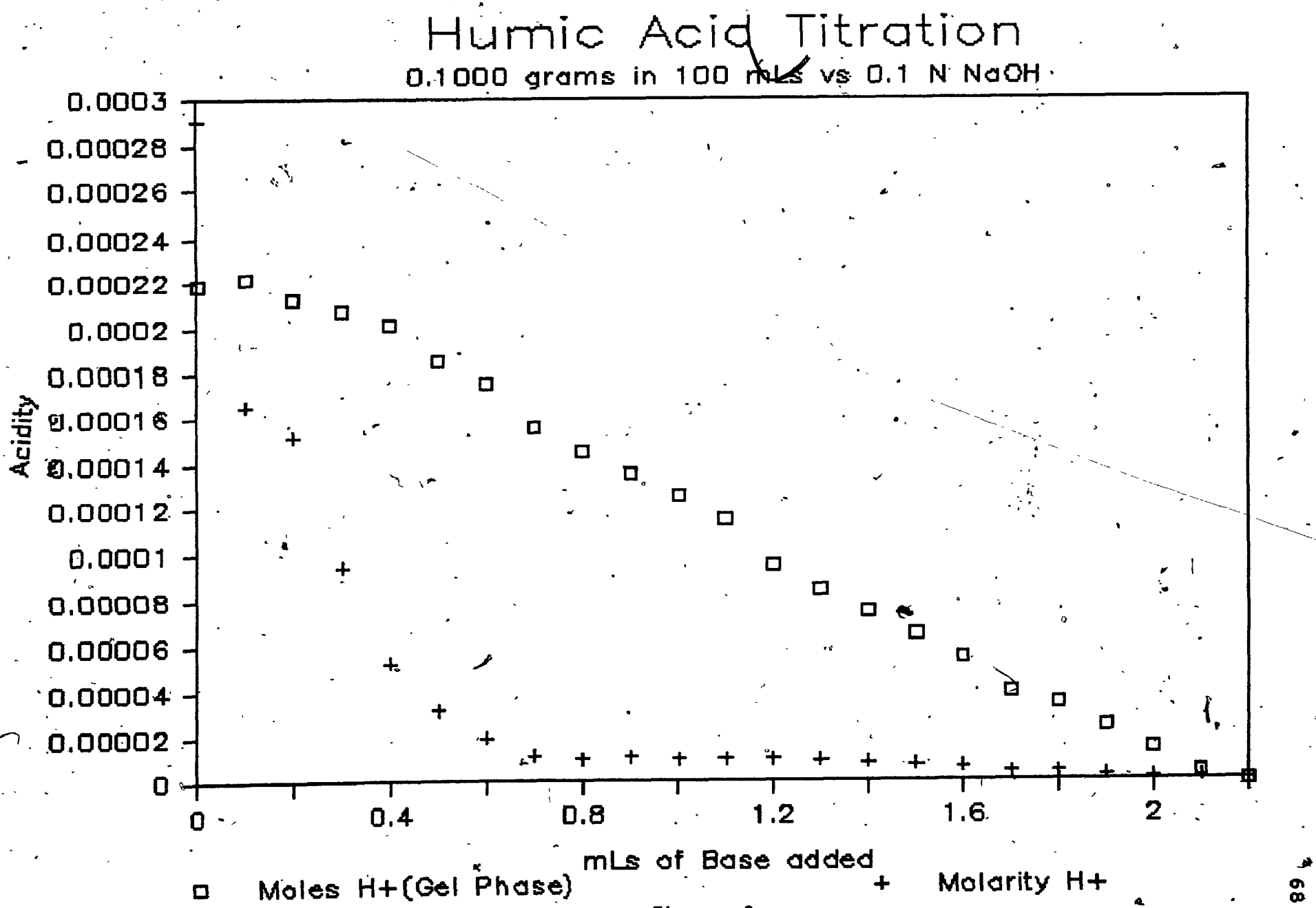
Humic Acid Titration
0.1000 grams in 100 mLs vs 0.1 N NaOH
Acidity
0.0003
0.00028
0.00026
0.00024
0.00022
0.0002
0.00018
0.00016
0.00014
0.00012
0.0001
0.00008
0.00006
0.00004
0.00002
0
0
0.4
0.8
1.2
1.6
2
mLs of Base added
Moles H+(Gel Phase)
Molarity H+

Figure 3

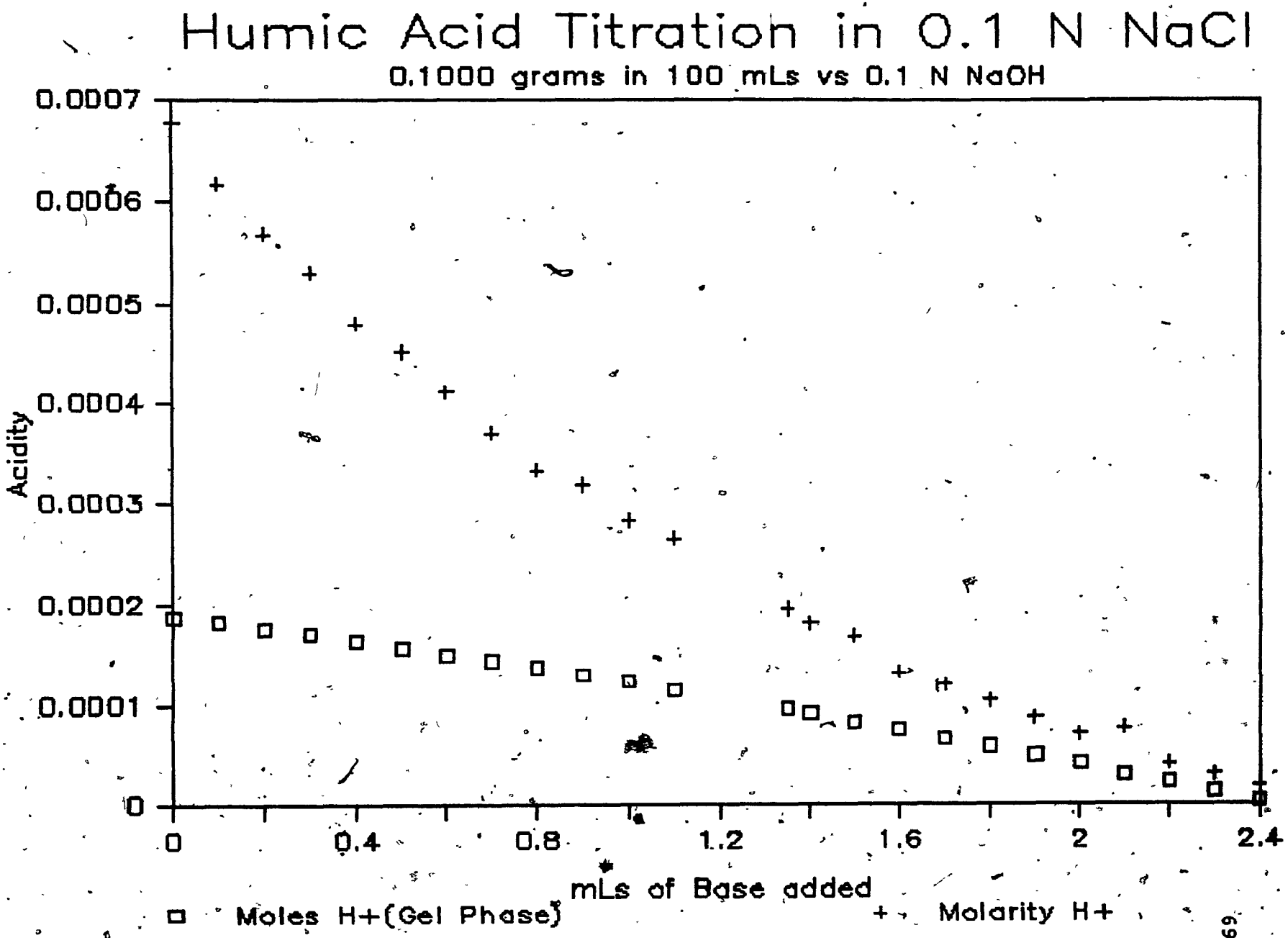
Humic Acid Titration in 0.1 N NaCl
0.1000 grams in 100 mLs vs 0.1 N NaOH
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
Acidity
0
0.4
0.8
1.2
1.6
2
2.4
mLs of Base added
Moles H+(Gel Phase)
Molarity H+

Figure 4

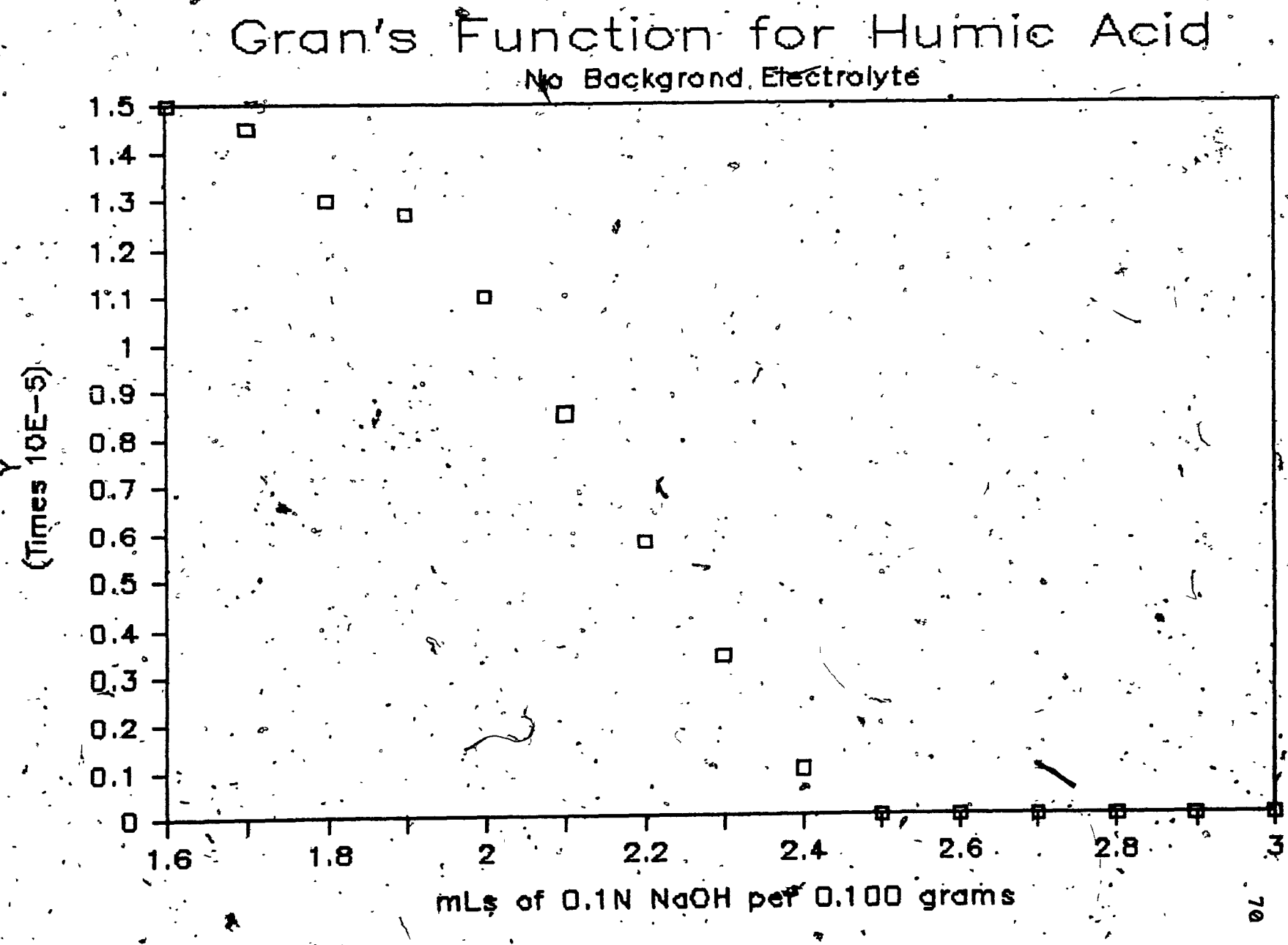
Gran's Function for Humic Acid
No Background Electrolyte
Y (Times 10E-5)
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
1.6
1.8
2
2.2
2.4
2.6
2.8
3
mLs of 0.1N NaOH per 0.100 grams

Figure 5

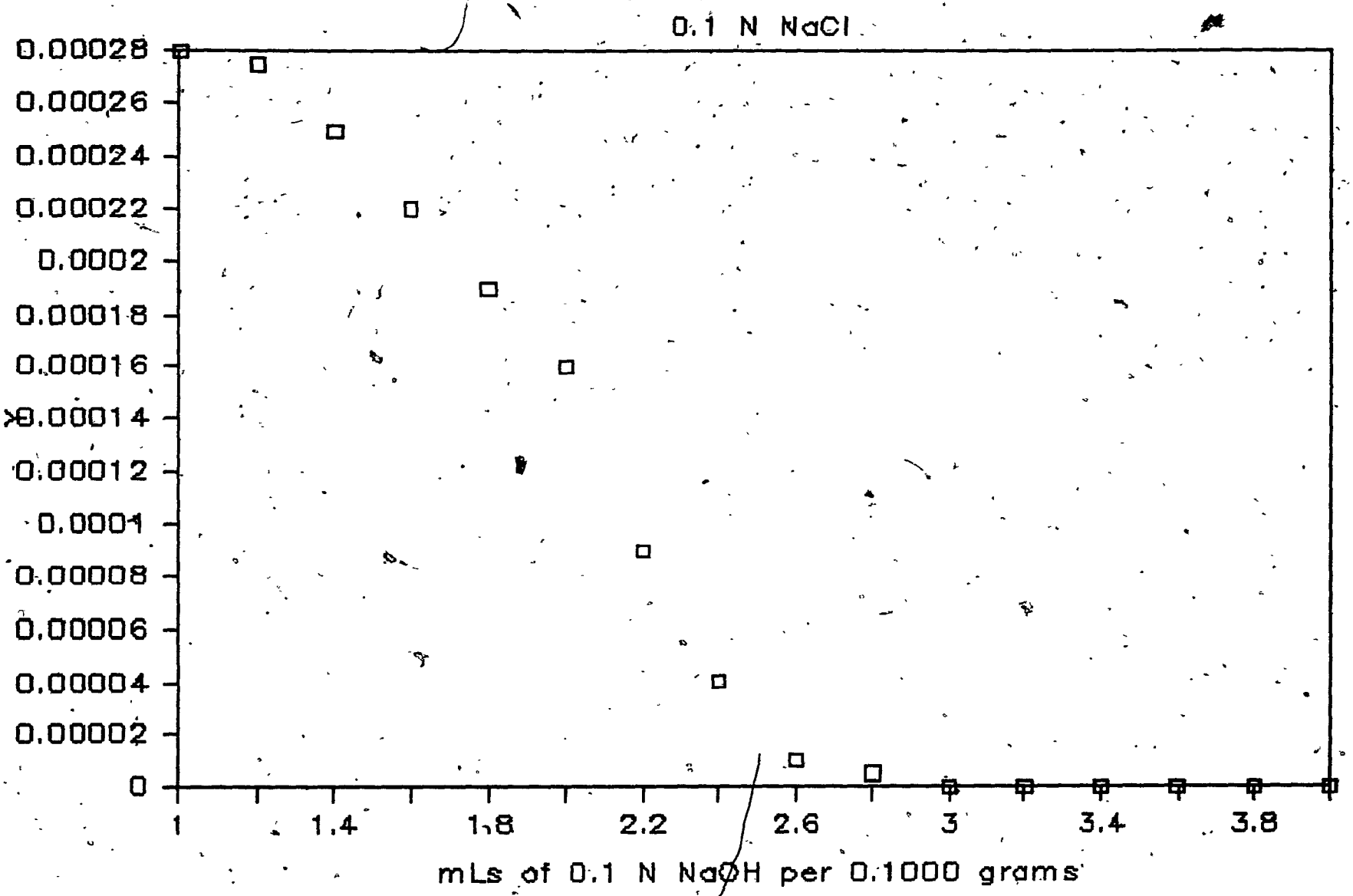
Gran's Function for Humic Acid
0.1 N NaCl
0.00028
0.00026
0.00024
0.00022
0.0002
0.00018
0.00016
0.00014
0.00012
0.0001
0.00008
0.00006
0.00004
0.00002
0
1
1.4
1.8
2.2
2.6
3
3.4
3.8
mLs of 0.1 N NaOH per 0.1000 grams

Figure 6

Table 5

Analytical Properties of Laurentide Humic Acid

Element	Content
C	51.9 %
O	39.9 %
H	5.5 %
N	2.3 %
S	0.26 %
Total Acidity	7.60 mmoles/gr 10%
COOH	2.50 mmoles/gr 5%
OH	5.1 mmoles/gr 10%
Ash	< 0.1%

In the case of humic acid at zero ionic strength, the amount of carboxyl groups ionized at pH 5.00 is less than the amount ionized at the same pH but in the presence of background electrolyte. This must be kept in mind when correlating binding capacities with carboxyl content.

For extrapolating purposes, the titration curve plotted as percent acid remaining in the gel phase against the volume of base at zero ionic strength, was fitted to a polynomial. This is shown in figure 7. It can be seen that Figure 4 has a smaller

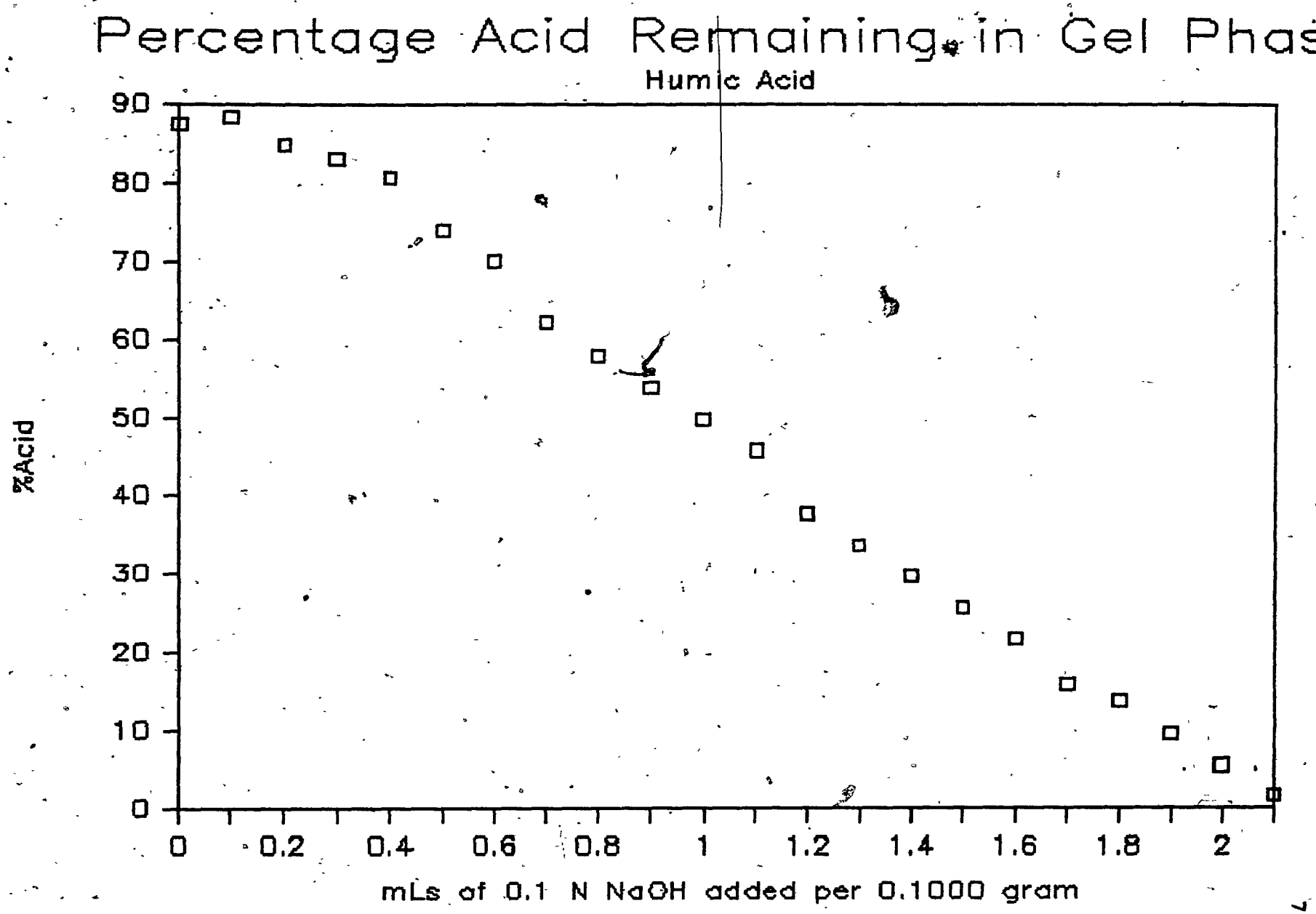
Percentage Acid Remaining in Gel Phase
Humic Acid
%Acid
90
80
70
60
50
40
30
20
10
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
mLs of 0.1 N NaOH added per 0.1000 gram

Figure 7

slope than the equivalent curve for the acid present in the external solution.

At pH 5.00 and zero ionic strength, the percentage of acid still in the gel is about 61.7% of the total amount. This represents only about 1.00 mmoles/gr of ionized sites.

The titration curve in the presence of background electrolyte 0.1 M NaCl is similar to the one in the absence of NaCl. In the former, the gel curve is flattened with respect to that in Figure 3. This is due to the ion exchange taking place between sodium and hydrogen ions. The initial pH is lower due to the release of protons by excess sodium ions. The decrease of the solution phase acid shows a smaller slope in the presence of sodium chloride. This can be explained by the fact that a larger fraction of the total acid has been released into solution, and the remaining amount of acid in the gel is relatively weak; this means that in order to see a larger decrease in the concentration of protons in the external solution a larger aliquot of base must be added, provided that the same concentration is used.

5.1.2. Redox Properties of Laurentide Humic Acid.

The analysis of the redox properties of humic substances is rather complicated. The origin of the complications lies in the heterogeneity of the functional groups making up the total

acidity of the sample and their polyelectrolytic character. Marinsky et al.(14,15,16) has developed a methodology useful in assessing the contributions of the polyelctrolyte effect to the dissociation functions of fulvic acids. The regolution of the electrostatic field component to the apparent pKa has been achieved in the case of various fulvic acid samples(15), by screening off the charge developed at the surface of the molecules during titration with standard base. For fulvic acids, at high background electrolyte concentrations, the plot of apparent pKa against the degree of ionization is an increasing function. This has been interpreted, as due to the heterogeneity of the acidic functionalities of the sample; since the polyelectrolyte effect has been minimized by the high the high concentration of background electrolyte.

At this point, resolution of the heterogeneity factor follows two main approaches. Marinsky(15) has pointed out, that the heterogeneity in these systems, can be sorted out by resorting to discrete sites. The other interpretations, put forward by Gamble(9), Buffle(50) and Perdue(51), among others, assumes the existence of a continuous distribution of sites, resulting from the similarities in pKa's; values of which are too close to be resolved. In the light of the evidence presented so far for the case of fulvic acids(15,16,52), a merging of the two models is needed.

5.1.2.1. Application of Marinsky's Methodology to the Potentiometric Data for Laurentide Humic Acid.

The potentiometric data obtained during titrations of Laurentide Humic Acid with standard base were analyzed using the methodology developed by Marinsky(15). Plots of apparent acidity constants (pK_{app}) against the degree of ionization were produced. The degree of ionization was estimated by subtracting the amount of acid remaining in the gel as determined by Equation (76) on Page (38) from the total carboxyl content.

Figure 8 shows the apparent pKa for humic acid plotted against the degree of ionization at two different ionic strengths. The most striking feature is that the variation of pK_{app} is not as prominent as has been reported for fulvic acids (15,16). This is not due to underestimations of the degree of ionization. The lower curve in Figure 8, indicates that variations of pK_{app} with the degree of ionization are very small.

The significance of these results is that the humic acid under investigation presents a rather simple spectrum of dissociation constants, modelled by a single discrete value. The intersection of the two curves in Figure 8 provides an estimate of an "intrinsic" pKa values of approximately 3.70.

Another piece of information that can be obtained is an estimate of the electrostatic field developed at the surface of the humic acid molecule. Assuming that the bottom curve in Figure 9 represents the situation where the electrostatic

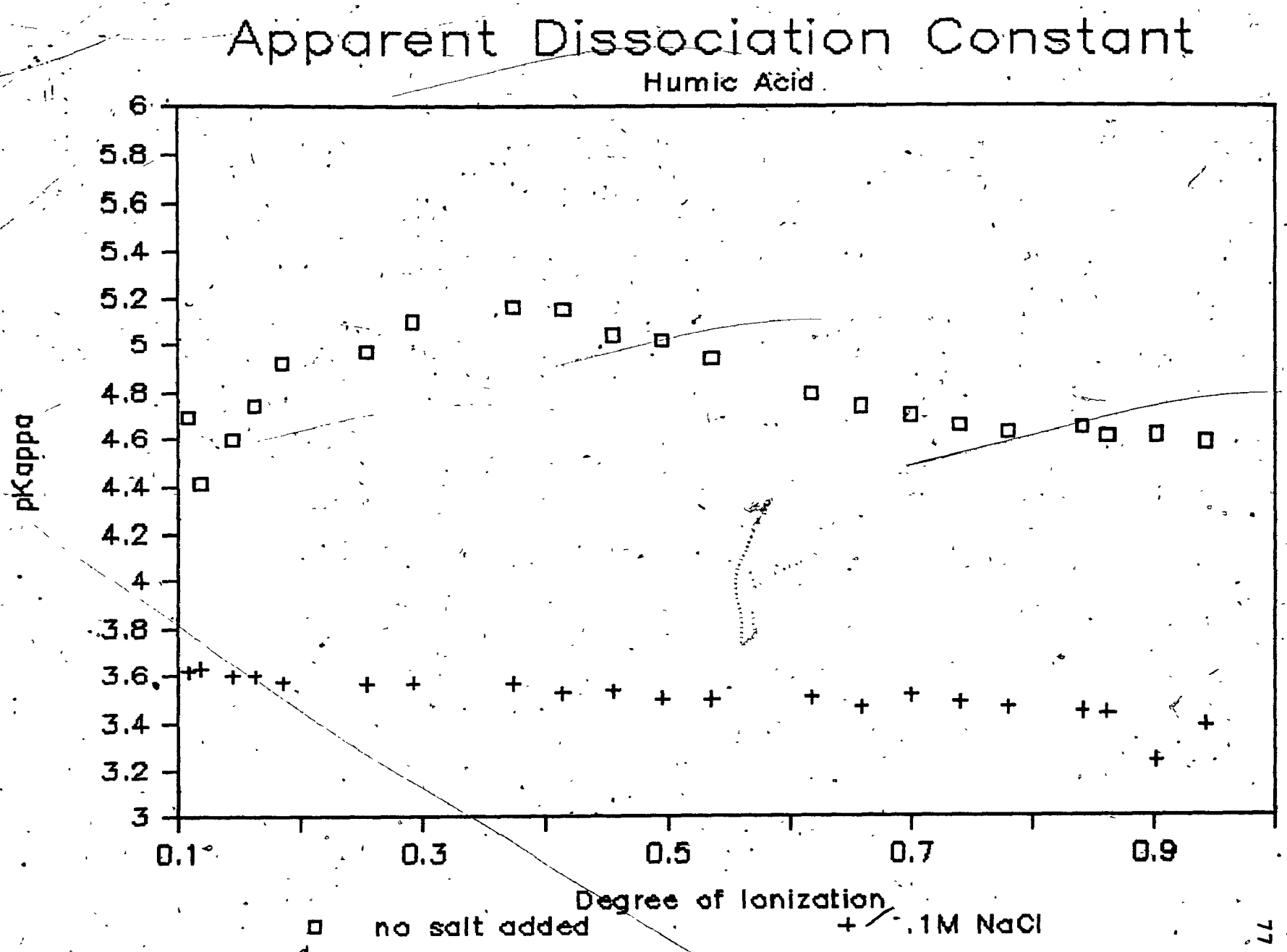
Apparent Dissociation Constant
Humic Acid
pKapp
6
5.8
5.6
5.4
5.2
5
4.8
4.6
4.4
4.2
4
3.8
3.6
3.4
3.2
3
0.1
0.3
0.5
0.7
0.9
Degree of Ionization
no salt added
.1M NaCl

Figure 8

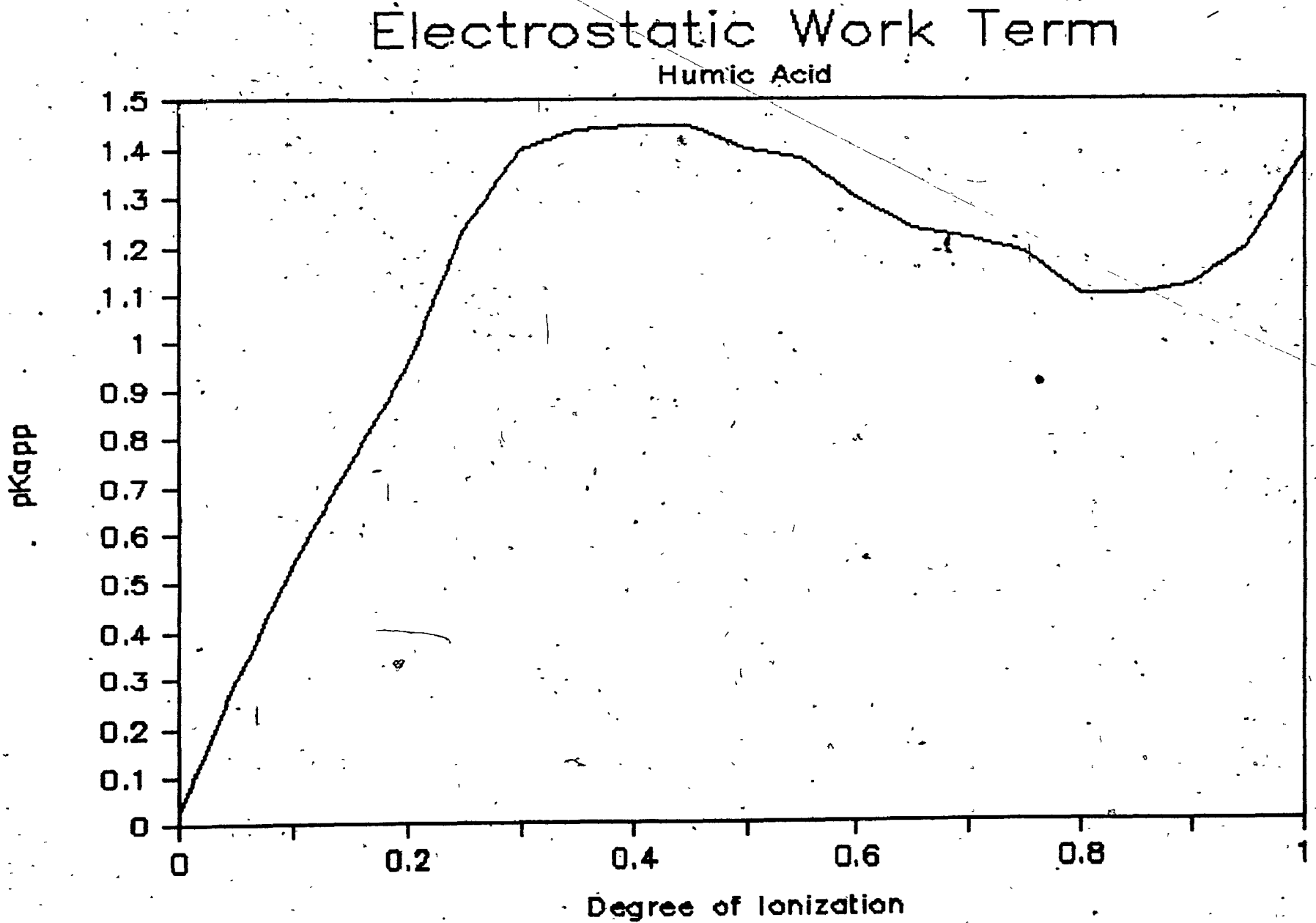
Electrostatic Work Term
Humic Acid
pKapp
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
Degree of Ionization

Figure 9

potential has been screened by background electrolyte, the difference between the upper curve and the bottom one provides an estimate of the electrostatic field at zero background electrolyte. This plot is shown in Figure 9.

The pK^{app} is a unique function of pH alone for a rigid gel impermeable to salt. This seems to be the case for the Laurentide Humic Acid which is rather surprising. A plot of apparent pK^a against pH in the external solution shown in Figure 10 indicates just that. There is a discontinuity in the function at about pH 5.00. The presence of a discontinuity as shown in the low ionic strength plot has been attributed by Marinsky to changes in the polymer configuration. The origin of the discontinuity seen here may be a change in the configuration of the humic acid polymer. The structure of humic acid goes through rather drastic changes during titration; from a gel phase into a "dissolved" polyelectrolyte. The position of the discontinuity can be located at about pH 5.00; it coincides with the almost total dissolution of the humic gel as detected by visual examination of the sample. This takes place at pH just below 5. "Precipitation" in the context of this discussion is taken as the situation in which large particles can be seen to settle by no other aid than the naked eye. It is understood that more sophisticated methods of detecting the onset of coagulation or precipitation can sharpen this observation.

In the potentiometric analysis done by Marinsky (53,54) on a

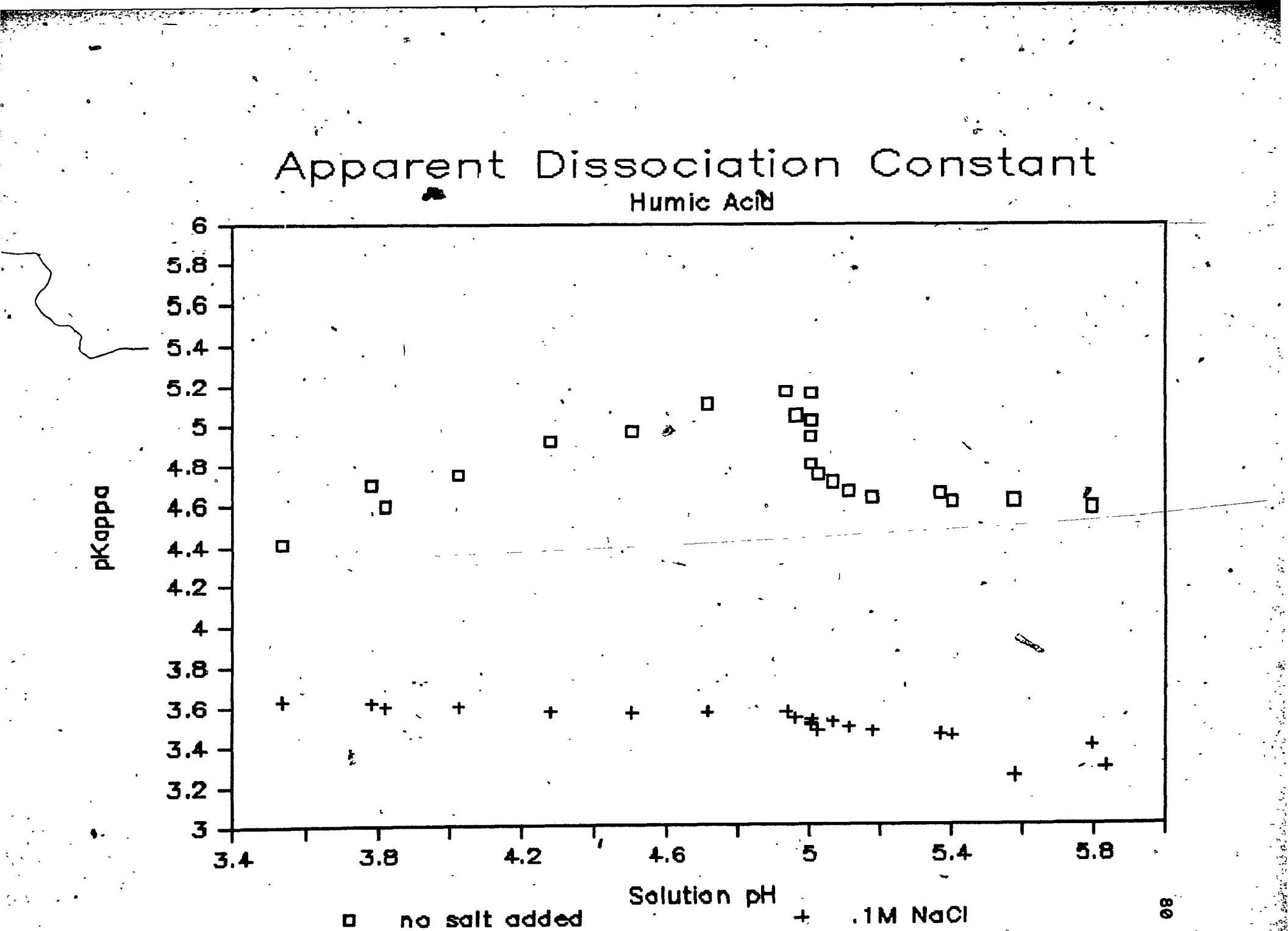
Apparent Dissociation Constant
Humic Acid
pKappa
6
5.8
5.6
5.4
5.2
5
4.8
4.6
4.4
4.2
4
3.8
3.6
3.4
3.2
3
3.4
3.8
4.2
4.6
5
5.4
5.8
Solution pH
no salt added
.1M NaCl

Figure 10

humic acid sample, this discontinuity was not present. This could have been due to the treatment that the humic acid sample underwent prior to titration. In that particular experiment, the sample was subjected to a cycle of acid-base treatment by adding stoichiometric amount of HNO_3 and NaOH alternatively. It was found, during the course of this study, that the dissolution-precipitation equilibrium for humic acid is quite dependent on the concentration of humic acid, At concentrations less than 0.1 gram per litre, precipitation of humic acid by addition of acid was not noticeable. Precipitation was evident to the eye at concentrations larger or equal to 1 gram per litre. The use of the treatment described by Marinsky could have been the cause for the disappearance of the discontinuity.

The results presented in this section indicate that the acidic functionalities titratable with base in aqueous medium for Laurentide humic acid could be modelled by single value for the ionization constant. This may be due to the low carboxyl content of the sample. A value of 3.70 has been resolved as the average intrinsic pK^a for the acidic sites. This result has a significant bearing on the interpretation of metal ion binding.

5.1.3. Paraquat Speciation Methodology.

The main problem in equilibrium studies in natural water systems is the speciation technique. That is, the researcher is

interested in obtaining a picture of the equilibrium situation at a given time with the minimum disturbance of the equilibrium itself. In the case of the interaction of a limited number of metal ions with humic substances, ion selective electrodes are available which make the problem of speciation easier or at least tolerable. Ion selective electrodes have their advantages and disadvantages in these studies, but an inspection of both is beyond the limit of this dissertation.

The problem is complicated in the case of herbicides and metal ions which cannot be detected by ion selective electrodes or any of the electrochemical technique available such as anodic stripping or potentiometric stripping analysis. In these situations, physical separation techniques are employed to differentiate between bound and free species.

The methodologies employed so far in the speciation of paraquat in humic acid suspensions have all involved dialysis or centrifugation combined with a detection technique, usually ultraviolet spectroscopy. Khan (38,55) reported the need for background correction in the analysis of supernatants after centrifugation due to peptization of humic acid. The fact that humic substances have a wide absorption spectrum which cover most of the visible and the ultraviolet creates problems in the analysis of substances by spectrophotometric analysis. Humic substances must be effectively removed from solution prior to analysis without perturbation of the equilibrium conditions. Guy

et al. (4,4a) employed dialysis as means of speciation in paraquat humic acid suspensions. There is a definite advantage in the use of dialysis-spectrophotometry as compared to the use of centrifugation-spectrophotometry. Dialysis allows for more control on the separation step by controlling the pore size of the dialysis material the retention of humic acid can be controlled. Another speciation (6) methodology reported in the literature (perhaps the first one applied to the study of paraquat humic acid suspensions) was the use of centrifugation coupled with counting of ^{14}C radioactivity.

One overlooked factor in equilibrium speciation techniques, including dialysis and centrifugation, is that humic substances change their configuration depending on the solution conditions. At low pH values and high ionic strength the humic acid molecule is out of solution in the form of aggregates, while at high pH values (higher than 4) the humic acid molecules are "dissolved" forming a polyelectrolyte solution or micro-gel suspension. The size of the humic moieties at different pH values will then, produce artifacts in the detection of substances by spectrophotometry and the conditions during the separation may vary enough to produce complex changes in the humic acid sample.

5.1.3.1. Ultrafiltration technique for the speciation of paraquat in humic acid suspensions.

The use of ultrafiltration as a speciation technique has

been widely reported (56,57,60). Most applications dealt with metal ion speciation. One of the first applications of ultrafiltration to the speciation of herbicides in humic material suspensions was reported by Haniff (5). A batch ultrafiltration method was developed for the speciation of atrazine in fulvic acids solutions. Up to now there are no reports in the literature on the application of ultrafiltration to the speciation of paraquat in humic acid suspensions.

The methodology employed for the case of paraquat and humic acid has been already developed by Gamble et. al.(58,59). The basics behind the method are described in the Appendix (1).

5.1.3.2. Ultrafiltration of paraquat-humic acid suspensions.

The membrane employed in this study was the Amicon YM2 which has a molecular weight cut-off of 1000. The retention of humic acid by YM2 membranes was monitored by taking spectrophotometric readings at 255 nm of the filtrates from suspensions at different pH values. Figure 11 shows the absorbance of the filtrates against the weight of humic acid used per 50 mls of suspension. The absorbance readings are constant and very close to zero for concentrations up to 0.3 grams per litre for all pH values. For higher concentrations, the absorbance of the filtrates increased dramatically. There is a clear dependence of the retention of humic acid by YM2 membranes and the concentration of humic acid. This is obviously due to the passage of humic acid through the

membrane as the concentration increases.

The use of UV spectrophotometry to detect paraquat in the filtrates will be affected by the concentration of humic acid in the suspension. This is seen in Figure 12. For concentration of humic acid in suspension greater than 0.3 grams per litre (about 2 mg) the apparent concentration of paraquat in the filtrate is grossly overestimated compared with the concentration as detected by HPLC. The advantage of HPLC over UV spectrophotometry is clear. The HPLC conditions used allow for a clean separation of the interference caused by humic acid in the filtrate. Another advantage of HPLC is that it requires little filtrate volume for analysis, filtrate volumes of less than 1 ml are enough to provide enough solution to clean the syringe and inject the sample into the chromatograph. Typical injection volumes were 25 microlitres. UV required larger filtrate volumes, between 1 and 5 mLs depending on the dilution that was to follow.

The main advantage of UV over HPLC is an improved detection limit since the cell path length used (1 cm) is much larger than that in the HPLC UV detector. Another advantage is the analysis time. The retention time for paraquat under the chromatographic conditions previously specified was approximately 8 minutes once the column had been equilibrated. Another problem encountered with HPLC was that after about twenty samples were analyzed, the column response began to deteriorate. This may be due to column blocking by some humic material remaining in

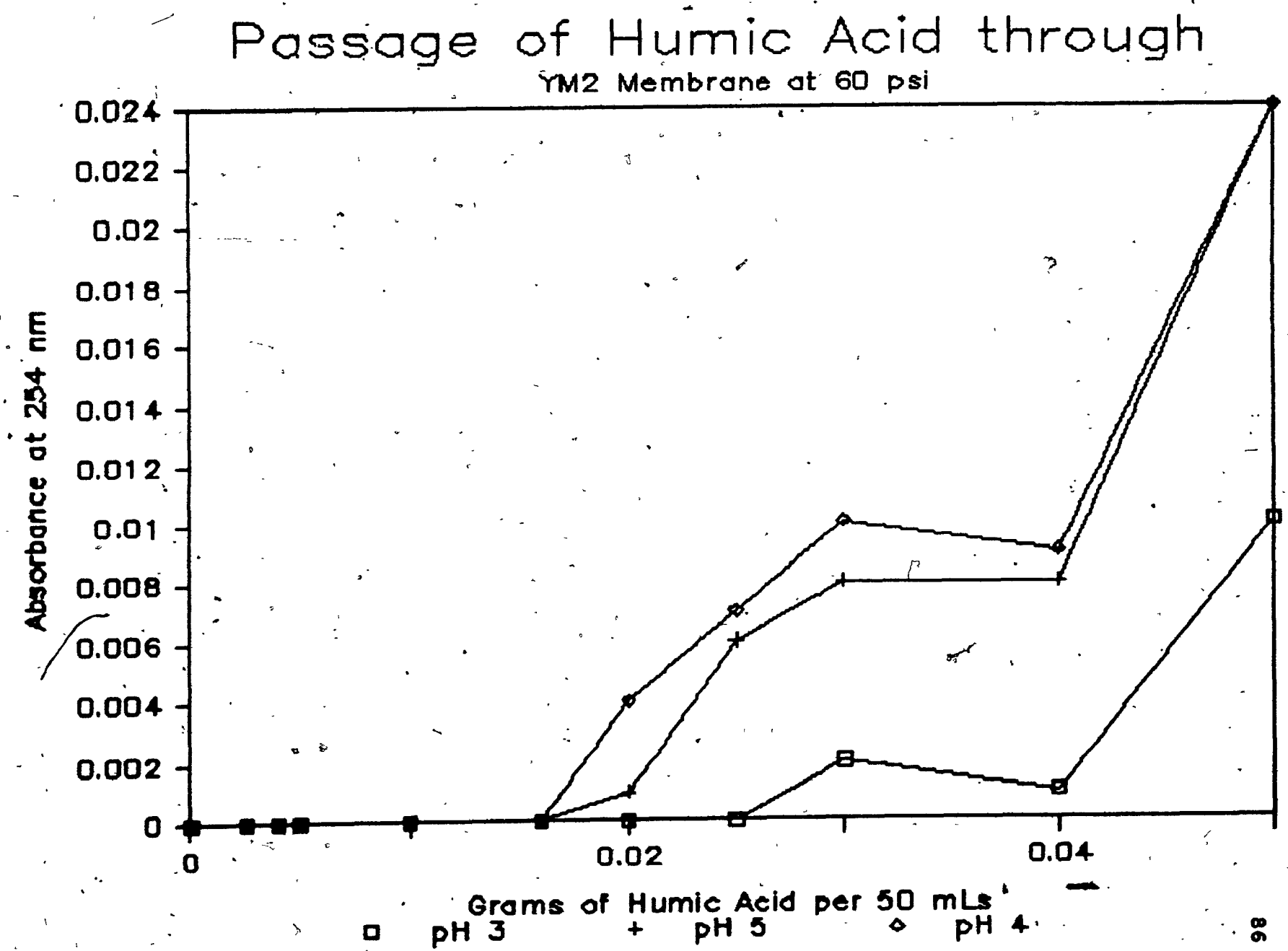
Passage of Humic Acid through
YM2 Membrane at 60 psi
Absorbance at 254 nm
0.024
0.022
0.02
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0
0.02
0.04
Grams of Humic Acid per 50 mLs
pH 3
pH 5
pH 4

Figure 11

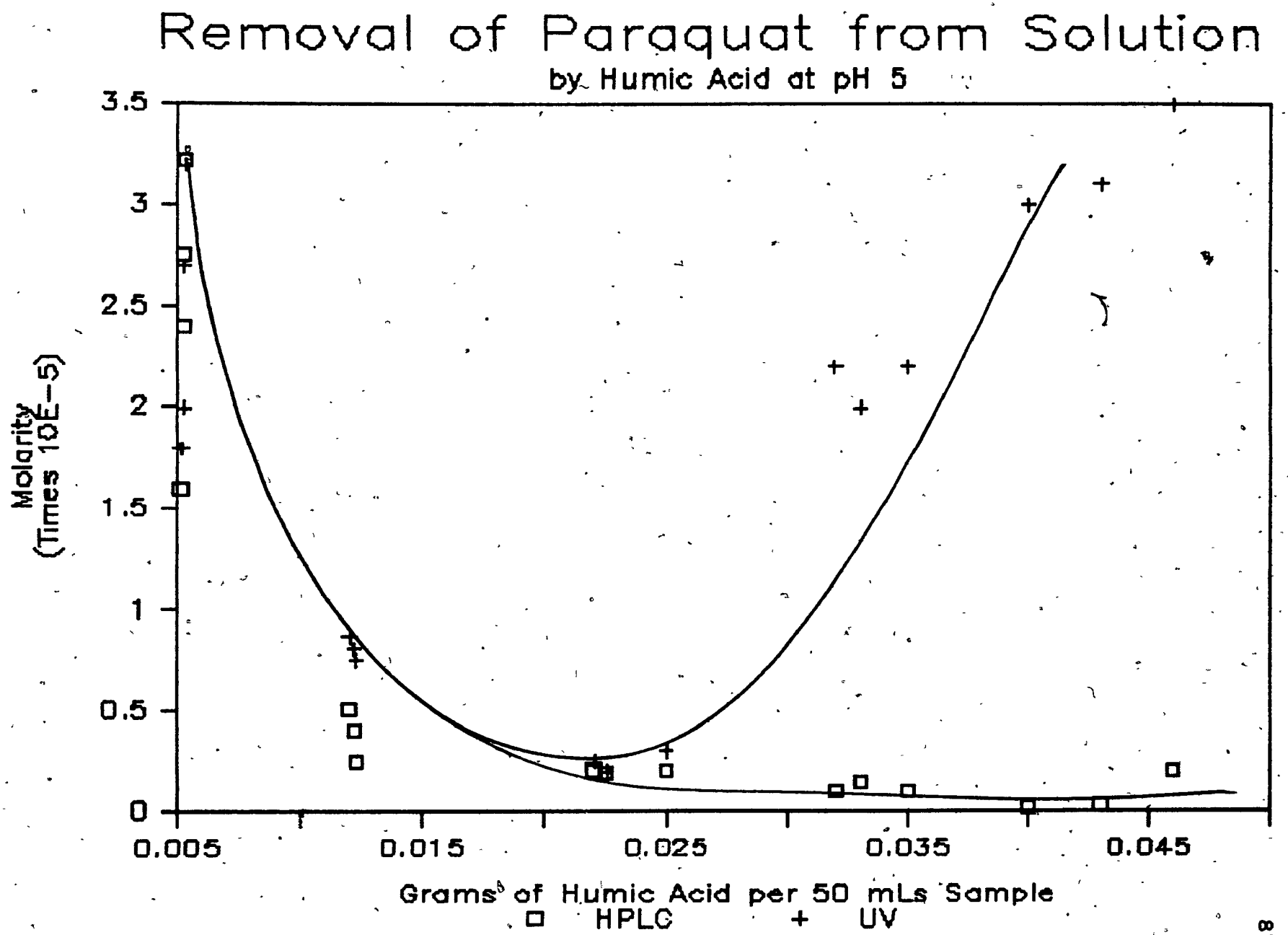
Removal of Paraquat from Solution
by Humic Acid at pH 5
Molarity
(Times 10E-5)
3.5
3
2.5
2
1.5
1
0.5
0
0.005
0.015
0.025
0.035
0.045
Grams of Humic Acid per 50 mLs Sample
HPLC
UV

Figure 12

the column. Extensive washing by flushing through large volumes of mobile phase was required to regenerate the column. The use of a column with a lager particle size did not improve the situation.

Based on the results shown in Figure 12 there is no significant difference in the detection of paraquat by HPLC or UV in samples containing 10 milligrams of humic acid per 50 milliliters. Due to a short supply of humic acid, the amount used for each batch experiment was approximately 12 milligram per 50 milliliters of suspension. UV was the method of chosen for analysis because it is rapid and gives a lower detection limit. To show the reproducibility of both methods a binding curve for paraquat on humic acid is shown in Figure 13. The analysis of paraquat after ultrafiltration was done by UV and HPLC. It can be seen that there is no significant difference in the binding curves obtained by the two methods. What difference exists can be attributed to the errors involved in both procedures. The UV method required dilution of the filtrate for the high concentration range tested. This involved pipetting of the filtrate and a dilution step. In contrast, the HPLC method required only that the filtrate be injected directly into the HPLC unit.

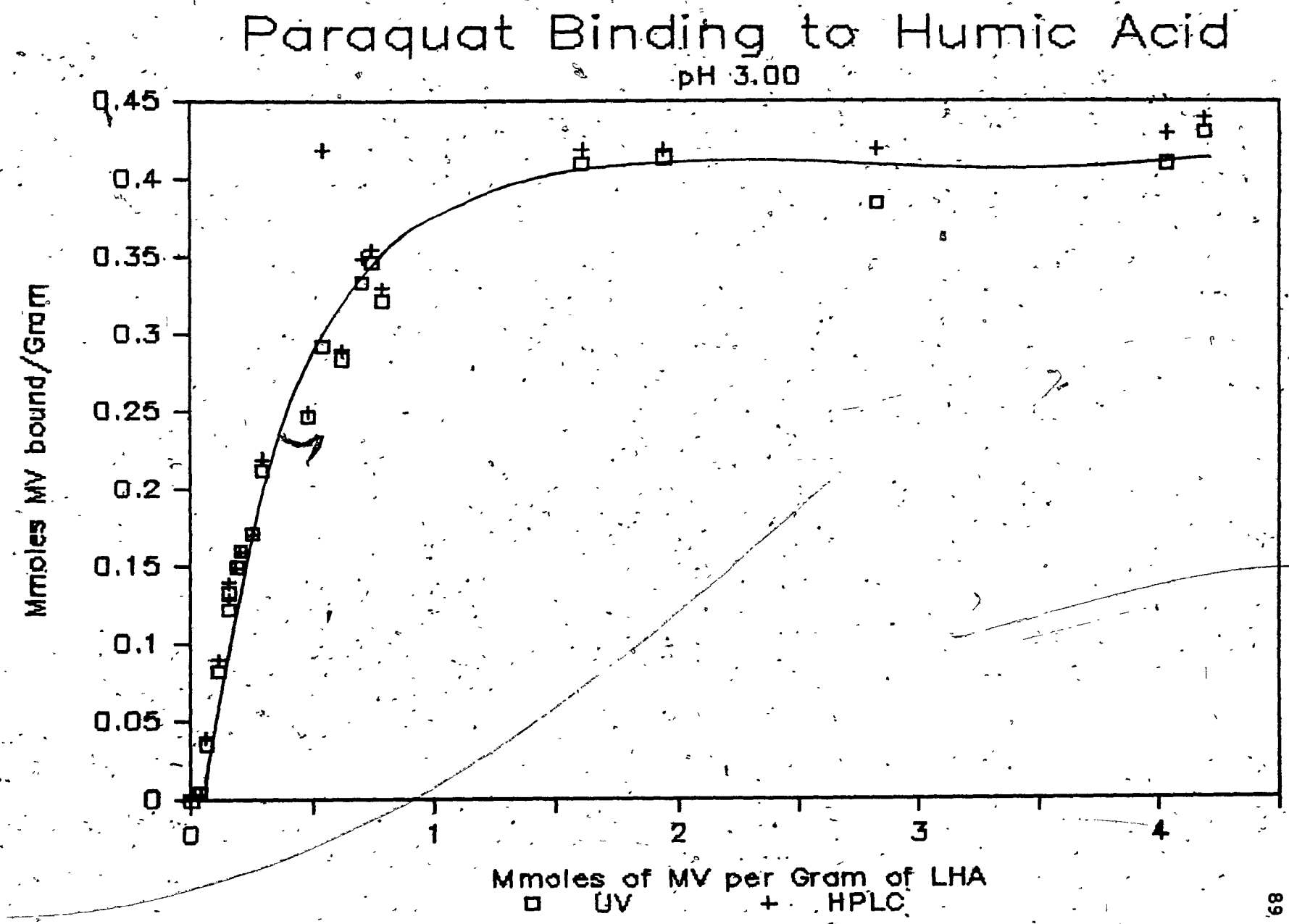
Paraquat Binding to Humic Acid
pH 3.00
Mmoles MV bound/Gram
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
1
2
3
4
Mmoles of MV per Gram of LHA
□ UV + HPLC

Figure 13

5.1.3.3. Batch ultrafiltration method for the speciation of paraquat.

Figure 14 shows a batch titration of Laurentide humic acid with paraquat at pH 3. The upper curve represents the results with the control samples, while the lower one represents the concentration of paraquat in the presence of humic acid. It can be seen that the curve for control is linear throughout the concentration range explored. The shape of the lower curve depends on the chemistry of the humic acid-paraquat system. The difference between the upper and lower curves represents the amount of paraquat bound to humic acid.

The utility of this type of plot has been extensively discussed by Gamble et al.(58,59). The upper curve provides a membrane calibration curve. In the absence of any membrane effects such as sorption and or rejection of paraquat, the slope of the control curve must be equal to the concentration of the stock solution divided by the sample volume and the intercept equal to zero. Undesirable membrane effects would show up on the slope and intercept of the control curve.

The sorption or rejection of paraquat by the membrane at low concentrations followed by breakthrough of paraquat at high concentration will show up as a negative intercept. Desorption of paraquat previously sorbed will be indicated by a positive intercept. Total rejection of paraquat would give a slope of

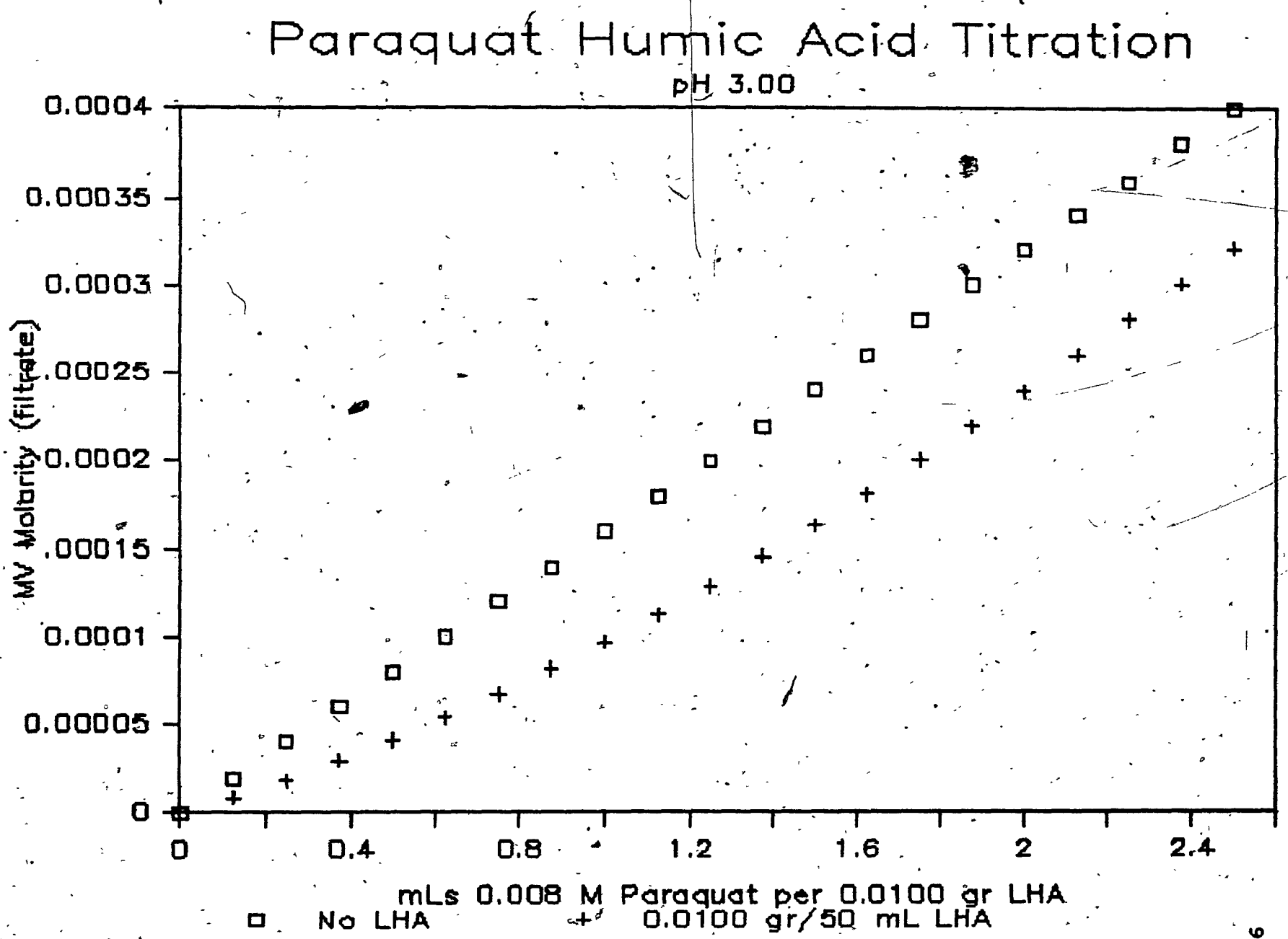
Paraquat Humic Acid Titration
pH 3.00
0.0004
0.00035
0.0003
.00025
0.0002
.00015
0.0001
0.00005
0
MV Molarity (filtrate)
0
0.4
0.8
1.2
1.6
2
2.4
mLs 0.008 M Paraquat per 0.0100 gr LHA
No LHA
0.0100 gr/50 mL LHA

Figure 14

zero. Partial rejection by the membrane will give a slope of less than the predicted value. In experimental situations the intercepts and slopes of the membrane calibration curves were not exactly as predicted above. In the case of paraquat and metal ions such as calcium, copper and magnesium, it was found that the intercepts and slopes deviated somewhat from the expected values. Typical ultrafiltration membrane control curve data for paraquat are shown in Table 6.

Table 6

Ultrafiltration Membrane Calibration Curves for Paraquat

pH	Slope		Intercept	Conditions
	theo	exp		
	x10+4 M/mls		x10+6 M	
3.00	1.636	1.603	6.176	----------
3.00	1.589	1.037	4.590	0.01M NaCl
3.00	1.589	1.006	2.281	0.10M NaCl
3.00	1.268	1.032	-6.598	0.01M $NaNO_3$
3.00	1.636	1.382	11.540	0.10M $NaNO_3$
3.00	0.939	0.945	-2.295	0.10M NaCl
5.00	1.482	1.347	-1.256	0.10M NaCl
5.00	1.482	1.400	-0.324	----------
3.00	1.246	1.013	2.527	Cu
4.00	0.530	0.520	2.920	Cu
5.00	0.400	0.416	-1.290	Ca,Mg
3.00	1.636	1.599	1.043	Mg
5.00	1.636	1.599	-0.156	Mg
3.00	1.636	1.579	-7.254	Ca
5.00	1.483	1.460	-0.636	Mg
2.00	1.375	1.339	-1.418	----------
5.00	1.375	1.340	-1.500	Mg
5.00	1.482	1.570	-1.173	----------

Standard deviation for intercept= 1.18×10^{-6}

intercept mean value= 7×10^{-6} M

There is a large experimental scatter in the slope and the intercepts. Correlation of the intercepts and slope with pH and ionic strength did not give any significant results. The deviations of the intercept from zero fall within experimental error. Similar errors were found for the case of atrazine and fulvic acid(58,59). The lack of correlation between the intercepts and parameters such as pH and ionic strength leads to the conclusion that the errors involved are random analytical errors inherent to the technique and the sample manipulation procedures involved. There was no difference in the errors observed using HPLC or UV spectrophotometry as detection systems.

The membrane calibration tests, as described above, allowed for empirical corrections in determining the amount of herbicide free in solution. The general procedure in the calculation of a batch titration curve, consisted in securing a membrane calibration curve first, followed by the curve produced by the sample solutions. In order to minimize errors due to repetitive calculations the preparation of a standard calibration curve for paraquat was bypassed. To do this, use was made of solutions of accurately known concentrations, therefore, the signal or absorbance read for each control solution was related directly to its concentration. (The alternative was to calculate each concentration by means of a calibration curve and then relating it to the volume of stock solution used, as shown in Figure 14.)

Since the weight of humic acid was not exactly the same for each sample in a batch titration, the control curve was expressed as absorbance (corrected for any dilution) versus millimoles of titrant, paraquat in this case. From this it was possible to determine millimoles of free paraquat, given the absorbance, for each sample to be obtained. In this situation, and in the absence of any membrane effects, the intercept of the control curve should be zero with the slope depending on the instrument as well as the concentration range used. Any deviation from zero will indicate the presence of undesirable membrane effects.

5.1.3.4. Speciation Techniques for Metal Ions.

The speciation technique used for copper, calcium and magnesium was the same as that used for paraquat.

Ultrafiltration has been used extensively in the speciation of metal ions in natural water samples, as well as in humic material suspensions. Guy and Chakrabarti(60) described the technique as applied to metal ions such as lead, copper and cadmium. Buffle(57) has, recently, investigated membrane effects on the ultrafiltration of a variety of metal ions.

Membrane test curves for copper, calcium, magnesium and paraquat are shown in Figures 15 to 18.

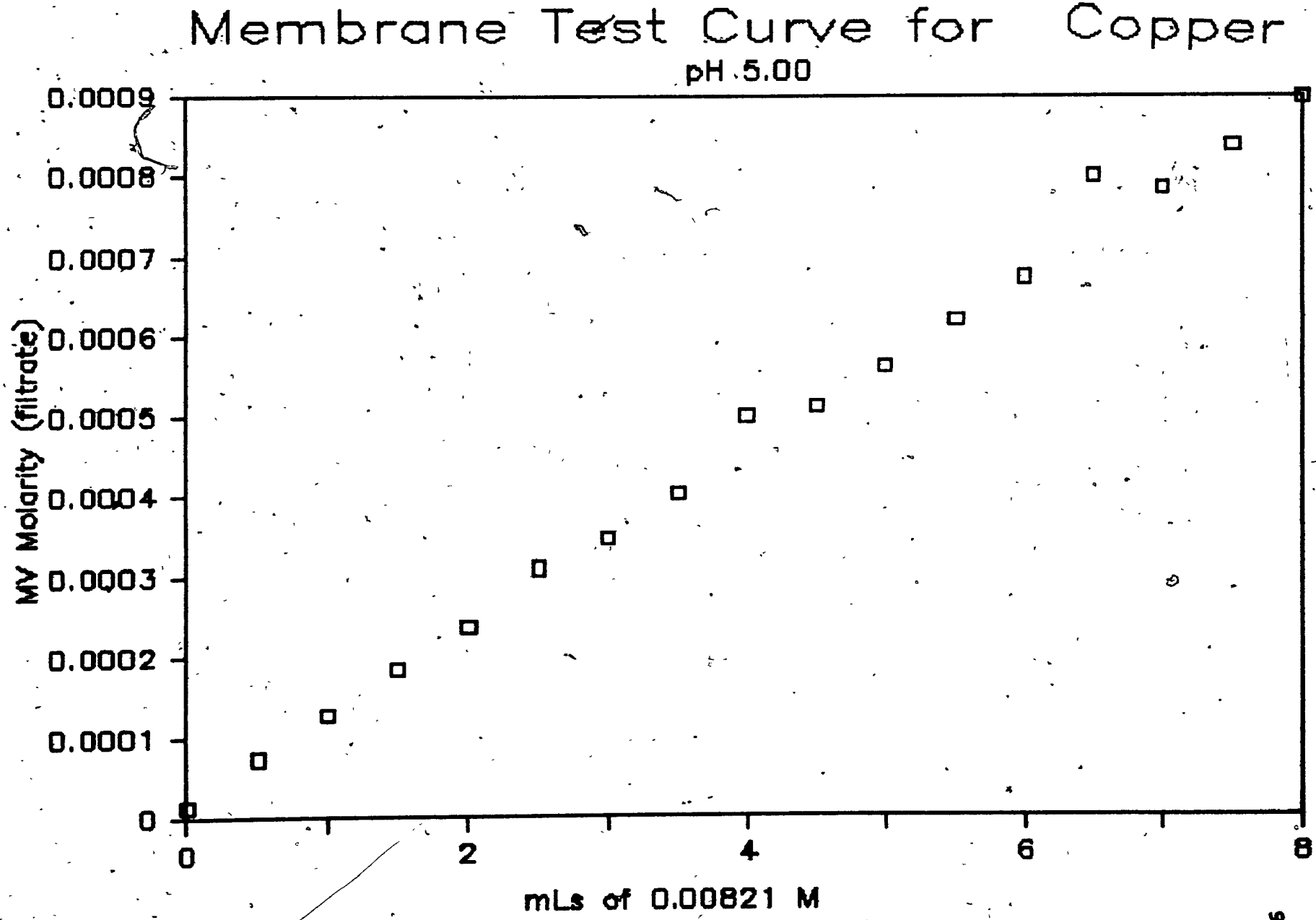
Membrane Test Curve for Copper
pH 5.00
MV Molarity (filtrate)
0.0009
0.0008
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
0
2
4
6
8
mLs of 0.00821 M

Figure 15

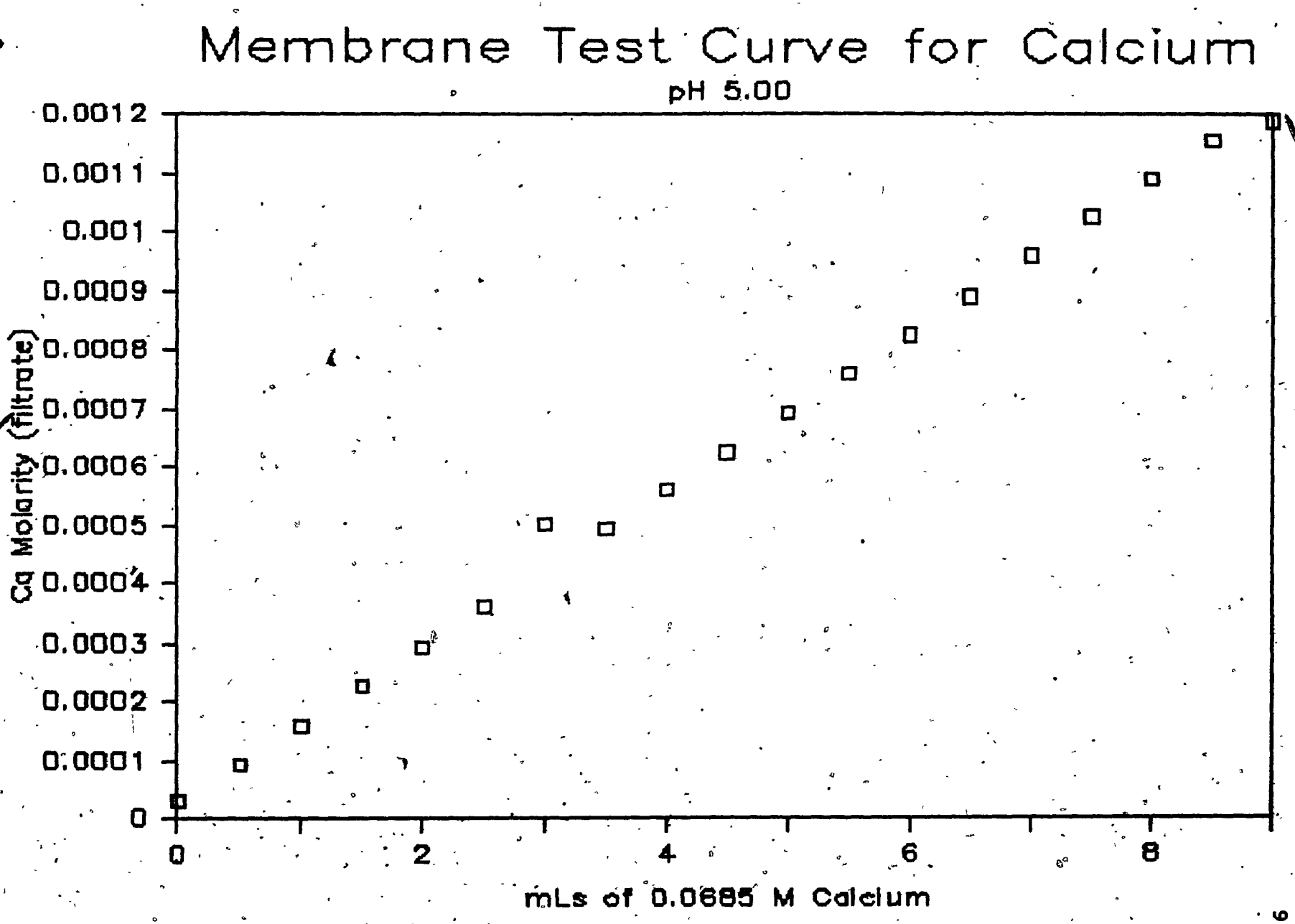
Membrane Test Curve for Calcium
pH 5.00
Ca Molarity (filtrate)
0.0012
0.0011
0.001
0.0009
0.0008
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
0
2
4
6
8
mLs of 0.0685 M Calcium

Figure 16

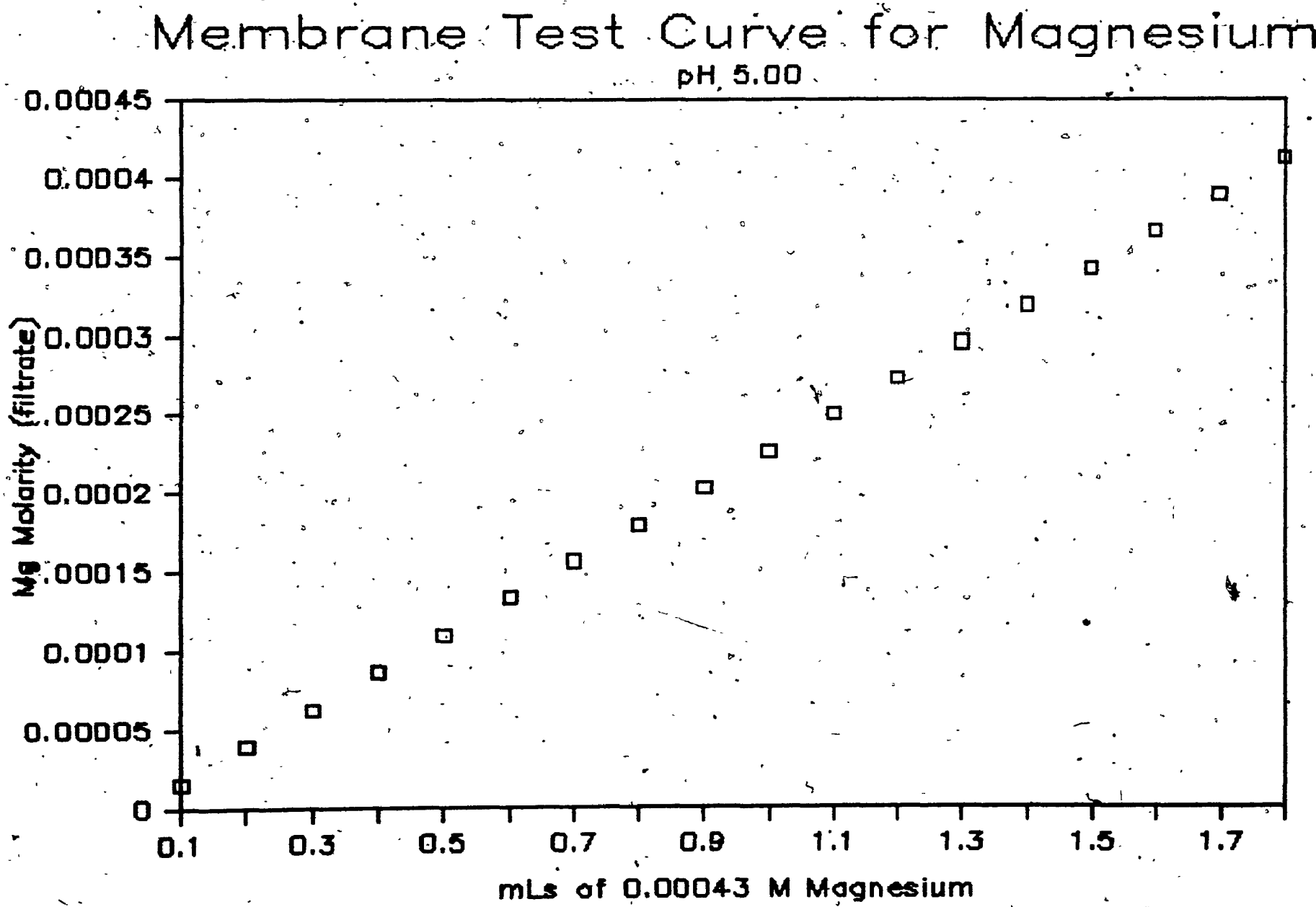
Membrane Test Curve for Magnesium
pH 5.00
0.00045
0.0004
0.00035
0.0003
0.00025
0.0002
0.00015
0.0001
0.00005
0
Mg Molarity (filtrate)
0.1
0.3
0.5
0.7
0.9
1.1
1.3
1.5
1.7
mLs of 0.00043 M Magnesium

Figure 17

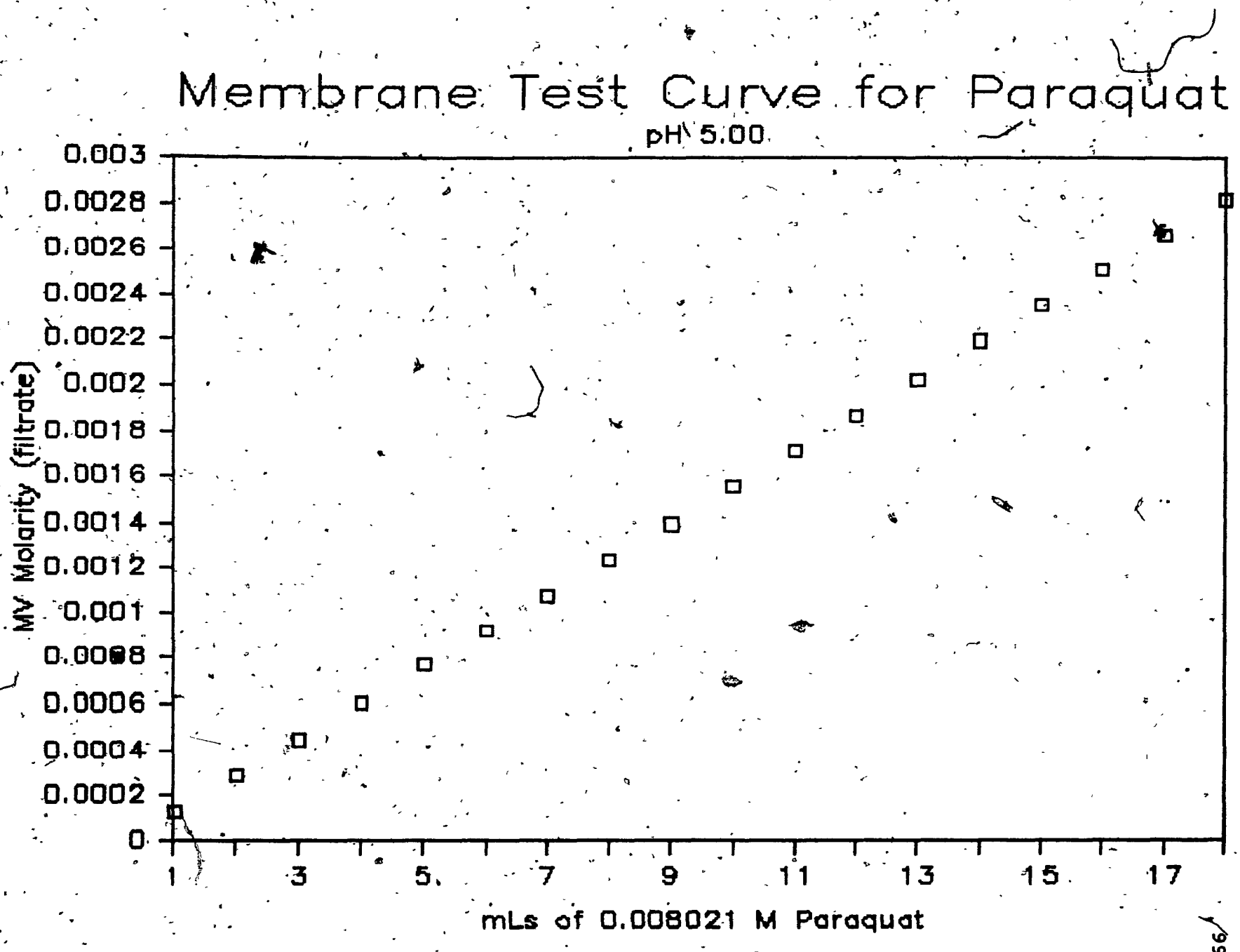
Membrane Test Curve for Paraquat
pH 5.00
MV Molarity (filtrate)
0.003
0.0028
0.0026
0.0024
0.0022
0.002
0.0018
0.0016
0.0014
0.0012
0.001
0.0008
0.0006
0.0004
0.0002
0
1
3
5
7
9
11
13
15
17
mLs of 0.008021 M Paraquat

Figure 18

Table 7

Ultrafiltration Membrane Calibration Curve Data for Calcium

pH	Slope		Intercept	Conditions
	theo	exp		
	x10+5 M/mls		x10+6 M	
3.00	4.004	3.725	-1.298	----------
3.00	4.004	3.729	-2.542	----------
5.00	4.004	4.156	-1.450	MV,Mg
5.00	3.929	3.426	-6.243	Mg
5.00	3.929	3.542	-8.750	MV
5.00	3.929	3.758	1.437	----------
5.00	3.929	4.220	-2.547	----------
5.00	3.540	4.046	3.334	----------
5.00	3.929	3.795	2.407	---------

Table 8

Ultrafiltration Membrane Calibration Curve Data for Magnesium

pH	Slope		Intercept	Conditions
	theo	exp		
	x10+5 M/mls		x10+6 M	
5.00	3.995	3.690	-5.390	----------
5.00	3.995	3.844	-3.744	MV,Ca
3.00	5.108	4.702	11.145	----------
3.00	5.108	5.020	1.124	----------

Table 9

Ultrafiltration Membrane Calibration Curve Data for Copper

pH	Slope		Intercept	Conditions
	theo	exp		
	x10+4 M/mls		x10+6 M	
4.00	1.995	1.900	-0.161	----------
3.50	6.000	6.372	2.920	MV
4.00	2.302	2.283	4.323	----------
3.00	1.246	1.013	2.527	----------
5.00	1.483	1.370	-1.418	----------
5.00	1.351	1.423	-1.755	MV

Examination of Tables 7-9 indicates that the type of errors involved are the same as in the case of paraquat. The concentration range covered in these experiments was from 10^{-6} to about 10^{-3} M. It was found , although not shown in the Tables, that for concentrations below this range, deviations from straight line behaviour became important. This limits the technique to the concentration range specified above. This also implies that using concentration values below this range gives much less reliable data. Using low concentrations, below the 10^{-6} M limit, interferences due to the membrane material itself become a source of error. Membranes must be washed carefully in order to get rid of any contaminants. Buffle et al.(57) found a

similar problem in the speciation of zinc in natural water samples using the same Amicon membranes.

Corrections for membrane effects in the case of constant cation concentration, as was the situation for most of the experiments, were made by multiplying the experimental concentration by the retention coefficient (R) as defined by the ratio of the concentration in the control cell to the filtrate. Table 10 shows some typical retention coefficients for copper, calcium, magnesium and paraquat. It can be seen that at the concentration levels used membrane effects, if present, are not critical.

Table 10

Retention Coefficients for Cations on YM2 Membranes

Cation	Molarity	R	Conditions
MV^{+2}	2.966×10^{-4}	0.9898	pH 5.00, Cu
MV^{+2}	5.145×10^{-3}	0.9879	pH 3.00, Cu
MV^{+2}	3.275×10^{-5}	1.0359	pH 5.00, Mg
MV^{+2}	5.145×10^{-3}	0.9978	pH 5.00, Ca
Ca^{+2}	1.050×10^{-4}	0.9599	pH 5.00, MV
Mg^{+2}	8.00×10^{-5}	0.9866	pH 5.00, Ca
Mg^{+2}	2.554×10^{-5}	0.9787	pH 5.00, MV
Mg^{+2}	5.108×10^{-4}	0.9800	pH 3.00, Cu
Cu^{+2}	4.050×10^{-4}	1.004	pH 3.00, Mg
Cu^{+2}	4.050×10^{-4}	1.120	pH 3.00, MV

The main advantage in using ultrafiltration for the speciation of copper, calcium and magnesium was that all cations, including paraquat, could be determined in the same solution volume. Collection of 5.00 mL of filtrate provided enough sample to analyze for each of the cations simultaneously.

5.1.3.5. Drawbacks of Ultrafiltration as Speciation Technique.

The main problem with ultrafiltration as a speciation technique, is the retention of metal ions at low concentration levels; that is, below 10^{-7} M in this particular case. Contamination by the membrane material and general irreproducibility of the measurements at these low concentrations makes operation difficult. At low concentrations it is possible to use any of the electrochemical methods available for detection of metal ions. Ion selective electrodes are the choice for copper, although their detection limit is not much lower than 10^{-7} M. If membrane irreproducibility and contamination could be eliminated, ultrafiltration would be limited only by the technique used to determine the analyte.

5.1.4. Determination of apparent binding capacity.

The term "apparent binding capacity" is defined in this work as the total number of millimoles of sites per gram of humic acid available to a particular cation. It is automatically assigned

to the "end point" in a "pseudo-titration" of humic acid with the cation in question. In practice, the actual value obtained for the apparent binding capacity depends on the sample conditions, the methodology employed in its determination as well as on the mathematical treatment applied to the titration data. This suggests that the "apparent binding capacity" is an operationally defined term. Despite its operational character, it can be related to the chemical properties of the system. This requires an identification of the elements responsible for the interaction between humic acid and the particular cation. Only then does the correlation of "apparent binding capacities" with chemical properties have any meaning.

In the study of the interaction of metal ions with humic substances, identification of the main sites involved in metal ion binding leads to rationalization of apparent binding capacities. Even in situations like this, however, there is always the possibility of not being able to account for all the sites involved in the interactions. Attempts to do the same for organocationic herbicide-humic acid interactions are complicated by the nature of the herbicides. Various types of interactions besides the rather obvious electrostatic attraction must be considered, i.e., charge transfer, dipole-dipole, ion-dipole, hydrophobic and hydrogen bonding.

As a first approximation, metal ions can be seen as spheres approaching ionogenic groups inside the interior of the humic

gel. Although the possibility of size exclusion from the interior of the gel is a valid one it may not be of great importance for medium size cations. In the case of an organocation such as paraquat, its entrance into the interior of the gel solution where ion exchange takes place may, depending on the ionic strength, pH , and other parameters, be limited by its size. Another aspect to consider is the need for a particular geometrical arrangement of ionogenic groups in order to match the spatial charge distribution on the organocation. For these reasons, prediction of binding capacities for organocations based on the accounting for potential binding sites may give erroneous estimates. Another aspect to be considered is the possibility for the organocation to interact with other parts of the "humic acid molecule" not involved in interactions with metal ions.

Given an acceptable speciation methodology, it is important to select an appropriate data handling routine in order to obtain meaningful information. The treatment of ultrafiltration data will be carried out using two approaches: the Gamble(58,57) and the Ruzic(61,62,63) methodologies.

Gamble's methodology has been successfully applied to the Atrazine-Fulvic Acid system(59). The titration curves obtained, were split into two linear sections, each of which was fitted to a straight line. The end point was evident at high additions of Atrazine, when the slopes of the titration curve and the control

curves were of the same magnitude. One problem with this method is that it cannot be applied to titration curves which do not show sharp end points, such as in the case in which the end point is asymptotically approached. Binding capacities are obtained from the intercept of the second branch of the titration curve or "post-complexing" region. The main advantage of the Gamble methodology is that it provides diagnostic tests for undesirable membranes effects and empirical corrections factors.

Ruzic methodology seem to be amenable to titration curves which do not show sharp end points and cannot be clearly divided into two straight line sections, such as some of the ones encountered in this work. Ruzic proposes a linearization method based on the assumption of 1:1 complex formation. It consists of plotting $[M]/([M]_t-[M])$ against $[M]$; where $[M]$ and $[M]_t$ are the free and total metal ion concentrations respectively. If the 1:1 complex formation assumption is followed, the resulting plot should be a straight line with slope $1/C_1$ and intercept $1/(C_1K)$, where C_1 is the ligand concentration or binding capacity in moles per litres, and K is the conditional stability constant, defined as :

$$\bar{K}_M = \frac{[M]_t - [M]}{[M]\,[L]}$$

where [L] is the concentration of free ligand.

One possible problem, is that the methodology assumes that the means of measuring the concentration of the "free" specie in solution is exact. This may not represent a drawback to the technique, since empirical corrections for membrane effects can be made easily.

Both methods were used to determine apparent binding capacities for different cations: Cu, MV, Mg and Ca. Comparison of both results for paraquat and copper are shown in Table 11.

The values shown in Table 11 deserve a few comments. The first observation is that values determined by the Ruzic method tend to be higher than those by the Gamble method. A possible explanation of this lies in the way the calculation of the end point is made. In the Gamble method, the end point is strongly dependent on the slope of the "post-complexing" region; this created problems in some of the titrations done in this work, since the slopes of the "post-complexing" regions were usually smaller than the expected values based on the slope of the control curve. The extrapolation of this line to obtain the end point, may be one cause of errors. This is reflected in lower apparent binding capacities, since the end point is underestimated. Ruzic method, on the other hand, estimates the capacity from the slope of the titration diagram, and considers the whole titration curve, instead of the "post-complexing" region only. This allows for better estimates of the binding capacity. One problem with this method is that quasi-linear

Table 11

Apparent Binding Capacities for Cations

In Humic Acid Suspensions

Comparison of Ruzic's and Gamble's methods

Titration	Ruzic mmoles/g (%10)	Gamble mmoles/g (%12)
Cu-Clay pH 3	0.186	0.171
MV-Clay pH 3	0.482	0.488
MV-HA pH 4	0.552	0.472
MV-HA pH 3*	0.552	0.372
Cu-HA pH 3*	0.649	0.605
Cu-HA pH 3**	0.980	0.860
Cu-HA pH 5*	0.970	0.940
Cu-HA pH 5**	1.120	0.720
Cu-HA pH 5	1.59	1.340
MV-HA pH 5	1.190	0.975
Cu-HA pH 3	0.815#	0.238***
MV-HA pH 3	0.512	0.411

** 0.01M NaCl; *0.1M NaCl; # estimated from asymptote

*** end point not reached.

behaviour can be observed much before the asymptote is approached, and there is no way of knowing how large the

deviation from the asymptote is. There is a tendency to underestimate the slope of the titration diagram, leading to larger values for the apparent binding capacity.

Differences between values obtained by both methods can be seen in Table 11. For the case of paraquat at pH 4 the value determined by the Ruzic method is larger than that obtained by using the Gamble method; similar differences are noted for copper at pH 3 at different ionic strengths. It is quite dramatic for the case of copper at pH 3 (one before last entry in Table 11), in which the slope of the post-complexing region for the Gamble plot has a value of 4.50×10^{-4} M per mLs; which is remarkably different from the expected value of 6.00×10^{-4} M per mLs. This represents one advantage of the Gamble method. It provides a quick check on how far the titration is from reaching the end point.

In these examples, the slopes corresponding to the Gamble plots were significantly smaller than those of their respective control curves. Ruzic plots for these cases showed quasi-linear behaviour, giving the "illusion" that the end point was reached. The problem concerning the estimation of apparent binding capacities by the Ruzic method has been recently discussed by Morel et al.(63a). At best, both methods provide estimates for apparent binding capacities, which must be taken with certain caution.

In the analysis of Ruzic diagrams, deviations from straight

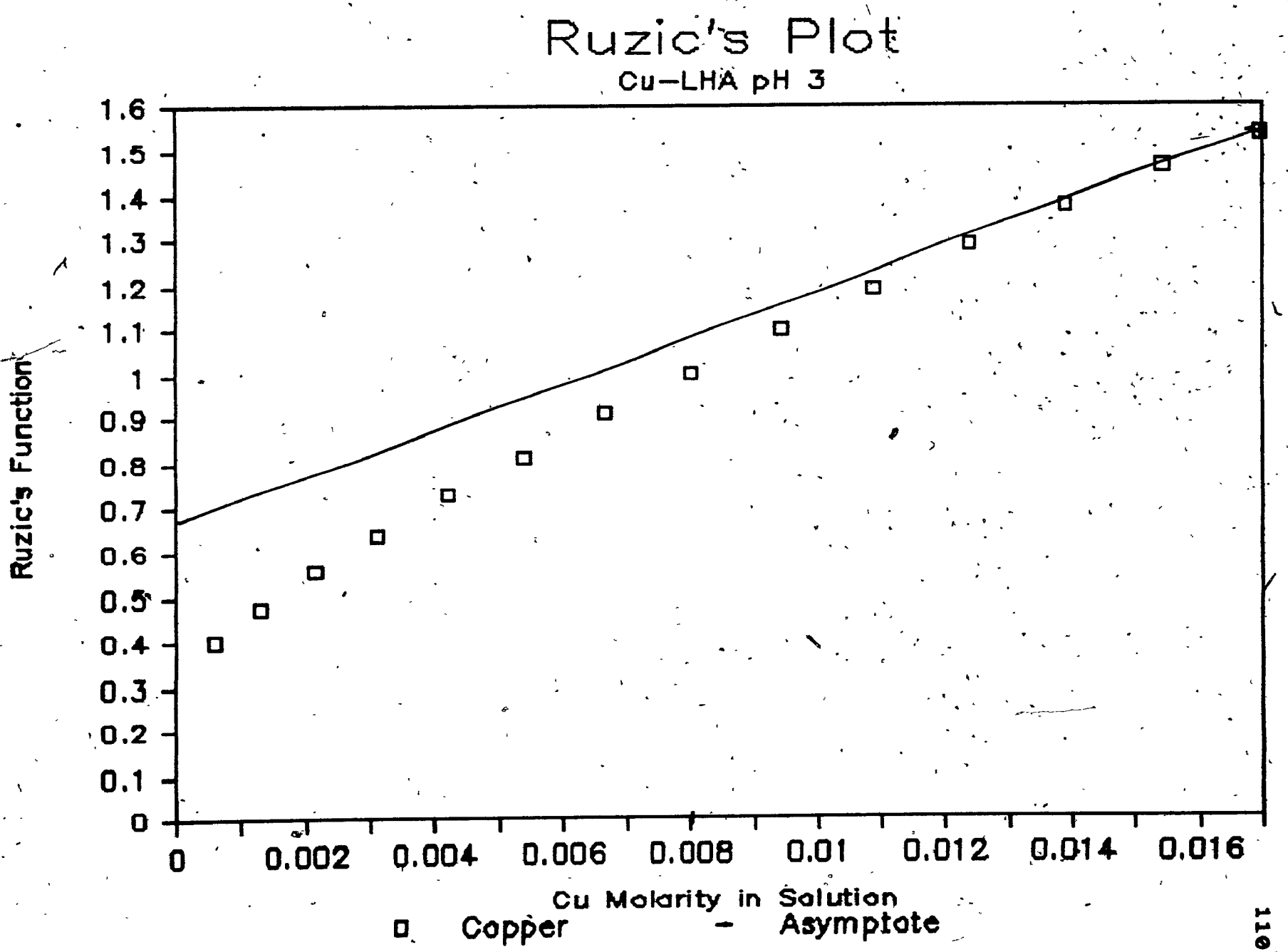
Ruzic's Plot
Cu-LHA pH 3
Ruzic's Function
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.002
0.004
0.006
0.008
0.01
0.012
0.014
0.016
Cu Molarity in Solution
Copper
Asymptote

Figure 19

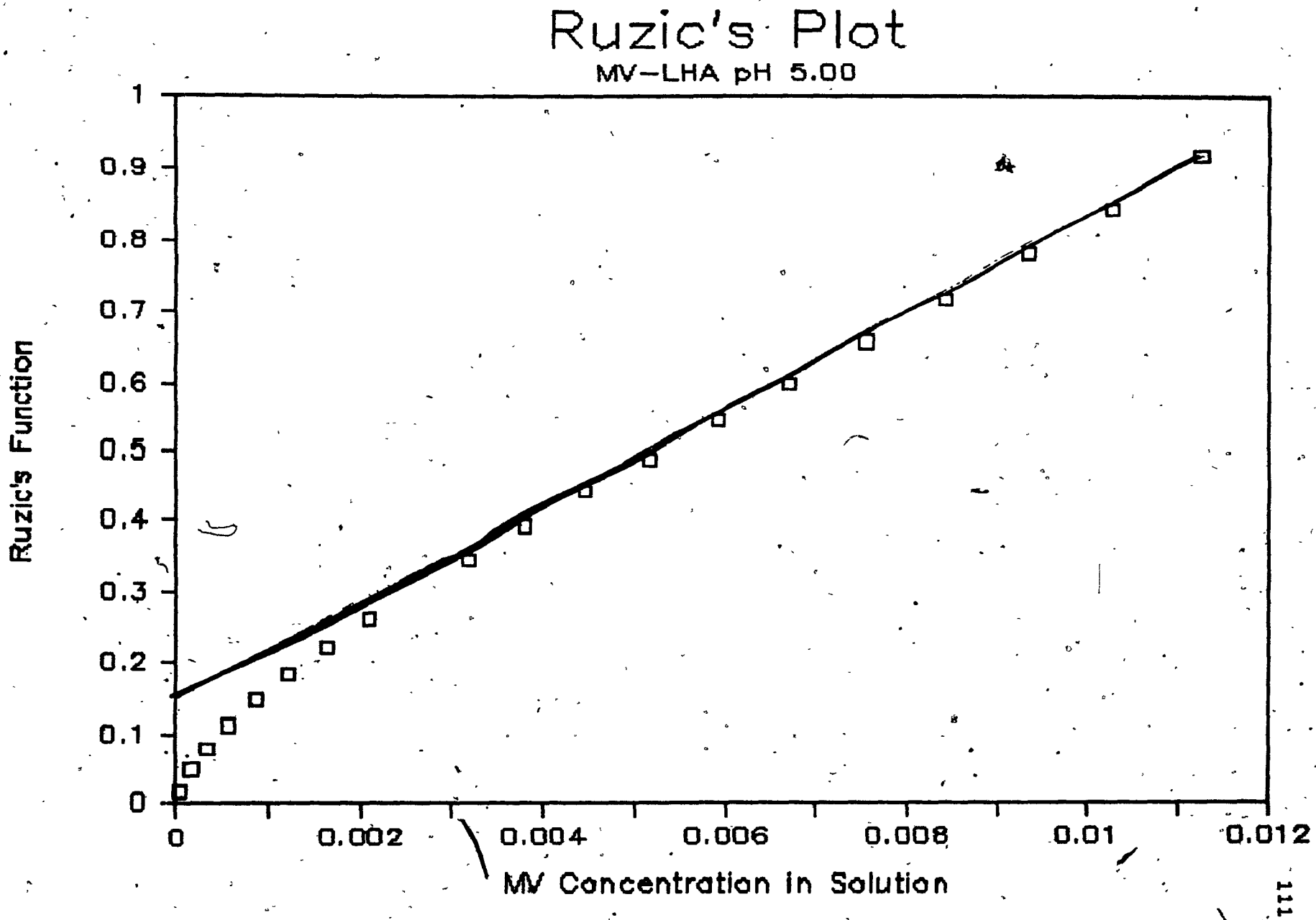
Ruzic's Plot
MV-LHA pH 5.00
Ruzic's Function
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.002
0.004
0.006
0.008
0.01
0.012
MV Concentration in Solution

Figure 20

line behaviour were noted for copper and paraquat. Figure 19 shows a typical Ruzic's diagram for the titration of Laurentide Humic Acid with copper at pH 3.00. It can be seen clearly that there is a deviation from straight line behaviour at low copper levels. A similar behaviour is seen for paraquat at pH 5.00. Figure 20 shows the Ruzic's diagram for the titration of LHA with paraquat at pH 5.00. It can be seen that at low total paraquat, the titration diagram deviates from straight line behaviour.The apparent binding capacity was determined measuring the slope for the asymptotic line (line A in Figures 19 and 20). Ruzic(62) interprets such deviations as evidence for the formation of two complexes, that is, each cation interacts with two different groups of sites.

This apparently contradicts the previous results on the existence of one type of carboxyl site in this humic acid, which predicts the formation of only one type of complex between cations and carboxyl sites. Deviations from straight line behaviour were not noticed for calcium and magnesium at different pH values, indicating that both cations are interacting with one type of site, as expected. In the case of copper, the deviations may be due to the formation of two different type of complexes, including carboxyl as well as hydroxy sites. An explanation for the case of paraquat may be more difficult to present, although the possibility of paraquat forming complexes with other sites besides carboxyl groups, may be considered.

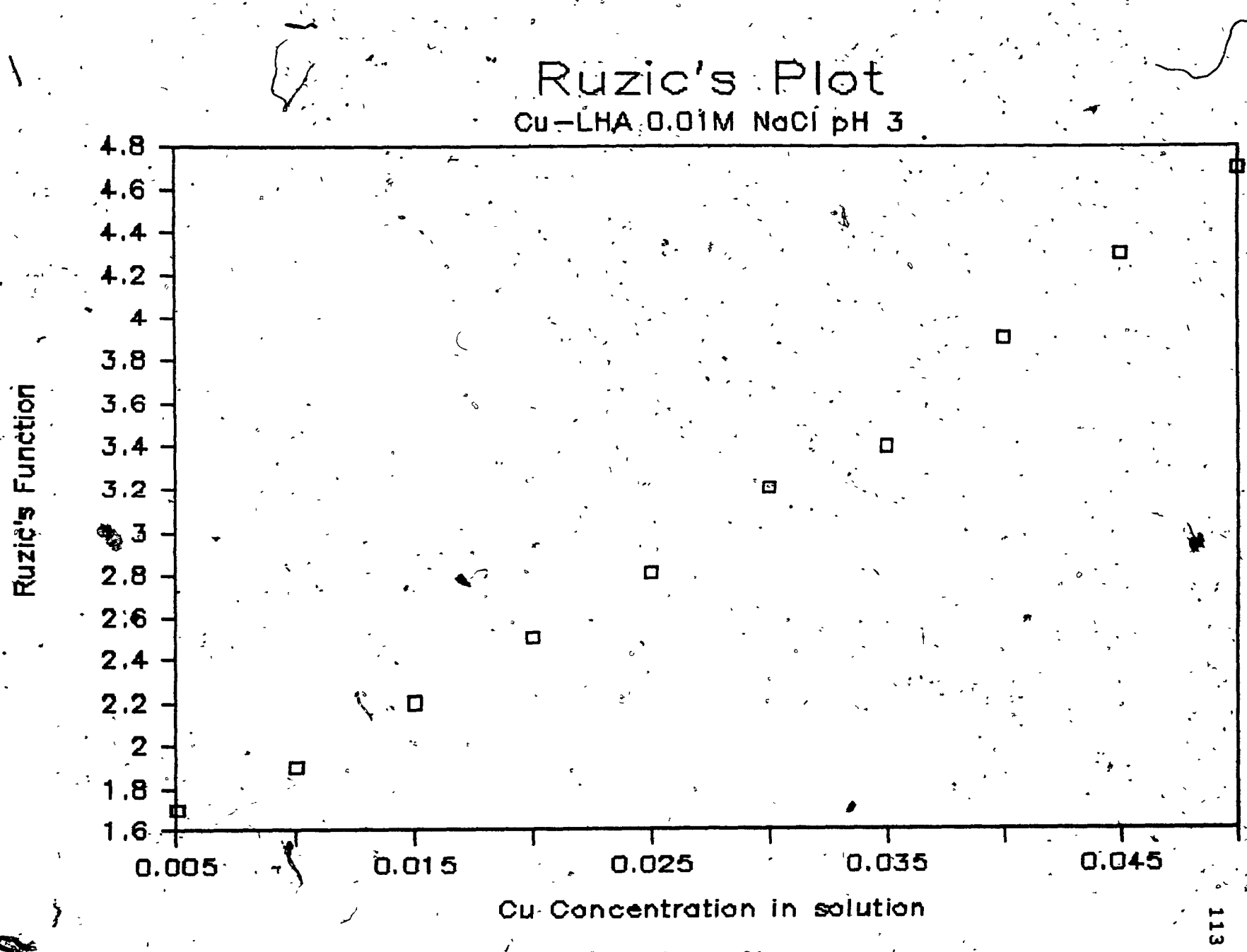
Ruzic's Plot
Cu-LHA 0.01M NaCl pH 3
Ruzic's Function
4.8
4.6
4.4
4.2
4
3.8
3.6
3.4
3.2
3
2.8
2.6
2.4
2.2
2
1.8
1.6
0.005
0.015
0.025
0.035
0.045
Cu Concentration in solution

Figure 21

Titrations in the presence of background electrolyte involving copper and paraquat did not show deviations from Ruzic behaviour (see Figure 21).

5.1.5. Paraquat Binding to LHA.

5.1.5.1. Ionic Strength and pH Effects.

Figure 22 shows average binding curves for paraquat on LHA at different pH values, all at zero ionic strength. The apparent binding capacity increases with pH. A similar effect has been reported in the literature(4). Changes in pH after equilibration were not detected. In the case of pH 3, any small release of hydrogen ions would have been obscured by the large concentration of hydrogen ions already present in solution. The constant pH, in the case of pH 5 may indicate that paraquat ions prefer to interact with already ionized acidic sites. The increase in apparent binding capacity with pH can be attributed to the decrease in the competition for ion exchange sites between paraquat and hydrogen ions although other effects such as structural changes in humic acid leading to exposure of sites otherwise not accessible to paraquat cannot be ruled out. Figures 23 and 24 show the binding of paraquat at different ionic strengths. Increasing the ionic strength of the external solution decreases the amount of paraquat bound. This can be explained by a reduction of the Donnan Potential and competition with sodium ions for sites. The ionic strength effects are

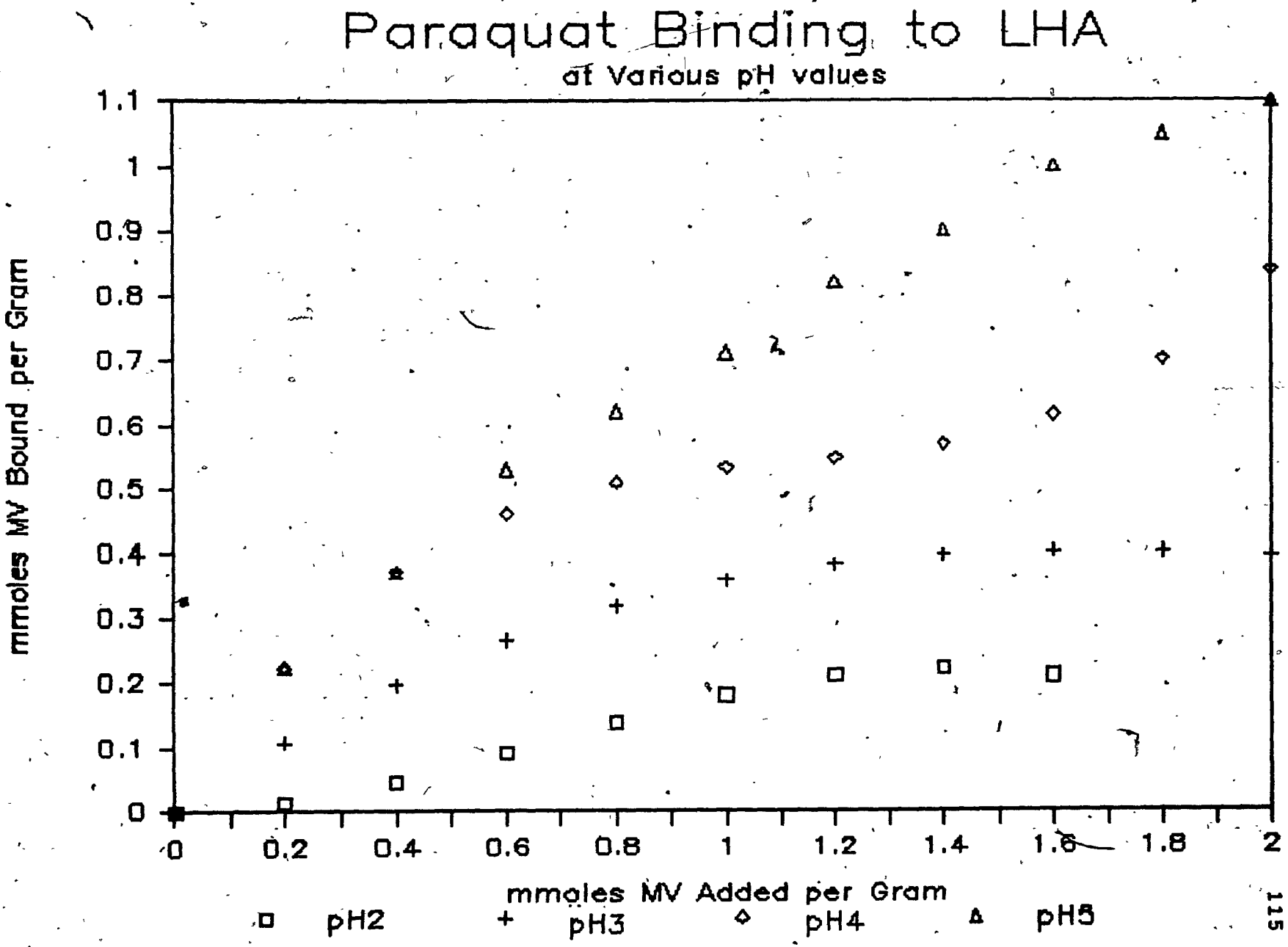
Paraquat Binding to LHA
at Various pH values
mmoles MV Bound per Gram
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
mmoles MV Added per Gram
pH2
pH3
pH4
pH5

Figure 22

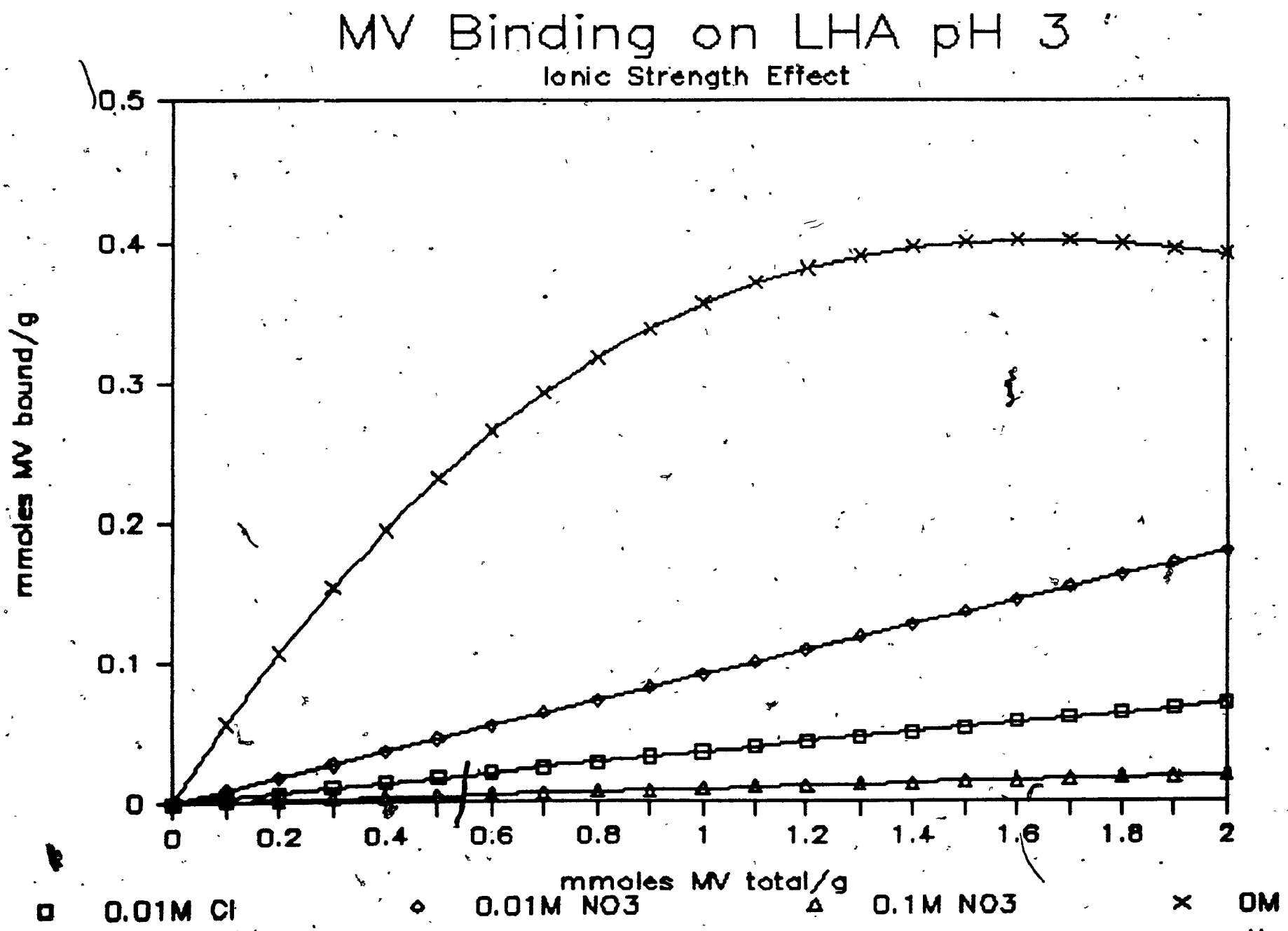
MV Binding on LHA pH 3
Ionic Strength Effect
mmoles MV bound/g
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
mmoles MV total/g
0.01M Cl
0.01M NO3
0.1M NO3
0M

Figure 23

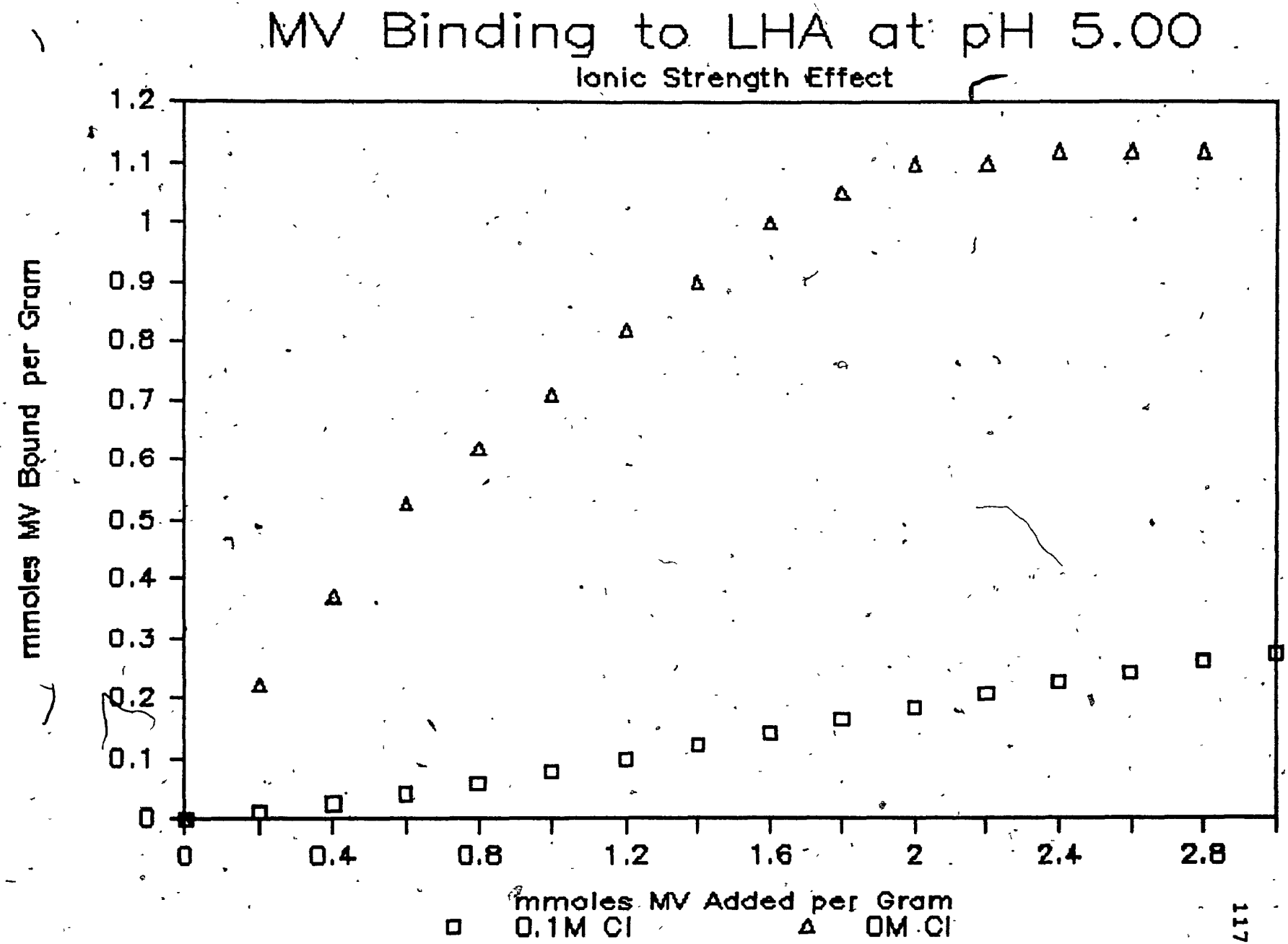
MV Binding to LHA at pH 5.00
Ionic Strength Effect
mmoles MV Bound per Gram
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.4
0.8
1.2
1.6
2
2.4
2.8
mmoles MV Added per Gram
0.1M Cl
0M Cl

Figure 24

similar to those for cations such as calcium and magnesium. Ionic strengths higher than 0.01M effectively excluded calcium and magnesium from the gel solution. Although the effect of sodium was not as dramatic for paraquat, the reduction in binding is significant. This is an indication that Donnan potential and electrostatic forces are keys to the binding mechanism of paraquat to LHA. Competition with sodium ions for ion exchange sites is also important. In this situation, one has to consider that there are three cations competing for sites, this includes, paraquat, sodium and hydrogen ions.

At 0.01M electrolyte concentration the Donnan potential must be much lower than in the absence of electrolyte. This, coupled with competition between sodium and paraquat for binding sites, explains why, in principle, the uptake of paraquat is less when either NaCl and $NaNO_3$ is present. Sodium chloride seems to be more effective in reducing the amount of paraquat bound. Two factors can provide clues to an explanation to this situation.

It is possible that, at the high concentrations of chloride ion, ion pairs are formed between paraquat and chloride(31,34). In this situation paraquat would be entering the gel domain as a monovalent cation, which would not be as attracted as a divalent one by the already weak Donnan potential. For this reason, the use of chlorides was avoided throughout this work. HNO_3 was used, instead of HCl for pH

adjustment. There is no report in the literature of paraquat-nitrate ion pair formation.

5.1.5.2. Paraquat Equilibrium Functions.

Figure 25 shows the average and differential ion exchange equilibrium functions for paraquat on LHA at pH 3.00 and zero ionic strength. The average equilibrium function was calculated by means of Equation(16) on Page (16). The assumption of a Donnan controlled mechanism calls for a stoichiometry of 1:1 between paraquat dications and bidentate sites. Plots of KX_{SH2} against X_{SH2} were fitted to polynomials in order to take the derivative of that particular function required by Equation (16) on Page (16). It can be seen that the differential equilibrium function is an order of magnitude greater than the average equilibrium function. The standard deviation of the average equilibrium function values over the range scanned was of about the same order as the experimental error involved and propagated throughout the calculations. This leads to the idea that the K values did not show the variation expected with site loading. One must look at this result carefully. From the data presented earlier for the redox properties of the humic acid involved in this investigation, the expected result would be a constant equilibrium function for cations interacting only with carboxyl groups. The constant value showed by paraquat may be a confirmation of this fact provided that it interacts with carboxyl groups only.

Table 12

Paraquat Equilibrium Function pH 3.00

X_{SH2}	$\overline{K}$ (M)	$\overline{K} X_{SH2}$
0.993	1.707×10^{-3}	1.694×10^{-3}
0.986	1.630×10^{-3}	1.606×10^{-3}
0.979	1.557×10^{-3}	1.525×10^{-3}
0.967	1.424×10^{-3}	1.377×10^{-3}
0.950	1.251×10^{-3}	1.189×10^{-3}
0.941	1.150×10^{-3}	1.081×10^{-3}
0.926	9.725×10^{-4}	9.007×10^{-4}

Average $\overline{K} = 1.366 \times 10^{-3} \pm 2.3 \times 10^{-4}$

The assumption of a 1:1 stoichiometry, as mentioned before, resulted from a consideration of the Donnan mechanism. The use of divalent sites is just to simplify calculations. The same assumption at pH 5.00, where the gel structure has suffered dramatic changes, may not be a valid one. In this case, paraquat may be forming 1:1 and 1:2 complexes with monovalent sites. The restrictions imposed by the more structured gel at pH 3 are no longer operating at pH 5; humic acid molecules have more freedom to change their conformation in solution.

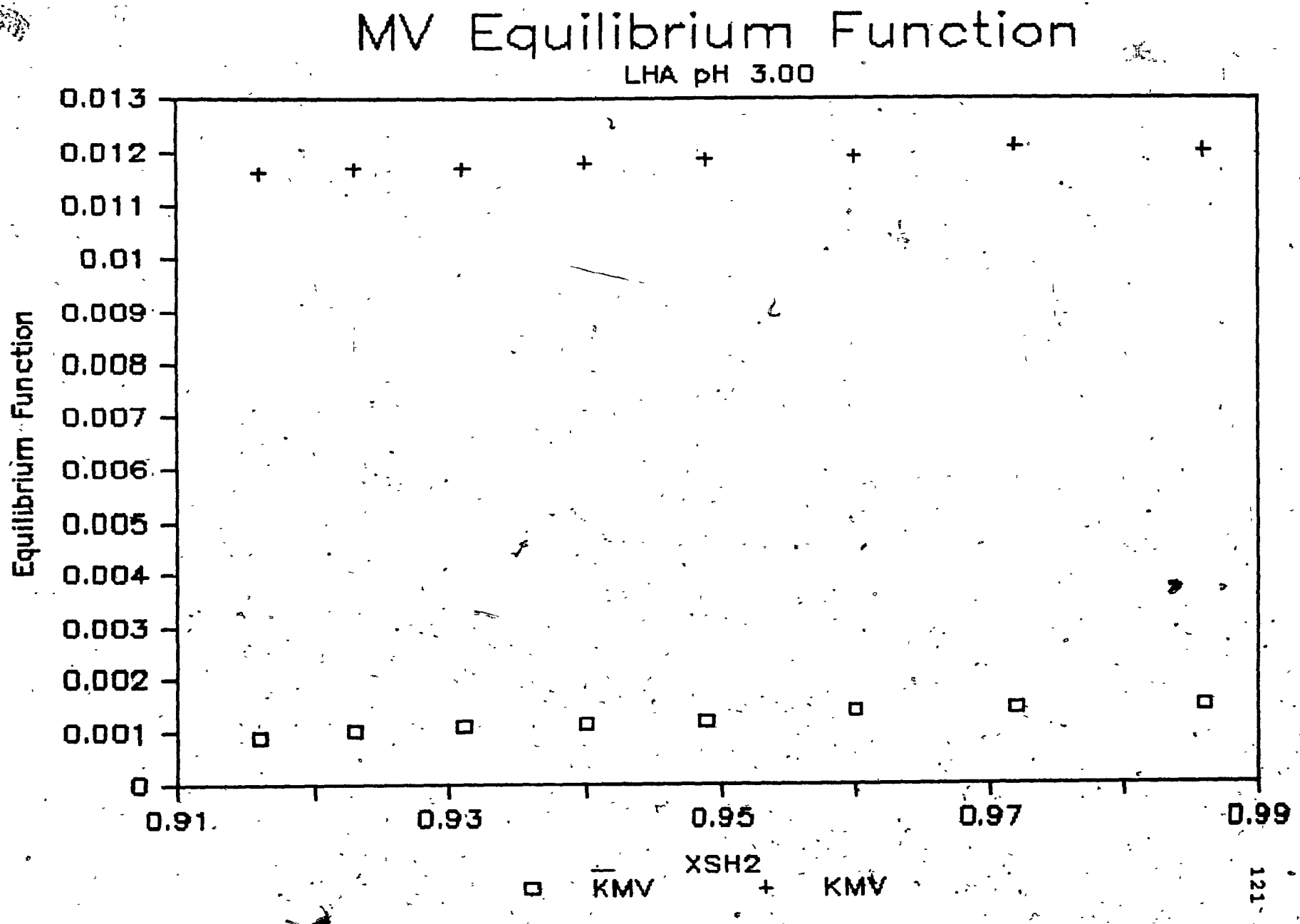
MV Equilibrium Function
LHA pH 3.00
Equilibrium Function
0.013
0.012
0.011
0.01
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0.91
0.93
0.95
0.97
0.99
XSH2
KMV
KMV

Figure 25

5.1.6. Interaction of Calcium and Magnesium with LHA.

5.1.6.1. Calcium-Humic Acid at pH 3.00.

Figure 26 shows the binding of calcium to Laurentide Humic acid at two different pH values. It can be seen that as the pH is increased the apparent binding capacity increases as well. This reflects the competition for binding sites between calcium and protons. Changes in pH after equilibration were not detected at the two pH levels studied, probably due to the small amount of hydrogen exchanged, especially so at pH 3. The constant binding at pH 5 indicates that in the range of concentration studied cations must be interacting with already ionized acidic groups. The uptake of calcium at low concentrations is close to 100 % indicating a strong affinity of humic acid for calcium ions.

The average equilibrium function for the calcium-humic acid interaction at pH 3 has been calculated, assuming a one to one stoichiometry with bidentate sites in the humic gel using Equation (16) (see Figure 27). The total number of potential sites available for interaction has been taken considering the total acidity of the humic acid sample. This includes, carboxyl as well as phenolic protons. The possibility that calcium may engage in chelate formation with salicylic-like structures in humic substances has been considered by Perdue(64) in explaining small increases in the total carboxyl content of fulvic acid titrated in the presence of calcium ions. The inclusion of the

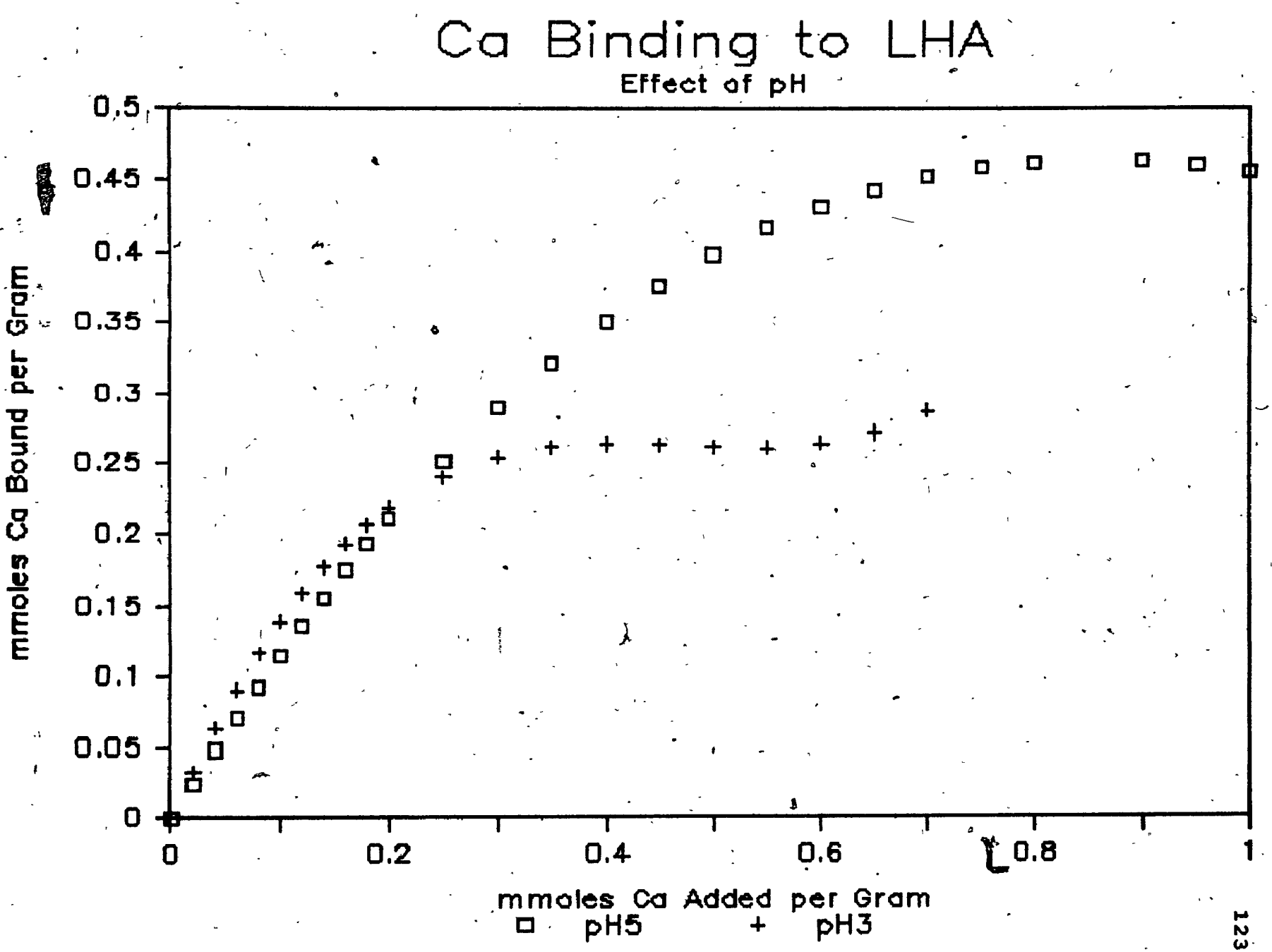
Ca Binding to LHA
Effect of pH
mmoles Ca Bound per Gram
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
0.2
0.4
0.6
0.8
1
mmoles Ca Added per Gram
pH5
pH3
123

Figure 26

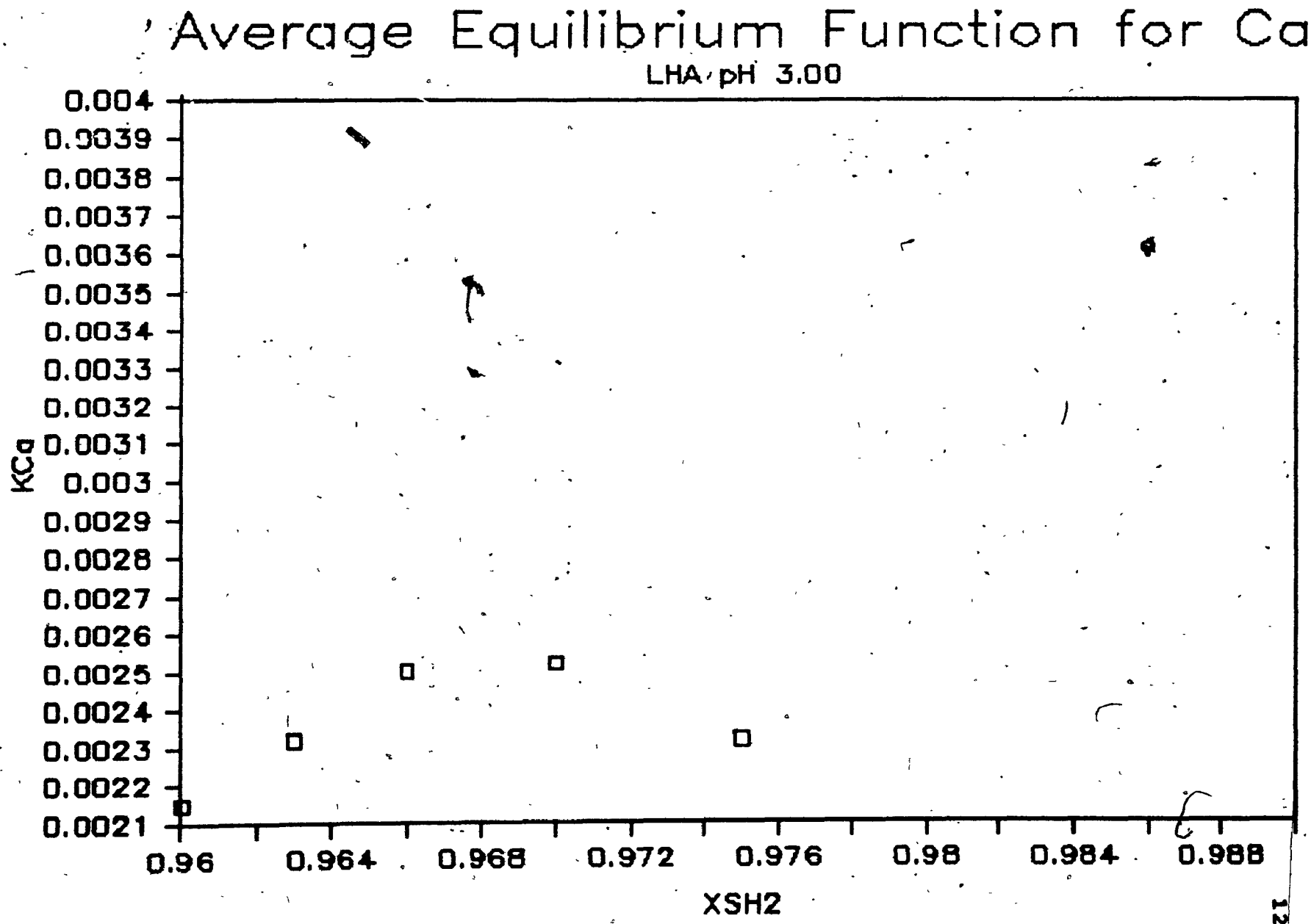
Average Equilibrium Function for Ca
LHA pH 3.00
KCa
0.004
0.0039
0.0038
0.0037
0.0036
0.0035
0.0034
0.0033
0.0032
0.0031
0.003
0.0029
0.0028
0.0027
0.0026
0.0025
0.0024
0.0023
0.0022
0.0021
0.96
0.964
0.968
0.972
0.976
0.98
0.984
0.988
XSH2

Figure 27

total acidity in the total number of potential sites has been done with this in mind. The average equilibrium function for calcium at pH 3.00 showed a constant behaviour indicating that all the sites available by calcium are very similar , or, that any variation has been obscured by experimental error. This seems to fit the one-site model presented earlier for the humic acid under investigation. Table 13 shows that average ion exchange equilibrium function for calcium at pH 3.

Table 13

Average Ion Exchange Equilibrium Function for Calcium at pH 3.00

X_{SH2} (±%7)	$\overline{K}_{Ca}$ (±%15)	$\overline{K}_{Ca} X_{SH2}$ (±%20)
0.994	5.25×10^{-4}	5.22×10^{-4}
0.987	1.32×10^{-3}	1.30×10^{-3}
0.980	1.99×10^{-3}	1.95×10^{-3}
0.975	2.39×10^{-3}	2.34×10^{-3}
0.970	2.54×10^{-3}	2.46×10^{-3}
0.960	2.11×10^{-3}	2.03×10^{-3}

5.1.6.2. Magnesium Binding to LHA pH 3.00.

Figure 28 shows the binding of magnesium to LHA at two different pH values. Increase in pH increased the apparent

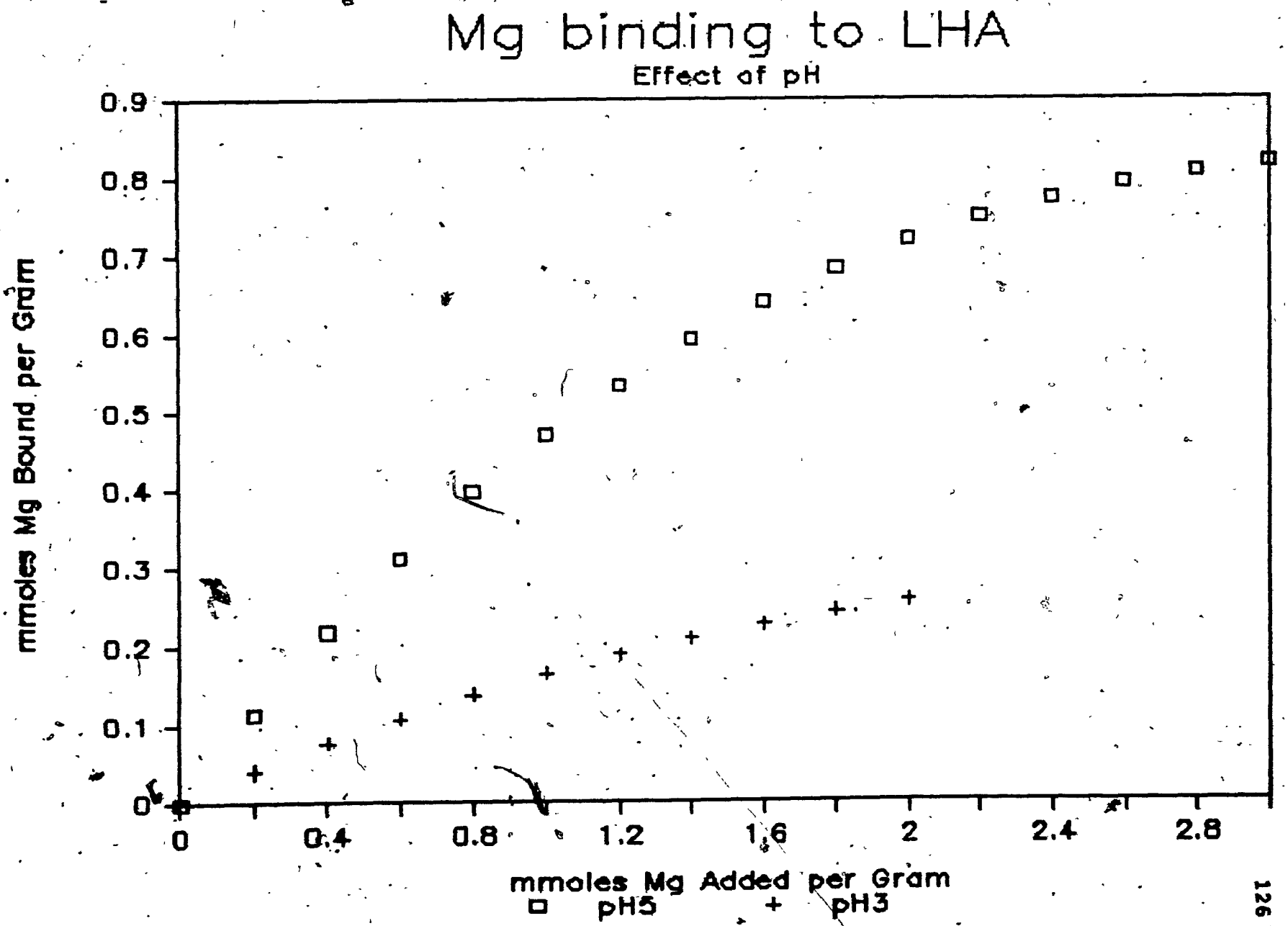
Mg binding to LHA
Effect of pH
mmoles Mg Bound per Gram
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.4
0.8
1.2
1.6
2
2.4
2.8
mmoles Mg Added per Gram
pH5
pH3
126

Figure 28

binding capacity. The increase is higher than in the case of calcium, previously shown. The apparent binding capacity at pH 3.00 is similar to that for calcium, although the uptake of magnesium at low concentrations is not as pronounced as in the case of calcium. As will be shown later, calcium effectively blocks ion exchange sites from magnesium when a humic acid suspension previously equilibrated with calcium is titrated with magnesium ions indicating that both cations compete for the same sites at pH 3.00. By looking at the average equilibrium functions for both cations in Figures 27 and 29, it is clear that the interaction of magnesium with the carboxyl groups in humic acid is much weaker than that of calcium. It may also provide an indication of the type of interaction between each cation and the ionogenic groups in humic acid. The order of magnitude difference in equilibrium constants between calcium and magnesium may be due to the formation of inner-sphere complexes in the case of calcium as compared to the formation of outer-sphere complexes in the case of magnesium; i.e., magnesium is reacting as the hydrated $[Mg(OH_2)_6]2^+$ cation while calcium as the bare cation.

The fact that calcium and magnesium have similar apparent binding capacities and compete for the same sites, provides clues on the fraction of exchangeable protons at pH 3.00. It is expected that magnesium and calcium will enter the gel phase displacing protons paired to carboxyl groups in order to fullfil the Donnan mechanism of ion exchange. Due to the pH of the

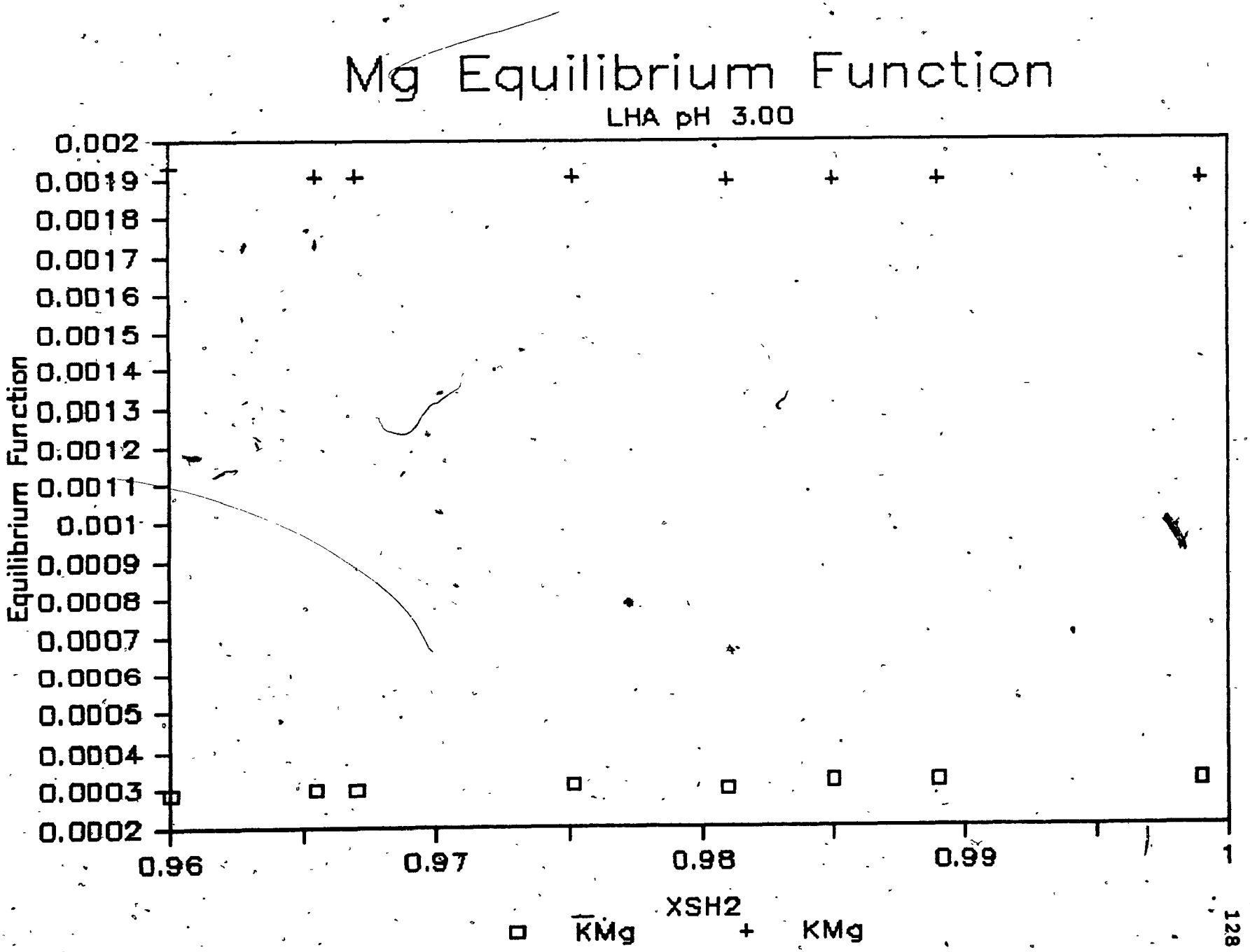
Mg Equilibrium Function
LHA pH 3.00
Equilibrium Function
0.002
0.0019
0.0018
0.0017
0.0016
0.0015
0.0014
0.0013
0.0012
0.0011
0.001
0.0009
0.0008
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.96
0.97
0.98
0.99
1
XSH2
KMg
KMg
128

Figure 29

external solution, most of the carboxyl groups will be covered by protons. The fraction of protons exchangeable for magnesium or calcium represent the strongest acidic portion of the collection of protons inside the gel phase at an external pH of 8.

The average equilibrium function for magnesium at pH 3 turns out to be rather constant as in the previous cases, as can be seen in Table 14 and Figure 29. If there is any variation with site loading, it has been obscured by experimental error. The average value for K_{Mg} is about an order of magnitude smaller than K_{Ca}. The interaction of calcium with the carboxyl groups in humic acid is stronger than that of magnesium; this is corroborated in Figure 30, which shows that magnesium cannot displace calcium ion from the gel phase in the concentration range shown. The preference of LHA for calcium over magnesium may be due, among other factors, to the possible formation of a specific interaction between calcium and the carboxyl groups. Kwak et al.(66) have shown a similar behaviour for magnesium and calcium on various polyelectrolytes containing carboxyl groups.

Page 130 omitted in page numbering

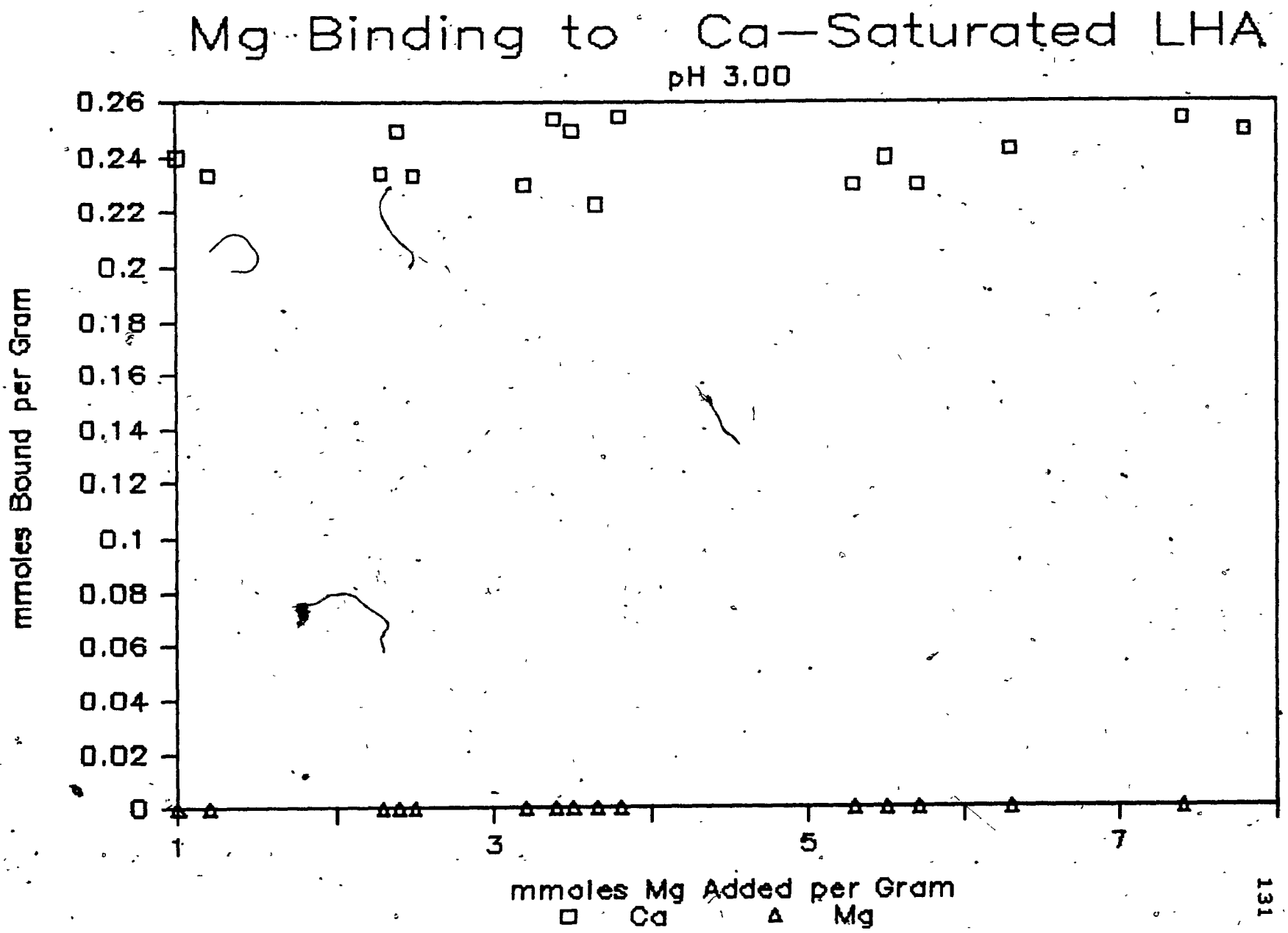
Mg Binding to Ca—Saturated LHA
pH 3.00
mmoles Bound per Gram
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
1
3
5
7
mmoles Mg Added per Gram
Ca
Mg

Figure 30

5.1.6.3. Calcium-Humic Acid and Magnesium-Humic Acid Interactions at pH 5.00.

The binding curves of calcium and magnesium on LHA at pH 5.00 are quite different from the case at pH 3.00. As can be seen by comparing Figures 26 and 28, the apparent binding capacity of calcium at pH 5 is about half that for magnesium, which was not the case at pH 3.00. An important qualitative observation is that in the titration of humic acid with calcium ions at pH 5, precipitation of humic species occurred very early. This phenomenon was not present in titrations involving magnesium ions under the same conditions. Depending on the concentration of calcium used, most of the humic acid could be removed from solution.

The precipitation of humic acid by calcium can be interpreted as the result of the formation of complexes in which calcium serves as a bridge between carboxyl groups located in different humic acid molecules. It is not an ionic strength or salting-out effect since the concentration of calcium was kept at the millimolar level and this phenomenon is not brought about by salts of monovalent cations. The formation of precipitates complicates the formulation of the equilibrium function for calcium-humic acid complexes, since two phases are now involved. This is not the case for magnesium, all magnesium-humic complexes formed remained in solution. At this point a formulation of equilibrium functions for magnesium and calcium is premature

since there is little information on the stoichiometry, although the differences in apparent binding capacities seem to indicate that calcium interacts in a 1:2 ratio with monovalent sites. This implies that magnesium interacts in a 1:1 ratio. Competitive experiments between calcium and magnesium will provide information needed to formulate the equilibrium for each individual ion.

5.1.6.4. Ionic Strength Effects.

Titrations of LHA with calcium and magnesium at pH 3 and 5 in the presence of 0.01 and 0.1 M NaCl, totally excluded both cations from the humic acid gel phase. It is possible that for the case of calcium some binding might have occurred at 0.01 M NaCl but the total amount of calcium needed to effectively displace sodium ions was very large. This made it difficult to detect sorption by difference, since the amount of calcium bound would be very small compared to the total amount added.

5.1.7. Copper Humic Acid interaction.

Copper binding to Laurentide Humic Acid at different pH values is shown in Figure 31. It can be seen that while the binding curve at pH 5.00 reaches a plateau at about 1.4 millimoles of copper per gram of humic acid, the curves for pH 2.00 and pH 3.00 do not. This is a clear evidence, as expected,

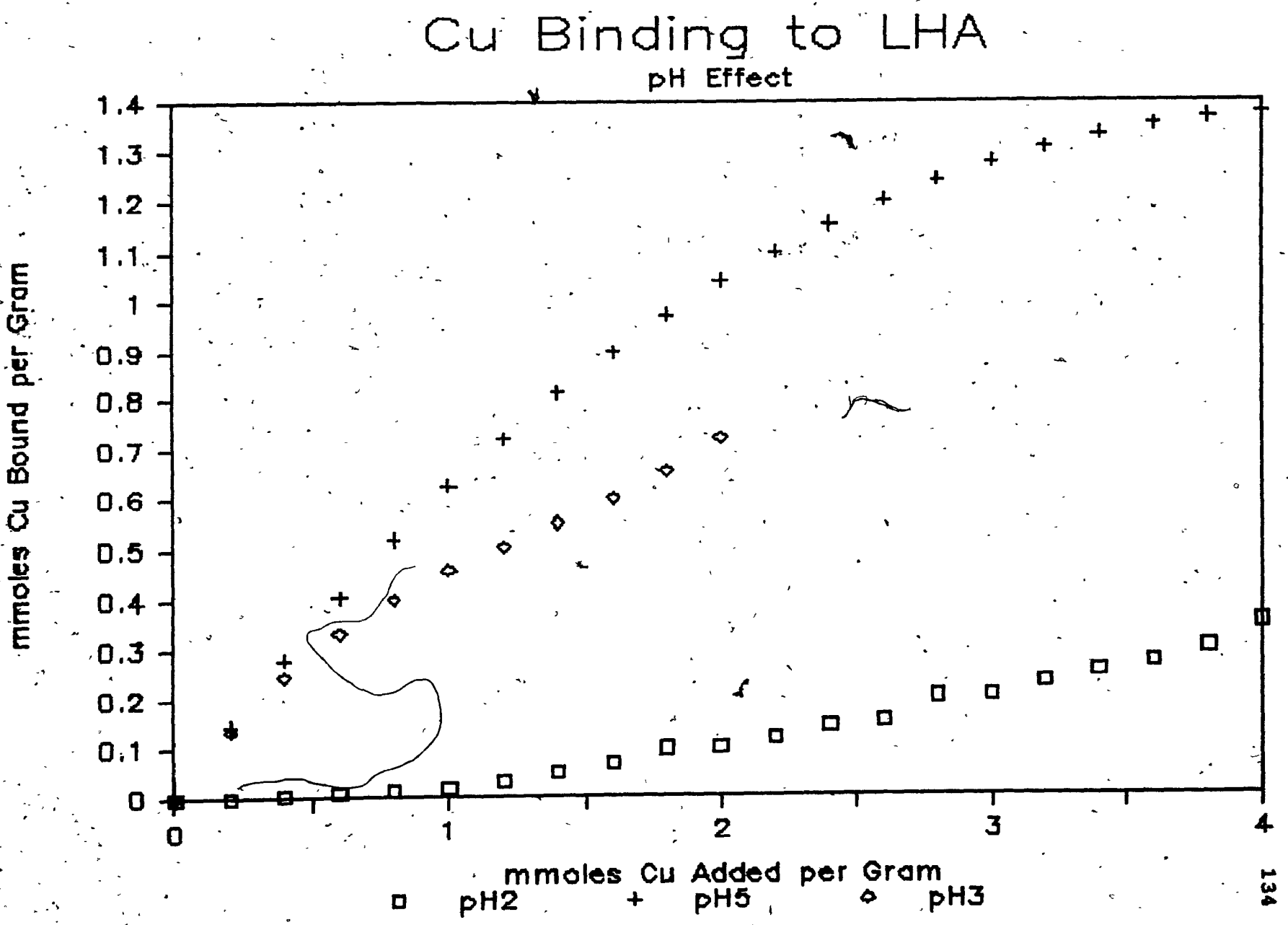
Cu Binding to LHA
pH Effect
mmoles Cu Bound per Gram
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
mmoles Cu Added per Gram
pH2
pH5
pH3

Figure 31

of competition between copper and protons for ion exchange sites. The effect of ionic strength on copper binding is shown in Figures 32 and 33. The lowering of the Donnan potential by the presence of neutral electrolyte reduces the amount of copper bound. Another factor which reduces the amount of copper bound is competition between sodium ions and copper for ion exchange sites. The decrease in the apparent binding capacity with increasing ionic strength reflects these facts.

The effect of neutral electrolyte seems to be greater at lower pH than at pH value such as 5.00. This may be a reflection of the gel character of humic acid at pH 3.00 resulting in the sorption of copper ions being controlled by the Donnan potential. The addition of electrolyte reduces this potential and as well as introduces another competing cation. Both factors contribute to the reduction in the amount of copper bound.

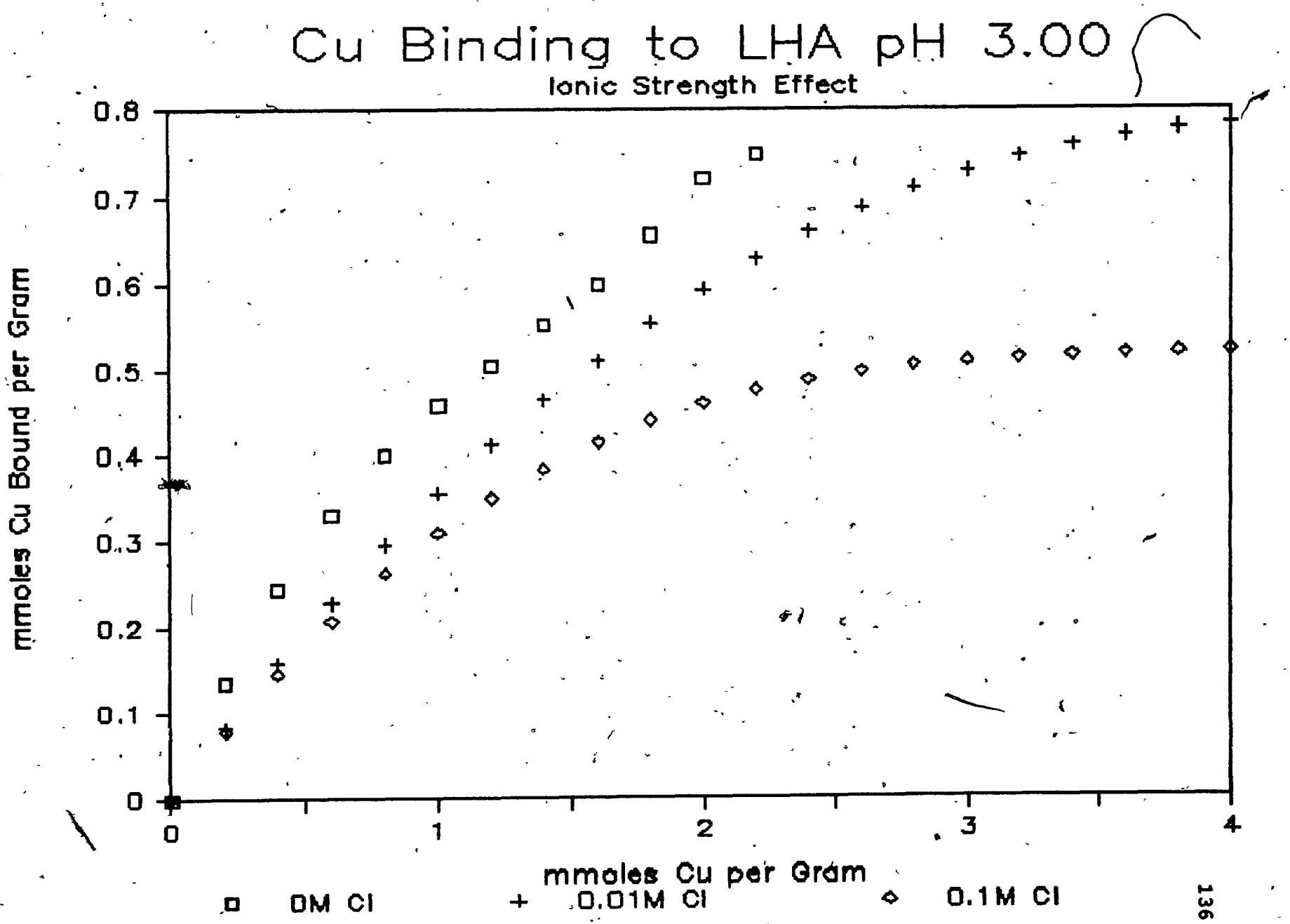
Cu Binding to LHA pH 3.00
Ionic Strength Effect
mmoles Cu Bound per Gram
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
mmoles Cu per Gram
0M Cl
0.01M Cl
0.1M Cl

Figure 32

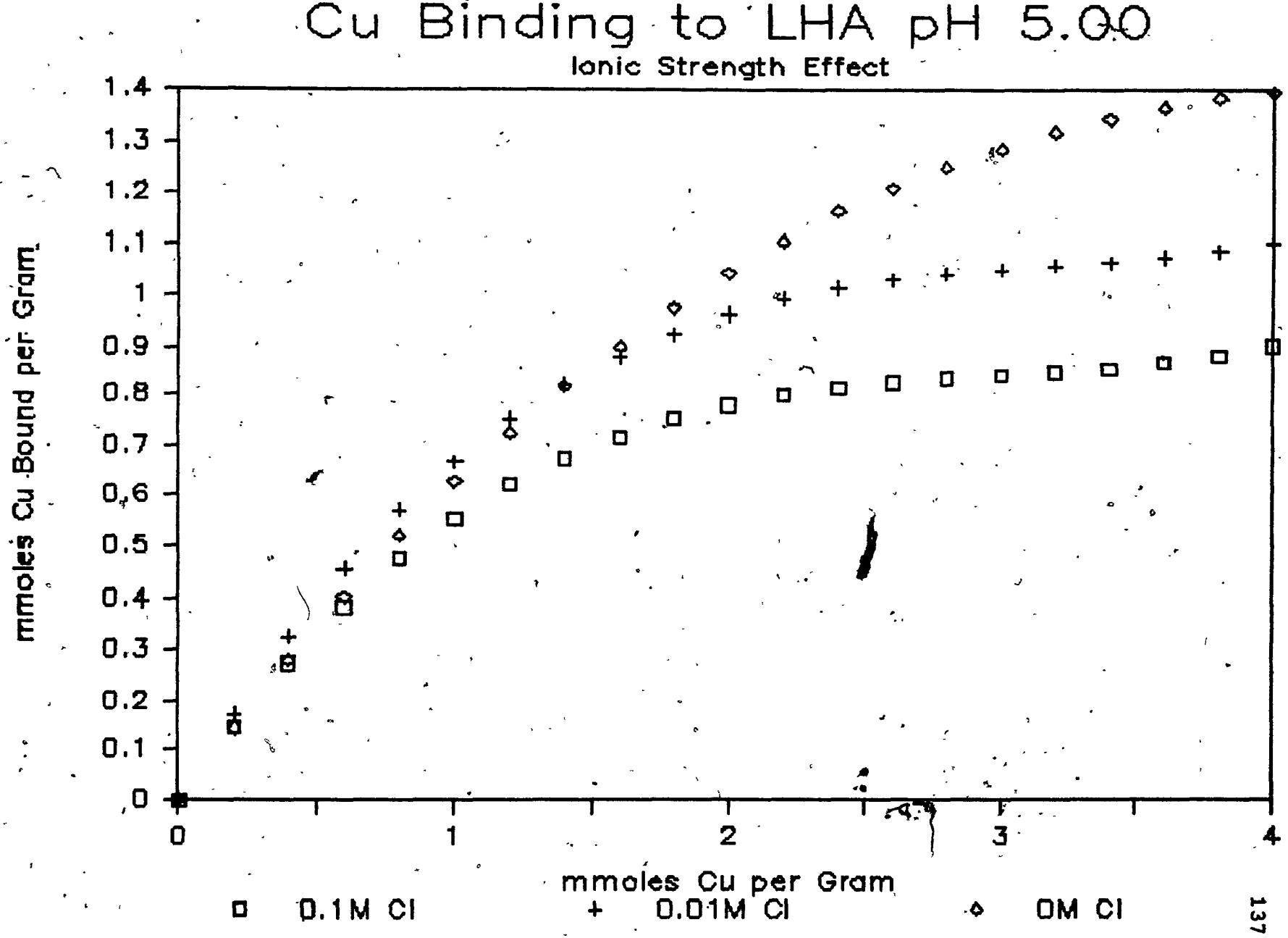
Cu Binding to LHA pH 5.00
Ionic Strength Effect
mmoles Cu Bound per Gram
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
mmoles Cu per Gram
0.1M Cl
0.01M Cl
0M Cl

Figure 33

Donnan effects are usually underestimated at pH values at which humic acid seems to be "dissolved". Marinsky(15) has pointed out the possible existence of micro-gels in humic substances. In these cases a Donnan behaviour may be noted at pH values when the macro-gel structure has been destroyed. The Donnan potentials developed in these systems may be much smaller than in macro-gel systems such as is the case of humic acid at low pH values. In the absence of specific interactions, cations are expected to be held in the gel phase by electrostatic attraction. In the presence of background electrolyte and a fixed degree of ionization the concentration of copper ions in both phase depends on concentration of background electrolyte in the gel phase. The greater dependence of the binding of copper to humic acid at pH 3 compared to the binding at pH 5 seems to reflect the possibility that the interaction between copper and humic acid at low pH is mainly electrostatic. While at pH 5 specific interaction may be contributing to the total binding.

The differences in the copper binding curves at pH 3 and 5, with no background electrolyte can be explained as follows. At low pH, there is a large number of ion exchange sites covered by protons. Copper has the tendency to displace them, despite the large concentration of protons in the external solution. Taking pK_{app} for humic acid as 3.7 and the average equilibrium ion exchange function for copper as 2×10^{-2} (see Table 15) will give an estimated association constant for copper-humate of

10^{+5}, compared to the association constant for proton-humate of 10^{+4}. This can explain why the binding curve for copper at low pH does not show a definite plateau region, copper ions are able to compete with protons for binding site even at relatively high concentration of protons in solution. At low copper loadings, the changes in pH were not detected by the pH electrode.

The situation is different at higher pH values. At pH 5, the copper binding curve approaches a plateau, reflecting the existence of a constant number of binding sites at that pH. Competition with protons is much less evident.

The behaviour of copper at pH 3 is in contrast to that of alkaline earth metal ions such as Ca and Mg. Both these cations show definite saturation regions.

5.1.7.1. Copper Equilibrium Function.

Copper ion exchange equilibrium function values, as calculated by Equation(16) on Page (16), are presented in Table 15. At low copper loadings, pH changes in the suspensions were not detected, especially at pH 3.00. A plot of the equilibrium function at pH 3.00 is shown in Figure 34. It can be seen that the range of sites covered by copper is larger than that for any of the other cations investigated. Values for the equilibrium function for copper are not very different from those for paraquat and calcium.

Table 15

Copper Ion Exchange Equilibrium Functions

pH 3.00

X_{BH2} (±%7)	$\bar{X}_{Cu}$ (±%10)	K_{Cu} (±%12)
0.981	3.32×10^{-3}	3.10×10^{-2}
0.965	2.84×10^{-3}	2.77×10^{-2}
0.950	2.47×10^{-3}	2.47×10^{-2}
0.937	2.18×10^{-3}	2.00×10^{-2}
0.923	1.94×10^{-3}	1.81×10^{-2}
0.914	1.75×10^{-3}	1.65×10^{-2}
0.905	1.57×10^{-3}	1.45×10^{-2}
0.896	1.44×10^{-3}	1.37×10^{-2}
0.888	1.34×10^{-3}	1.26×10^{-2}

The one-site model presented for this particular humic acid implies that the interaction of cations with carboxyl groups should be reflected in constant values for the equilibrium function, as was the case for calcium and magnesium where the range of sites scanned is small. Based on this and assuming that the main groups to which copper binds involve carboxyl groups in one way or another, i.e. as dicarboxyl or salicylic sites, the dependence of K_{Cu} on X_{BH2} represents the effect of the polyelectrolytic character of humic acid. The reduction of the electrostatic field near the site of the reaction, i.e., inside

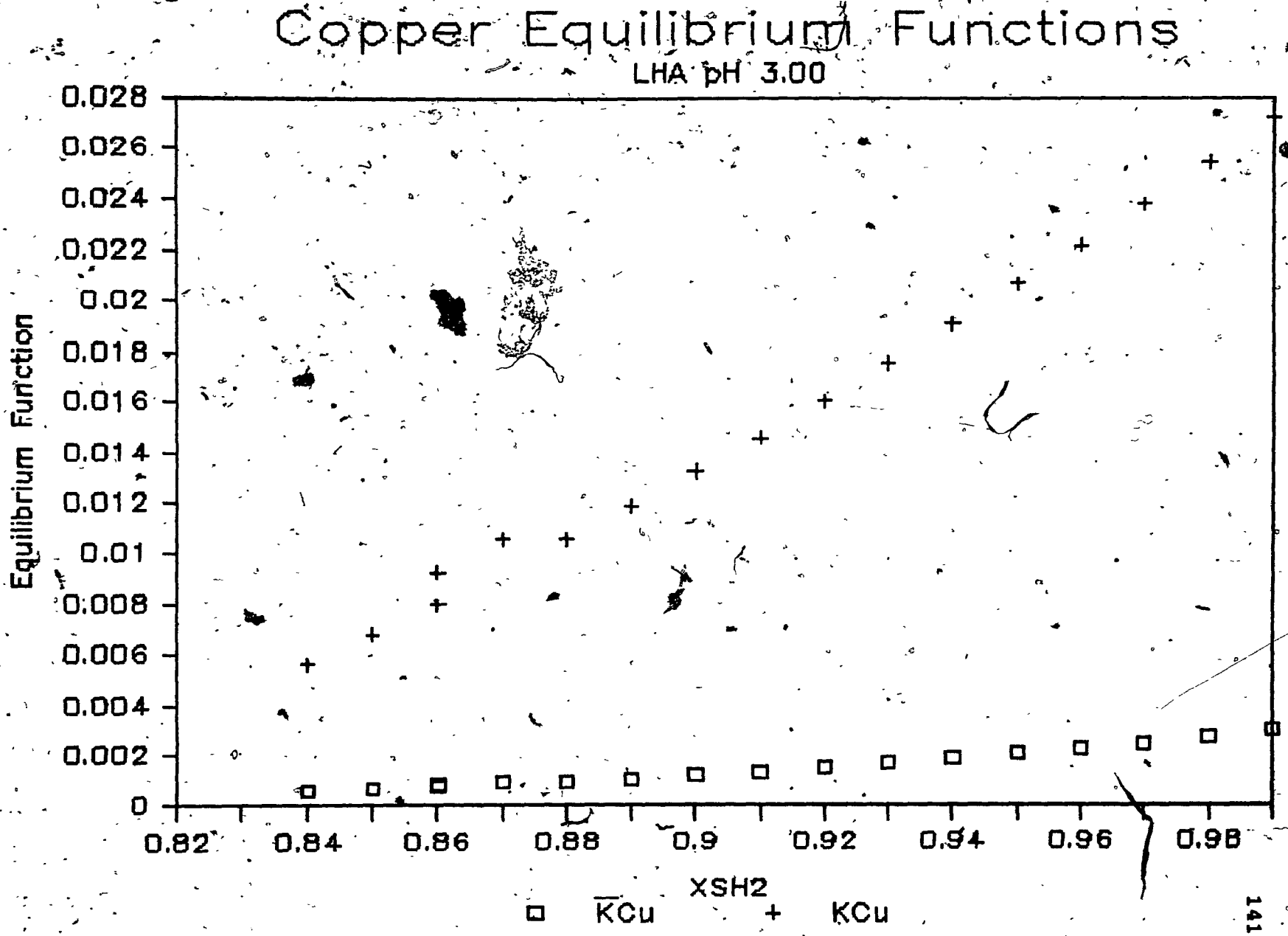
Copper Equilibrium Functions
LHA pH 3.00
Equilibrium Function
0.028
0.026
0.024
0.022
0.02
0.018
0.016
0.014
0.012
0.01
0.008
0.006
0.004
0.002
0
0.82
0.84
0.86
0.88
0.9
0.92
0.94
0.96
0.98
XSH2
KCu
KCu

Figure 34

the gel solution, as copper ions are bound, produces a reduction on the attractive forces with concomitant decrease of the average equilibrium function.

The plot of the average, and differential equilibrium functions for copper at pH 3.00 is shown in Figure 34. As the site coverage increases, the average and differential functions converge to a common value. Changes ion the differential function with respect to total copper added are much smaller that those for the average equilibrium function; this indicates that the sites to which copper binds are rather homogeneous, in corroboratfon of the one-site model proposed earlier.

5.1.7.2. Copper Binding to LHA at pH 5.00:

The binding of copper to LHA at pH 5.00 was studied at different ionic strengths. (Figure 33). One important qualitative observation is that in all cases humic acid precipitated very early in the titration. In most cases, the supernatant solution was perfectly clear to the naked eye. The formation of aggregates large enough to produce precipitation of humic moieties must be due to the linking of molecules via copper bridges. A similar situation was found by Saar and Weber(65) for fulvic acids interacting with lead ions. Underdown et al.(13), found the same effect in the interaction of a soil fulvic acid and copper ions, although in the latter case, precipitation, as detected by the settling of visible

precipitates, was not seen. Calcium showed the same effect as copper for LHA at pH 5.00. The formation of bridges between molecules in fulvic acid has been postulated to explain copper complexation by carboxyl groups in two different molecules(13). It is quite possible that a similar mechanism would be valid for LHA copper complexation.

The total number of potential sites in humic acids is smaller that in fulvic acids. This, in conjunction with a larger average molecular weight, may enhance coagulation and precipitation effects in humic acid systems.

The fact that precipitation occurs rather early in the titration (after the addition of between 0.5 and 1 millimoles of copper per gram of humic acid), indicates that the complexation process inducing it, takes priority over any other process. Extending this line of thought further leads to the hypothesis that dicarboxlylic-copper interaction (with carboxyl groups in different molecules) is the main binding mechanism at pH 5.00 for LHA. The concentration of salicylic sites, may be much less than that of dicarboxyl sites, probably due to structural reasons, i.e, few hydroxyl groups adjacent to benzoic acid moieties. Figure 34a shows a possible structure for the copper-dicarboxylic complexes in LHA.

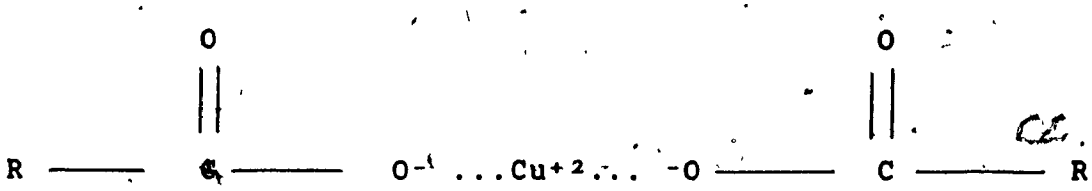

Figure 34a

As in the case of copper-fulvic acid, the interaction of copper and humic acid deserves an in detailed study, including some light scattering measurements to follow the titration procedure. The formation of bridging complexes in fulvic acid required relatively high concentrations of fulvic acid, about 1 g/L; even at this concentration, precipitation did not occur. In the experiments with LHA, concentrations of 0.1 to 0.2 g/L were enough for aggregation/precipitation to occur at relatively low loadings of copper. This can be explained by the fact that humic acid has a larger average molecular weight and lower oxygen content than does fulvic acid.

The formation of precipitates complicates the equilibria that take place at pH 5.00, due to the existence of solution phase, as well as, solid phase copper-humate complexes. The final form of the equilibrium expression should reflect all these components.

5.1.8. Paraquat-Copper-Laurentide Humic Acid System.

5.1.8.1. Experiments with excess Paraquat.

The main aim of these experiments is to see to what extent paraquat and copper compete for the same sites in humic acid. The amount of paraquat per gram needed to saturate humic acid was previously determined from paraquat titrations of humic acid at pH 3.00. By equilibrating the appropriate amount of paraquat with a known amount of humic acid the MV-LHA "complex" was formed. The humic acid paraquat samples were initially equilibrated for 12 hours in order to ensure the formation of the paraquat-humic complex. All the sites available to paraquat in the humic acid sample at that particular pH and ionic strength were covered.

Figure 35 shows the binding curve of copper ion the presence of paraquat. The actual release of paraquat from humic acid by addition of copper is seen in Figure 36.

Experiments in which humic acid saturated with paraquat was titrated with copper, showed that although copper displaced most of the paraquat initially bound, the total amount of copper bound cannot be directly correlated to the amount of paraquat released. The actual amount of copper bound is in fact higher than the amount of paraquat released. Copper, therefore, must be interacting with other sites as well. The amount of paraquat released after each addition of copper corresponds to a fraction of paraquat bound to sites shared by both cations. Under the conditions of these experiments, it is valid to assume that the release of paraquat is due only to ion exchange by copper ions,

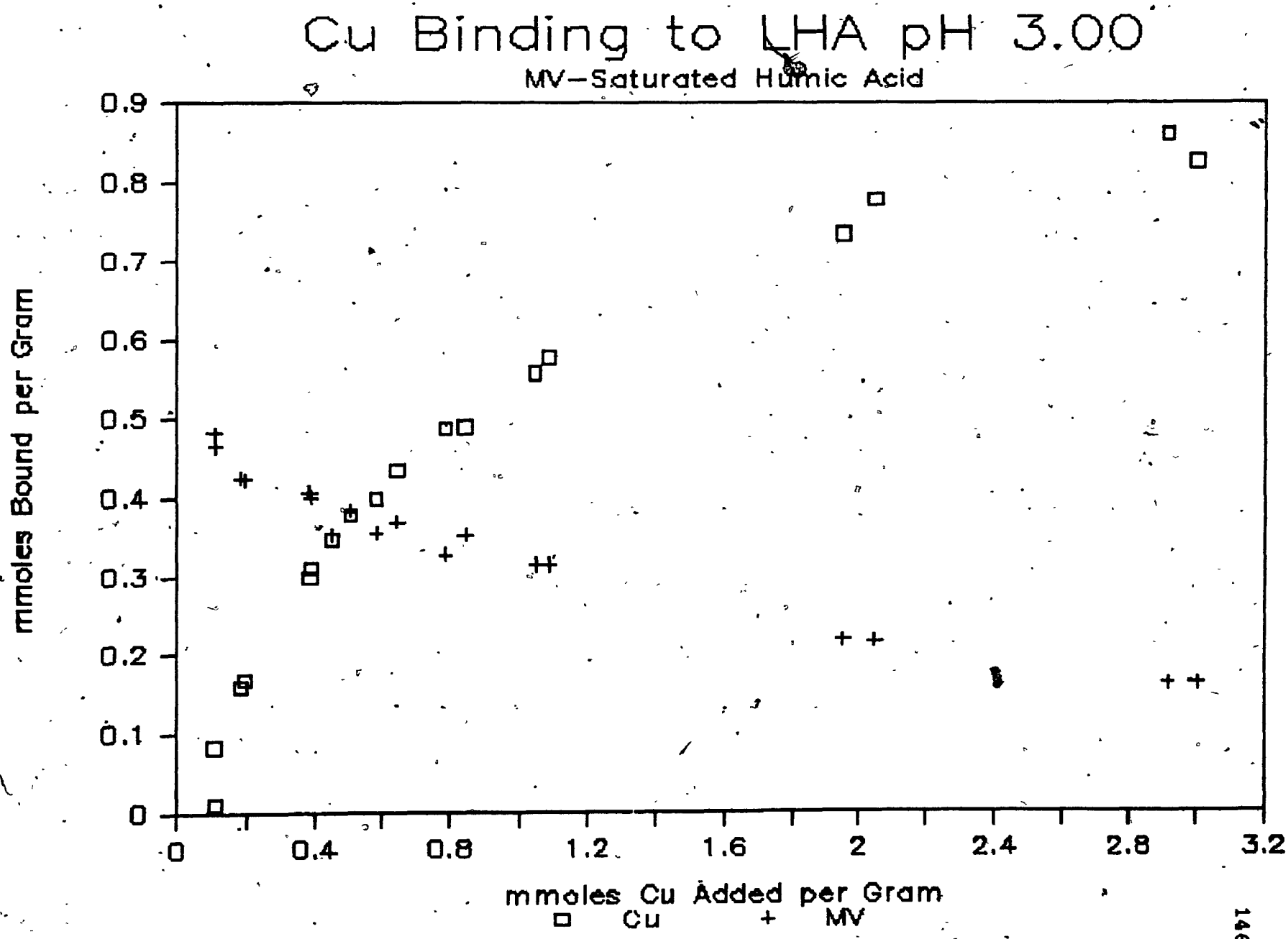
Cu Binding to LHA pH 3.00
MV-Saturated Humic Acid
mmoles Bound per Gram
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.4
0.8
1.2
1.6
2
2.4
2.8
3.2
mmoles Cu Added per Gram
Cu
MV

Figure 35

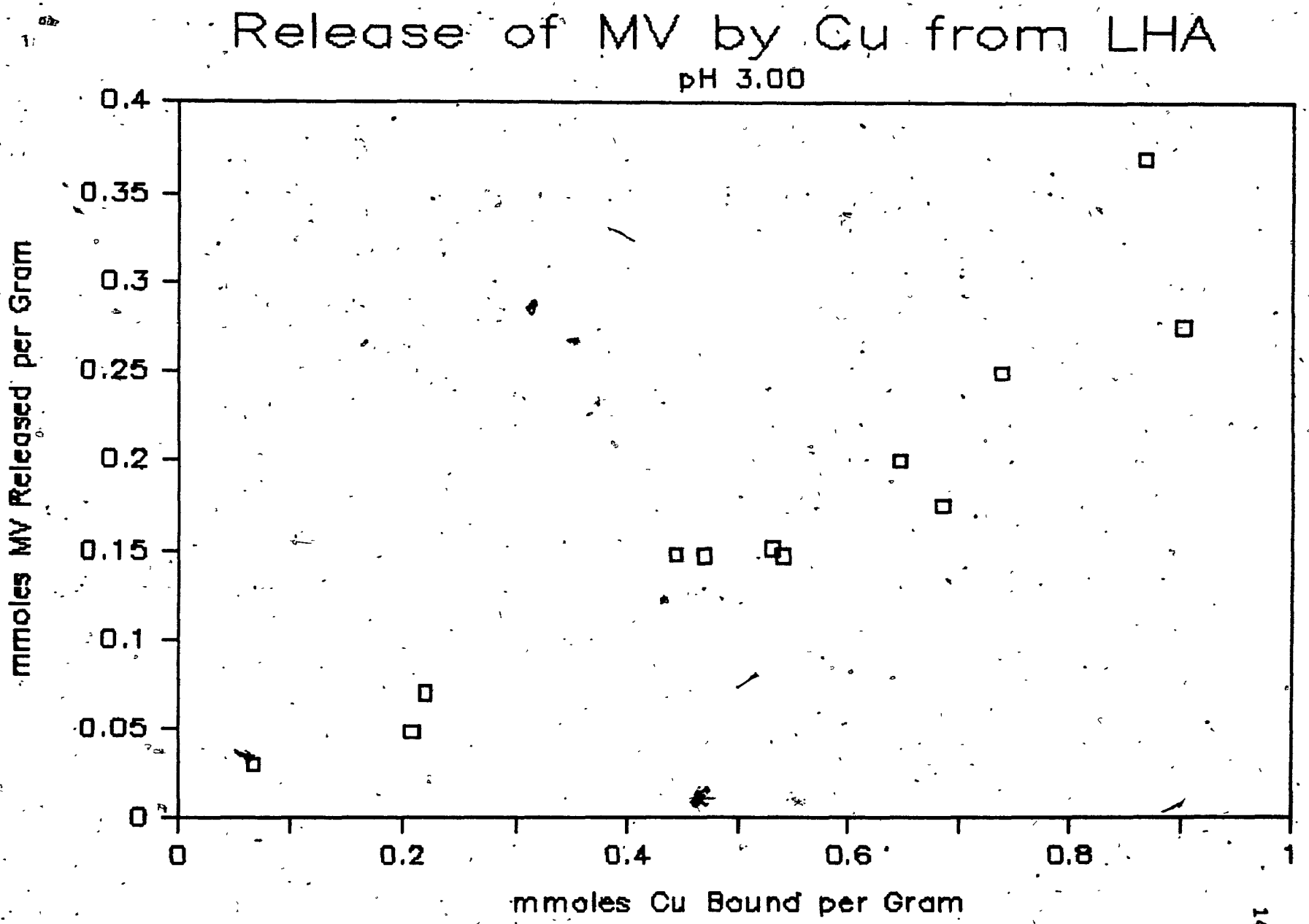
Release of MV by Cu from LHA
pH 3.00
mmoles MV Released per Gram
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
0.2
0.4
0.6
0.8
1
mmoles Cu Bound per Gram

Figure 36

that is the fraction of paraquat bound via ion exchange; thus the stoichiometry is of 1:1. The fraction of copper not engaged in displacing paraquat must be binding to sites initially covered by protons.

5.1.8.2. Mole Fraction Plots

The slopes of the mole fraction plots are given in Table 16. Actual mole fraction are given in Table 17. As can be seen in the last column in Table 16, the summations of the slopes corresponding to copper and paraquat are very close to unity, indicating self consistency in the data analysis.

Table 16

Paraquat-Copper Mole Fraction Relationships

Experiment	Cation	X_{SH2}	dX_C/dX_{SH2}	dX_C/dX_{SH2}
Constant	Cu	0.710	5.67×10^{-2}	
Copper	MV	0.710	-1.06	-1.00
Constant	CU	0.850	-1.525	
Paraquat	MV	0.850	0.521	-1.00
Constant	Cu	0.775	-0.447	
Copper	MV	0.775	-0.431	-0.878
Constant	Cu	0.740	-1.445	
Paraquat	MV	0.740	0.446	-0.999

Table 17

Ion Exchange Equilibrium Functions'

Paraquat-Copper-LHA at pH 3.00

X_{MV} (±%5)	X_{Cu} (±%5)	X_{SH2} (±%7)	K_{MV} (±%10)	K_{Cu} (±%10)
0.097	0.017	0.886	7.31×10^{-4}	1.08×10^{-3}
0.092	0.054	0.8854	9.17×10^{-3}	3.52×10^{-3}
0.066	0.057	0.877	6.61×10^{-3}	2.29×10^{-3}
0.067	0.116	0.817	6.68×10^{-3}	4.19×10^{-3}
0.062	0.122	0.814	6.32×10^{-3}	3.03×10^{-3}
0.063	0.141	0.797	6.29×10^{-3}	2.33×10^{-3}
0.062	0.138	0.799	6.20×10^{-3}	1.35×10^{-3}
0.049	0.168	0.784	4.85×10^{-3}	1.22×10^{-3}
0.052	0.178	0.770	5.20×10^{-3}	1.04×10^{-3}
0.037	0.192	0.770	3.73×10^{-3}	8.73×10^{-3}
0.032	0.226	0.742	3.26×10^{-3}	7.72×10^{-3}

Total Paraquat added 1 10^{-3}M per 0.1 grams of LHA in 50.00 mLs.

Table 18

Ion Exchange Equilibrium Functions

Paraquat-Copper-LHA at pH 3.00

X_{MV} (±%5)	X_{Cu} (±%5)	X_{BH2} (±%7)	K_{MV} (±%10)	K_{Cu} (±%10)
0.121	0.003	0.876	1.13×10^{-3}	1.85×10^{-4}
0.126	0.022	0.853	1.29×10^{-3}	5.21×10^{-3}
0.110	0.043	0.846	1.09×10^{-3}	7.78×10^{-3}
0.111	0.042	0.848	1.14×10^{-3}	7.43×10^{-3}
0.105	0.081	0.814	1.03×10^{-3}	5.34×10^{-3}
0.106	0.078	0.816	1.06×10^{-3}	4.70×10^{-3}
0.100	0.099	0.801	9.42×10^{-4}	4.26×10^{-3}
0.092	0.090	0.918	8.64×10^{-4}	4.40×10^{-3}
0.096	0.113	0.790	8.69×10^{-4}	3.23×10^{-3}
0.093	0.104	0.803	8.52×10^{-4}	3.04×10^{-3}
0.086	0.127	0.788	7.61×10^{-4}	2.29×10^{-3}
0.092	0.127	0.781	8.21×10^{-4}	2.12×10^{-3}
0.082	0.150	0.767	7.00×10^{-4}	1.82×10^{-3}
0.082	0.150	0.767	7.08×10^{-4}	1.74×10^{-3}
0.057	0.203	0.740	4.46×10^{-4}	9.61×10^{-4}
0.057	0.192	0.751	4.48×10^{-4}	8.89×10^{-4}

Total Paraquat 4×10^{-3}M per 0.1 grams LHA in 50.00 mLs

Figures 37-40 show various mole fraction plots for copper and paraquat at pH 3.00. These plots have been interpreted by Gamble et al.(9) as elution plots. They indicate that as the mole fraction of protons increases in the exchanger, cations are released; this is manifested as a negative slope. A positive slope, on the other hand, indicates that the binding of that particular cation increases as the mole fraction of protons increases, which implies that particular cation can only compete for sites with protons. The situation in paraquat-saturated humic acid experiments involving copper is different. Since paraquat has reached its saturation value it can be released only by copper ions or protons. As copper ions are bound paraquat and proton mole fractions decrease, leading to a positive slope for the paraquat mole fraction plot. The coefficients for paraquat, in the constant copper runs, reveal that it is interacting with humic acid, with minimum copper exchange. This verifies the qualitative picture coming out of the binding curves.

The removal of paraquat by copper ions, under the specified conditions, was not complete. Saturation of available sites for copper is reached without total displacement of paraquat. This implies that in the concentration range scanned there is a residual binding of paraquat which cannot be accounted for on the basis of ion exchange with copper ions and by mass balance. Also there is still a number of protons which cannot be displaced by copper.

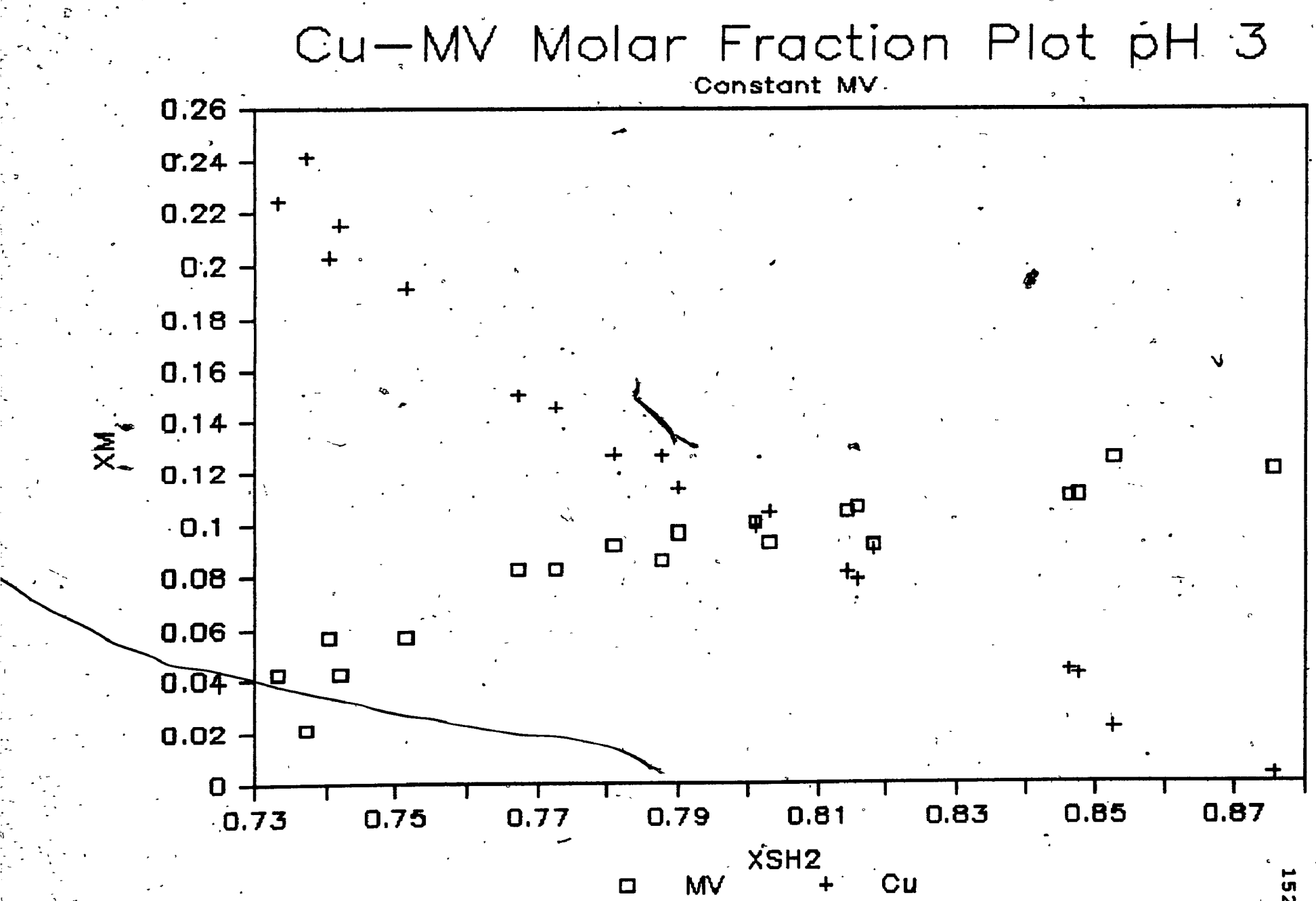
Cu—MV Molar Fraction Plot pH 3
Constant MV
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
XM
0.73
0.75
0.77
0.79
0.81
0.83
0.85
0.87
XSH2
MV
Cu

Figure 37

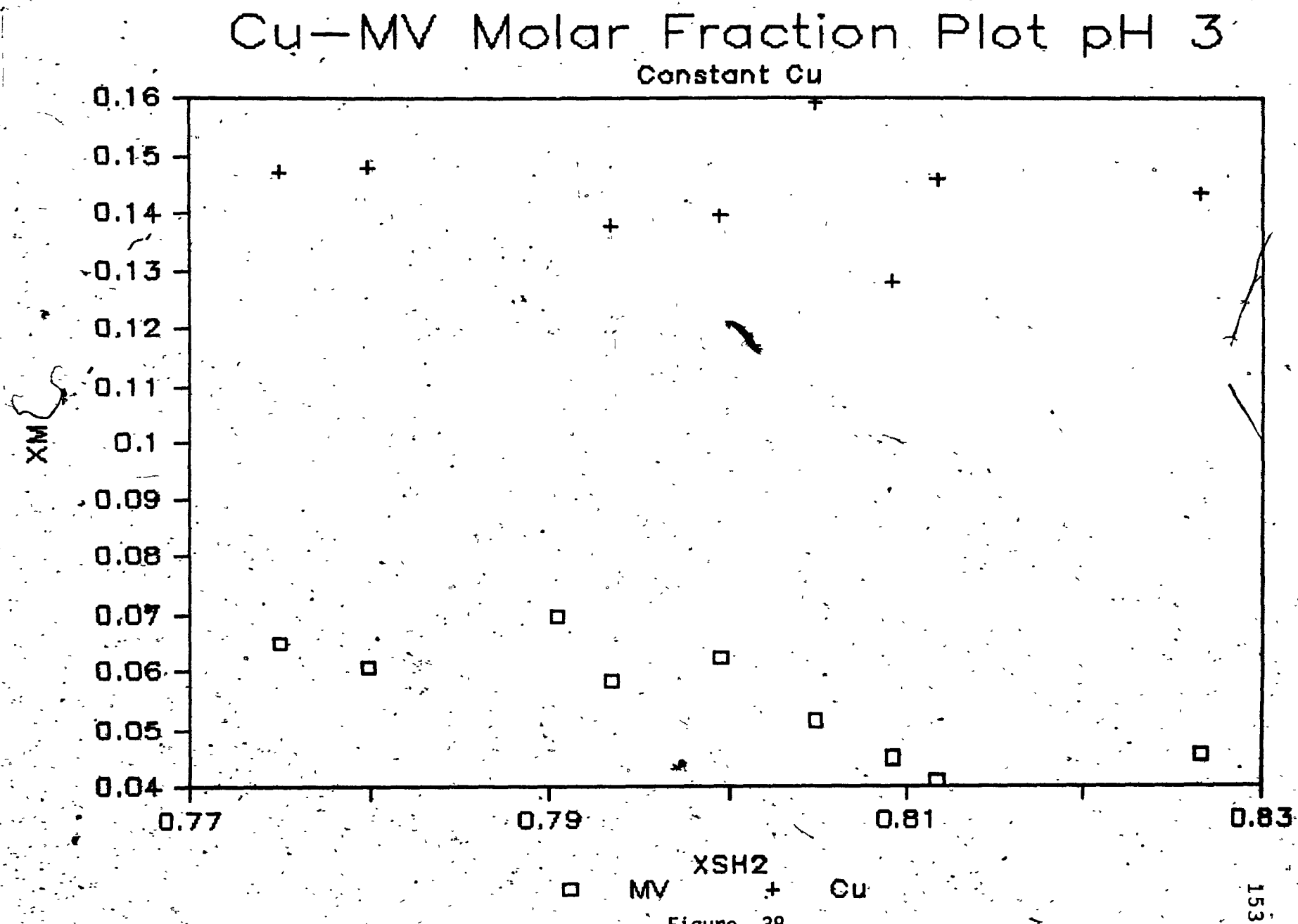
Cu—MV Molar Fraction Plot pH 3
Constant Cu
0.16
0.15
0.14
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
XM
0.77
0.79
0.81
0.83
XSH2
MV
Cu

Figure 38

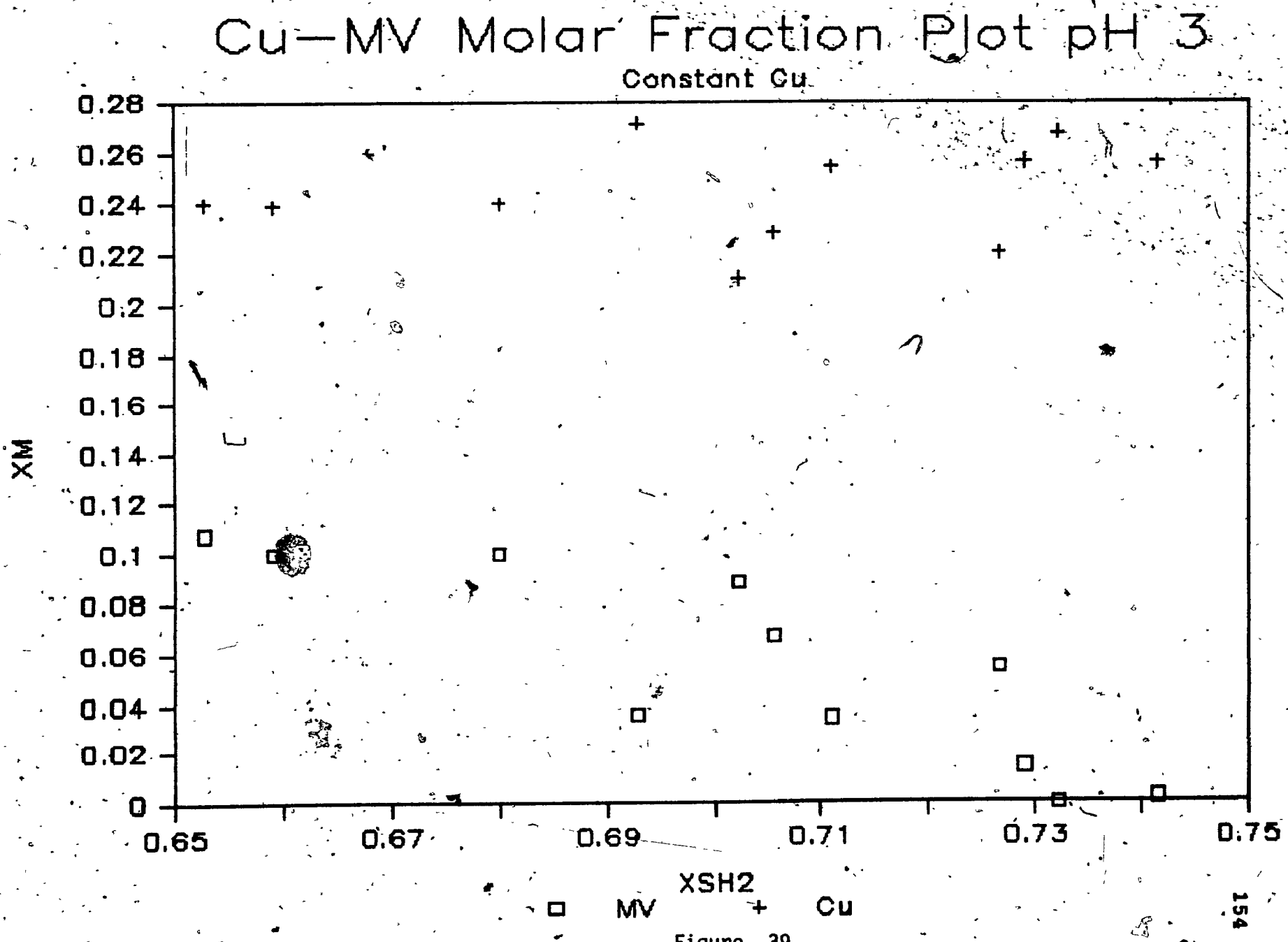
Cu—MV Molar Fraction Plot pH 3
Constant Cu
XM
0.28
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0.65
0.67
0.69
0.71
0.73
0.75
XSH2
MV
Cu

Figure 39

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Interactions of Paraquat with Humic Acid: The Effect of Cations

Luis Eduardo Sojo Lopez

A Thesis

in

The Department

of

Chemistry

Presented in Partial Fulfillment of the Requirements
for the Degree of Doctor of Philosophy at
Concordia University
Montréal, Québec, Canada

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ABSTRACT

Interactions of Paraquat with Humic Acid: The Effect of Cations

Luis Eduardo Sojo Lopez, Ph.D.
Concordia University, 1988

The interactions between the herbicide paraquat with a well characterized humic acid were studied under low ionic strength conditions and various pH values, in the presence of cations such as calcium, magnesium and copper. The humic acid under investigation was standardized by titration using Gran's equivalent point determination. The carboxyl content was determined to be 2.45 ±1% (mmoles/g). An intrinsic pKa value of 3.7 was resolved for Laurentide Humic Acid. Variations in the dissociation function are attributed to polyelectrolyte effects, not to site heterogeneity. The apparent binding capacities for each cations at pH 3 and 5 and at zero ionic strength were found to be: Cu (0.82), MV(paraquat) (0.45), Ca (0.26), Mg(0.25) and Cu(1.34), MV(0.90), Mg(0.92), Ca(0.45) (mmoles/g) respectively. At low ionic strength and pH 3 when Donnan potentials control cation uptake, 50% of the total number of sites available to paraquat are shared with calcium and magnesium. Copper shares about 75% of all the sites available to paraquat. Approximately 25% of these sites do not interact with calcium, magnesium or

copper. The type of sites shared by paraquat with calcium or magnesium are identified as carboxyl groups, while those shared with copper may include carboxyl as well as groups involving phenolic moieties, such as salicylic or α-hydroxy sites. The interaction between paraquat and the sites not shared by the other cations is likely to be charge transfer complexation.

To

Liliana and Alexandra

Many Thanks to Dr. R. H. Zienius for the opportunity to work in his Laboratory. Thanks to Dr. C. H. Langford for valuable discussions and infinite thanks to Dr. D. S. Gamble for sharing his ideas and enthusiasm.

Glossary of Terms

Symbol	Meaning	Units
A-	Fully protonated Humic Acid monovalent site	
aH+	Hydrogen ion activity	Molar
aNa+	Sodium ion activity	Molar
CS	Total number of bidentate sites per gram of Humic Acid	
	Activity Coeffivient	
ΔGe	Average Electrostatic Free Energy of binding	Kjoules/mole
HA	Fully protonated HUmic Acid monovalent sites	
$\overline{KM}$	Weighted Average Ion Exchange Function for Cation M	Molar
KM	Differential Ion Exchange Function for Cation M	Molar

Symbol	Meaning	Units
KMi	Ion Exchange Constant for cation M and site i	Molar
$\bar{K}$SMAn	Weighted Everage Solubility Function for M-Humate	
$\bar{K}$SHA	Weighted Average Solubility Function for Humic Acid	
LHA	Laurentide Humic Acid	
MV+2	Paraquat Cation	
MVCl2	Paraquat Duchloride	
P	Pressure inside Humic Acid gel particles	
Po	Pressure outise Humic Acid gel particles	
Pi	Osmotic Pressure	

qH	Millimoles of protons inside Hunmic Acid gel	Moles/gram
qM	Millimoles of cation M inside Humic Acid gel	Moles/gram
qS	Millimoles of sites free of cations inside Humic gel	Moles/gram
R	YM2 Membrene retention coefficient	
S-2	Fully deprotonated bidentate site	
SH-	Partially protonated bidnetate site	
SH2	Fully protonated bidentate site	
SM	Cation-HUmic Acid conplex	
μ	Chemical Potential	Kjoules/mole
V	Total sample Volume	Litres

VNaCl	Sodium Chloride Partial Molar Volume	Litre/mole
VHCl	Hydrogen Chloride Partial Molar Volume	Litre/mole
Vg	Internal Gel Solution Volume	Litres
XM	Mole Fraction of sites covered by cation M	
XMi	Mole Fraction of sites i covered by cation M	
XS	Mole Fraction of sites free of cations	
XSH2	Mole Fraction of sites covered by protons	
XSH2i	Mole Fraction of sites i covered by protons	

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Chapter 1

1.1. Introduction.

Since the introduction of paraquat as a herbicide in the mid 1950's, its use has been extended to almost all parts of the western world. Paraquat is widely used in North America(1), as well as Europe, England being the country in where it is most extensively used(2). The massive explosion in the development of agrochemicals which took place after the second world war and our times has provided enough surplus herbicides, that industrialized countries export them to third world countries. Paraquat is one of those herbicides, which has found its way into the third world.

The extensive use of such chemicals in agriculture, has produced the need for scientifically sound methods for monitoring their persistance in the environment. This depends on their interactions with the different components making up the whole environment. The partition of herbicides among the different compartments is of vital importance in order to have a clear picture of the fate of these chemicals in the environment. This partition will depend on the physical chemistry between the herbicide and the soil or aqueous compartment. Different compartments will have different affinities for a given herbicide. The interaction of all factors will provide an average behaviour of the herbicide in a particular environment.

The transport of herbicides from their place of application to other regions by ground waters, rain, etc, depends on their mobility in the soil solution. The mobility is linked to the physico-chemical form in which the herbicide is present. Soluble species are likely to be transported by run-off waters, more readily than solid-bound species. On the other hand solid-bound species may not be as dangerous to life as soluble ones. A case in point is paraquat which is inactivated by the presence of montmorillonite. The solid bound species (paraquat-montmorillonite complex) is not toxic (3). All these aspects must be considered when monitoring herbicides. This all leads to the important consideration; speciation. No monitoring protocol will be effective if the speciation of the herbicide in question is not sorted out.

The only study done taking into consideration speciation of paraquat in natural water environments is the one by Guy et al. (4). They suggested an operational speciation scheme based on the interaction of paraquat with humic acids and clay minerals and the effect of parameters such as pH and ionic strength. The different species of paraquat present in a natural water environment were then categorized as shown in Figure (1). The salt labile paraquat fraction is that portion of the total paraquat removable by simple salts such as sodium chloride; free paraquat represents the fraction dialysible through a 4.8 nm pore size membrane; particulate paraquat represents the fraction

removed from the humic acid and clay particles by H_2SO_4 digestion; and the pH labile paraquat represents the fraction removed by acidification.

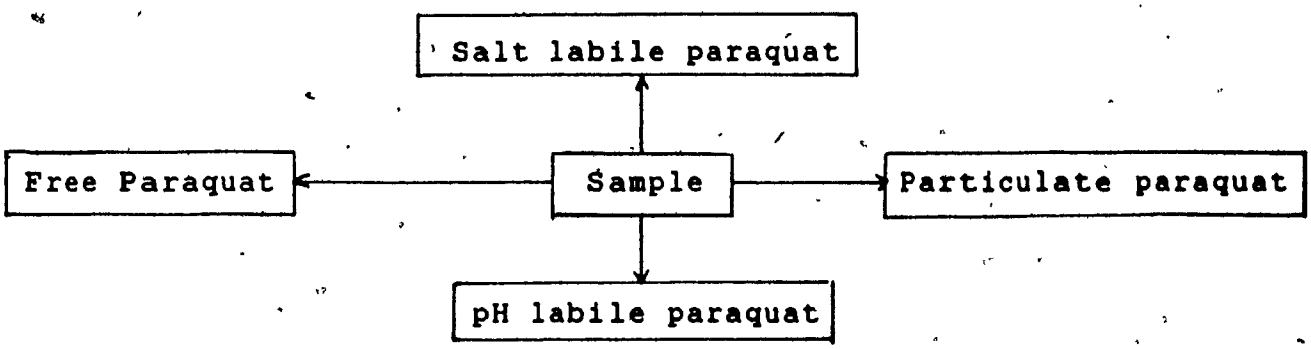


Figure 1

Suggested speciation scheme for paraquat in natural waters.

The speciation scheme presented above is operationally defined, but nevertheless it reflects, only partially, the nature of the interaction between paraquat and humic acids. The salt labile and the pH labile portions are consequences of the electrostatic character of the binding of paraquat to humic acids. This may be an over-simplification of the facts. The operationally defined species respond to a "bulk stimulus", such as changes in ionic strength or pH. This allows assumptions about the mechanism involved, but does not define the microscopic interactions and their intrinsic mechanisms. Changes in the amount bound introduced by changes in ionic strength may be the result of a much more complex situation than simple electrostatic

effects. A case in point is the reduction of the apparent binding capacity of atrazine on fulvic acid with increasing ionic strength (5). In this situation, the reduction of the apparent binding capacity is due to the displacement by potassium ions, of protons from carboxyl groups which otherwise would be available to form hydrogen bonds with atrazine.

The effect of different cations on paraquat speciation in humic suspension may differ. Different cations will interact with different sites in humic acids. Some of them will interact with the same sites as paraquat does. Other will not, particularly at low ionic strengths. Other factor not taken into account in the speciation scheme is possible changes in the structure of humic acid with changes in ionic strength and pH. Changes in the humic acid structure may lead to exclusion of sites which would be available otherwise.

Nevertheless, the speciation scheme presented by Guy et al, represents a practical approach to the problem, especially when considering the release of paraquat from particulate matter into estuaries. The conditions in estuaries are such that high ionic strength prevails. In soil solution where the ionic strength is much lower (1×10^{-3} M), Donnan potentials control the sorption of electrolytes on humic acids. In this situation it is worthwhile looking at the competition among metal ions and paraquat for ion exchange sites on organic as well as on inorganic matter. A detailed study of the range of sites

interacting with metal ions and paraquat is needed.

The ratio of paraquat to humic acid used in desorption studies by Guy et al(4), did not permit a total scan of all the sites available to paraquat. This resulted in an incomplete characterization of the interactions.

In order to be able to come up with a sound speciation scheme which reflects the chemistry of the system in soil solutions, there is also the need to understand the nature of the main adsorbing species, namely humic acid. In most of the studies to date (4,6,7), little information is given on the nature of the humic acid involved. Important parameters such as degree of ionization, physical state and number of potential sites available have been over looked. Structural considerations have also been underrated when interpreting the binding of paraquat to humic acids(4,6,7).

1.2. Objective.

In order to be able to predict the fate of herbicides in the soils knowledge of the interactions between the herbicide in question and the soil components and the effects of various other agents present in the soil solution must be acquired. This involves the physico-chemical categorization of the interactions as well as a detailed study of the factors influencing sorption and descrption from soil colloids. A large number of studies have been done on the interactions of paraquat and soil components (4,6,7). Most of these studies did not pay enough

attention to the effects of metal ions on the interaction of paraquat with humic acids. Competition for ion exchange sites between paraquat and metal ions has not been studied in detail. It is the aim of this work to study the effect of major ions, namely magnesium and calcium, present in soil solutions and trace metal ions such as copper on the interactions of paraquat with an organic soil component: Humic acid.

Chapter 2

2.1. Theory.

2.1.1. General equations for ion exchange in humic gels at low pH and low ionic strength.

At low pH values, most of the ionogenic groups present in humic acids are covered by protons. The main agents responsible for their ion exchange properties are the carboxyl groups. The existence of amine and other nitrogen bearing moieties, as well as sulfur containing groups, does not provide a significant contribution to ion exchange, mainly due to their low concentration. These groups are present in trace quantities in most humic acids of terrestrial origin.

The bulk average dissociation "constant" for the carboxyl groups present in humic acids is in the pKa range of 4 to 5. This explains why at pH lower than 4, the majority of the carboxyl groups are unionized. It is theorized that the true nature of ion exchange expressions are functions, not constants, for two main reasons: first, the heterogeneity of the humic polymer makes each carboxyl groups nonidentical to its nearest neighbor. The difference in pKa would be small but nevertheless significant and would be felt when a scan across the mixture of sites is done. Second (the more obvious) as metal ions are "bound" to the exchanger, they affect the electrostatic potential

at the site of the reaction. The next ions to enter the exchanger would " feel" a smaller electrostatic attraction. This is a well documented situation occurring in polyelectrolytes (8).

The ion exchange reactions between cations and protons in humic acids can be described by:

$$n\,\widetilde{HA} + M^{+n} \rightleftharpoons \widetilde{MA}_n + nH^+ \qquad (1)$$

where the ~ symbols represents species in the gel domain. The establishment of this equation allows for the expression of the equilibrium by means of the law of mass action as proposed by Gamble et al. (9).

$$\overline{K_M} = \frac{X_M \quad [H^+]^n}{X_{SH2}\,[M^{+n}]} \qquad (2)$$

where X_M and X_{SH2} are the mole fractions of the species in the gel domain and the symbols in brackets represent the molarities of species in the external solution. The law of mass action in these systems is controlled by the Donnan potential developed between the inside and the outside of the humic gel for humic acid suspensions at low ionic strength.

An important feature of ion exchange in humic acids is their solubility dependence on pH. Upon titration with standard base humic acids dissolve as the pH of the external solution goes up.

This solubility dependence on pH is linked to the solubility of the alkali-humate formed during titration. The replacement of protons by alkali metal ions (usually Na) disrupts the forces holding together the tridimensional network making up the humic gel. The nature of these forces is likely to be hydrogen bonds between electron donor groups (mainly oxygen) and protons. It is quite possible that at low pH ion exchange may cause dissolution of humic gels, especially when exchange occurs between protons and some weakly "bound" cations such as magnesium. Visual examination of humic acid suspensions at low pH in the presence of magnesium revealed that some of the humic acid goes into solution.

Accounting for the possible dissolution of the products of ion exchange at low pH leads to the establishment of the following equilibrium reactions:

$$\widetilde{H^+\ A^-} \rightleftharpoons H^+\ A^- \qquad (3)$$

$$\widetilde{M^{+n}\ A^-} \rightleftharpoons M^{+n}\ A^- \qquad (4)$$

The law of mass action describing these equilibria takes the form:

$$\overline{K}_{BHA} = \frac{[H^+]\ [A^-]}{\{H^+\}\ \{A^-\}} \qquad (5)$$

$$\overline{K}_{SMA_n} = \frac{[M^{+n}]\,[A^-]}{\{M^{+n}\}\,\{A^-\}} \qquad (6)$$

The ion exchange law of mass action expression can then be written as:

$$\overline{K}_M = \frac{(\overline{K}_{SHA})^n}{\overline{K}_{SMA_n}} \qquad (7)$$

Free cations in the gel phase are ion paired to ionized carboxyl groups making up the ion exchanger. Direct measurement of the molarity of cations inside the gel solution cannot be done because the gel volume is unknown. This is complicated by the fact that its volume changes in the course of an acid base titration due to dissolution of humic acid.

$$\overline{K}_M = \frac{\{M^{+n}\}\,[H^+]^n}{\{H^+\}^n\,[M^+]} \qquad (8)$$

Expressing the molarity of species inside the gel solution as the ratio of the number of moles of cations divided by the gel solution volume leads to:

$$\overline{K}_M = \frac{V_{g(n-1)}\,q_M\,[H^+]^n}{q_H{}^n\,[M^{+n}]} \qquad (9)$$

In the case of ion exchange between protons and univalent cations the gel volume terms is unity. The molarity of free protons inside the gel solution must be equal to the molarity of ionized carboxyl groups to which they are paired. The above expression is not very useful since the gel volume term is unknown.

The ion exchange law of mass action can be rewritten in order to exclude the volume term:

$$\overline{K}_M = \frac{\{SM\}\,[H^+]^2}{\{SH_2\}\,[M^{+2}]} \qquad (10)$$

where the SM and SH_2 represent bidentate ion exchange sites covered by cations and protons respectively in order to simplify the expression when dealing with divalent cations. The assignment of a cation to a particular binding site is rather convenient for mathematical manipulations, although it may not reflect the truth; especially when territorialy bound cations are involved. This may also be true for other cations, since at low pH the structure of the sites inside the gel solution may not be clearly defined due to the confinement of a charge to compact tridimensional network.

The molarity terms in the gel solution can be transformed into their respective moles per volume expressions:

$$\{SM\} = \frac{q_M}{V_g} \qquad (11)$$

$$\{SH_2\} = \frac{q_{SH2}}{V_g} \qquad (12)$$

In this way the volume terms cancel and:

$$\overline{K_M} = \frac{q_M \quad [H^+]^2}{q_{SH2} \quad [M^{+2}]} \qquad (13)$$

The term q_{SH2} represents the number of moles of bidentate sites occupied by protons. Mole fraction can be introduced easily at this point:

$$\overline{K_M} = \frac{X_M \quad [H^+]^2}{X_{SH2} \quad [M^{+2}]} \qquad (14)$$

$$\overline{K_M} = \frac{X_M \quad [H^+]^2}{(1-X_M) \cdot [M^{+2}]} \qquad (15)$$

The ion exchange equilibrium expressions are mathematical devices that allow us to interpret the chemical events taking place. A few comments are important at this point. First, the law of mass action has been employed using molarities instead of

activities. Activity coefficients in soil solutions are rather difficult if not impossible to obtain. Sposito (10) very recently has tackled the possibility of measuring activity coefficients in soil solutions, including single ion activities. Until activity coefficient data become readily available, molarity units are the only accessible pieces of information the soil scientist can obtain without extensive mathematical manipulations involving approximations. Second, a consideration rather crucial to the forthcoming discussion is the fact that the law of mass action as described for humic substances is not a constant, but rather, a function that depends on the heterogeneity of the system as well as its polyelectrolytic nature. Law of mass action ratios are then functions of the loading of metal ion as well as the electrostatic field developed at the site of the reaction. The latter is also a function of site coverage.

It has been proposed by Gamble et al. (10) that in order to be able to describe ion exchange equilibrium in humic gels in a quasi-thermodynamic fashion it is necessary first to clarify the heterogeneity factor. This can be achieved by a series of mathematical manipulations which lead to the definition of differential equilibrium functions. The bulk average equilibrium values experimentally determined are the weighted average of an infinite number of ion exchange constants due to reactions between metal ions and an infinite number of chemically similar

ion exchange sites. As these sites are covered by metal ions, each cation entering into the gel solution will "see" a slightly chemically different environment. It is theoretically to write, therefore, that;

$$K_{Mi} = \frac{XM_i \ [H^+]^2}{X_{SH2} \ [M^+]} \qquad (16)$$

This represents the law of mass action applied to a small "i" portion of the total number of ion exchange sites. This expression can be expanded to include an "intrinsic" ion exchange constant and its electrostatic term:

$$K_{Mi} = K_{Mi}^{o} \exp(-\Delta G_{ei} / RT) \qquad (17)$$

K_{Mi}^{o} represents the heterogeneity factor and the exponential term represents the polyelectrolytic nature of humic acid.

The link between the experimentally determined equilibrium value and the intrinsic equilibrium constant leads to:

$$X_{Mi} = \frac{K_{Mi} \ (X_{SH2})_i \ [M^{+2}]}{[H^+]^2} \qquad (18)$$

Mass balance for the total amount of metal "bound" and the total number of ion exchange sites leads to:

$$X_M = \sum_{i=1}^{n} X_{Mi} \qquad (19)$$

$$X_{SH2} = \sum_{i=1}^{n} (X_{SH2})_i \qquad (20)$$

substituting equations (19) and (20) into equation (18):

$$X_M = \sum_{i=1}^{n} K_{Mi} (X_{SH2})_i \frac{[M^{+2}]}{[H^+]^2} \qquad (21)$$

Substituting equation (21) into equation (14):

$$\overline{K_M} = \sum_{i=1}^{n} \frac{K_{Mi}(X_{SH2})_i [M^{+2}]/[H^+]^2 ([H^+]^2)}{X_{SH2} [M1^{+2}]} \qquad (22)$$

$$\overline{K_M} = \sum_{i=1}^{n} \frac{K_{Mi} (X_{SH2})_i}{X_{SH2}} \qquad (23)$$

In the light of the recent interpretations of the

heterogeneity of humic substances (11,12), it is important to point out that the previous expression is perfectly valid for both the case of continuous and discrete site distribution models. In the case of discrete site distributions, some authors (11,12) suggest the use of two or three sites at the most. This assumption has little chemical meaning. It is only the result of the best number of sites to fit a particular set of data. For a three sites model, equation (23) will take the form:

$$K_M = \frac{K_{M1}(X_{SH2})_1 + K_{M2}(X_{SH2})_2 + K_{M3}(X_{SH2})_3}{X_{SH2}} \quad (24)$$

The use of a continuous distribution of binding sites model requires the mathematical device of infinitesimal sites, which can be described as the infinitely small portion of the total number of sites with a distinct or "intrinsic" equilibrium constant; this lead to:

$$\overline{K_M} = \frac{1}{X_{SH2}} \int_0^{X_{SH2}} K_M \, dX_{SH2} \quad (25)$$

The importance of equation (25) lies in the fact that by determining the average equilibrium function one can get an insight into the "intrinsic" or differential equilibrium function K_M. Rearranging and taking derivatives of equation (25):

$$K_M = \frac{d\,(\bar{K}_M\, X_{SH2})}{d\, X_{SH2}} \qquad (26)$$

Equation (26) implies that K_M is a function of the mole fraction of sites covered by protons . Scanning the mixture of sites will provide information on how K_M changes with site coverage. This change reflects changes in the electrostatic field at the site of the reaction, as well as changes due to the heterogeneity of the ion exchange sites.

At constant low pH (< 3), the electrostatic contribution to the differential equilibrium function is not as large as in the case of a scan across a wide range of pH values. More precisely, due to the fact that only a very small fraction of the ion exchange sites is actually dissociated inside the gel solution, the electrostatic field developed would be more or less constant at low metal loadings. Any deviation from a constant average equilibrium function would then be due mainly to the heterogeneous component contribution to the average equilibrium function.

2.1.1.1. Cation competition for ion exchange sites in humic gels.

The effect of other cations on the ion exchange equilibrium function of any one cation can be described using the proton as a reference cation (10). This means that independent law of mass action expressions can be written for each cation in the system which will include the proton as one of the exchanging species. The total number of bidentate sites is composed of the summation of all the metal covered sites plus the sites covered by protons:

$$X_{SH2} = 1 - (X_{M1} + X_{M2} + X_{M3} + \ldots + X_{Mn}) \qquad (27)$$

$$X_{SH2} = 1 - \sum_{i=1}^{n} X_{Mi} \qquad (28)$$

$$X_{SH2} = 1 - X_{M1} - \sum_{i=2}^{n} X_{Mj} \qquad (29)$$

where X_{M1} represents the cation of interest.

$$dX_{SH2} = -dX_{M1} - \sum_{J=2}^{n} dX_{Mj} \qquad (30)$$

The differential equilibrium function takes the form:

$$dK_{M1}\, X_{BH2} = -K_{M1}\, dX_{M1} - \sum_{j=2}^{n} dX_{Mj}\, K_{Mj} \qquad (31)$$

The bulk average equilibrium function for this particular case is:

$$K_{M1} = \frac{-1}{X_{BH2}} \int_0^{XM_1} K_{M1}\, dX_{BH2} - \sum_{j=2}^{k} \int_0^{X_{Mj}} K_M dX_{Mj} \qquad (32)$$

Expression (32) deserves a few comments. The effect of other cations on the equilibrium function of M_1, for example, depends on the extent of loading on the sites as well as the kind of site to which binding occurs. A total loading of cation M_2, for example, may not give the same equilibrium position for M^1 as the same loading of M_3. This depends on the nature of the sites to which M_2 and M_3 bind and the interaction itself. Structural differences in ion exchange sites may lead to selective binding of one cation over another. This will have an effect on the binding behaviour of M^1. Expression (32) provides a way of probing the spectrum of sites to which M_1 binds. The use of a cation known to bind preferentially to a given type of sites may help in assessing the type of site to which M^1 binds. This is particularly of interest in the case of the interaction between organocations and humic acids. Organocations such as paraquat present more stringent requirements for ion exchange to be

possible, than do metal ions which can be considered, as a first approximation, as positively charged spheres for ion exchange purposes.

Mass balance relationships between the total number of cations in the gel phase provide an internal experimental check on the data. Gamble et al.(9) described the use of mole fraction relationships as follows:

$$\sum_{i=1}^{n} \frac{dX_{Mi}}{dX_{BH2}} = -1 \qquad (33)$$

Competition between cations and protons is manifested by a negative value in the summation terms. It is expected that the absolute values of these coefficients will be less than unity. These are considered to be first order interactions. Positive values were identified by Gamble et al. (9) as an indication of second or higher order interactions, i.e. cations being released by protons allowing for the interaction of other cations with previously proton covered sites. The use of mole fraction relationships implies a prior knowledge of the stoichiometry of the ion exchange reaction. A 1:1 stoichiometry is usually assumed when considering divalent cation and bidentate sites.

2.1.2. Interaction of cations with humic acid at high pH values.

The pH dependent solubility of humic acid introduces a variable which must be accounted for in order to describe cation-humic interactions. At pH values higher that 4.5 humic acid dissolves providing a polyelectrolyte "pseudo-solution". The consequence of this is that a large electrostatic field develops on the surface of the humic acid molecules due to the ionization of carboxylic sites. The macro-gel structure has been totally or partially disrupted. Under these conditions humic acid behaves like a fulvic acid in solution, which can be described as pointed out by Marinsky et al.(15,16) as a micro-gel system impermeable to electrolytes. Any equilibrium description must take this into account.

Cations such as magnesium and calcium will interact with already ionized carboxyl groups, which will presumably hold the cations in the polyelectrolyte domain. Metal ions such as copper will also interact with phenolic protons, presumably those next to already ionized carboxyl groups. This is a consequence of copper being able to form inner sphere complexes. The forces involved in the binding of calcium and magnesium are presumably electrostatic, while those involved in the binding of copper will exhibit some covalent character. Results reported by Underdown et al. (13) considering the energy of binding show that this is true in the case of fulvic acid and copper interactions

at low copper loadings. Salicylic type sites are rather selective towards copper ions.

At pH 5.00, when visual inspection indicated that humic acid has gone into solution, a large fraction of the carboxyl groups are ionized (50%) based on acid-base titrations results. Under these conditions five generic groups of bidentate sites can be postulated:

1.- Type A : fully protonated dicarboxylic sites

2.- Type A1 : partially ionized dicarboxylic sites

3.- Type B : partially ionized salicylic sites

4.- Type B1 : fully deprotonated dicarboxylic sites

Experimental results based on the monitoring of hydrogen ion release at low loadings of calcium and magnesium indicate that these cations will likely interact with type A sites while copper will interact with all of them. This permits writing of possible reaction stoichiometries between carboxyl sites and divalent cations:

$$Mg^{+2} + S^{-2} \rightleftharpoons SMg \qquad (34)$$

$$Ca^{+2} + S^{-2} \rightleftharpoons SCa \qquad (35)$$

$$MV^{+2} + S^{-2} \rightleftharpoons SMV \qquad (36)$$

$$Cu^{+2} + S^{-2} \rightleftharpoons SCu \qquad (37)$$

$$Cu^{+2} + SH^{-} \rightleftharpoons SCu + H^{+} \qquad (38)$$

$$Cu^{+2} + SH_2 \rightleftharpoons SCu + 2H^{+} \qquad (39)$$

The stoichiometric expressions written above allow for the description of the equilibria under specified conditions.

In general, at low magnesium, calcium or paraquat loadings:

$$M^{+2} + S^{-2} \rightleftharpoons SM \qquad (40)$$

$$\bar{K}_M = \frac{X_{SM}}{X_S \quad [M^{+2}]} \qquad (41)$$

$$X_S = \frac{\text{moles of ionized carboxyl sites}}{\text{number of total sites ionized}} \qquad (42)$$

$$X_{SM} = \frac{\text{moles of cation M in gel}}{\text{number of total sites ionized}} \qquad (43)$$

Under low loading conditions, the average equilibrium function is given by:

$$\bar{K}_M = \frac{1}{X_S} \int_0^{X_S} K_M \, X_S \, dX_S \qquad (44)$$

A similar function can be defined for an infinitesimal fraction of the mixture of sites:

$$K_M = \frac{dX_S}{dX_S \quad [M^{+2}]} \qquad (45)$$

$$K_M = \frac{1}{X_B} \int_0^{X_B} K_M \exp(-\Delta G_e/RT) dX_B \qquad (46)$$

The differential equilibrium function has the same properties as described before. Contributions from the electrostatic term are expected to be more significant than in the case at low pH. The electrostatic term has been identified by Marinsky(14,15,16) as a contribution to the deviation from constancy in plots of apparent pKa versus the degree of ionization of the polyelectrolyte. Large deviations are found at high pH values indicating a significant contribution from the electrostatic term. In the case of cations such as magnesium, K_M values may be very small compared to the electrostatic contribution. An important consequence of this fact is that by studying the interaction between humic acid and magnesium one can obtain an estimate of the electrostatic term.

In the above derivations, a 1:1 stoichiometry was assumed. This takes for granted certain stereochemical constraints. For the binding of cations by bidentate sites as postulated above, the carboxyl groups participating in the interaction must be located in such a way that the distance between the two groups is close enough for binding as a bidentate site. This implies that carboxyl groups closely spaced in the same molecule will provide the optimum conditions for binding. This has been

considered in Figure 2. This simple steric consideration implies that not all the sites will be available as bidentate sites. The possibility of bridging two molecules via cation interaction with carboxyl groups in separate molecules must also be considered. It is expected that in this situation the binding will be sensitive to the ligand concentration.

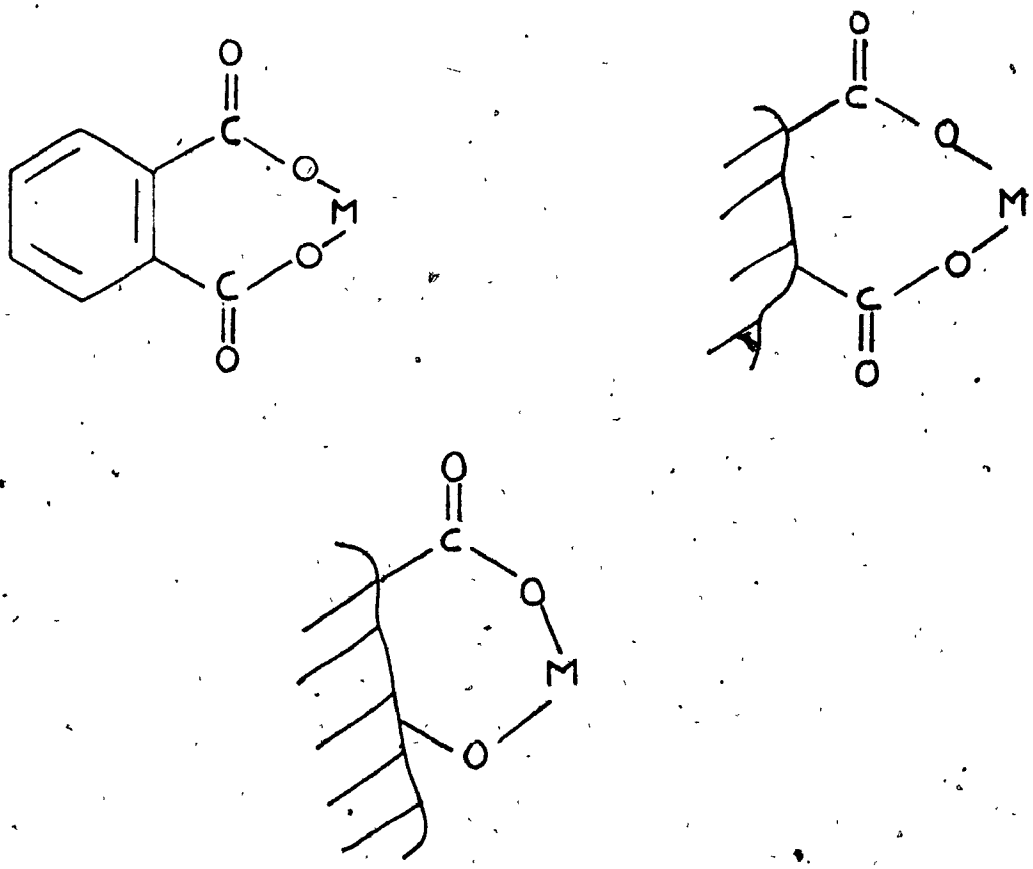


Figure 2.

Postulated Cation Binding Sites in Humic Acids

2.1.3. Mole fraction relationships.

The description of the equilibrium between cations and humic substances requires the establishment of the stoichiometry of the ion exchange reactions taking place. The key is the recognition of which functional groups are responsible for the ion exchange reactions. It is one of the aims of this work to confirm this requirement.

Ion exchange reactions taking place in humic substances can be correlated to the operationally defined number of acidic groups present in the sample. Carboxyl and phenolic protons are prime candidates for ion exchange sites as has been shown in numerous studies(14,15,16,). As a first approximation, the total number of millimoles of acidic hydrogen can provide an estimate of the apparent binding capacity for metal ions. Based on the total number of sites potentially available, mole fraction relationships can be written to describe the system.

The total number of potential ion exchange sites for divalent cations can be estimated to equal half of the total acidity. This represents an upper limit and does not provide an absolute value. The actual number of sites available will depend on the solution conditions, the cation involved, etc. Phenolic protons have been included with a purpose since there is the possibility of certain cations interacting with sites containing phenolic hydrogen. A case in point is copper which prefers to interact with salicylic type of sites in fulvic acids. The

contribution of sites involving only phenolic protons to cation binding is expected to be negligible at low pH values. An important consequence of this is that the total number of carboxyl groups will limit the maximum amount of cation binding.

The total number of sites is given by:

$$C_S = m_S + n_1 m_{M1} + n_2 m_{M2} + \ldots + \quad (47)$$

where C_S is the total number of moles of bidentate sites per gram in a particular sample, m_{Mn} equals the moles of bidentate sites occupied by cations and m_S the moles of sites free of cations. The coefficients, n_n, are the stoichiometric parameters for the ion exchange reactions. Introducing mole fractions:

$$1 = X_S + n_1 X_{M1} + n_2 X_{M2} + \ldots + \quad (48)$$

In the case of a multiple n-cation system, where all cations compete for binding sites, the previous equation becomes a multivariable expression, depending on the extent of the binding of each individual cation. A n-space coordinate system would be required to represent such a system.

One way of obtaining information concerning stoichiometric parameters is to control the number of cations interacting with the humic acid sample. The simplest system

would consist of one cation, M_1, and the proton. This system would not provide enough information on stoichiometry unless there was information from ancillary pH data as to the number of sites free of cations. This may not be a problem for relatively large samples in which pH can be easily monitored.

A practical and interesting way of simplifying the system and obtaining enough information to formulate the stoichiometry of the reaction is to use a "probe cation". In this case the system consists of two cations, M_1 and M_2, and the proton. The mole fraction expression is then reduced to:

$$1 = X_S + n_1 X_{M1} + n_2 X_{M2} \qquad (49)$$

Two extreme possibilities exist: first, that both cations interact with the same sites; and second, both cations interact with different sites. Any combination of these two scenarios is possible. The careful choice of the probe cation can help in simplifying the scheme. The probe cation is added to the system so as to saturate the sites in the humic acid sample. This saturation of sites represents the apparent binding capacity for the probe cation under the specified conditions. It may be different for the other cation. Equation (49) can be rearranged to give:

$$X_{M1} = \frac{1 - X_S}{n_1} - \frac{n_2}{n_1} X_{M2} \qquad (50)$$

In the most general case X_{M1} would be a function of X_S and X_{M2}. The differential of X_{M1} provides information on the coefficients $1/n_1$ and n_2/n_1:

$$dX_{M1} = \frac{1}{n_1} X_S \, dX_S - \frac{n_2}{n_1} X_{M2} \, dX_{M2} \qquad (51)$$

Equation (51) can be simplified further. The case in which both cations compete for the same sites is of practical importance. Assuming that M_1 has saturated the sites, it is expected that X_{M1} will decrease as X_{M2} increases. M_2 will displace M1 from the exchanger sites. This will keep X_S constant or equal to zero in the case where all the sites were initially occupied by M_1. It is important to remember that the apparent binding capacity for M_2 and M_1 may not be the same and that it may be very well less than the total number of sites available.

In the situation described above, the mole fraction function will take a linear form. The slope of the line representing the ratio of the stoichiometric coefficients and the intercept, the mole fraction of M_1 at the saturation level. It is quite common to find deviations from straight line. In most such cases, however, the plot can be divided in two linear sections. A slope of zero will simply mean that M_2 must be binding other sites not including those already occupied by M_1.

2.1.4. Humic acid-base equilibrium.

Contrary to fulvic acid which is soluble in acidic solutions, humic acid remains out of solution as a second physical phase. The physical chemistry of the system under these conditions is quite similar to that of a weakly cation exchange gel. The majority of the acidic functional groups will be located inside the gel solution. Addition of electrolyte lowers the pH of the external solution due to ion exchange taking place between protons in the gel solution and cations from the external solution.

Addition of sodium chloride to humic acid suspensions followed by sodium hydroxide promotes ion exchange. Protons being released by sodium exchange are neutralized by base in the external solution. This simple ion exchange mechanism is complicated by two factors. First, humic acid ion exchange sites, presumably carboxyl groups, are not all chemically identical, due to the heterogeneity of the sample, but they are similar. This results in a continuum of sites with very close pKa values. Also contributing to this variation is the polyelectrolyte effect. Second, humic acid dissolves as the pH of the external solution goes up past 4 or 5 pH units. This latter phenomenon creates a rather complicated situation, since in the pH range mentioned, the humic acid sample is consisting of a dissolved polyelectrolyte and a cation exchange gel in contact with an aqueous phase.

Treatment of titration data must be done keeping these facts in mind. Previous researchers (4,6,7) did not pay much attention to these phenomena when dealing with humic acids. The physical chemistry of the system must be sorted out, before a valid interpretation of titration data can be rendered.

Marinsky et al.(14,15,16) has proposed a unified physico-chemical description of the potentiometric properties of gels and polyelectrolytes. His description takes into consideration the ion exchange properties of these materials, including humic and fulvic acids. An analysis made by Merle et al.(17) of the potentiometric properties of sphagnum peat, considered the fact that there are volume changes inside the gel phase as titration proceeds. His calculation of the volume of the gel solution at each step in the titration is not explicit. In this analysis, the main assumption seemed to be that any volume changes were due to swelling and not gel dissolution. This approach has been applied to fulvic acid, which is soluble in all pH ranges and does not present the problem of the existence of a two phase system at low pH values.

2.1.4.1. Interpretation of Humic Acid Titration Data.

The pH dependent solubility of humic acid can be linked to the dissolution of the metal-humate formed during titration. Dissolution of humic acid in the protonated form is expected to be very small, but nevertheless, it may contribute to the total change in the volume of the gel.

$$(\widetilde{H^+ + A^-}) \rightleftharpoons (H^+ + A^-) \quad (52)$$

$$(\widetilde{Na^+ + A^-}) \rightleftharpoons (Na^+ + A^-) \quad (53)$$

$$\bar{K}_{SHA} = \frac{[H^+]\,[A^-]}{\{H^+\}\,\{A^-\}} \quad (54)$$

$$\bar{K}_{SNaA} = \frac{[Na^+]\,[A^-]}{\{Na^+\}\,\{A^-\}} \quad (55)$$

Equations (54) and (55) represent the average solubility functions for humic acid and sodium humate respectively. The ion exchange taking place between sodium and hydrogen ions is described by:

$$\{H^+ + A^-\} + Na \rightleftharpoons \{Na^+ + A^-\} + H^+ \quad (56)$$

The selectivity function is given by:

$$\bar{K}_{H,Na} = \frac{\{Na^+\}\,[H^+]}{[Na^+]\,\{H^+\}} \quad (57)$$

which can be expressed as the ratio of the solubility functions:

$$\bar{K}_{H,Na} = \bar{K}_{SHA} / \bar{K}_{SNaA} \quad (58)$$

The volume inside the gel solution, V_g, is not accessible to measurements, but it cancels out in the solubility functions:

$$\overline{K}_{H,Na} = \frac{Q_{Na}\ [H^+]}{Q_H\ [Na^+]} \qquad (59)$$

where Q represents the number of millimoles of each cation in the gel phase. At this point, it is important to look at the physical chemistry of the system. At equilibrium, the chemical potential of the diffusing species must be the same in both phases. That is:

$$\tilde{\mu}_{H^+} = \mu_{H^+} \qquad (60)$$

$$\tilde{\mu}_{Na^+} = \mu_{Na^+} \qquad (61)$$

$$\tilde{\mu}_{H2O} = \mu_{H2O} \qquad (62)$$

Notice, that the use of single ion activities is implied in equations (60) and (61). Although thermodynamically unacceptable, it will be adopted here to simplify the expressions. The chemical potential of each component can be described by a function of its molarity and its osmotic pressure:

$$\tilde{\mu}_{H^+} = \mu_{H^+} + RT \ln a_{H^+} + (P-P_o)\,\overline{V}_{H^+} \qquad (63)$$

$$\tilde{\mu}_{H^+} = \mu_{H^+} + RT \ln a_{H^+} + (P-P_o)\,\overline{V}_{H^+} \qquad (64)$$

$$\tilde{\mu}_{Na^+} = \mu_{Na^+} + RT \ln a_{Na^+} + (P-P_o)\,\overline{V}Na^+ \qquad (65)$$

$$\tilde{\mu}_{Na^+} = \mu_{Na^+} + RT \ln a_{Na^+} + (P-P_o)\,\overline{V}Na^+ \qquad (66)$$

where P_o and P are the pressures outside and inside the gel solution, V terms are the partial molar volumes of the solutes outside and inside the gel solution. The equilibrium expression for the exchange reaction according to Marinsky (16) is then:

$$RT \ln \frac{[a_{H^+}]\,[a_{Na^+}]}{\{a_{H^+}\}\,[a_{Na^+}]} = + P_i(V_{Na^+} - V_{H^+}) \qquad (67)$$

Equation (67) is the result of choosing the same standard state in the gel as well as the external solution phases.

According to Marinsky et al.(14) in most gel phases the term involving the osmotic pressure is very small when compared with the logarithmic term in equation (67), This allows the expression of equation (67) as :

$$\ln \frac{[H^+]}{[Na^+]} = \ln \frac{\{H^+\}}{\{Na^+\}} \qquad (68)$$

In equation (68) a further assumption is made involving the activity coefficients in the gel and solution phases; i e. the ratio of activity coefficients is assumed to be equal to unity:

$$\frac{\tilde{\gamma}_{H^+}\,\tilde{\gamma}_{Na^+}}{\gamma_{H^+}\,\gamma_{Na^+}} = 1 \qquad (69)$$

The selectivity function is now defined as:

$$\overline{K}_{H,Na} = \frac{1}{*} \qquad (70)$$

since the activity in both phases must be the same.

The number of millimoles of any cation inside the gel solution is given then:

$$Q_{Na^+} = \frac{[Na^+] \quad Q_{H^+}}{[H^+]} \qquad (71)$$

As humic acid dissolves, carboxyl groups go into solution. The more general situation is one in which carboxyl groups, both ionized and unionized, are released into the external solution by the dissolution of the gel. Using mass balance relationships, the total amount of carboxyl groups making up the system can be written as:

$$Q_A = q_{HA} + q_A + [A^-]\,V \qquad (72)$$

where q_{HA} and q_A represent the millimoles per gram of undissociated and dissociated groups, $[A^-]$ the molarity of carboxyl groups in solution and V the sample volume.

The amount of carboxyl groups inside the gel solution can be further split into groups paired to protons and groups paired to sodium ions;

$$q_A = q_H + q_{Na} \qquad (73)$$

Mass balance considerations applied to the amount of base added at each point during the titration leads to:

$$Q_B = q_{Na} + [Na]\,V - [Cl]\,V \qquad (74)$$

where [Na] and [Cl] are the molarities of sodium and chloride ions in the external solution and Q_B is the number of millimoles of base added. The term involving chloride concentration will not be present in the case of titrations not involving NaCl as background electrolyte.

At each point during the titration, the total number of acid remaining in the sample will be equal to the total carboxyl content minus the amount of carboxyl groups neutralized.

$$Q_H = Q_A - Q_B \qquad (75)$$

This quantity can be further broken down into:

$$Q_H = Q_H^* + [H]\,V - [OH]\,v \qquad (76)$$

$$Q_H^* = q_H + q_{HA} \qquad (77)$$

where Q_H^* is the amount of acid remaining in the gel. For ion exchange purposes it will be useful to have information on the amount of ionized carboxyl groups as well.

The amount of ionized carboxyl groups in the gel is given by:

$$q_A = q_H + ([Na]/[H])\, q_H \qquad (78)$$

$$q_H = Q_B + \frac{v\,([H]-[OH]) - [A]\,V}{[Na]/[H]} \qquad (79)$$

The term containing the molarity of carboxyl groups in solution is an unknown, since it is not possible to determine their concentration. Equation (79) can be useful, nevertheless, at low pH if it is assumed that the concentration of carboxyl groups in the external solution is negligible. This approximation is valid only at pH values were no dissolution of humic acid takes place.

Equation (79) takes an interesting form when no base has been added to the system, and only background electrolyte is present. If [A] V term is taken as zero:

$$q_H = \frac{V\,([H] - [OH])\,[H]}{[Na]} \qquad (80)$$

In this situation, the amount of ionized carboxyl groups can be estimated. The amount of acid remaining in the gel can be monitored as it decreases with titration progress by means of equation (76).

Chapter 3

3.1. Chemistry of Paraquat.

Paraquat belongs to a family of chemicals called viologens. It is a 1,1'disubstituted-4,4' bipyridinium ion commonly available as chloride and bromide salts. Paraquat or methyl viologen (MV), was originally investigated as a redox indicator in the studies of biological systems by Michaelis(1). It was not until the late 1950's that its herbicidal properties were discovered.

Earlier studies have demonstrated a correlation between the herbicidal properties of viologens and their redox potentials. Paraquat itself, has one of the lowest redox potentials of any known organic compound (-456 millivolts vs SCE). This makes it easily reduced to the radical mono-cation as shown below:

$$MV^{+2} + e^- \rightleftharpoons MV^{+\cdot}$$

$$MV^{+\cdot} + e^- \longrightarrow MV^{\circ}$$

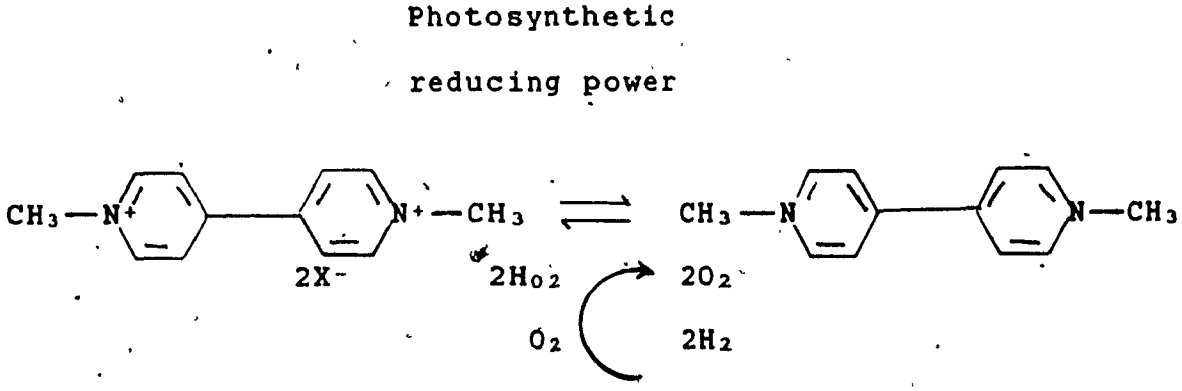
The first reaction is totally reversible on the scale of most electrochemical processes. The second reduction is considered to be irreversible. The mono-cation formed in the first reduction step has a deep blue colour in aqueous solutions. The paraquat dication is very stable in aqueous solutions under a wide range of pH, from very acidic (pH < 1) to mild alkaline conditions (pH = 10). Ledwith and Stam(18) have reported the dealkylation of paraquat under alkaline conditions.

3.1.1. Herbicidal properties.

As was previously mentioned, the herbicidal properties of paraquat are associated with its redox potential. In the viologen family, only those members with a redox potential less negative that -800 millivolts (vs SCE) display herbicidal activity. Paraquat, with a redox potential of -446 millivolts vs SCE makes a suitable herbicide.

Paraquat and the closely related diquat are widely used as general contact weed controlling agents. Paraquat is directly applied to the foliage. It is easily translocated to different parts in plants. The contact action of paraquat is rapid and its effects are seen within hours of its application.

It is believed that the key mechanism of action of paraquat and related compounds is their ability to form and induce the formation of free radicals because of their low redox potentials. They act as catalysts in the formation of free radicals and superoxides in living organisms(19).



This reaction forms ·OH and $^1O_2$ radicals. The fact that paraquat is reduced in the photosynthetic reaction was demonstrated by Horowitz in 1952(19).

3.1.2. Metabolism.

It has been demonstrated(20) that paraquat is not broken down by organisms such as tomatoes, potatoes, etc, which extends its persistance in these organisms as well as in the soil environment. It is broken down to a significant extent by sunlight.

3.1.3. Toxicological Properties.

Acute toxicity or oral LD_{50} in rats is 120 mg of paraquat cation per Kg. Paraquat presents subacute toxicity (dermal) in rabbits at LD_{50} greater than 24 mg per Kg. While the acute oral toxicity of paraquat is well documented (21), the hazard to humans through other routes of low level exposures such as inhalation have not been systematically studied(22). Recently, a study among Quebec farmers(23) suggested a possible link between prolonged paraquat exposure and early onset of symptoms similar to Parkinson's disease. Paraquat affects levels of glucose, insulin, cathecolamines and enzyme activity. Regardless of the route of exposure, paraquat toxicity is usually centred at the lungs resulting in the development of pulmonary fibrosis.

Recently(24), public organisms in the U.S.A. have questioned the exposure of agricultural workers to paraquat. In third world

countries, the lack of any supervision of the spraying of paraquat has made it one of the most dangerous agrochemicals available to farmers.

3.1.4. Analytical Chemistry.

The spectrophotometric and electrochemical properties of paraquat have been exploited as detection and determination techniques(24). One of the oldest methods of analysis, frequently used, is the detection of the formation of the blue radical monocation upon the reduction of paraquat with sodium dithionate. The main problem with this method is that reoxidation to the clear divalent cation is easily achieved by traces of oxygen or any oxidizing agent present in solution. This makes deaeration of the sample a must for precise analysis.

Another method, recommended by the Weed Science Society of America (24a), consists in the UV detection of paraquat as 254 nm in acetate buffer at pH 4.5.

Both methods require sample clean up prior to analysis. This is particularly critical in the case of soil extracts; since traces of organic materials interfere in the detection.

Electrochemical methods, such as DC polarography and Voltammetry(26), surprisingly enough, are not as common as the two mentioned spectrophotometric techniques. Direct application of electrochemical methods to the analysis of paraquat in soil solutions has not yet been reported(25).

Other methods for the analysis of paraquat in soil solutions and body fluids such as urine and serum include, HPLC and UV. HPLC allows the detection of paraquat in the presence of small amounts of chromatographically resolvable interferences but still requires clean up procedures. Fairly recently(27), an enzyme-linked immunosorbent assay (ELISA) for paraquat was developed.

3.1.5. Paraquat interactions.

3.1.5.1. Interactions with phenolic compounds.

Phenolic materials are present in a variety of forms in natural environments. Humic substances and tannin acids are just two examples of the many forms in which phenol containing substances occur(28). Polyphenolic substances are also present in plants. The wide distribution of phenolic materials in soil and aquatic environments makes it worthwhile to study the interactions between paraquat and these substances.

Ledwith et al. (29) carried out an investigation of the formation of stable crystalline complexes between paraquat and a variety of phenols. The mixing of paraquat and phenols in appropriate solvents gave colored solutions, which provided an indication of the formation of charge transfer complexes. The composition of the complexes formed depended on the phenol involved and the conditions of the reactions. The isolation of chloride salts of these complexes gave information on the

stoichiometry of the reactions. Phenol, o-cresol, p-cresol, phloroglucinol and pyrogallol reacted with paraquat in a 4:1 stoichiometry. 4,4'-Dihydroxy-biphenyl reacted in a 2:1 ratio at pH values higher than 9 and in a 1:1 ratio under acidic conditions. Phenolate ions, which have lower ionization potentials that the parent compounds gave rise to a lower energy charge transfer transitions. There is an approximately linear relationship between the charge transfer l_{max} and the oxidation potential at pH 5 for the phenols investigated. An interesting results of the apparent stoichiometry is that each cationic charge in the paraquat cation seems to interact with two phenolic groups, not necessarily present in the same molecule. Therefore, monohydric phenols such as cresol, reacted in a 4:1 ratio. The stoichiometry ratio was invariant with pH; results at low pH and high pH values gave the same ratios. The only difference was the counter ion composing the salt. At low pH, chloride salts were isolated, while at pH higher than 9, phenolates were isolated. Acidification of alkaline solutions of paraquat and phenolic compounds allowed complete recovery of the neutral phenol from paraquat complexes.

The interaction of paraquat and 4,4'-Dihydroxy-biphenyl is a special case since it does not follow the pattern of two aromatic hydroxy groups per cationic charge. Salts of complexes between paraquat and this compounds all gave 1:1 products. At low pH the counter ions were chloride while at pH higher than 9 they were

pheholates. This behaviour may be due to the special geometry of this particular compound. The distance between the positively charged centres in the paraquat cation and the distance between the phenolic oxygens are approximately the same. This may enhance charge transfer interactions, making it the most stable configuration. Although formation constants for the complexes were not reported, they are expected to be larger than for the complexes of paraquat and hydroquinone, which has a formation constant of 5.2 M^{-1} (30).

The type of forces involved in these interactions depend on pH. Thus under acidic conditions all phenolic compounds are fully undissociated. This results in dipole-dipole forces holding the complex together, which, depending on incidental orbital overlap, would lead to charge transfer complexes. In alkaline solutions, the ionization of phenols provides anions capable of strong coulombic interaction with paraquat cations. Again, if the geometry of the complex is favorable, charge transfer will occur. The inability of paraquat to displace phenolic protons is evident, especially at low pH values, where complexes were isolated as chloride salts.

The type of phenolic moieties present in humic acids are likely to have various geometrical configurations and show different chemical environments. Since the stoichiometry of paraquat-phenol complexes varies with the phenol involved, it would be quite difficult to assign a given stoichiometry to

possible paraquat-phenolic humic complexes.

3.1.5.2. Interactions with -donor molecules.

White(30) studied the formation of charge transfer complexes between paraquat and a series of -donor molecules. Table 1, taken from White(30) gives a list of some of the donor molecules studied as well as properties of the complexes formed between the donors and paraquat.

Table 1

Complexes of paraquat and various donor molecules

Adduct	ratio	colour	m.p C°
Urea	1:2	white	140
Thiourea	1:4	yellow	160
Phenol	1:4	yellow	
Hydroquinone	1:1	red	241
Cathecol	1:1	red	208
Phloroglucinol	1:3	orange	105
3,4-Dihydroxy benzoic acid	1:1	orange	194

3.1.5.3. Ion Pairs Complexes.

Paraquat is known to form ion pair complexes with a variety of anions. Aqueous solutions of paraquat show a ground state spectrum which can be identified as a charge transfer band, due to the interaction of the divalent cation with chloride ions

(31). The formation of the charge transfer complex $MV.CL^+$ in dilute aqueous solution occurs to a very small extent. The predominant species in aqueous solution is the divalent ion(32). Much less then 8% of the total paraquat is in the form of $MV.Cl^+$. Complexes involving two halide anions have also been reported (31). The formation constants are very small. $MV^{+2}.2Cl^-$ complexes have a formation constant in water of about 1.4 M^{-1}. Paraquat also forms ion pair complexes with anions solutes such as EDTA, hexametaphosphate, acetate, citrate and sulfide ions (33,34). The complex formed between paraquat and acetate ions forms the basis for its analysis.

3.1.5.4. Interaction of paraquat with polyelectrolytes.

The ability of polyelectrolytes to separate differently charged ions, has made them useful in the study of water splitting reactions. One of the elements involved in such systems is paraquat. Due to its suitable redox potential for reducing water to hydrogen, it is widely used as an electron relay in photochemically stimulated electron transfer reactions.

The interactions of paraquat and polyelectrolytes such as sodium poly(styrene sulfonate)) (PSS) and sodium poly(vinyl-sulfonate) (PVS) have been studied using fluorescence quenching techniques (35), as well as electrochemical methods (36). Paraquat is territorialy bound to PSS and PVS. The binding constants as determined from the slopes of binding curves were

about an order of magnitude different, being 800 M^{-1} and 8 x 10^{+3}, for PSS and PVS, respectively. The binding constant for polymetacrylic acid (PMA) was about the same magnitude as that for PVS(35). The big difference in binding constants for PSS and PVS was explained on the basis of differences in charge density, being higher in PVS and PMA. Sodium ions present in large excess were found to exclude paraquat from the polymer domain. The main mechanism of binding was identified as electrostatic binding for both polyelectrolytes. The possibility of specific binding in the case of PSS was interpreted to suggest charge transfer or electron donor-acceptor complex formation as a result of the electrostatic interaction leading to overlap of electron deficient zones in paraquat with phenyl rings of PSS.

3.1.5.5. Interaction of paraquat with humic substances.

The type of chemical moieties present in humic materials provide a wide range of structures and potential sites for interaction with herbicides. The chemical nature of both participants in the reaction must be known in order to be able to formulate models that could help in predicting herbicide behaviour in soils. A first approach to the problem must be the description of the chemical characteristics of the herbicide involved. A full description of the nature and chemistry of humic substances will not be attempted since it is a rather extensive and controversial matter. Instead, an operational outline of the

chemically relevant points in humic acid chemistry will be addressed.

Paraquat is known to become inactive in highly organic soils (37). The adsorption of paraquat by organic matter was demonstrated by the reduction of its phytotoxicity to plants grown in media containing highly organic soils (37). The degree of adsorption of paraquat to humic acids has been found to depend of the cation initially present on the humic material. Khan (38) has found that adsorption of paraquat followed the order : $Al^{+3} < Fe^{+3} < Cu^{+2} < Ni^{+2} < Zn^{+2} < Co^{+2} < Mn^{+2} < H^{+} < Ca^{+2} < Mg^{+2}$. This order seems to correlate with the sequence for the stability or strength of cation binding to humic acid as determined by Van Dijk (39). This sequence is based on the determination of conditional stability constants which may not reflect the real chemistry of the interaction. Nevertheless, the sequence suggests a dependency on the saturating cation. The pH drop after the addition of paraquat to suspensions made of humic acid saturated with various cations was explained by Kahn (37,38) as due to the hydrolysis of polyvalent cations released from humic acid by paraquat. The release of cations from humic acid by paraquat implies that some sort of ion exchange mechanism is involved in the interaction.

Metal ions, depending on their ability to form outer or inner spheres complexes, will interact with a different categories of sites in humic acid. Straight comparison of this

interaction with that of an organocation such as paraquat has to be done with certain restrictions. The mechanism suggested by Khan (38) involved ion exchange between chelated metal ions and paraquat. This considered the displacement of cations from salicylic like-sites by paraquat. This mechanism, although attractive, is not likely to represent the reality well, since a simple consideration of the size of the paraquat cation suggests that the charge separation in a salicylic-like site is much too small to fit the charge separation in paraquat. The paraquat cation presents more severe steric requirements to a "chelating" site than does a divalent metal ion. The configuration of the ion exchange sites is definitely more important to paraquat than to a metal ion. This suggest that paraquat may not be able to interact in a specific way with all the potentially available ion exchange sites in humic acid, particularly at low pH, since the structure of humic acid is expected to be rather fixed(28). This means that if the geometry of the sites is not the appropriate, specific interactions, may not be possible.

The existence of ion exchange as the main mechanism for the interaction of paraquat and humic acid has been extensively documented in a qualitative form. Best et al. (40), performed studies involving paraquat, humic acid and calcium. Calcium was able to compete for ion exchange sites in humic acid with paraquat. Burn et al. (6,7) and Khan (38) also detected the release of hydrogen ions upon equilibration of humic acid

suspensions with paraquat. This was attributed to the displacement of protons from carboxyl (and even phenolic groups) in humic acid. More recently, Narine et al.(41) presented evidence that no hydrogen ion was released by paraquat upon binding. This may be due to the relative amounts of humic acid and paraquat present in the experiments. The binding of paraquat was, nevertheless affected by cations such as calcium and magnesium present in the suspensions. Effects due to ionic strength on the binding of paraquat were reported by Guy et al.(4). All this evidence points to an ion exchange and or an electrostatic interaction mechanism. Other qualitative evidence for ion exchange is obtained by IR monitoring of the carboxyl and carbonyl band in humic acid before and after treatment with paraquat (38). The intensity of the carboxyl band was shown to increase in the presence of paraquat while that correponding to the carbonyl of the acid diminished. This suggested the conversion of COOH groups into COO^-. These qualitative results also point to the fact mentioned earlier concerning the inaccessibility of all the ion exchange sites to paraquat. The diminution of the acid carbonyl band was not total even after saturation of the sites with paraquat, indicating that a large portion of the COOH was inaccessible to paraquat.

Besides ion exchange, other secondary forces are likely to act in the binding of paraquat to humic acid. Best et al. (40) suggested the possibility of weak attractive forces such as van

der Waals's forces. A non ion exchange contribution has been proposed by Burns (6) and Sojo et al.(42). McCall et al.(43) provided evidence concerning paraquat binding to non-ionic resins. Charge transfer complexation between paraquat and humic acid has been shown to occur (37,38), possibly involving donor sites in humic acid and the electron deficient paraquat ring system. At this point it is important to mention that paraquat forms charge transfer complexes with oxygen donor molecules.

3.1.5.6. Interaction with clay minerals.

The inactivation of paraquat in the presence of clay suspensions has been recognized for quite some time (44). In the early periods in the manufacture of paraquat, clay suspensions, mainly montmorillonite, were used as antidotes in the case of paraquat ingestion. The binding of paraquat to clay minerals such as montmorillonite is irreversible. Although the mechanism involves exchange of cations initially held near the negatively charged sites in the clay's interlayer surfaces, it cannot be strictly considered to be ion exchange, due to its irreversibility. Weber et al.(44,45) studied the adsorption of paraquat on montmorillonite and kaolinite and concluded that the adsorption takes place up to the cation exchange capacity of the clay mineral. It is believed that the herbicide occupies the interlayer spaces in montmorillonite. Its flat geometry allows for maximum interaction with the negatively charged surface.

Weber et al.(44) found that the removal of paraquat from montmorillonite by 1 M $BaCl_2$ was far from complete. Only about 5% of the total amount of paraquat bound was released. This is in contrast to the case of kaolinite, in which 80% of the total herbicide was displaced by $BaCl_2$.

The adsorption of paraquat by montmorillonite is not affected by the cation initially bound to the clay surfaces according to Weber(45), the small release of paraquat from montmorillonite by inorganic salts only represents the fraction externally bound. X-ray diffraction evidence (47) supports the notion that the adsorption of paraquat produces a collapse of the interlayer spaces in montmorillonite, making it difficult for other cations to displace paraquat. It has been shown(47) that the forces involved in holding together the montmorillonite-paraquat complexes are charge transfer forces between the negatively charges in the clay surface and the electron deficient ring system in the paraquat cation.

Chapter 4

4.1. Experimental.

4.1.1. Extraction of Laurentide Humic Acid.

Humic acid was extracted from a soil sample donated by Professor S. Visser from Universite Laval, Ste Foy, Quebec. The extraction procedure was similar to the one employed by Schnitzer et al.(48).

Two kilograms of soil were air dried and sieved through a medium size sieve in order to remove large size materials. The soil sample was placed in a 25 litre plastic container to which 20 liters of 0.5 M NaOH solution were carefully added. The contents were swirled and pre-purified nitrogen gas was initially bubbled into the resulting suspension containing the soil extract. The extraction was allowed to take place for 24 hours. To avoid oxidation of the humic material a blanket of pre-purified nitrogen was kept above the extract surface. The container was shaken by a mechanical shaker while the extraction took place.

The collected soil extract was centrifuged at 3500 rpm in order to remove any solid material, and the dark brown and thick supernatant liquid was then passed through an ion exchange column containing Dowex-50 ion exchange resin in the H-form. The column was 124 cm long and 12 cm in internal diameter. The effluent of this column was directed to a smaller column made of the same ion exchanger. The aim of the second column was to remove further trace metals that escaped retention by the first column. Humic acid precipitated in the first column.

The recovery of humic acid was carried out by eluting the precipitate in the first column with 0.1 M NaOH. Approximately eleven liters of effluent were collected. This eluent contained mainly sodium humate. This preparation was acidified with 6 M HCl to a pH of 1.5. At this point most of the humic acid was

precipitated. This precipitate was allowed to age overnight and then separated from the supernatant by decantation. The resulting humic slurry was called LHA. It was suspended in deionized water and dialyzed using dialysis tubing of 1000 molecular weight cut-off in order to get rid of remaining HCl and excess salts. The disappearance of HCl was monitored by testing the external solution for chlorides with silver nitrate. The external solution was replaced every 24 hours until no more chloride was detected.

The dialyzed humic acid sample was then freeze-dried. A dark brown powder was obtained. It was ground to fine particles. Humic acid samples were stored in dark brown containers kept in a desiccator in order to avoid moisture.

An alternative extraction procedure was also carried out which involved omission of the ion exchange columns. The cleaned soil extract, after centrifugation, was acidified with 6 M HCl in order to precipitate the humic acid. From this point on, the procedure was exactly as before. Infrared spectra for both preparations failed to indicate any differences between the two.

4.1.2. Humic Acid Titrations with Standard Base.

Approximately 0.1000 grams of freeze-dried humic acid were accurately weighted and transferred quantitatively into a 150 mL titration vessel. One hundred milliliters of previously boiled deionized water were added to the titration vessel containing the

humic acid sample. The resulting suspension was stirred by means of a magnetic stirrer. The titration vessel was kept at 25° C using a water jacket. The humic acid suspension was carefully degassed by gently bubbling through pre-purified nitrogen for 15 minutes. After this period, a blanket of nitrogen gas was kept over the suspension. The titration vessel was closed with a rubber stopper containing ports for the burette, the pH electrode, and nitrogen inlet and outlet.

Addition of titrant was done from a ten mL burette. 0.050 mL aliquots of 0.1 M NaOH were added at a time. Millivolt readings were taken every ten minutes after addition of base, with a previously calibrated pH electrode with a built-in reference electrode. About 100 titration points were collected for each run. At least five titrations were secured for each experiment.

Similar titrations were carried out in the presence of background electrolyte 0.1 M NaCl.

4.1.3. Determination of total acidity.

The determination of the operationally defined total acidity was carried out using the method employed by Schnitzer and described by Stevenson(28). 0.100 grams of humic acid were accurately weighted and transferred to a 100 mLs round bottom flask. 25 mLs of 0.1 M $BaCl_2$ were added followed by deaeration with gently bubbling nitrogen for ten minutes. The flask was tightly closed with a glass stopper surrounded with Parafilm

paper. A similar solution was prepared but without humic acid for use as a control. Both sample and control flasks were shaken for 24 hours. After this period, sample and control, were titrated with 0.05 M HCl to pH 8.00 as determined with a pH electrode. Triplicate results were secured.

Total Carboxyl Content:

The total carboxyl content was determined from pH titrations with standard 0.1 M NaOH. The end point was determined by finding the intercept in the abscissa of the Gran's function plot, Y = $[H^+]$ V against V.

Phenolic Content:

Phenolic content was determined by subtracting the total carboxyl content from the total acidity as determined by the Baryta adsorption method.

4.1.4. Humic Acid Copper Titrations.

A series of 12 to 15 humic acid samples weighing approximately 0.0100 grams were equilibrated with 50.00 mls of copper solutions of increasing concentration. Initially, 25.00 mL of double deionized water were added to each of the samples. The pH of the resulting suspension was adjusted to the desired value (usually 3 or 4) by the addition of dilute HNO_3 or NaOH. This was followed by addition of an aliquot of copper stock solution whose pH was previously adjusted to the desired value. The volume of the resulting suspension was increased to 50.00 mLs by adding double deionized water which was previously

adjusted to the desired pH values(Table 2). Control samples were prepared in the same way as described above, but without humic acid. Both, controls and samples, were shaken for a period of three days to ensure equilibrium.

After the equilibration period, the pH of the suspensions was measured. This was followed by ultrafiltration on a YM2 1000 molecular weight cut-off membrane purchased from Amicon. 5.00 mL filtrates were collected for each sample and control at 60 psi. Filtrates were diluted when required with 15% HNO_3 and analyzed for copper by flame atomic absorption spectrometry on a Perkin Elmer Spectrophotometer Model 305. The wavelength used for the analysis was 324.8 nm.

Table 2

Copper-Humic Acid Titration

Weight	mLs H_2O*	mLs Cu^{+2}*
0.00998	49.90	0.10
0.01077	49.80	0.20
0.01048	49.70	0.30
0.01019	49.60	0.40
0.01036	49.50	0.50
0.01000	49.40	0.60
0.01020	49.30	0.70
0.01379	49.20	0.80

* Previously adjusted to the appropriate pH.
Copper stock solution 1.60×10^{-3} M

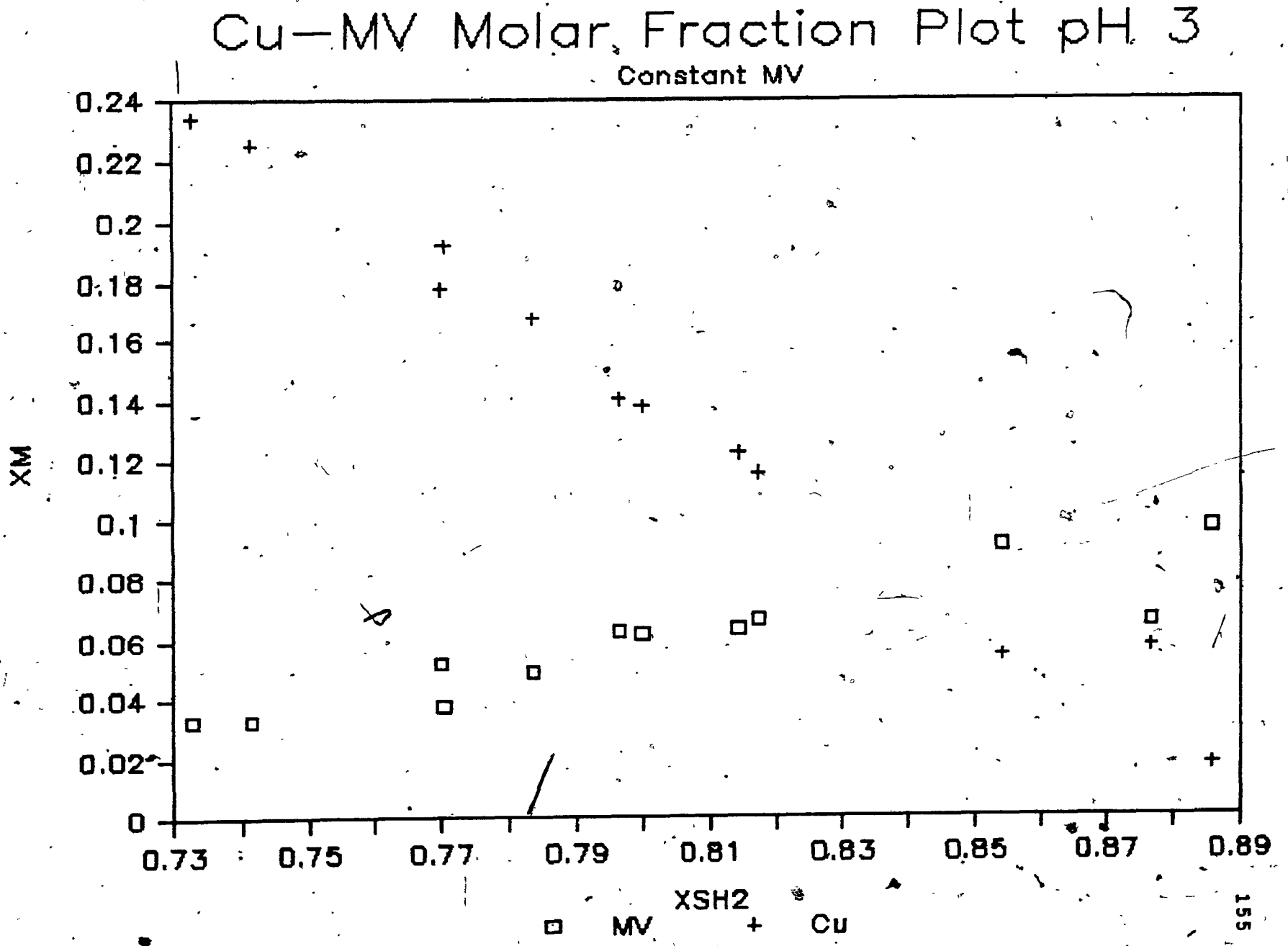

Cu—MV Molar Fraction Plot pH 3
Constant MV
XM
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0.73
0.75
0.77
0.79
0.81
0.83
0.85
0.87
0.89
XSH2
MV
Cu

Figure 40

The possibility that these sites are involved in the binding of paraquat in the presence of excess copper cannot be ruled out.

5.1.8.3. Excess Copper Experiments.

Humic acid saturated with copper at pH 3.00 was equilibrated with increasing amount of paraquat. The paraquat-saturated humic acid results demonstrated that both cations, copper and paraquat, share some binding sites in common. Figure 41 shows the binding curve of paraquat in the presence of a constant loading of copper. The experiment was done at different levels of added constant copper concentrations. The most important fact in these experiments, is that paraquat binds to humic acid with a minimum disturbance of the copper-humic acid equilibrium. This is exactly the opposite to what was found in the reverse situation.

At low copper loadings (see Figure 42), paraquat binding is very similar to that in the absence of copper ions. Increasing total copper concentration in solution (Figure 41), decreases paraquat binding. This decrease indicates, as expected, that there is some competition between both cations.

The displacement of copper, if any, does not account for the binding of paraquat. This indicate that paraquat interacts with other sites as well. The nature of which is such that they are not available for copper binding at pH 3. This is particularly true for the case (Figure 41) in which all

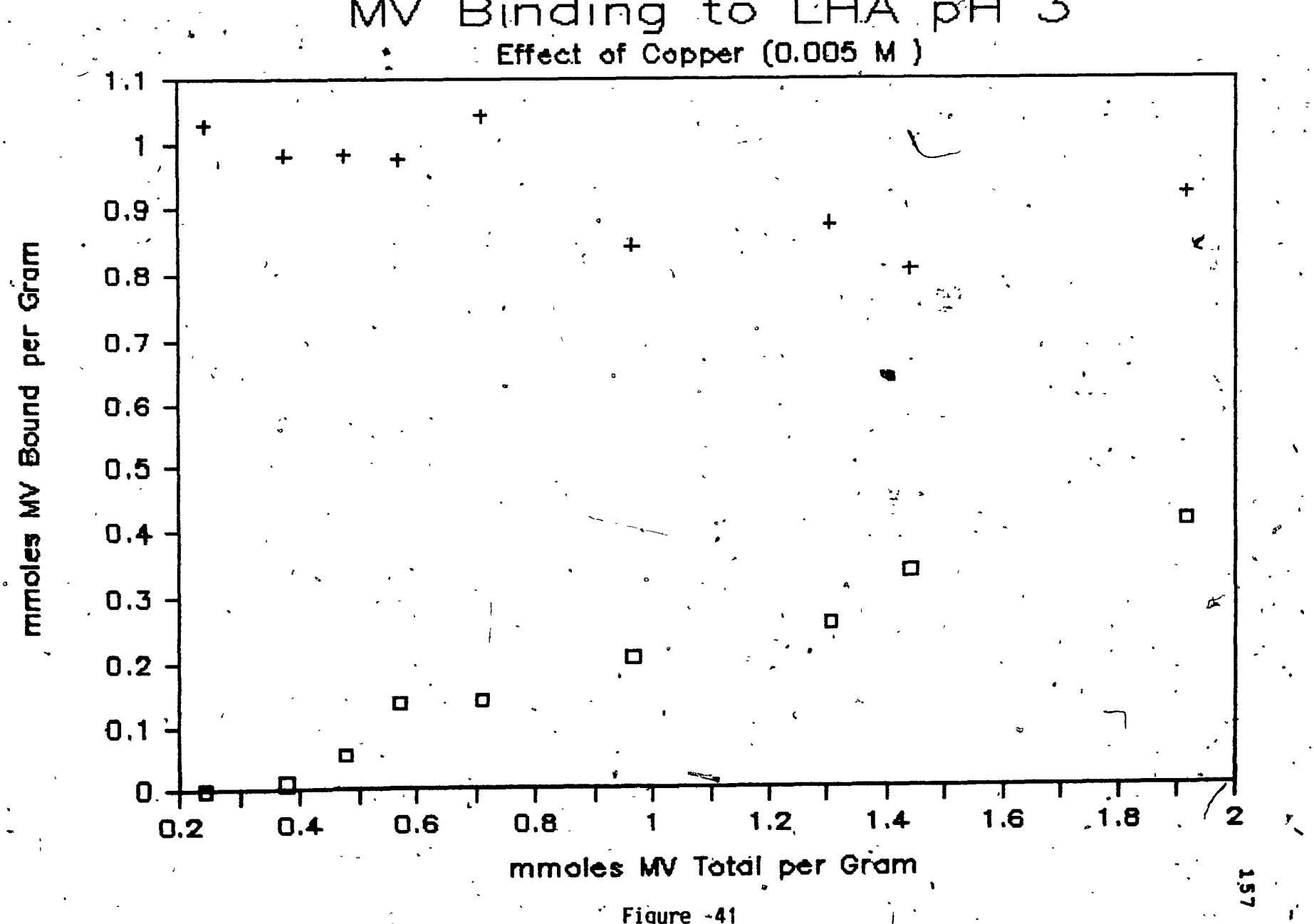

MV Binding to LHA pH 3
Effect of Copper (0.005 M)
mmoles MV Bound per Gram
mmoles MV Total per Gram
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
1.1
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2

Figure -41

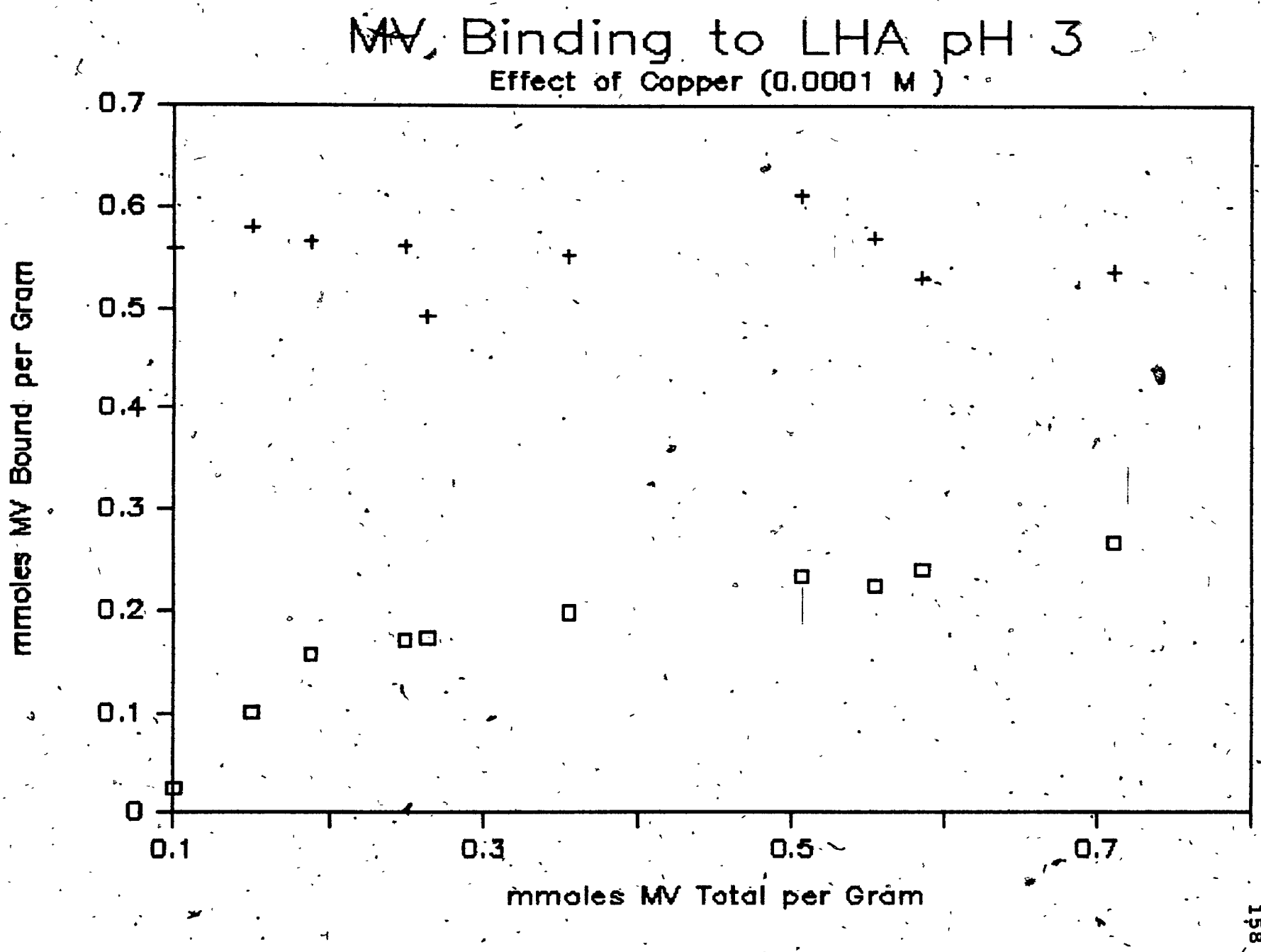

MV Binding to LHA pH 3
Effect of Copper (0.0001 M)
mmoles MV Bound per Gram
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.1
0.3
0.5
0.7
mmoles MV Total per Gram

Figure 42

the sites available to copper have been covered. Based on literature reports (29), it may be hypothesized that paraquat binds to phenolic groups at low pH values without displacing protons. These groups, which could be present in humic acid, may be responsible for the observed residual binding of paraquat which is not accounted for by ion exchange.

Mole fraction plots at constant copper concentrations are shown in Figures 37-40. The actual data is in Tables 19 and 20.

Table 19

Ion Exchange Equilibrium Function

Copper-Paraquat-LHA pH 3.00

X_{MV} (±%5)	X_{Cu} (±%5)	X_{SH2} (±%7)	K_{MV} (±%10)
0.041	0.147	0.812	8.32×10^{-3}
0.044	0.146	0.809	3.58×10^{-3}
0.045	0.128	0.827	2.60×10^{-3}
0.052	0.144	0.805	1.94×10^{-3}
0.061	0.159	0.780	1.45×10^{-3}
0.059	0.148	0.793	9.93×10^{-3}
0.062	0.138	0.800	8.84×10^{-3}
0.070	0.140	0.790	8.13×10^{-3}

Total copper added 2×10^{-3}M per 0.01 gram of LHA in 50 mLs

Table 20

Ion Exchange Equilibrium Function

Copper-Paraquat-LHA pH 3.00

X_{MV} (±%5)	X_{Cu} (±%5)	X_{SH2} (±%7)	K_{MV} (±%10)
0.000	0.268	0.752	-------
0.002	0.256	0.742	3.70×10^{-5}
0.014	0.257	0.729	2.07×10^{-4}
0.034	0.255	0.711	4.73×10^{-4}
0.036	0.272	0.693	4.01×10^{-4}
0.054	0.220	0.727	4.24×10^{-4}
0.066	0.228	0.706	4.40×10^{-4}
0.088	0.210	0.702	5.12×10^{-4}
0.108	0.240	0.652	4.95×10^{-4}

Total copper 5×10^{-3}M per 0.01 grams of LHA in 50.00 mLs

5.1.8.3. Equilibrium Functions.

Plots of the equilibrium functions for copper-constant paraquat and paraquat-constant copper systems at pH 3 are shown in Figures 43 and 44 respectively. It can be seen that both curves show two main regions: a relatively flat portion from about 0.650 to 0.70 X_{SH2} and a steep region from about 0.80 to 1 X_{SH2}.

Cu Equilibrium Function pH 3 and 3.5

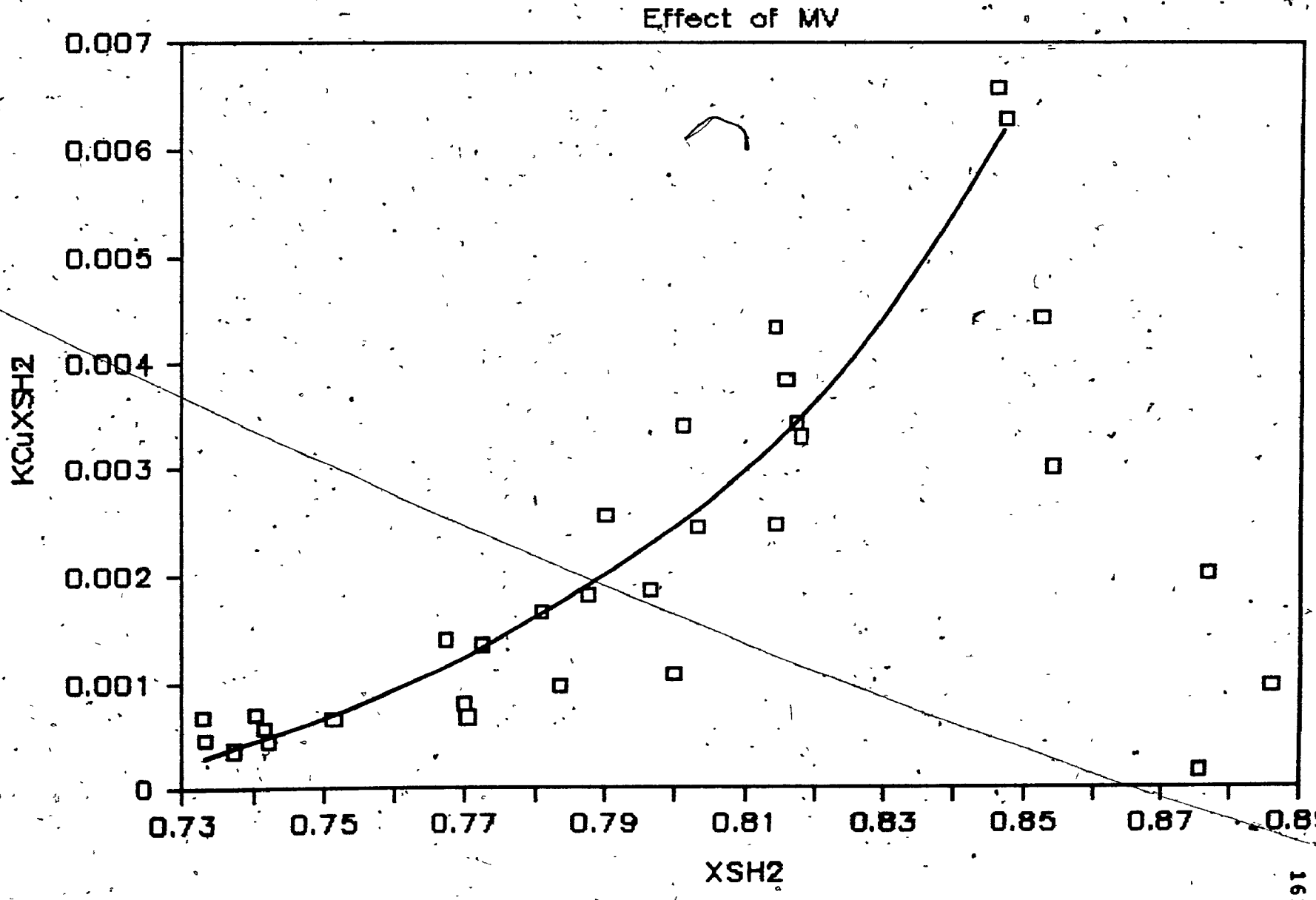


Figure 43

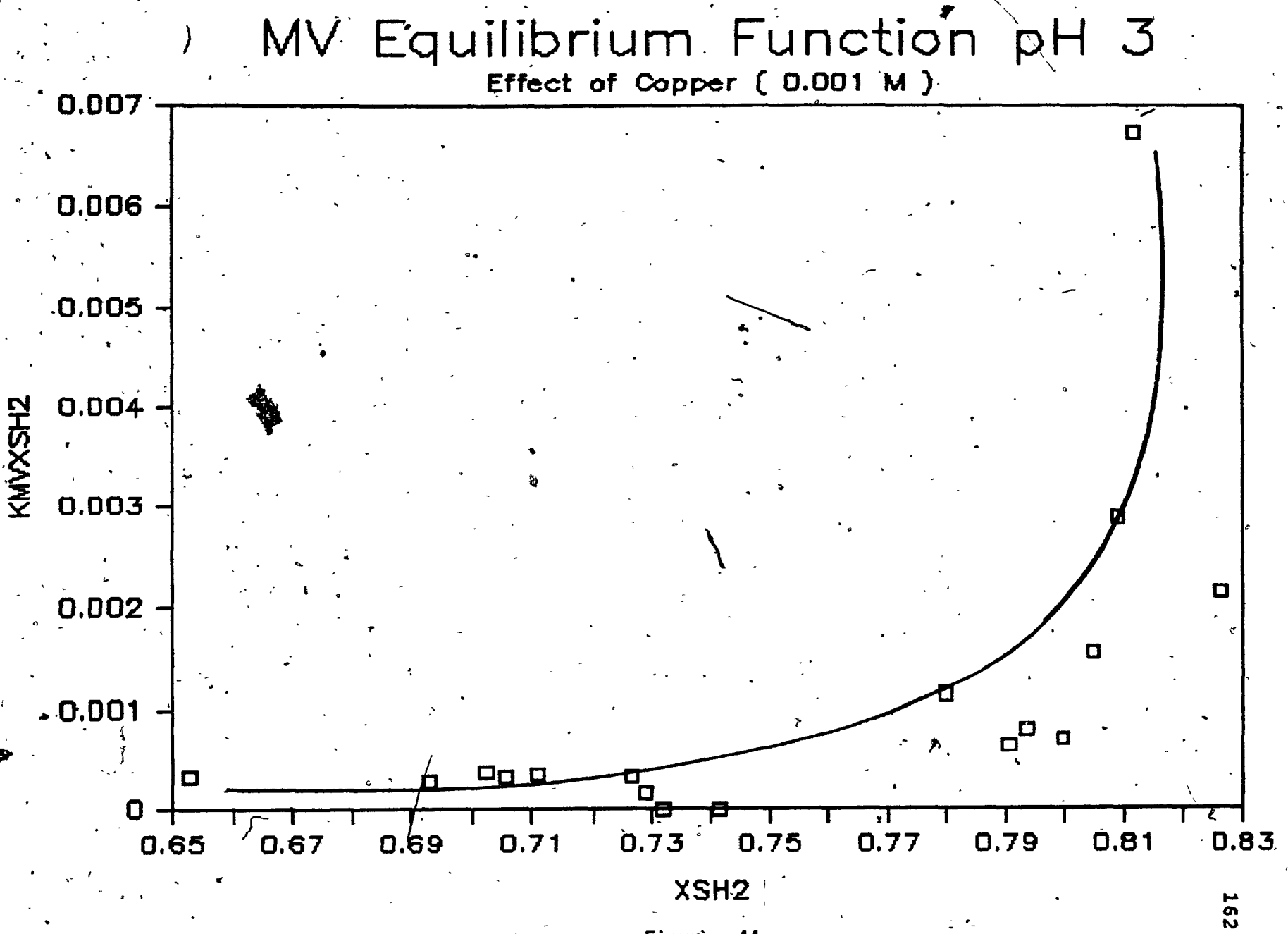

MV Equilibrium Function pH 3
Effect of Copper (0.001 M)
KMVXSH2
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0.65
0.67
0.69
0.71
0.73
0.75
0.77
0.79
0.81
0.83
XSH2

Figure 44

The region near 0.70 X_{SH2} for paraquat is steeper than for copper. There seems to be a maximum between 0.840 and 0.850 X_{SH2}, for the case of copper and at about 0.81 for paraquat. Gamble(9) noticed the existence of such maxima or discontinuities for copper at higher X_{SH2} for a different humic acid. Following the same trend as found by Gamble et al.(9), the copper equilibrium function determined here is about an order of magnitude greater in the steeper region. K_{Cu} values, are slightly higher than K_{MV} values in the flat region of the plots, while the reverse is true for the steeper region.

Binding curves for paraquat and copper in which both cations were added in similar amounts show a rather interesting feature (Figures 45 and 46). Both cations bind as if the other cation is not present particularly at low loading levels. This indicates that each cation interacts independently with different sites. Under these conditions, the binding capacity for paraquat does not seem to be much affected.

Figure 47 and 48 show the K_M X_{SH2} function plots for copper and paraquat corresponding to Figures 45 and 46. The shapes of these curves are very similar to those in the presence of excess copper or excess paraquat.

Mole fraction plots corresponding to Figure 45 and 46 are shown in Figure 49. Table 21 contains the equilibrium differential functions as calculated from equation 16 for the copper-paraquat-LHA systems at pH 3.00.

Table 21

Copper-paraquat-LAH system pH 3

Differential Equilibrium Functions

Humic Gel	Cation	Kc (±%14)	$\Delta G + \ln\left[\frac{\tilde{\gamma}_M \tilde{\gamma}_N^2}{\tilde{\gamma}_H^2 \gamma_M}\right]$	X_{sH2} (±%7)
MV-HA	Cu	3.27×10^{-2}	8.48	0.730
	Cu	9.24×10^{-2}	5.90	0.850
Cu-HA	MV	1.64×10^{-2}	10.20	0.700
	MV	4.39×10^{-2}	2.00	0.820
HA	Cu	5.93×10^{-3}	13.00	0.800
	Cu	8.93×10^{-2}	6.00	0.860
	MV	3.23×10^{-3}	14.00	0.800
	MV	1.03×10^{-1}	5.60	0.860

At similar X_{sH2}, paraquat and copper show similar values for their respective differential equilibrium functions. This is also reflected in the values of the free energy of binding. The similarities in free energy may provide some clues with respect to the nature of the sites involved in the interaction, provided that both cations interact with the same range of sites. For the paraquat-saturated-humic acid system the early displacement of paraquat by copper indicates that both cations interact with the same sites at low loading of copper. This is not the case for the copper-saturated humic acid runs. In the light of this it

is very difficult to compare free energies and make appropriate assessments concerning the binding process. Taking this into consideration it is clear that paraquat displacement by copper is not a reversible process even though both cations show similar binding free energies.

Gamble(9) has reported similar values for the free energy of binding for copper ions interacting with humic acid in the presence of ten different inorganic cations. The free energy of binding as calculated here and in Gamble's work includes the term containing the ratio of the activity coefficients in the gel phase for the cations involved. Assuming that the omission of this term does not introduce a significant error in the free energy estimates, one can say that the energy involved in the binding process is mainly electrostatic.

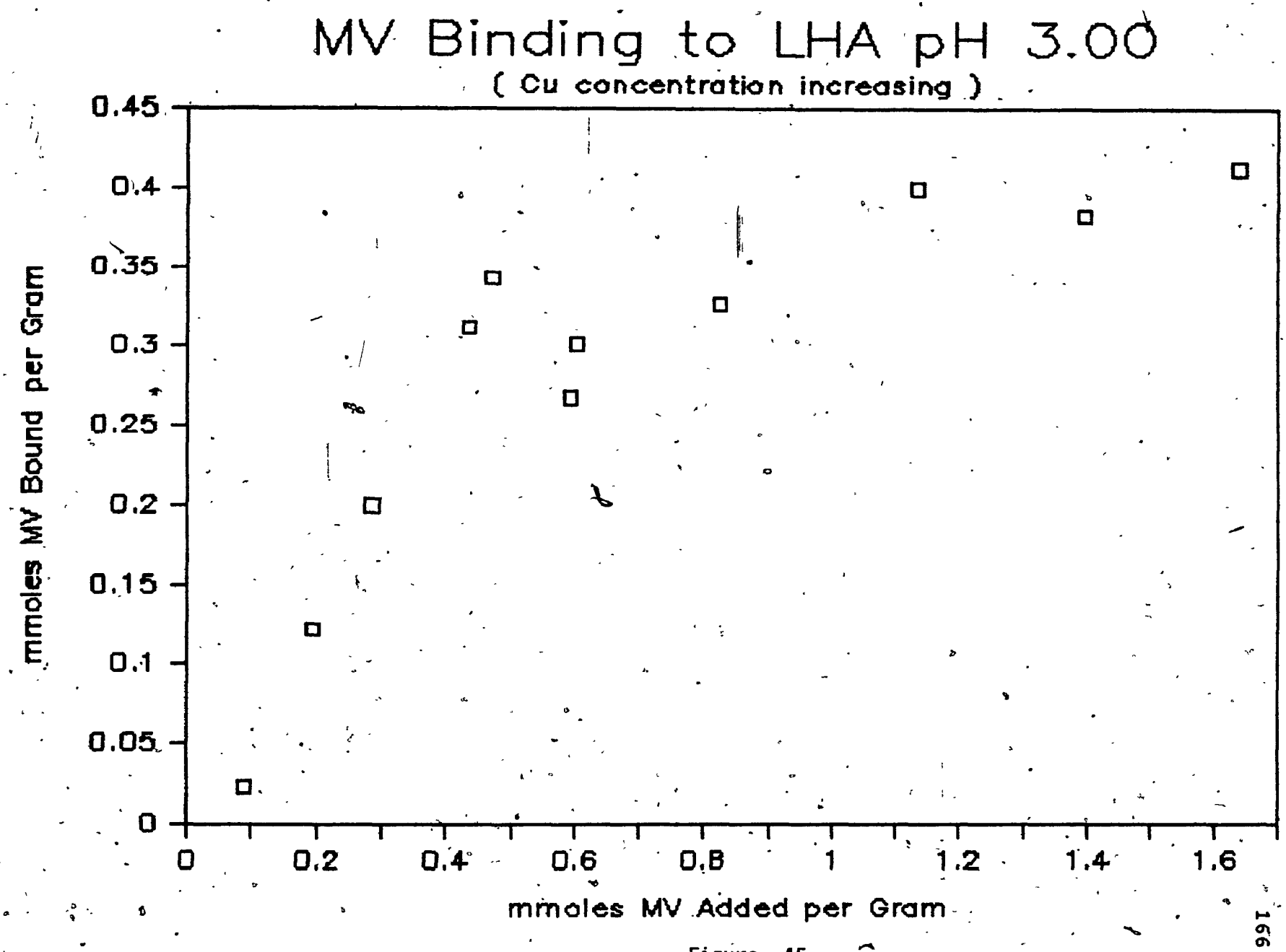

MV Binding to LHA pH 3.00
(Cu concentration increasing)
mmoles MV Bound per Gram
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
mmoles MV Added per Gram

Figure 45

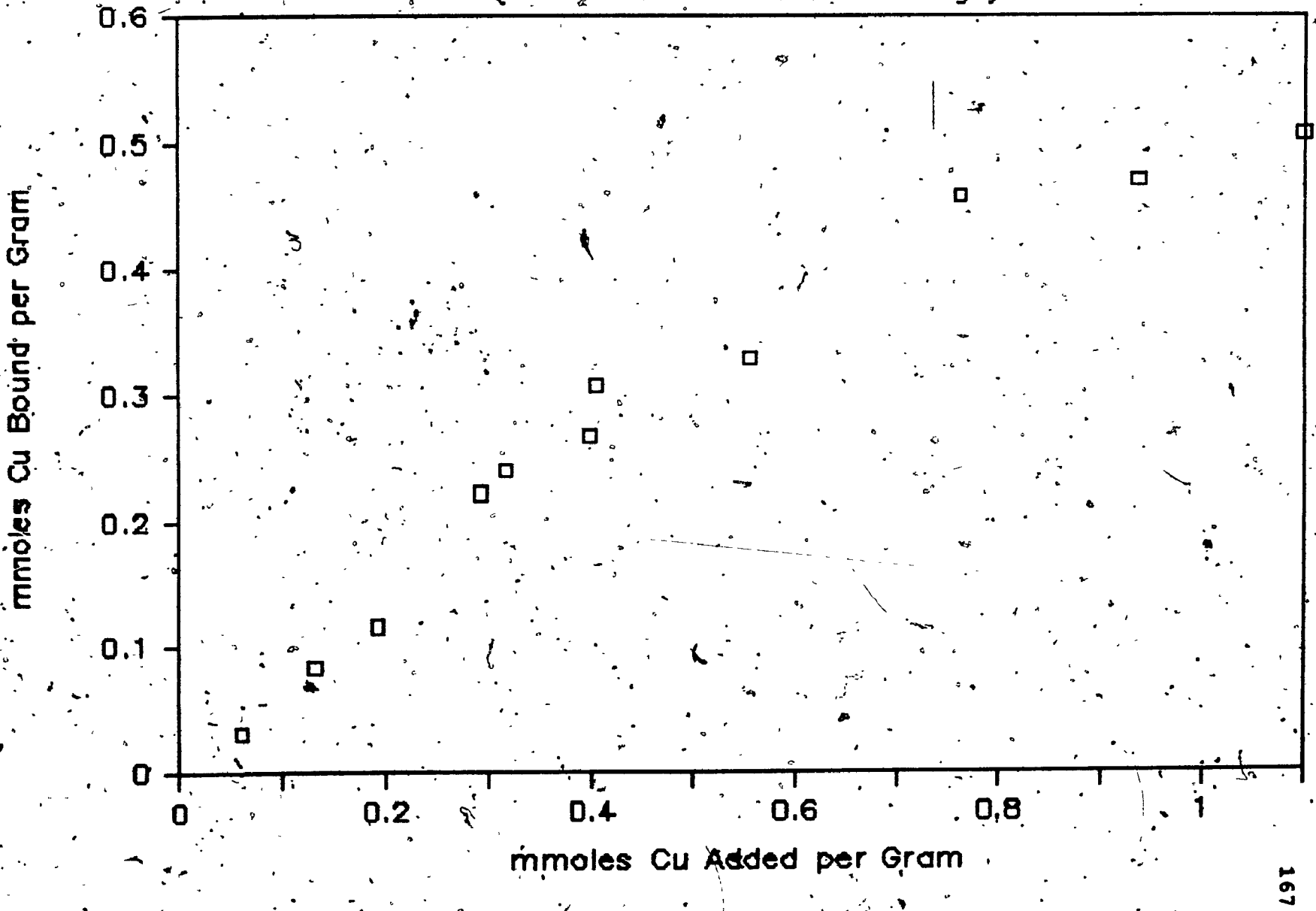

Cu Binding to LHA pH 3.00
(Mv concentration increasing)
mmoles Cu Bound per Gram
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
mmoles Cu Added per Gram

Figure 46

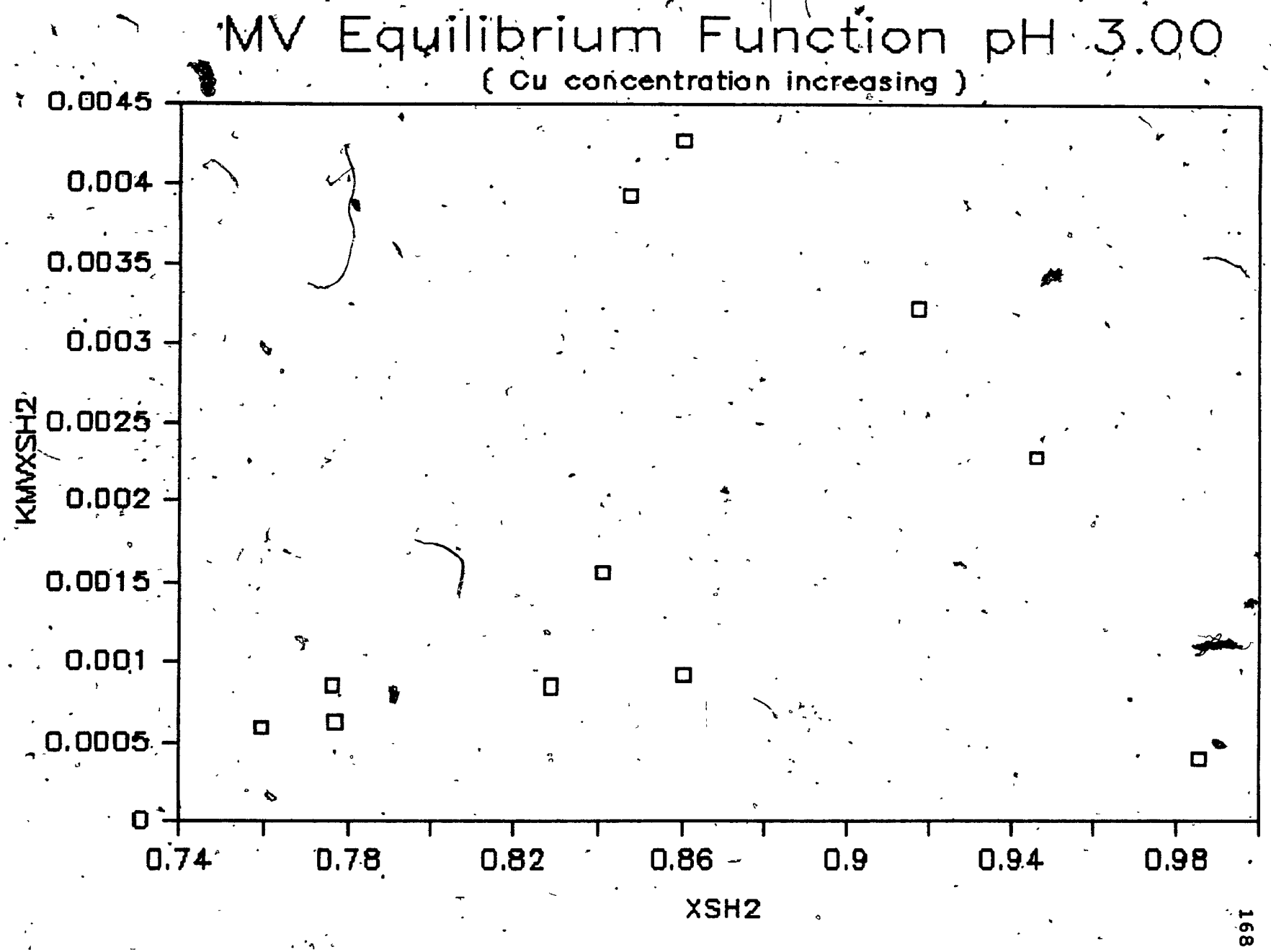

MV Equilibrium Function pH 3.00
(Cu concentration increasing)
KMVXSH2
0.0045
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
0.74
0.78
0.82
0.86
0.9
0.94
0.98
XSH2

Figure 47

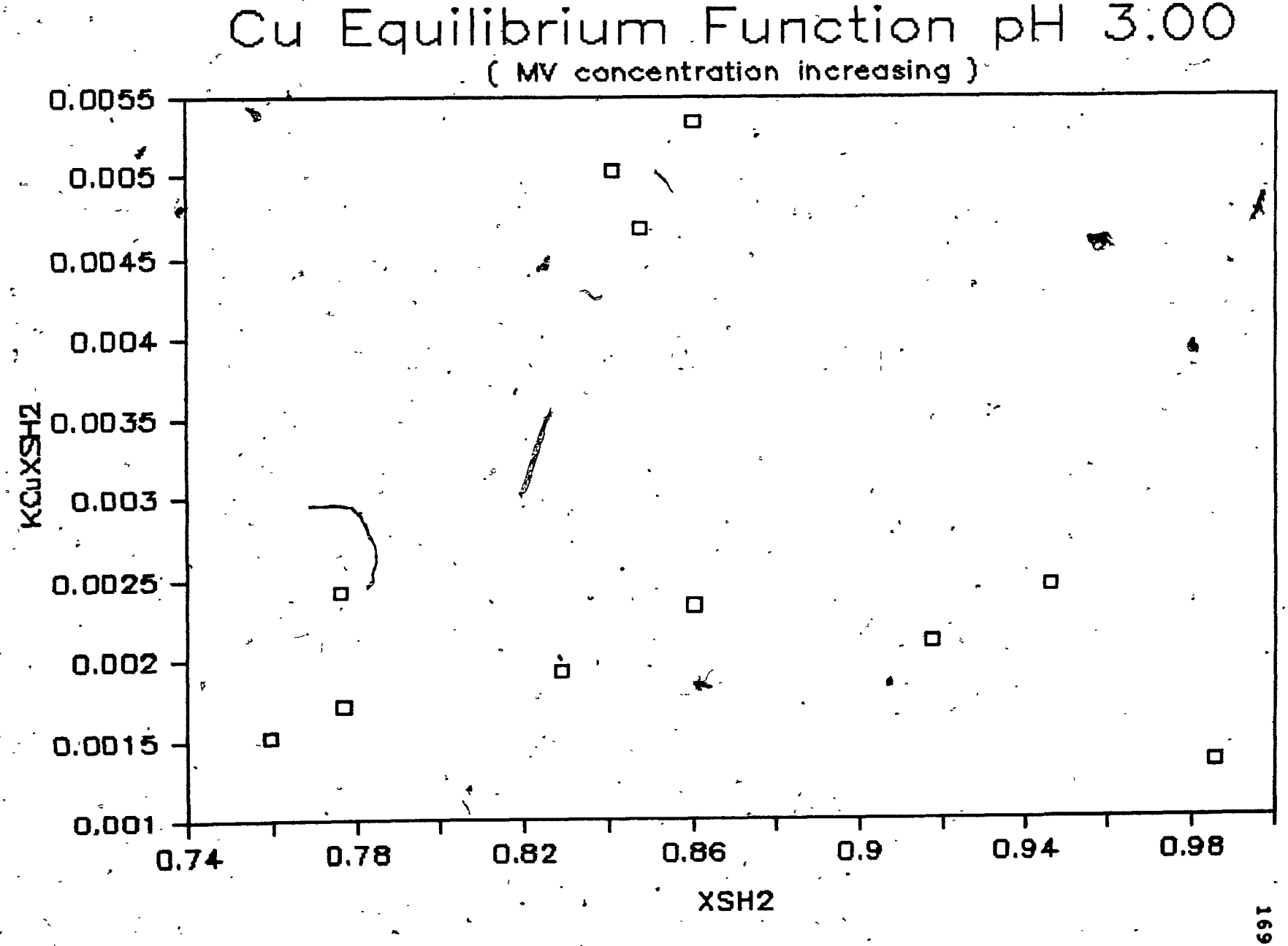

Cu Equilibrium Function pH 3.00
(MV concentration increasing)
0.0055
0.005
0.0045
0.004
0.0035
0.003
0.0025
0.002
0.0015
0.001
KCuXSH2
0.74
0.78
0.82
0.86
0.9
0.94
0.98
XSH2

Figure 48

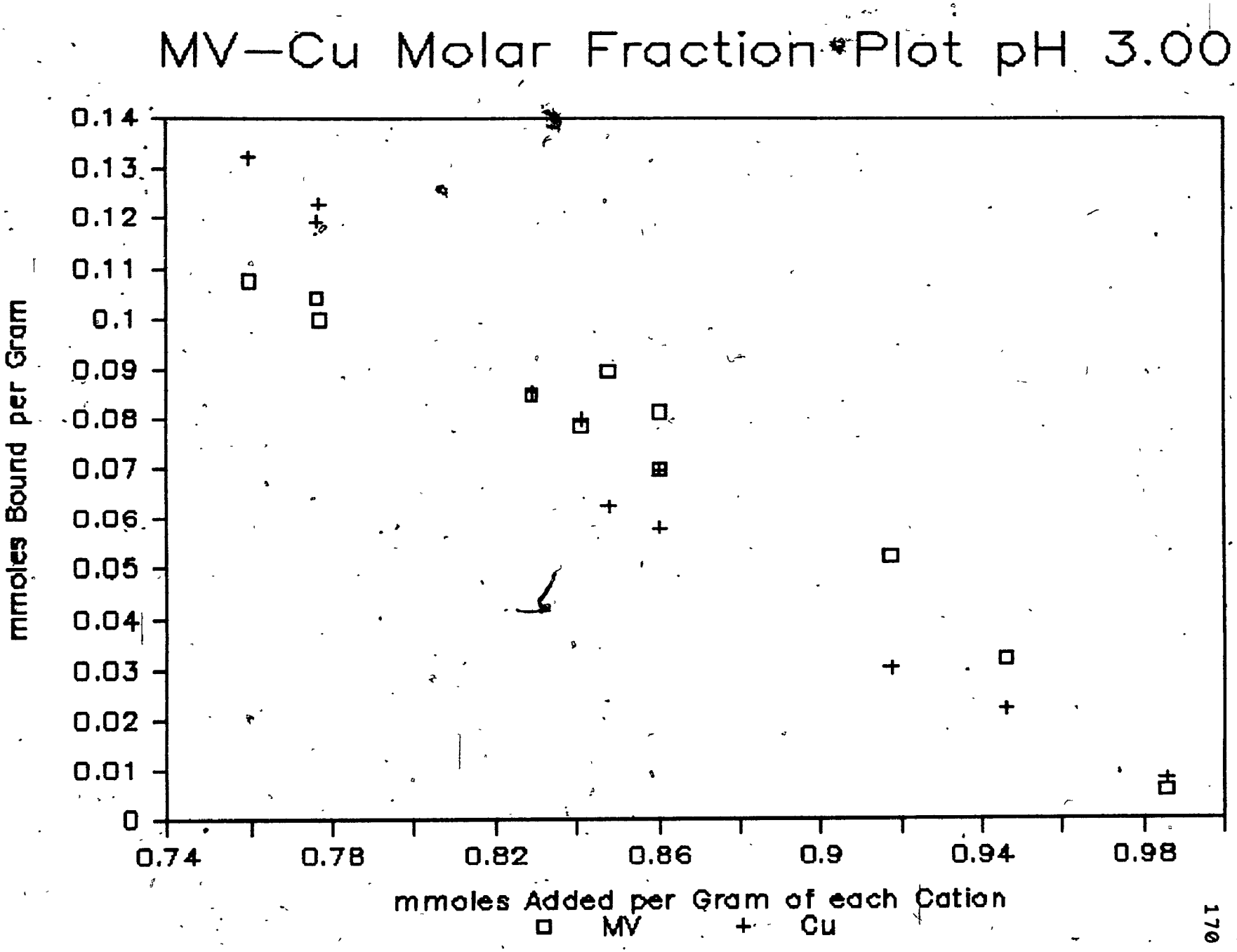

MV—Cu Molar Fraction Plot pH 3.00
mmoles Bound per Gram
0.14
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0.74
0.78
0.82
0.86
0.9
0.94
0.98
mmoles Added per Gram of each Cation
MV
Cu

Figure 49

5.1.9. Calcium-Paraquat and Magnesium-Paraquat systems.

A comparison of the plots for the binding of paraquat in the presence and absence of calcium indicates that paraquat competes with calcium for some of the sites (Figure 50). In addition it must interact with other sites not available to calcium ions. No displacement of calcium from the gel was evident in the concentration range studied. It is anticipated that at higher concentrations paraquat will start displacing calcium. A similar behaviour is noted in Figure 51 where the concentration of calcium was increased four fold.

Magnesium was not as effective as calcium in blocking ion exchange sites (Figure 52). This is a consequence of the smaller average equilibrium function for magnesium as compared to paraquat; as paraquat is added, a partial release of magnesium occurs.

These results corroborated those in Figure 30, which showed that calcium effectively blocks the ion exchange sites from magnesium. An important conclusion from this is that both cations, calcium and magnesium, interact with the same sites on humic acid.

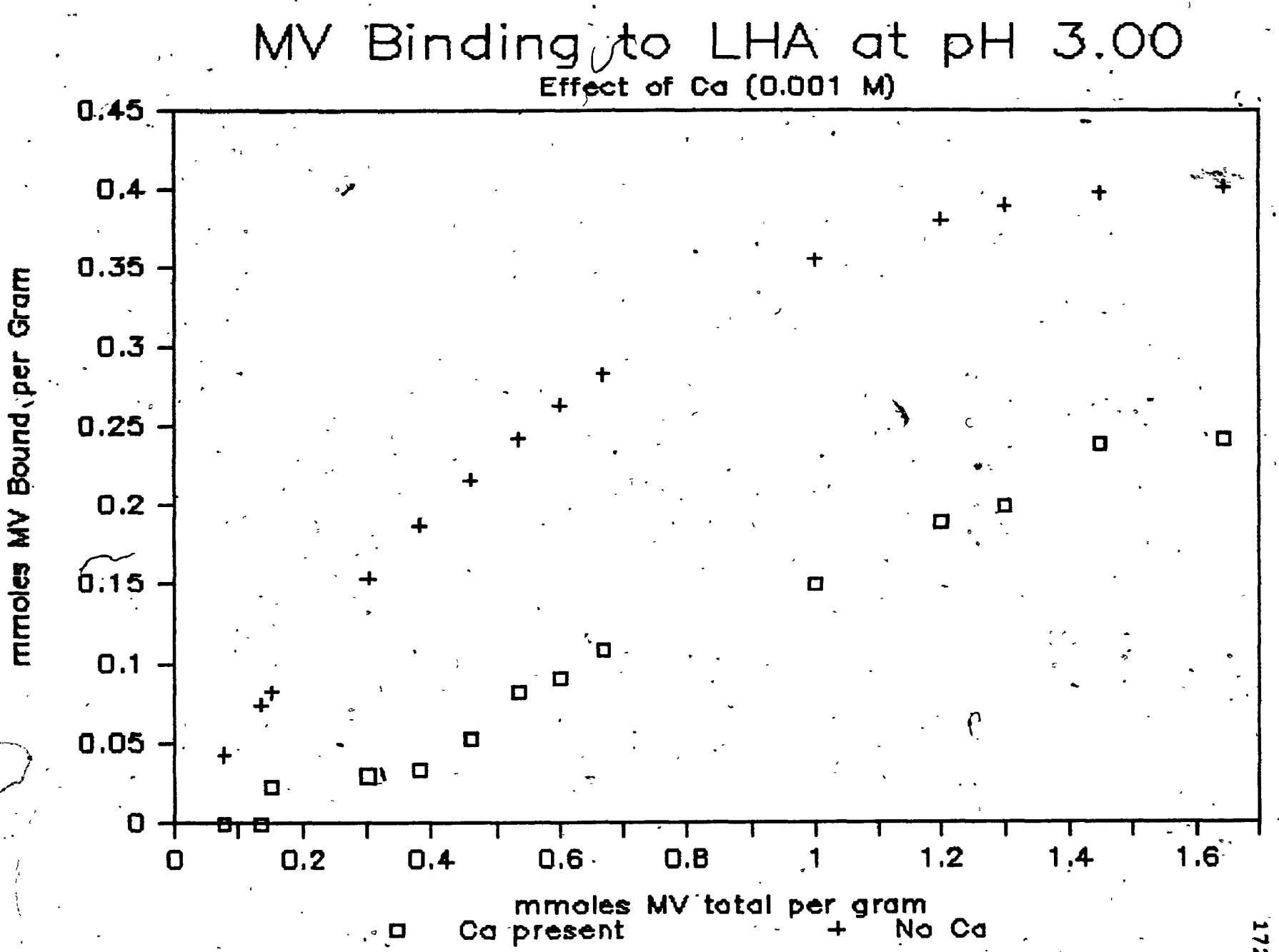

MV Binding to LHA at pH 3.00
Effect of Ca (0.001 M)
mmoles MV Bound per Gram
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
mmoles MV total per gram
Ca present
No Ca

Figure 50

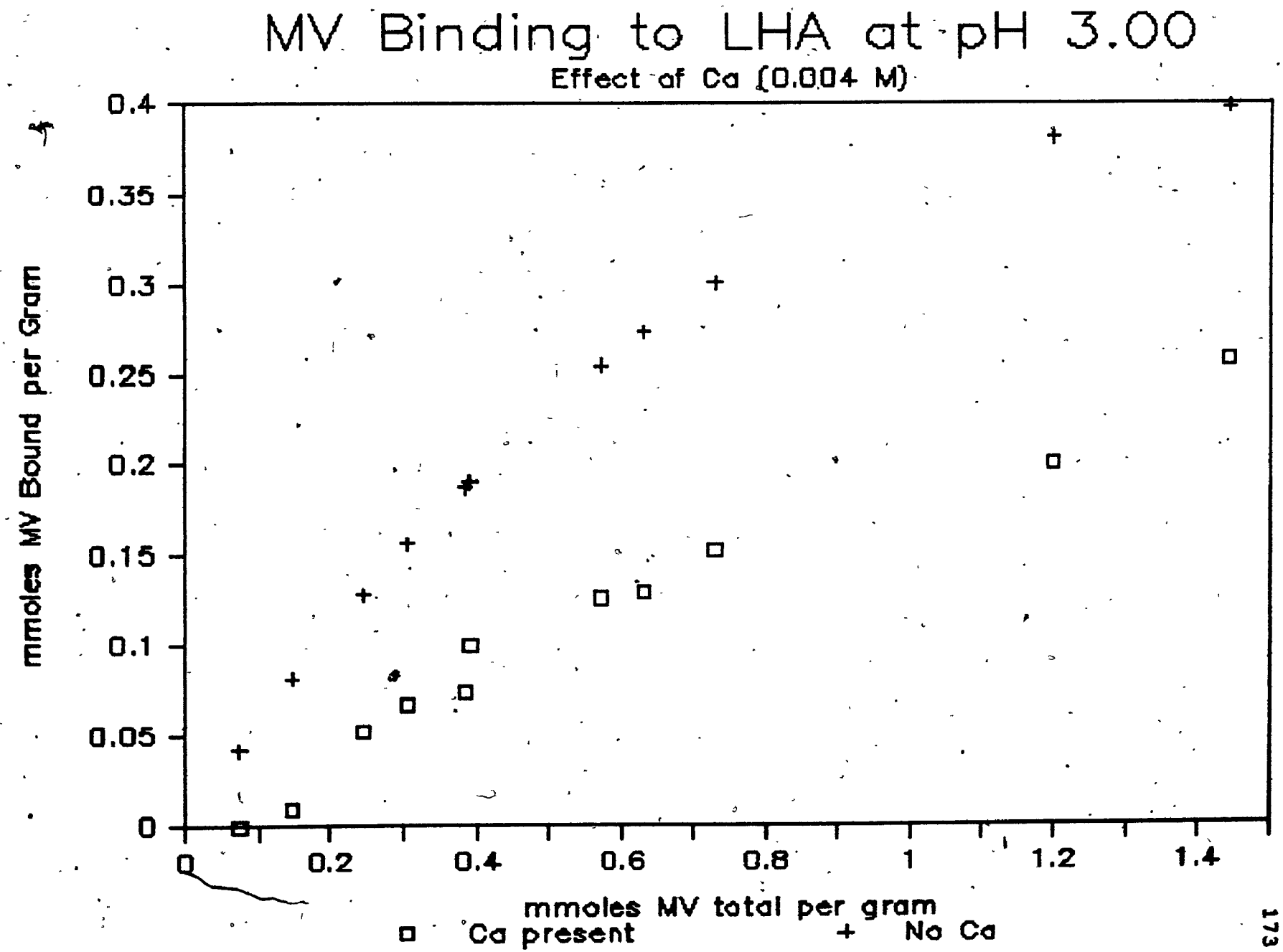

MV Binding to LHA at pH 3.00
Effect of Ca (0.004 M)
mmoles MV Bound per Gram
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
0.2
0.4
0.6
0.8
1
1.2
1.4
mmoles MV total per gram
Ca present
No Ca

Figure 51

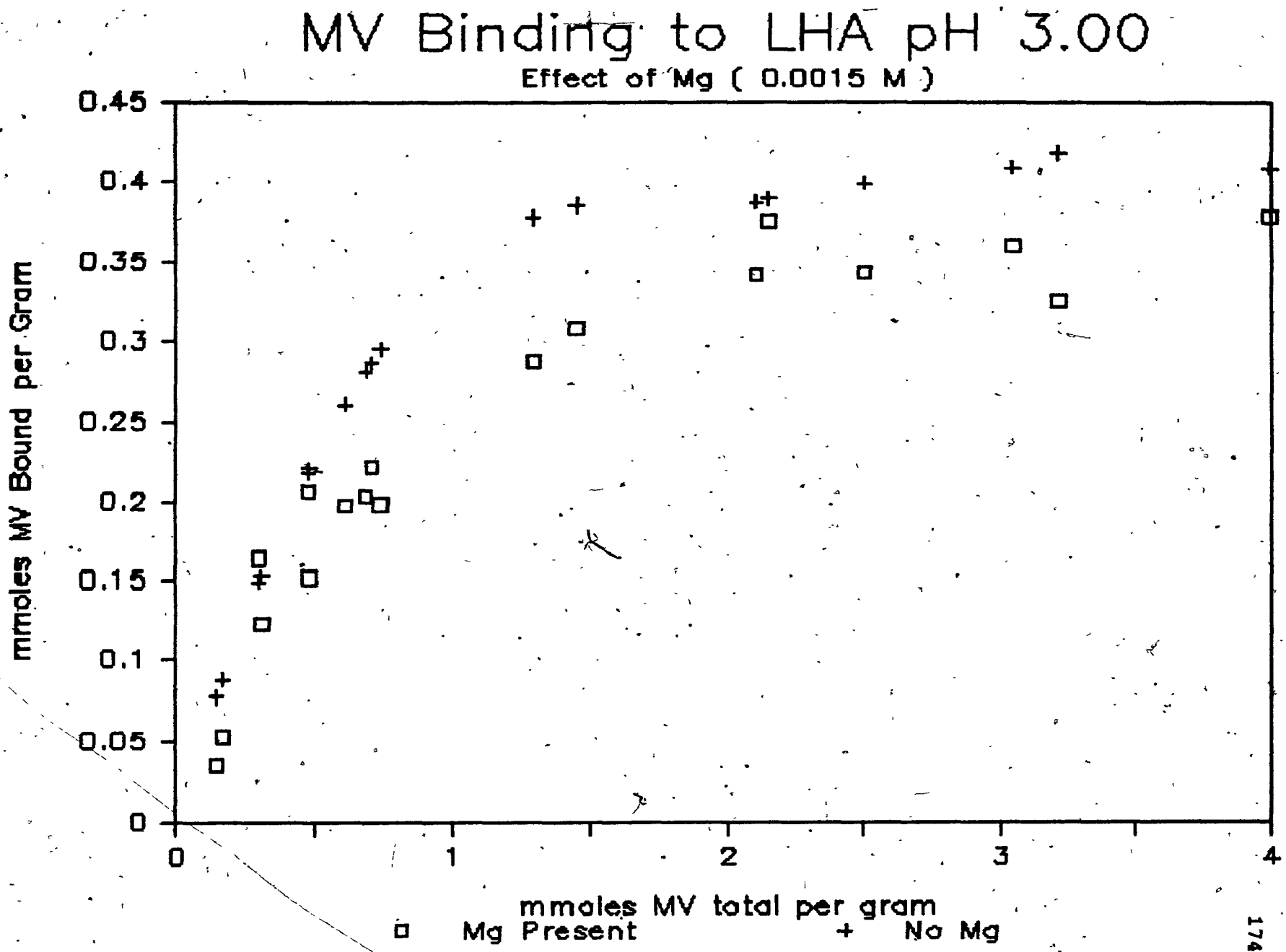

MV Binding to LHA pH 3.00
Effect of Mg (0.0015 M)
mmoles MV Bound per Gram
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
1
2
3
4
mmoles MV total per gram
Mg Present
No Mg

Figure 52

Mole fraction plots for paraquat in the presence of calcium and magnesium are shown in Figures 53 to 55. Mole fractions were calculated assuming that the number of potential binding sites totaled 3.80 millimoles per gram (Table 22). Figures 56 and 57 shows a plot to the K_{MV} X_{SH2} function against the mole fraction of proton covered sites (Figure 57 includes calcium and magnesium effects). Although there is a lot of scatter a trend can be seen to be emerging. There is an apparent maximum between 0.89 and 0.90 X_{SH2}. The binding intensity decreases on both sides of this maximum to relatively constant values which are about one order of magnitude smaller than the values at the maximum. The values at the maxima are very close to the average equilibrium function value at that particular loading. The similarity of this behaviour with the case of the copper-paraquat system is obvious. Differential equilibrium function values were obtained from Figure 56 for the magnesium saturated LHA case.

It is expected that the effect of copper, which binds preferentially to salicylic like sites, would be different from that of calcium and magnesium. Figure 44 shows that even though the amount of copper bound is greater than the amounts of calcium or magnesium bound (Figures 51 and 52), the effect on the paraquat differential function is less pronounced. Values are almost one order of magnitude larger in the presence of copper ions. This clearly shows that calcium

and magnesium are more effective than copper in competing with paraquat, despite the larger average equilibrium function for copper. The range of sites covered by copper includes some of the sites available to paraquat, calcium and magnesium, as well as other sites.

Cations such as magnesium and calcium, will interact preferentially with carboxyl groups. Their pronounced effect, compared to copper, on paraquat binding implies that there are more similarities between the sites covered by calcium, magnesium and paraquat, than between those covered by paraquat and copper.

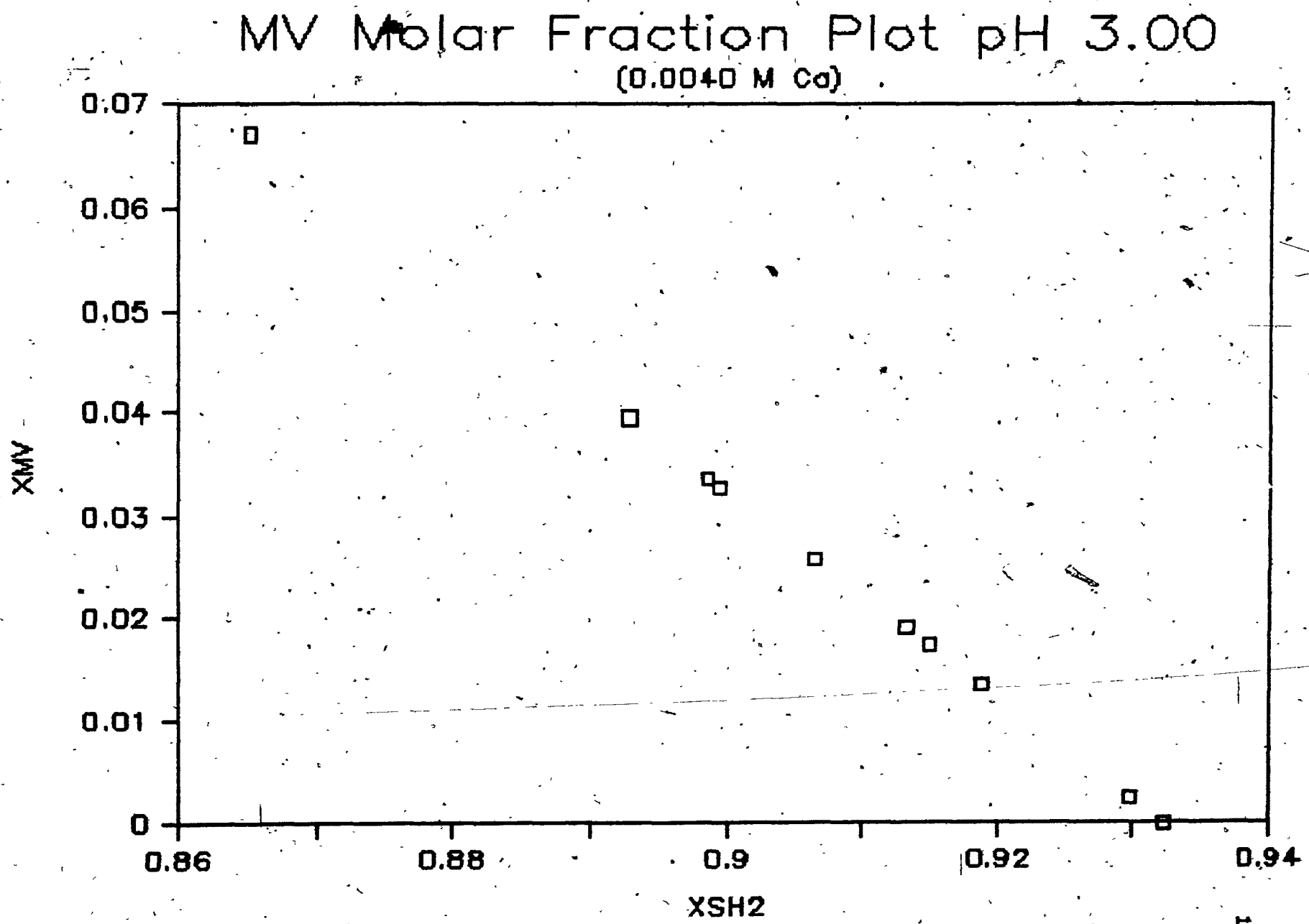

MV Molar Fraction Plot pH 3.00
(0.0040 M Ca)
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
XMV
0.86
0.88
0.9
0.92
0.94
XSH2

Figure 53

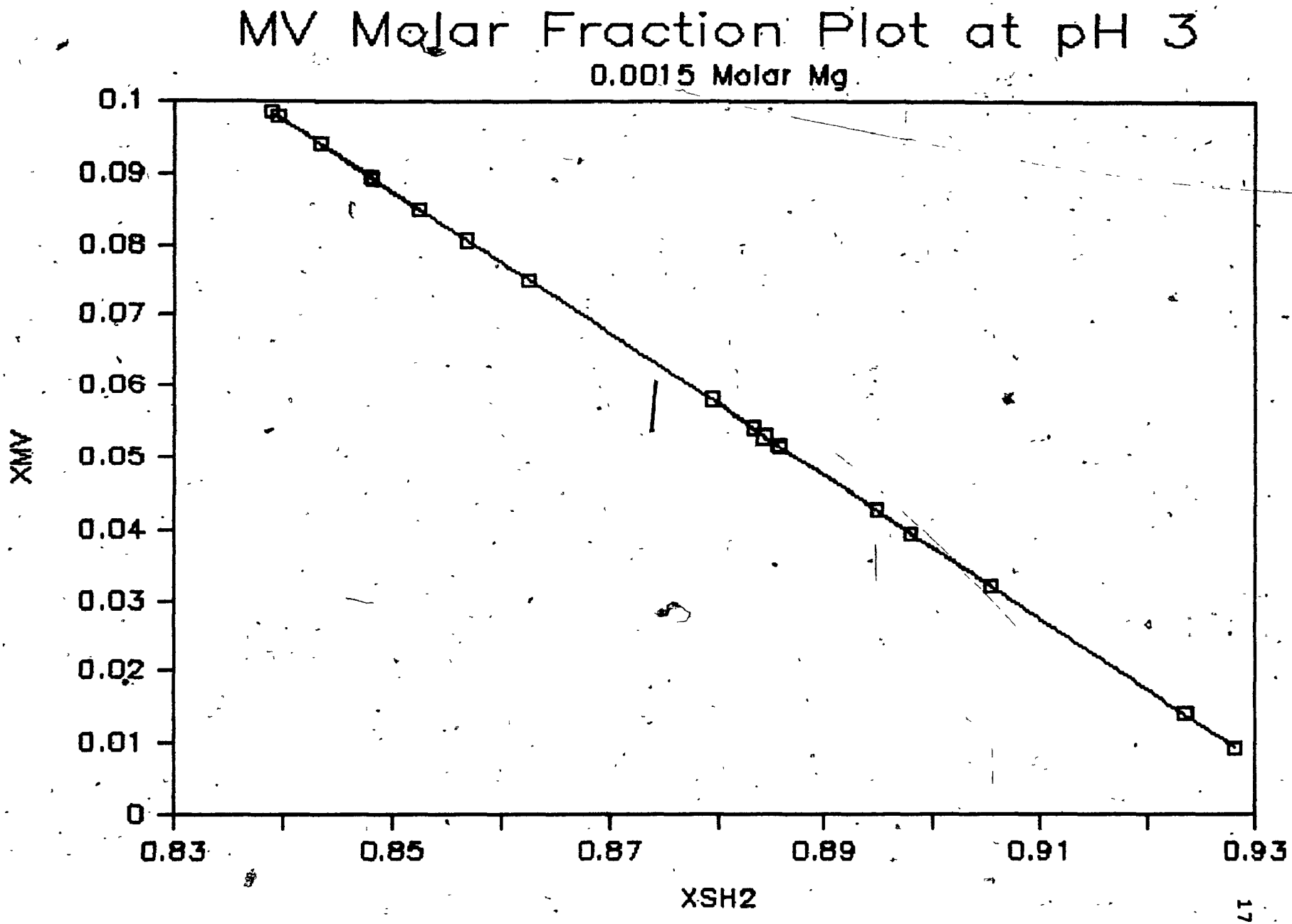

MV Molar Fraction Plot at pH 3
0.0015 Molar Mg
XMV
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
0.83
0.85
0.87
0.89
0.91
0.93
XSH2

Figure 54

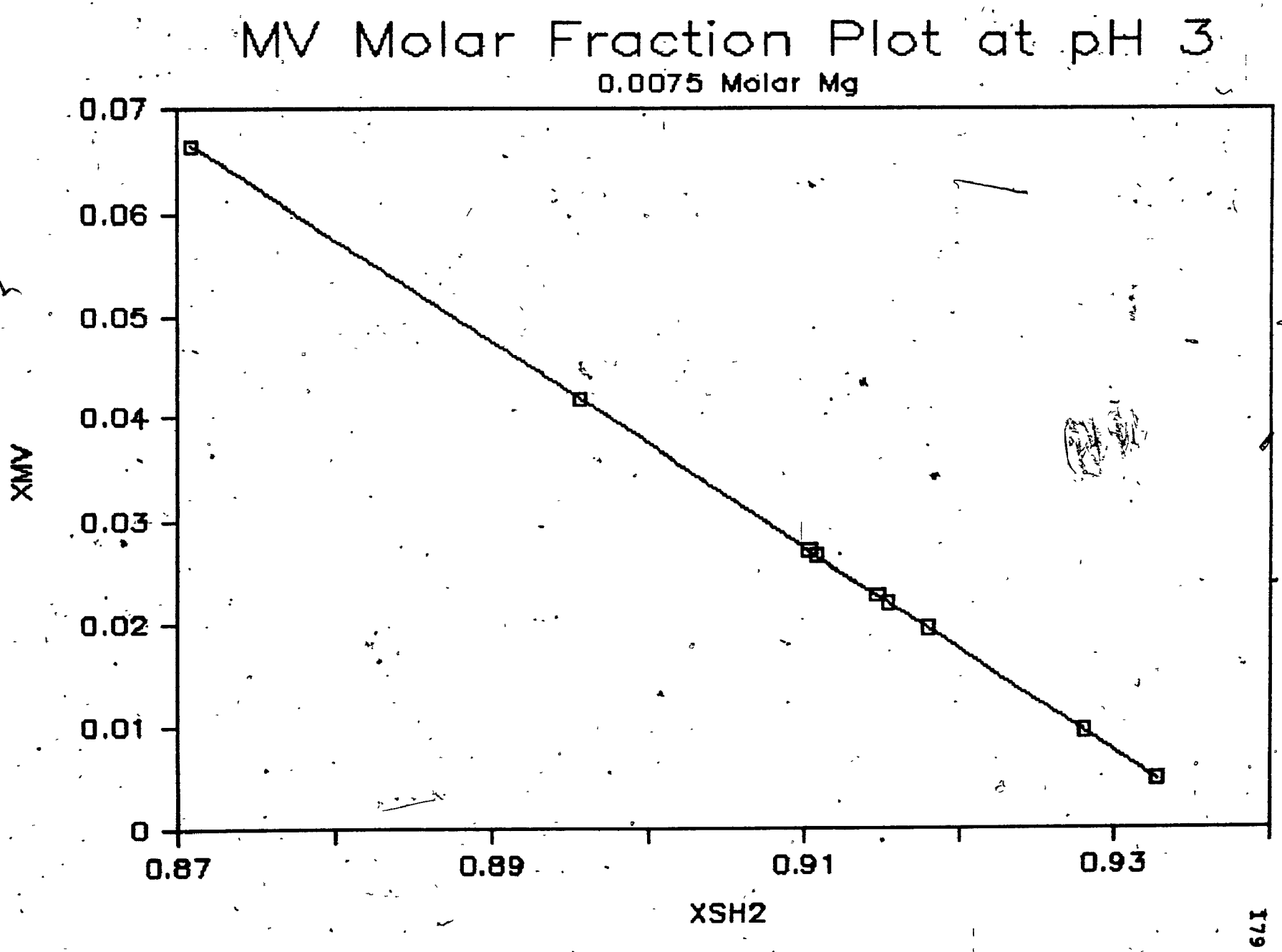

MV Molar Fraction Plot at pH 3
0.0075 Molar Mg
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
XMV
0.87
0.89
0.91
0.93
XSH2

Figure 55

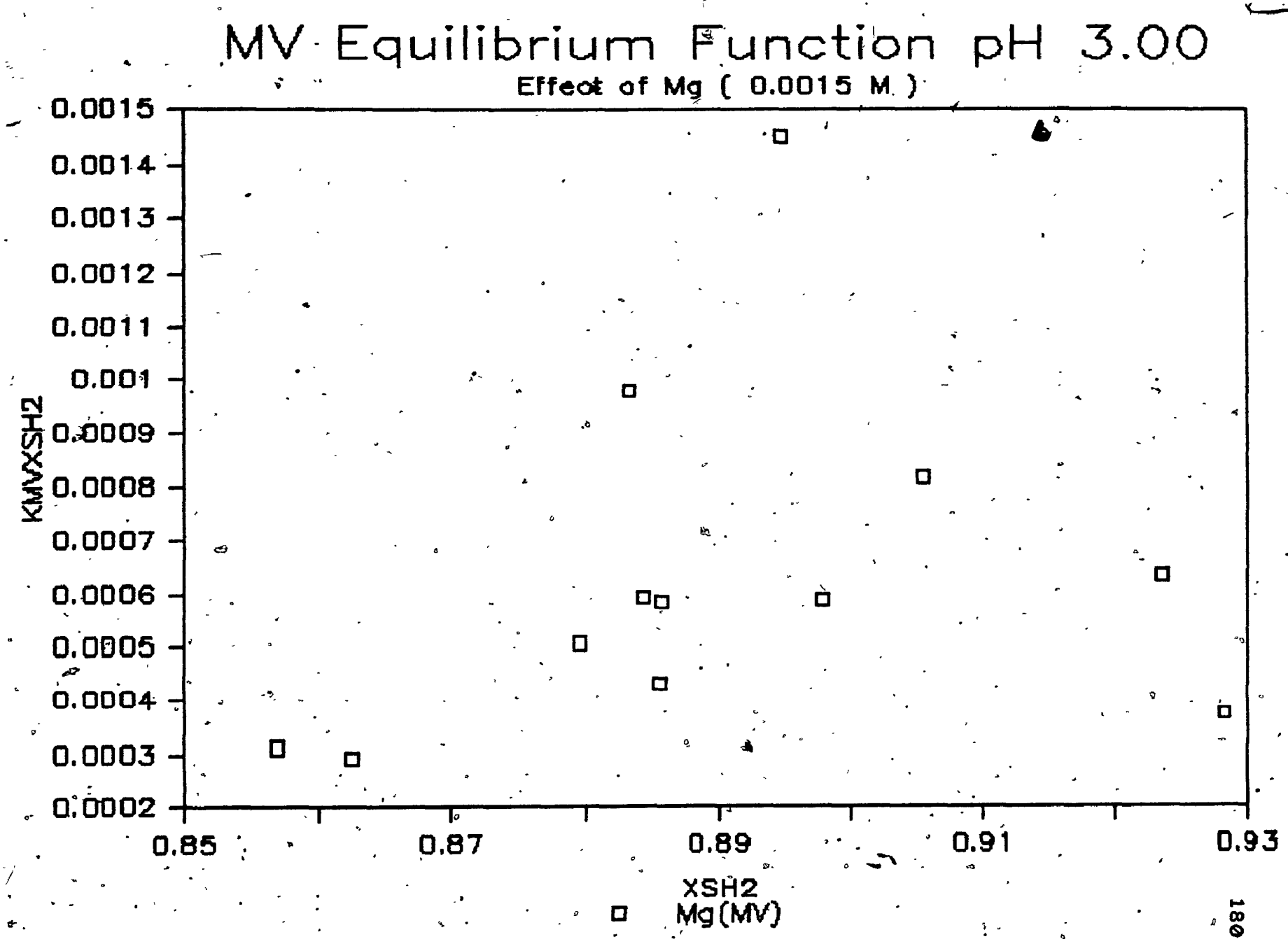

MV Equilibrium Function pH 3.00
Effect of Mg (0.0015 M)
KMVXSH2
0.0015
0.0014
0.0013
0.0012
0.0011
0.001
0.0009
0.0008
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.85
0.87
0.89
0.91
0.93
XSH2
Mg(MV)

Figure 56

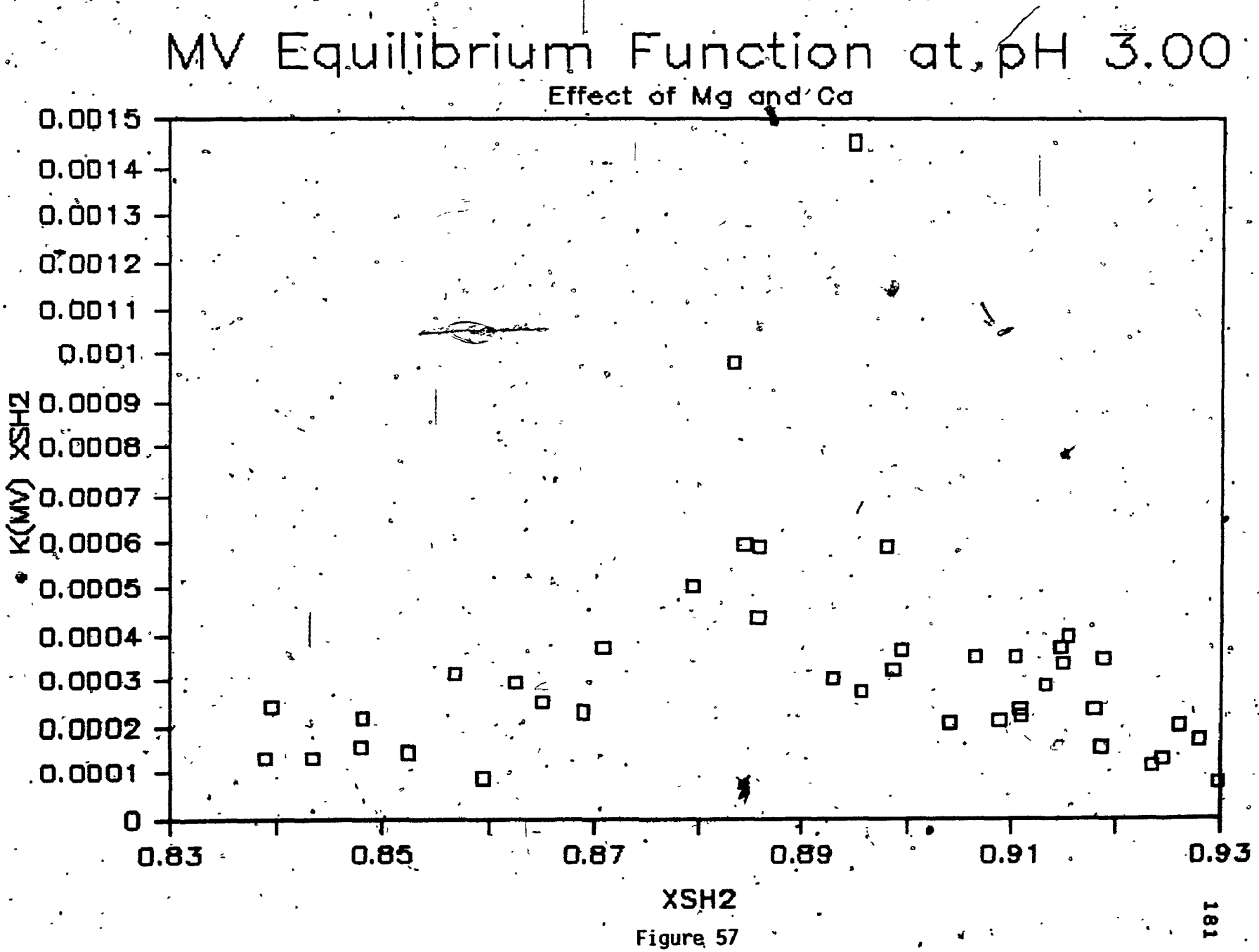

MV Equilibrium Function at pH 3.00
Effect of Mg and Ca
K(MV) XSH2
0.0015
0.0014
0.0013
0.0012
0.0011
0.001
0.0009
0.0008
0.0007
0.0006
0.0005
0.0004
0.0003
0.0002
0.0001
0
0.83
0.85
0.87
0.89
0.91
0.93
XSH2

Figure 57

Table 22

Paraquat-Humic Acid pH 3.00

Effect of Calcium on K_{MV} values

X_{MV} (±%4)	X_{Ca} (±%5)	X_{SH2} (±%10)	K_{MV} (±%15)
0.006	0.068	0.926	2.17×10^{-4}
0.008	0.068	0.925	1.43×10^{-4}
0.090	0.068	0.923	1.28×10^{-4}
0.014	0.068	0.919	1.70×10^{-4}
0.021	0.068	0.910	2.43×10^{-4}
0.026	0.068	0.909	2.32×10^{-4}
0.028	0.067	0.904	2.27×10^{-4}
0.063	0.067	0.869	2.61×10^{-4}

Humic acid concentration 0.2g/Lt. Total Ca added 4×10^{-3} M.

Table 23

Paraquat-Humic Acid pH 3.00

Effect of Magnesium on K_{MV} values

X_{MV} (±%4)	X_{Mg} (±%5)	X_{BH2} (±%10)	K_{MV} (±%15)
0.004	0.063	0.933	1.81×10^{-4}
0.009	0.063	0.982	2.51×10^{-4}
0.020	0.063	0.920	4.31×10^{-4}
0.022	0.063	0.915	3.85×10^{-4}
0.023	0.063	0.914	2.57×10^{-4}
0.027	0.063	0.910	4.06×10^{-4}
0.027	0.063	0.910	3.02×10^{-4}
0.042	0.063	0.896	4.18×10^{-4}
0.067	0.063	0.870	3.74×10^{-4}

Humic acid concentration 0.2 g/ Lt. Total Mg added 8×10^{-3} M in 50 mLs.

Table 24

Paraquat-Humic Acid pH 3.00

Effect of Magnesium on K_{MV} values

X_{MV} (±%4)	X_{Mg} (±%5)	X_{BH2} (±%10)	K_{MV} (±%15)
0.009	0.063	0.928	4.02×10^{-4}
0.014	0.063	0.924	6.87×10^{-4}
0.032	0.063	0.906	9.02×10^{-4}
0.040	0.063	0.898	6.56×10^{-4}
0.052	0.063	0.886	6.63×10^{-4}
0.052	0.063	0.886	4.90×10^{-4}
0.053	0.063	0.884	6.72×10^{-4}
0.054	0.063	0.883	1.10×10^{-4}
0.058	0.063	0.880	5.72×10^{-4}
0.075	0.063	0.863	3.41×10^{-4}
0.081	0.063	0.857	3.65×10^{-4}

Humic Acid concentration 0.2 g/L. Total Mg added 1×10^{-3} Molar in 50 mLs.

Table 25

Paraquat-Humic Acid pH 3.00

Effect of Calcium on K_{HV} values

X_{HV} (±%4)	X_{Ca} (±%5)	X_{BH2} (±%10)	K_{HV} (±%15)
0.003	0.068	0.930	8.60×10^{-5}
0.014	0.068	0.919	3.79×10^{-4}
0.017	0.068	0.915	3.71×10^{-4}
0.019	0.068	0.913	3.14×10^{-4}
0.026	0.068	0.906	3.88×10^{-4}
0.033	0.068	0.899	4.08×10^{-4}
0.034	0.068	0.898	3.69×10^{-4}
0.040	0.068	0.893	3.40×10^{-4}
0.067	0.068	0.865	2.88×10^{-4}

Humic Acid concentration 0.2 g/L. Total Ca added 1.10^{-3} Molar in 50 mLs sample.

5.1.10. Calcium-Magnesium system at pH 5.00.

In order to identify the type of sites with which cations such as magnesium and calcium interact, humic acid previously saturated with one of the two cations (calcium or magnesium) was titrated with the other cation. The amount of magnesium or calcium needed to saturate the sites available to it estimated on previous experiments involving magnesium or calcium alone was added.

Figure 58 shows the binding curve for calcium on a magnesium saturated humic acid at pH 5.00. The sample was initially equilibrated with a magnesium solution at a concentration level sufficient to saturate all the sites available to magnesium. It can be seen that as calcium binds to humic acid magnesium cations are released. Calcium is able to displace all of the magnesium initially bound. This indicates that calcium competes effectively with magnesium for the same sites. Approximately 2 moles of magnesium are released per mole of calcium bound as can be seen in Figure 59. The slope of the "release" plot is 1.98, the intercept was almost zero. This is a rather unusual result since electroneutrality does not seem to be maintained if one calcium ion displaces two magnesium ions from humic acid. Under the conditions of these experiments, the fraction of magnesium ions forming positively charged ion pairs

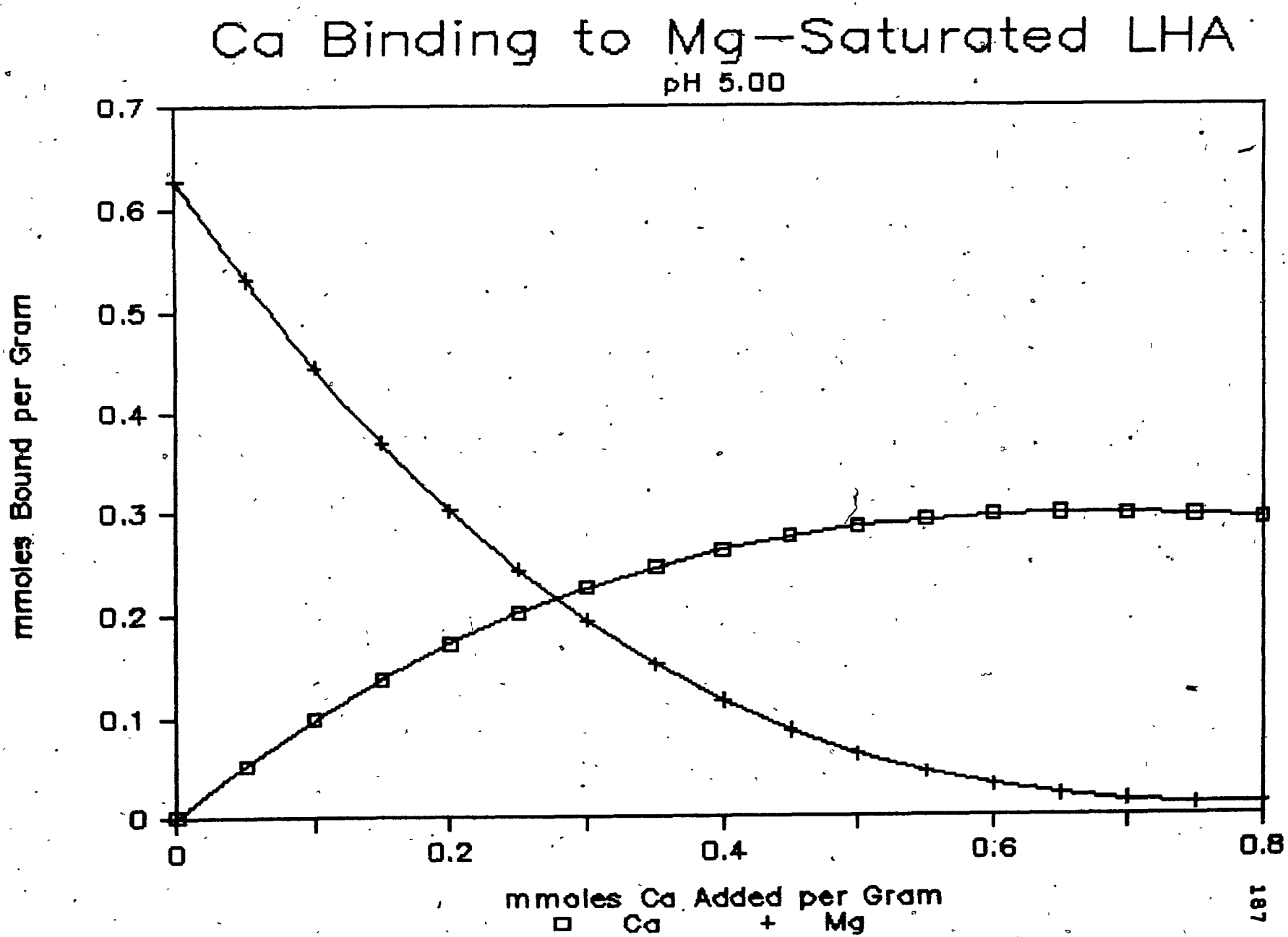

Ca Binding to Mg-Saturated LHA
pH 5.00
mmoles Bound per Gram
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
mmoles Ca Added per Gram
□ Ca + Mg
187

Figure 58

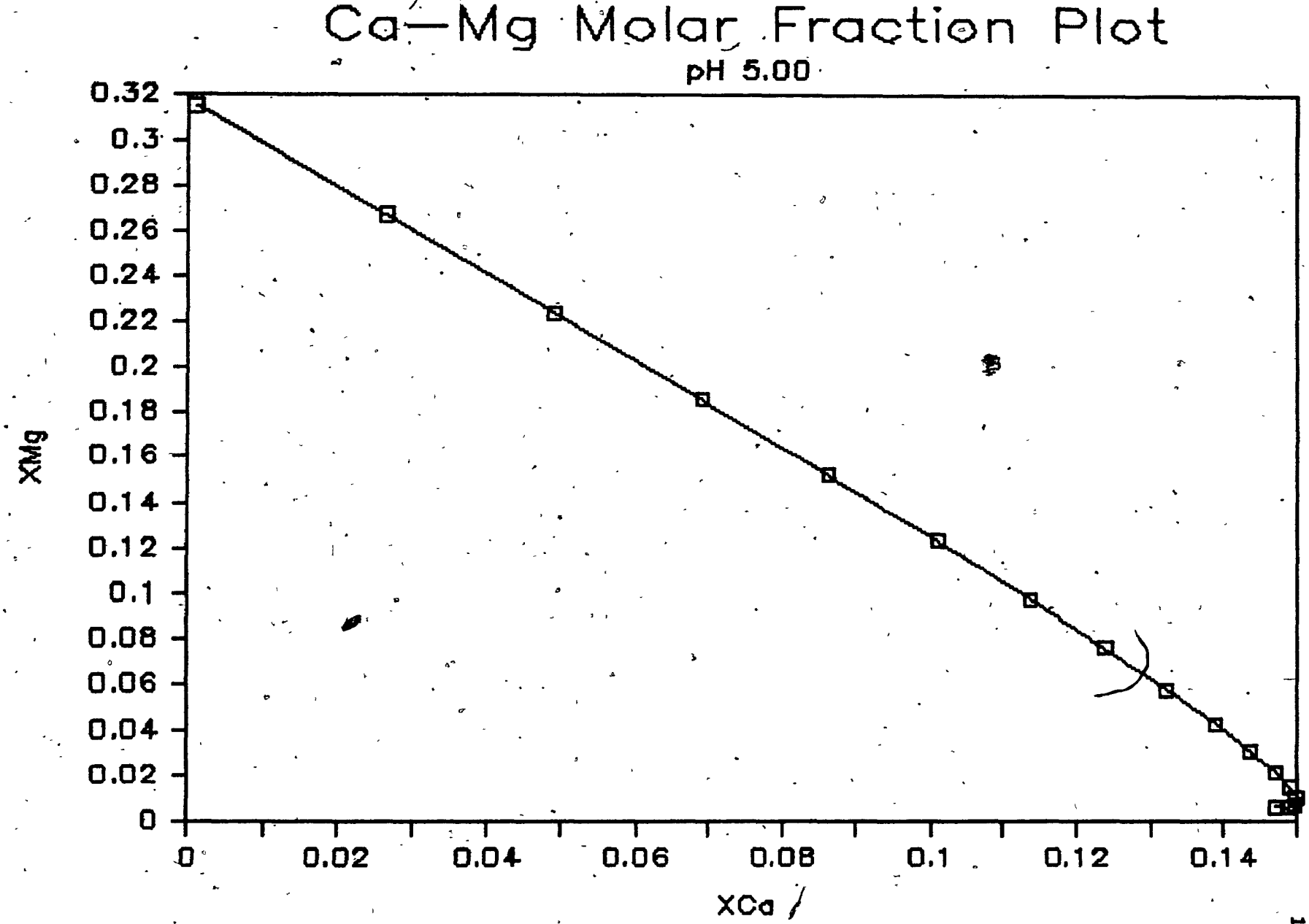
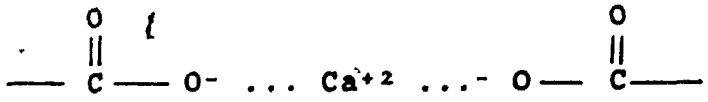

Ca—Mg Molar Fraction Plot
pH 5.00
XMg
0.32
0.3
0.28
0.26
0.24
0.22
0.2
0.18
0.16
0.14
0.12
0.1
0.08
0.06
0.04
0.02
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
XCa

Figure 59

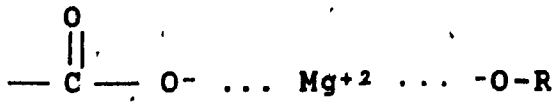
with inorganic anions is insignificant. Electroneutrality calculations based on the concentration of cations in the filtrates indicated that there is a fraction of positive charge which cannot be balanced by inorganic anions such as OH^-, Cl^- and CO_3^{-2}. Small organic anions released from humic acid and able to pass through the YM2 membrane may account for this. Even if the above assumptions are correct the fraction of unbalanced charge does not account for the total amount of magnesium released. At this point there is no explanation for this behaviour.

The reverse experiment consisting of a calcium saturated humic acid being titrated with magnesium gave results which imply that magnesium is not able to displace calcium from humic acid within the range of concentration scanned.

The coagulation of humic acid in the presence of calcium ions indicates that calcium must be binding carboxyl groups in adjacent molecules as well as adjacent groups within the same molecule. The formation of bridge complexes such as shown below has been postulated by Underdown et al.(13) in order to explain the effects of copper on the Raleigh scattering behaviour of fulvic acid.



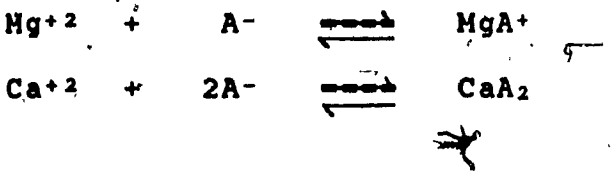
The behaviour of magnesium can only be explained by the formation of charged complexes between one carboxyl group and one divalent magnesium ion as shown below:



where -O-R represents a monomeric anion in solution.

The possibility of organic monomeric anions being attracted to the charged complex cannot be ruled out. This must be taken into account when considering a divalent calcium ion approaching a magnesium covered ion exchange site.

The proposed stoichiometry is compatible with the observed apparent binding capacities for magnesium and calcium. The establishment of the stoichiometry allows for the description of the equilibria involved as being:



where A- stands for a single negatively charged binding site.

Average equilibrium functions calculated using Equation 41 for magnesium and calcium are shown in Figure 60. The binding function for calcium is several orders of magnitude larger than that for magnesium based on results from the magnesium-saturated-

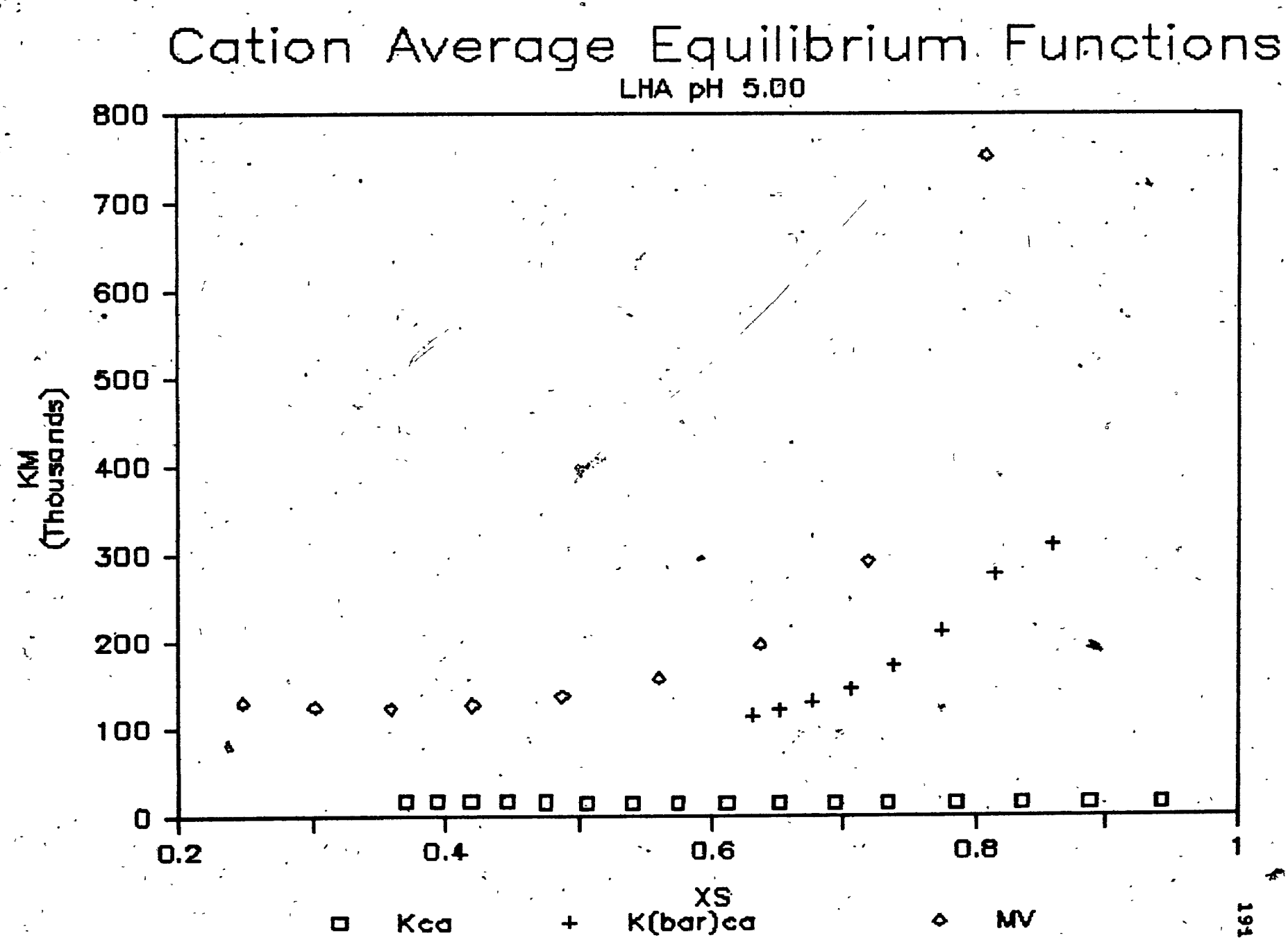

Cation Average Equilibrium Functions
LHA pH 5.00
800
700
600
500
400
300
200
100
0
KM
(Thousands)
0.2
0.4
0.6
0.8
1
XS
Kca
K(bar)ca
MV

Figure 60

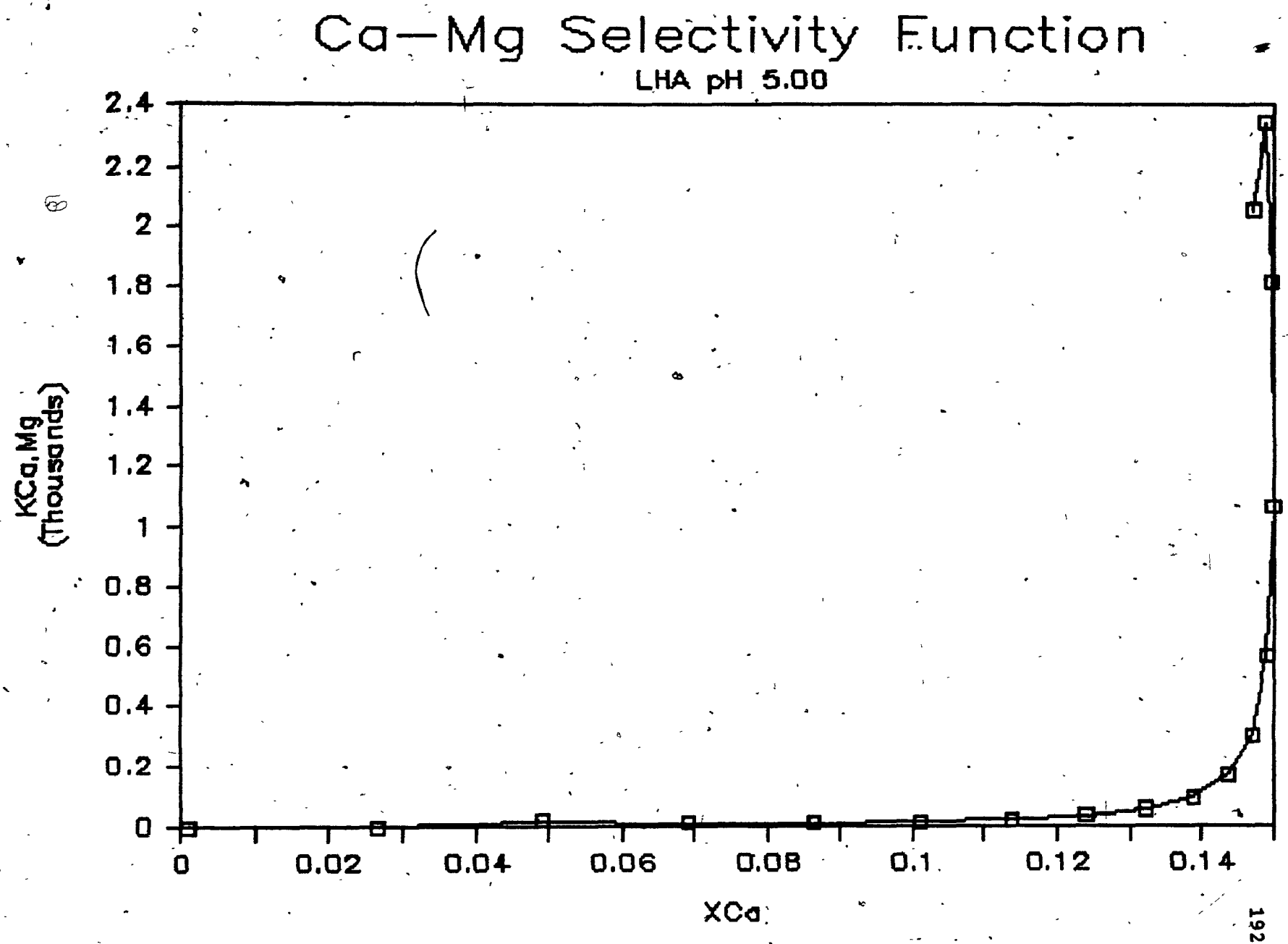

Ca—Mg Selectivity Function
LHA pH 5.00
KCa,Mg (Thousands)
2.4
2.2
2
1.8
1.6
1.4
1.2
1
0.8
0.6
0.4
0.2
0
0
0.02
0.04
0.06
0.08
0.1
0.12
0.14
XCa

Figure 61

humic acid experiment. The variation of the equilibrium functions with increasing calcium on the exchanger is expected for mainly two reasons: the polyelectrolyte effect and the removal of humic acid from solution as the binding of calcium proceeds. The ion exchange selectivity quotient is shown in Figure 61 for the magnesium saturated humic acid experiment. It decreases with decreasing calcium content in the exchanger.

The definition of the ion exchange selectivity quotient as:

$$\overline{K}_{Ca,Mg} = \frac{\{Ca^{+2}\}\ [ROMg^{+}]^2}{\{ORMg^{+}\}^2\ [Ca^{+2}]}$$

can also be expressed as the ratio of the formation constants for each individual complex:

$$\overline{K}_{Ca,Mg} = \frac{\overline{K}_{Ca}}{\overline{K}_{Mg^2}}$$

5.1.11. Magnesium Paraquat System at pH 5.

The interaction of paraquat with magnesium saturated humic acid and the interaction of magnesium with paraquat saturated humic acid were studied at pH 5.

The apparent binding capacity of paraquat at pH 5.00 is quite similar to that of magnesium. Binding curves for paraquat

in the presence of different levels of magnesium in solution are shown in Figures 62,63 and 64. The most evident feature is that magnesium is able to reduce the apparent binding capacity of paraquat. Unlike the displacement of magnesium by calcium the displacement of magnesium by paraquat was not complete. Results for experiments with high magnesium levels showed that the displacement of magnesium is similar to that for the low magnesium levels. In both situations paraquat displaced only about 0.6 millimoles of the initially bound magnesium.

Examination of the binding curve for paraquat in the presence of magnesium (Figure 64) indicates that the apparent binding capacity for paraquat is less than when no magnesium is present in solution. At both magnesium concentration levels the paraquat saturation values have been reduced to about 0.7 millimoles per gram, compared to approximately 0.9 millimoles in the absence of magnesium. Sites equivalent to approximately 0.3 millimoles of paraquat per gram are being effectively blocked by magnesium or, do not interact with paraquat.

In order to establish the stoichiometry of the ion exchange reaction between magnesium-saturated humic acid and paraquat a molar fraction plot has been prepared. Figure 65 shows X_{Mg} versus X_{MV} at high and low magnesium levels. The low magnesium level results can be fitted to a straight line, the slope of -0.8232 indicates that the ratio of the stoichiometric coefficients (n_{MV}/n_{Mg}) is close to unity. This substantiates the

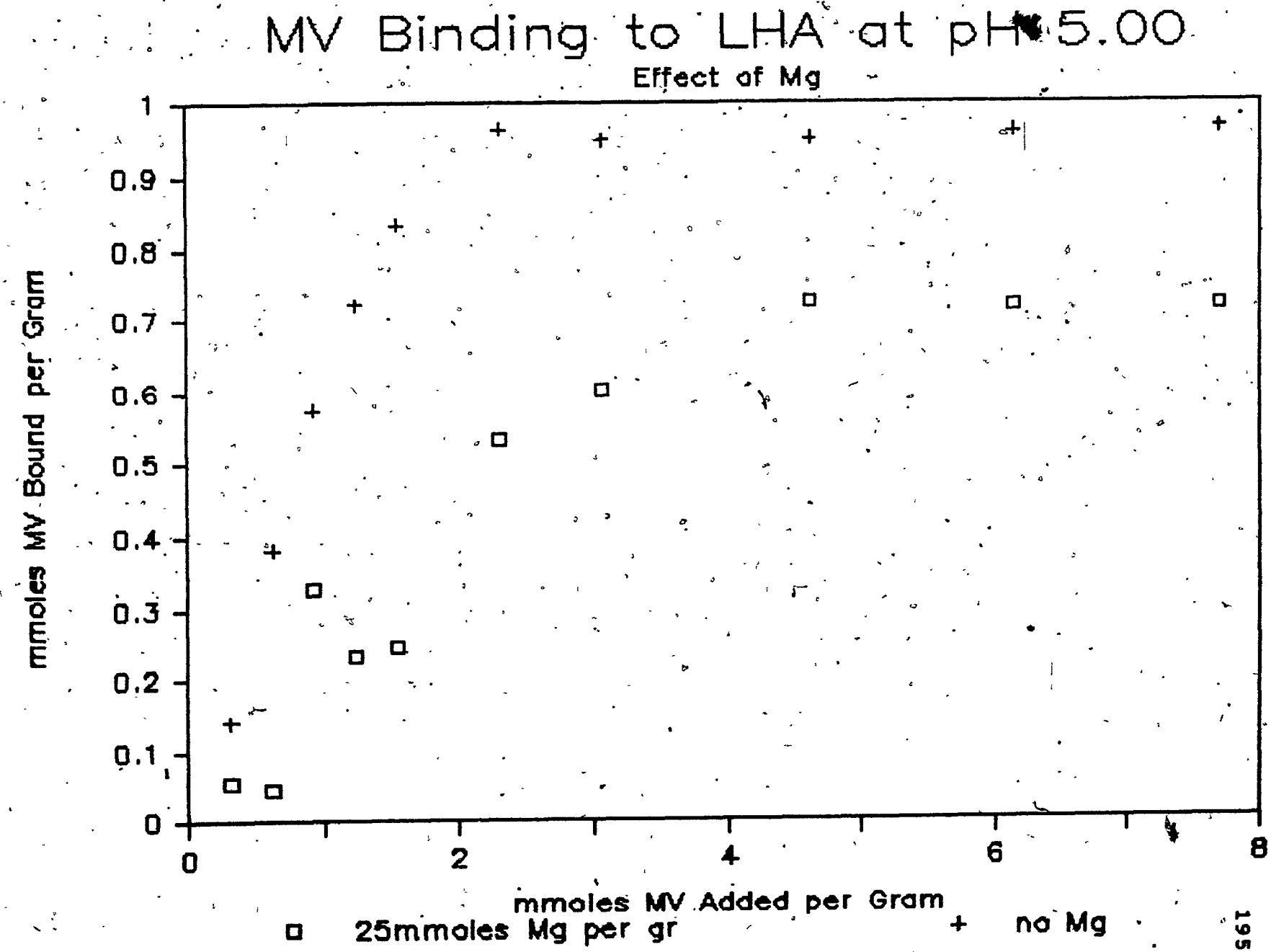

MV Binding to LHA at pH 5.00
Effect of Mg
mmoles MV Bound per Gram
0
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
0.9
1
0
2
4
6
8
mmoles MV Added per Gram
25mmoles Mg per gr
no Mg
195

Figure 62

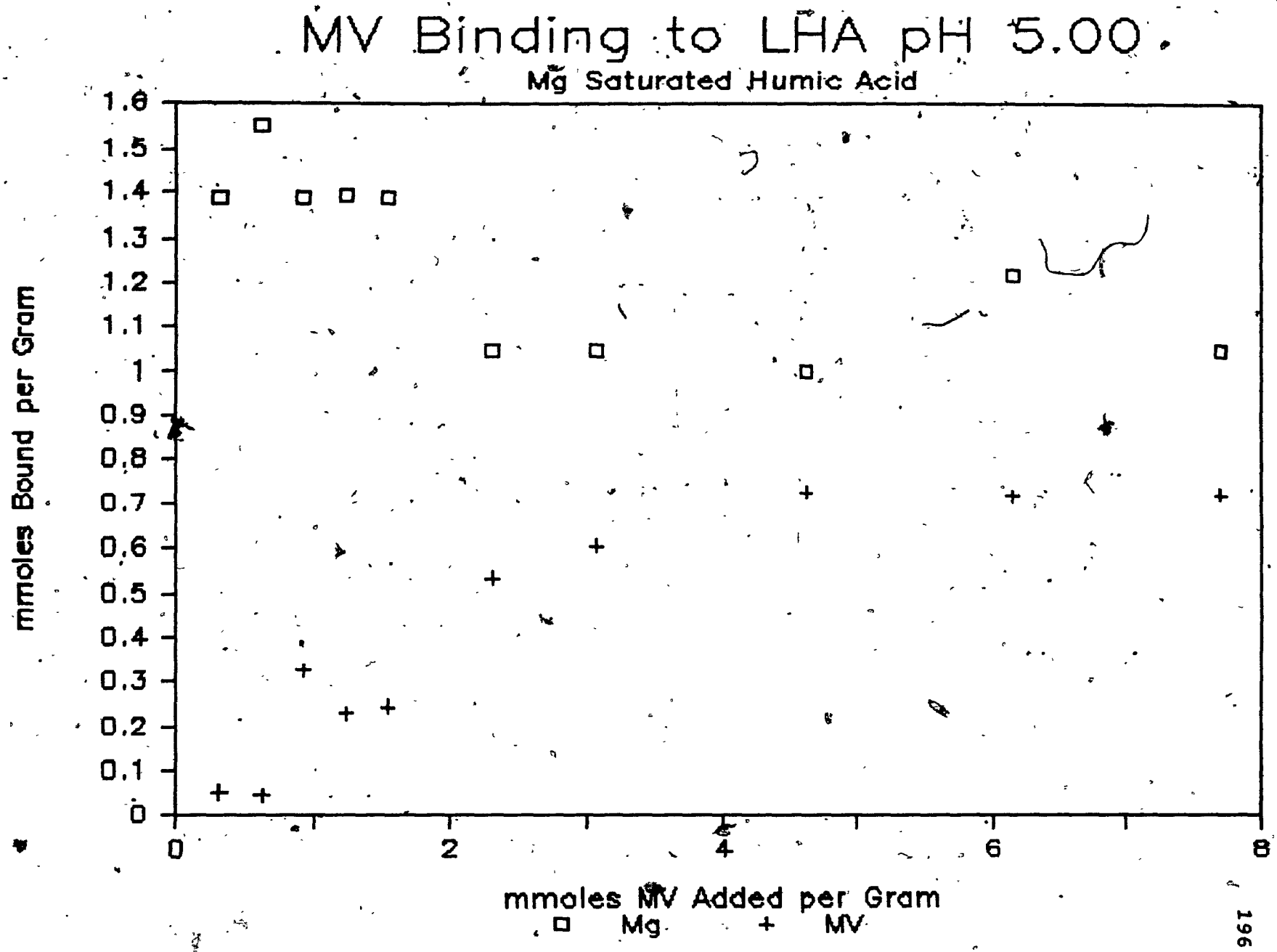

MV Binding to LHA pH 5.00
Mg Saturated Humic Acid
mmoles Bound per Gram
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
8
mmoles MV Added per Gram
Mg
MV
196

Figure 63

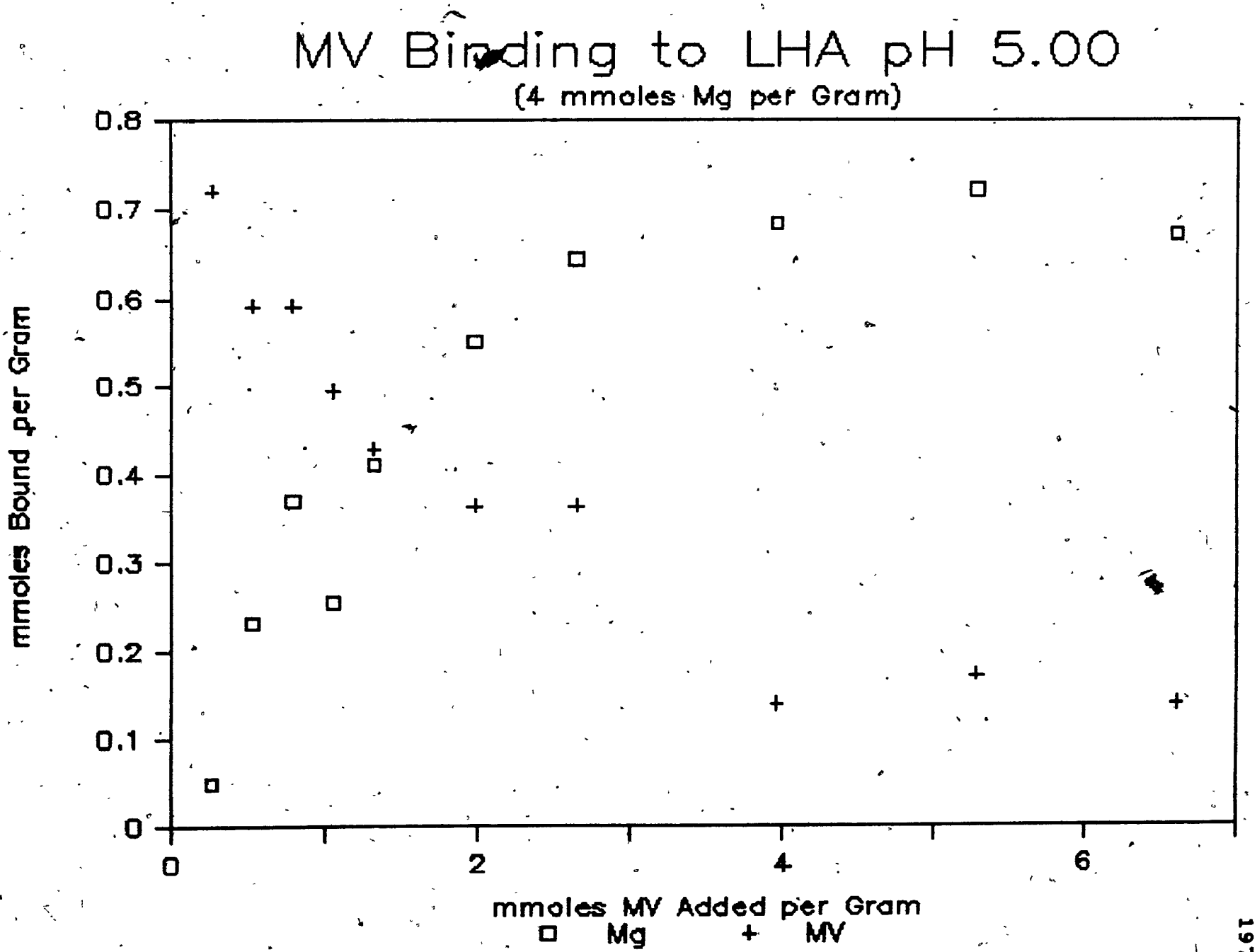

MV Binding to LHA pH 5.00
(4 mmoles Mg per Gram)
mmoles Bound per Gram
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
mmoles MV Added per Gram
Mg
MV

Figure 64

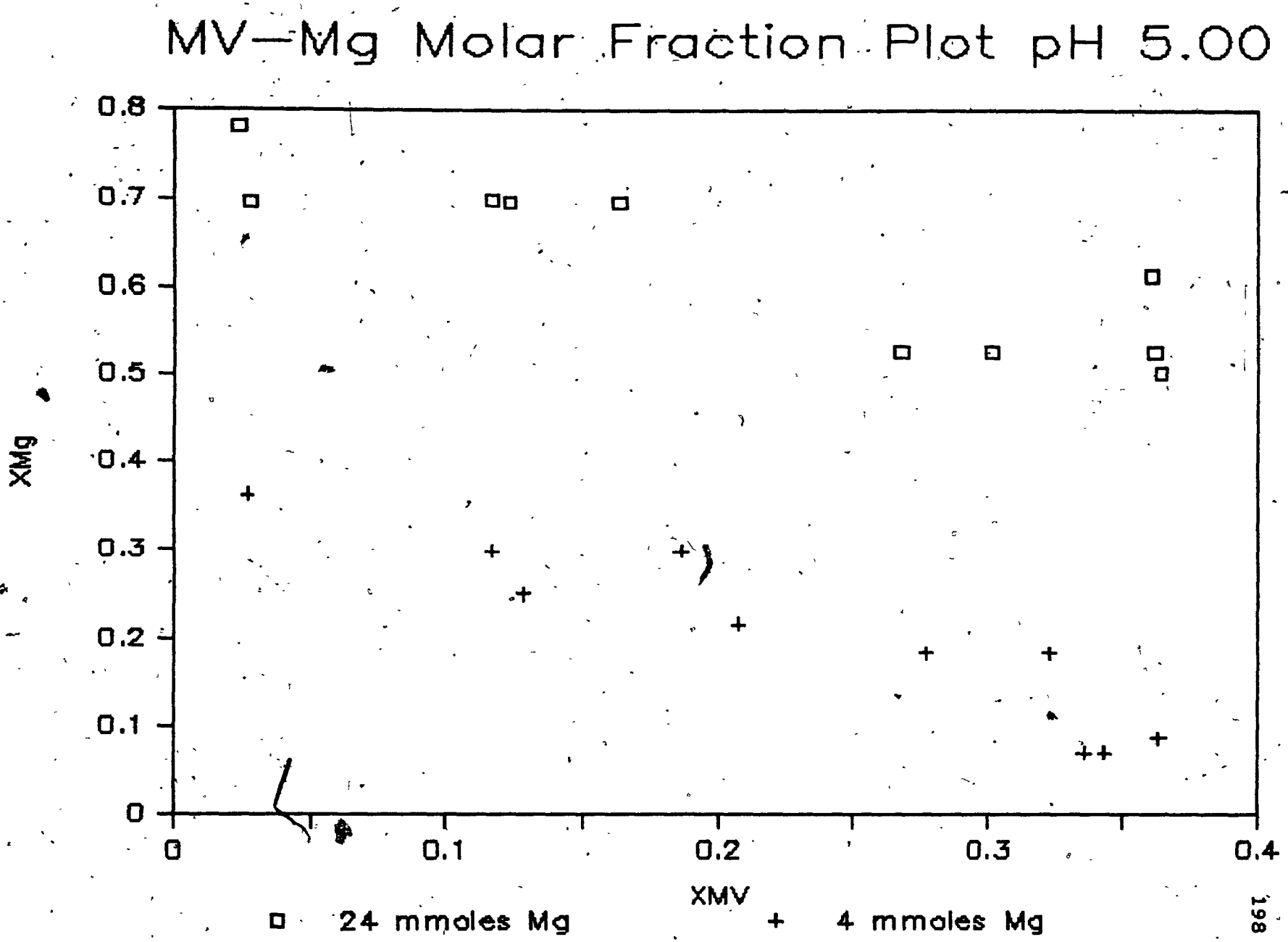

MV—Mg Molar Fraction Plot pH 5.00
XMg
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.1
0.2
0.3
0.4
XMV
24 mmoles Mg
4 mmoles Mg
198

Figure 65

hypothesis that paraquat is actually displacing magnesium ions and that interaction with other sites not occupied by magnesium is small. At both magnesium levels the mole fraction plot can be fitted to be a single function of the paraquat loading. As can be seen in Figure 65, the mole fraction of magnesium in humic acid decreases with increasing mole fraction of paraquat. This happens from the beginning of the titration. The slope of the plot indicates, again, a 1:1 stoichiometry for the paraquat-magnesium exchange.

This result is confirmed by a release plot for magnesium, the slope of which is 0.85 (Figure 66).

The exchange reaction between paraquat and magnesium saturated humic acid in the presence of low free magnesium in solution can be expressed as:

$$MgS^{+} + MV^{+2} \rightleftharpoons MVS^{+} + Mg^{+2}$$

A consequence of the 1:1 stoichiometry is that paraquat must form charged complexes in the same way as magnesium.

The slopes of the mole fraction plots ,although close to unity, were not the results of excellent linear fits. In an ideal situation, the value of X^{s} should remain constant for a 1:1 stoichiometry. This is a consequence of the fact that the

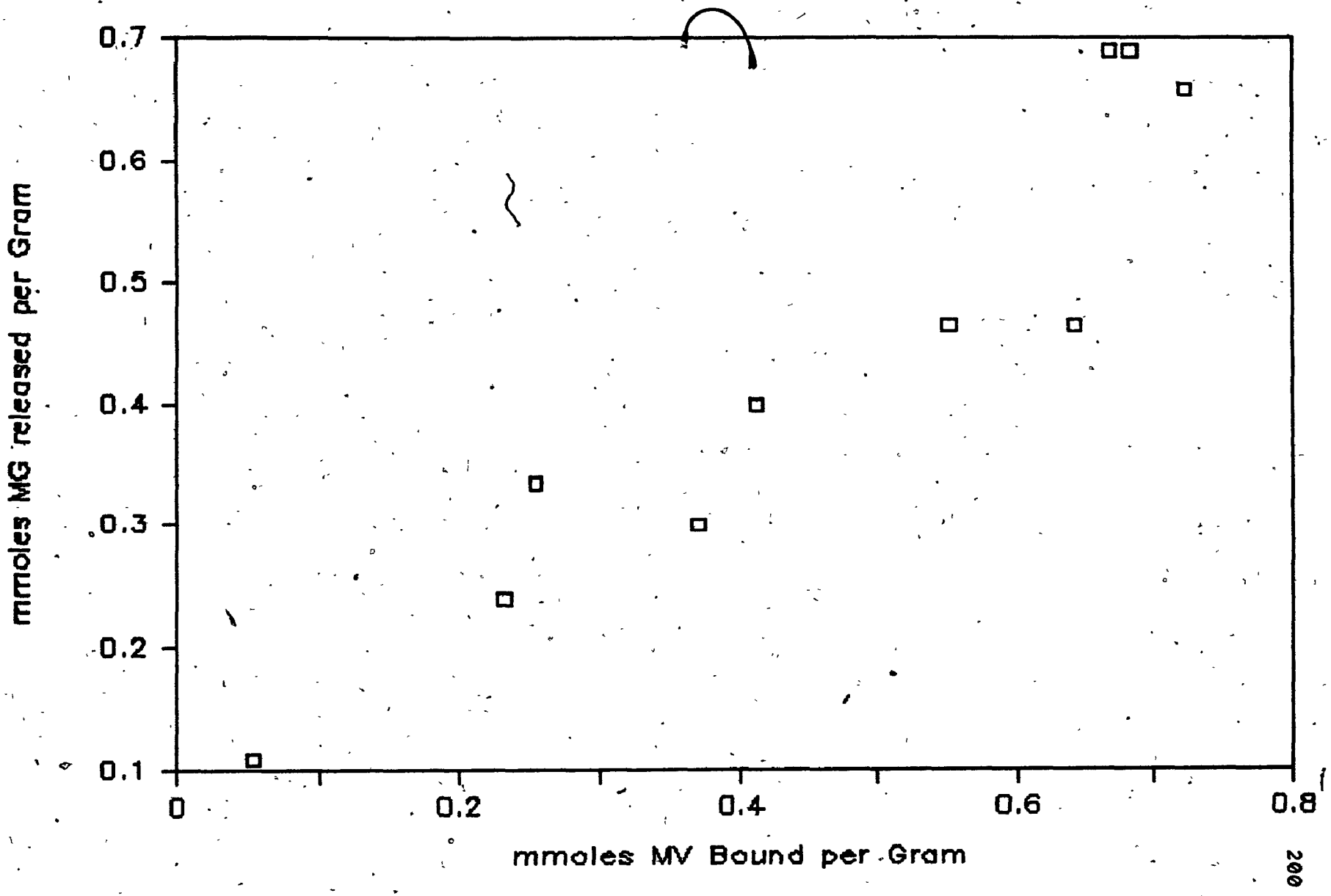

Release of Mg by MV on LHA pH 5.00
mmoles MG released per Gram
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0.2
0.4
0.6
0.8
mmoles MV Bound per Gram
200

Figure 66

exchange reaction occurs between cations already in the exchanger and the incoming ones. A good example is the case of the exchange reaction between calcium and magnesium. Variations in X^s were very small. The relative deviation was less than 2%. The X^s values for the paraquat-magnesium system varied widely as is shown in Table 26 on Page 222. This is reflected in the linear fit imposed on the mole fraction relationship. The non constancy of X^s implies that paraquat interacts with sites accessible to magnesium as well as with sites that do not interact with magnesium.

The total binding site for magnesium can be split into two fractions, one which is exchangeable by paraquat and the other which is not. Approximately 0.60 mmoles/ g of the total apparent binding capacity of magnesium is exchangeable with paraquat. This corresponds to 67 % of all the sites available to magnesium. The fraction of the magnesium sites not available to paraquat may be sites from which paraquat is excluded by size considerations.

The release of paraquat from humic acid by magnesium at pH 5.00 is minimal.

A further analysis of the binding curve for paraquat and magnesium gives information concerning the speciation of paraquat in humic acid suspension. Figure 67 shows the paraquat binding curve in the presence of magnesium. Curve A represents the total amount of paraquat bound, curve B, the amount of magnesium

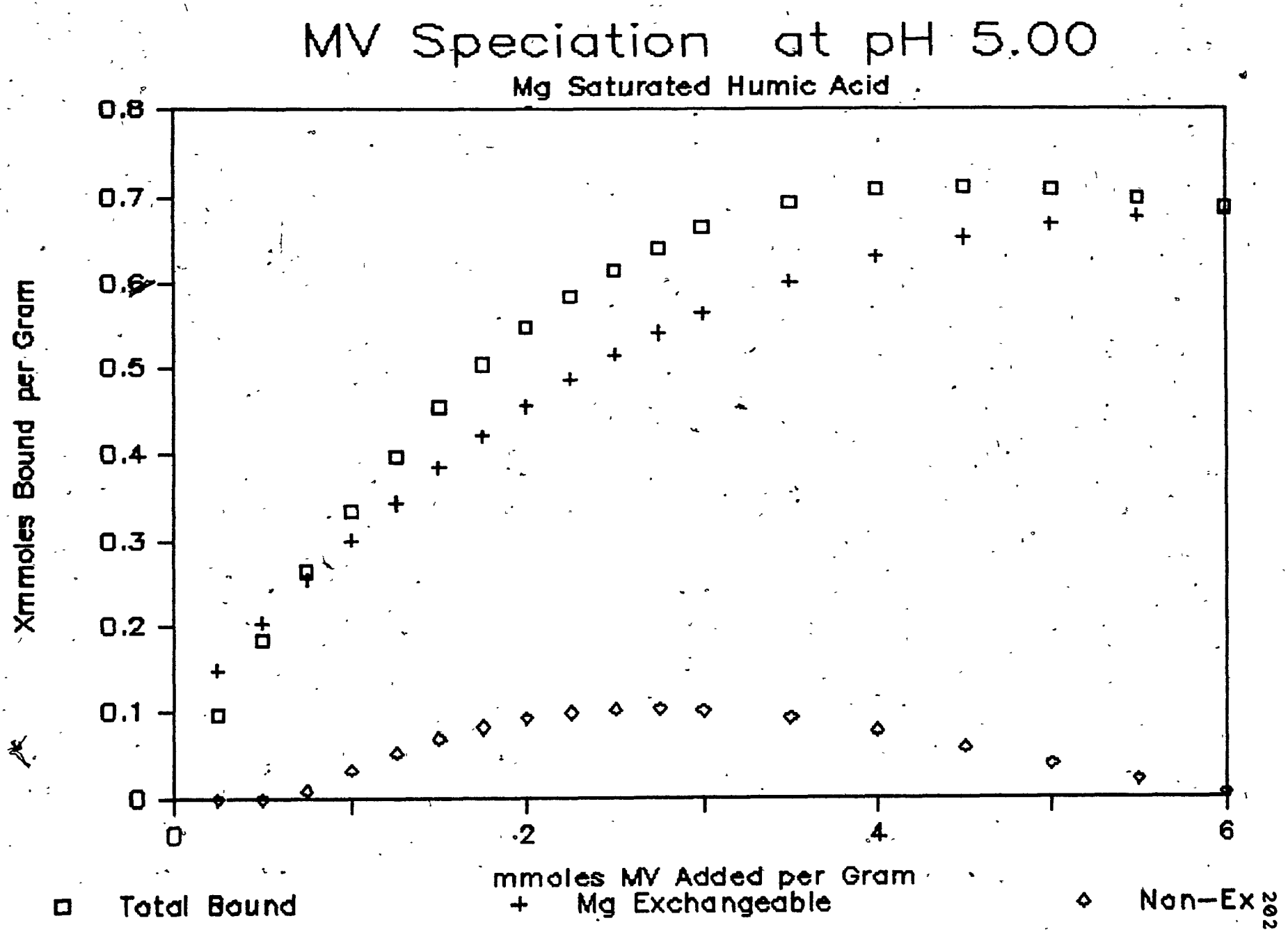

MV Speciation at pH 5.00
Mg Saturated Humic Acid
Xmmoles Bound per Gram
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
.2
.4
.6
mmoles MV Added per Gram
Total Bound
Mg Exchangeable
Non-Ex

Figure 67

released (magnesium-exchangeable fraction of paraquat bound) and C the difference between A and B. This difference can be assigned to a non-exchangeable fraction of the total paraquat bound. It appears to increase to a peak value of approximately 0.1 millimoles per gram. This value is quite close to the fraction of non-exchangeable paraquat bound in the copper-paraquat system at pH 3.00.

5.1.12. Copper - Paraquat -Humic acid system at pH 5.00.

Figure 68 shows the binding curve for copper at pH 5 in the presence of a constant amount of paraquat. Prior to the addition of paraquat, the physical appearance of the samples indicated the presence of two physical phases. As in the copper humic acid experiments, addition of copper produced coagulation and precipitation of humic acid. The amount of paraquat initially bound to humic acid decreased as copper was bound, to an approximately constant value of 0.2 millimoles per gram. A plot of the release of paraquat by copper suggests that the copper displaces paraquat in a one to one ratio (Figure 68a). A mole fraction plot of X_{MV} against X_{Cu} gives an almost linear relationship (Figure 69). The mole fraction of sites occupied by paraquat was calculated based on a total of 1.02 millimoles of carboxyl groups ionized. The same total number of sites was assumed for the copper mole fraction calculation.

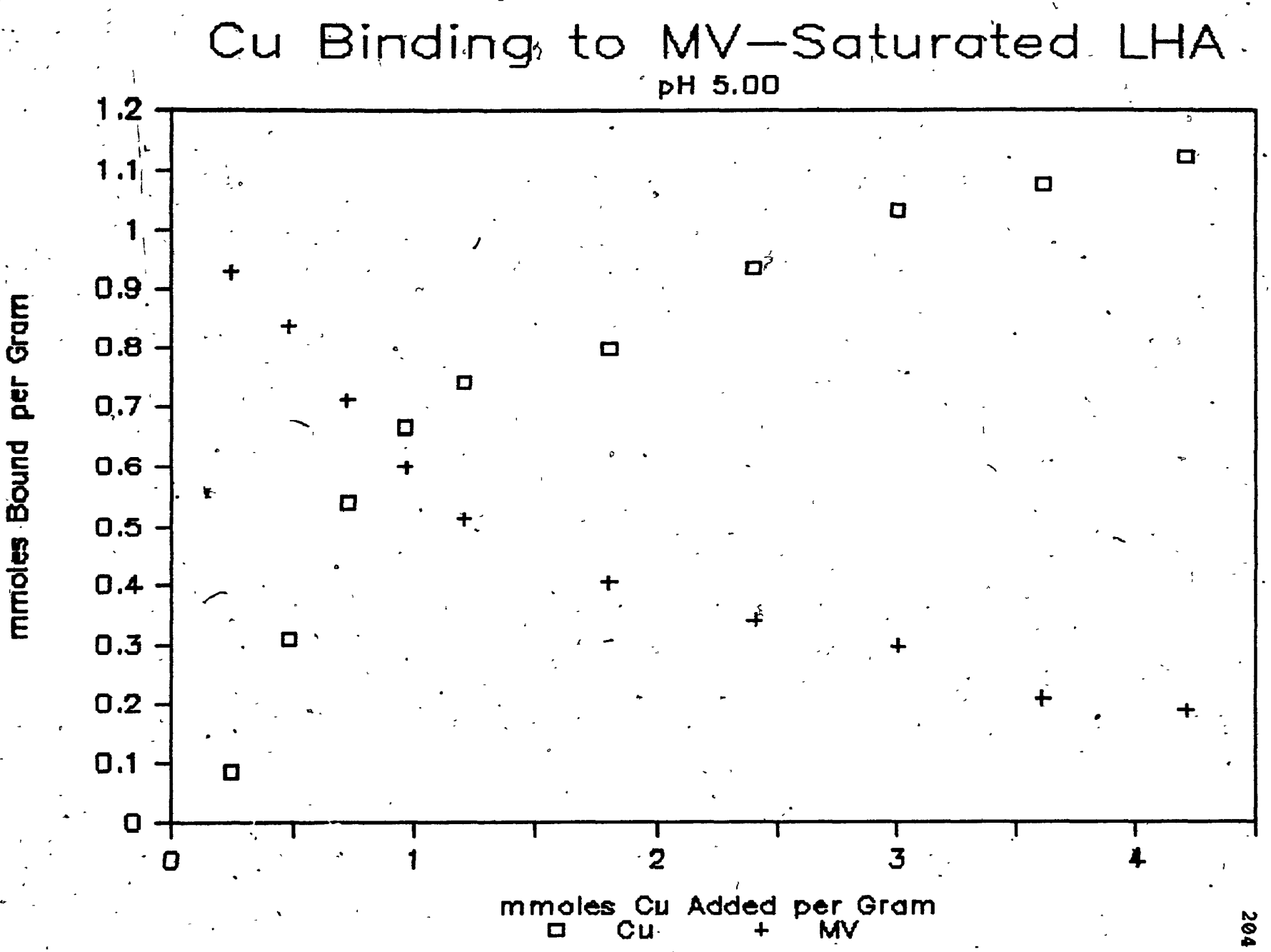

Cu Binding to MV—Saturated LHA
pH 5.00
mmoles Bound per Gram
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
mmoles Cu Added per Gram
Cu
MV

Figure 68

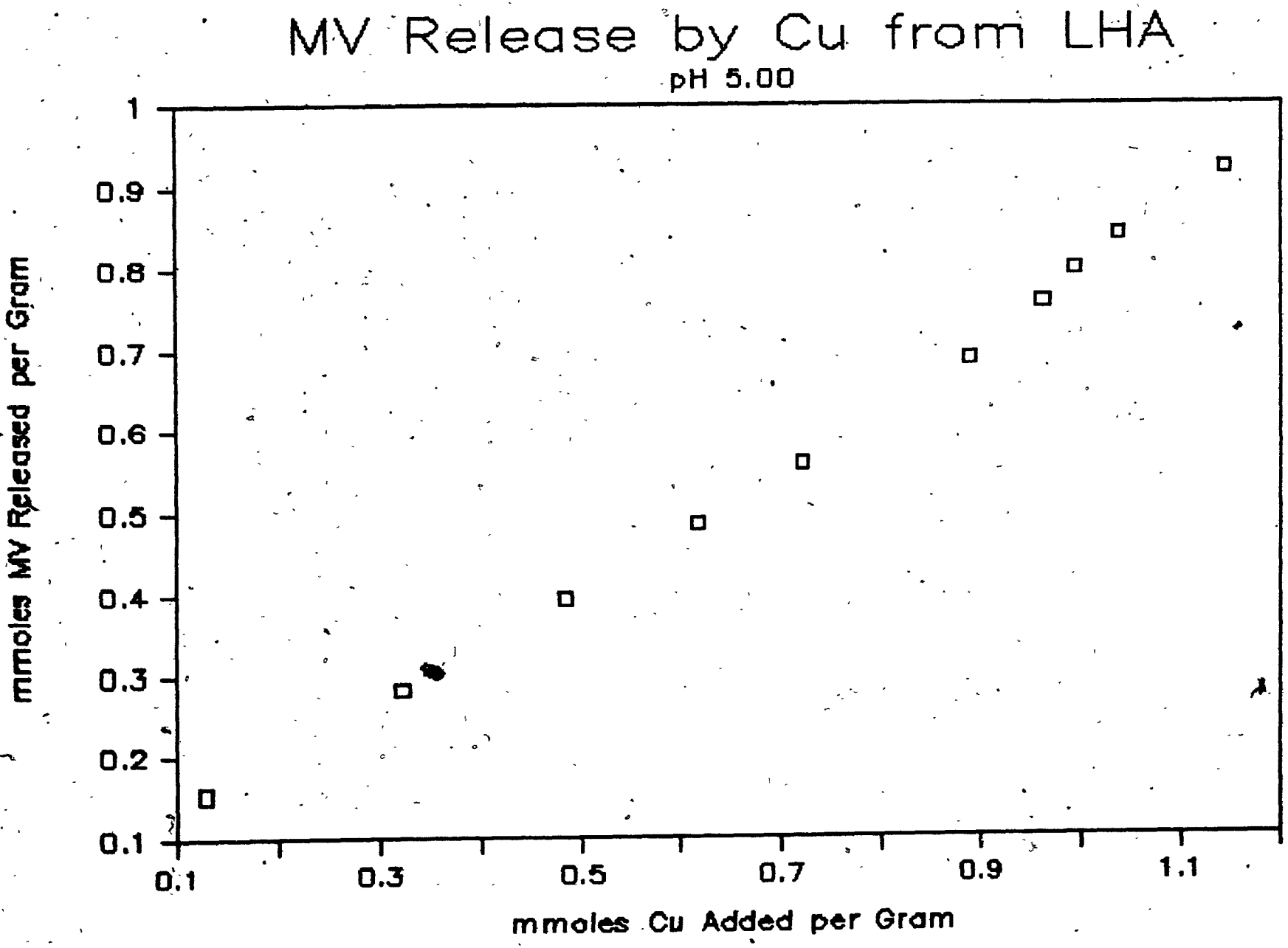

MV Release by Cu from LHA
pH 5.00
mmoles MV Released per Gram
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.1
0.3
0.5
0.7
0.9
1.1
mmoles Cu Added per Gram

Figure 68a

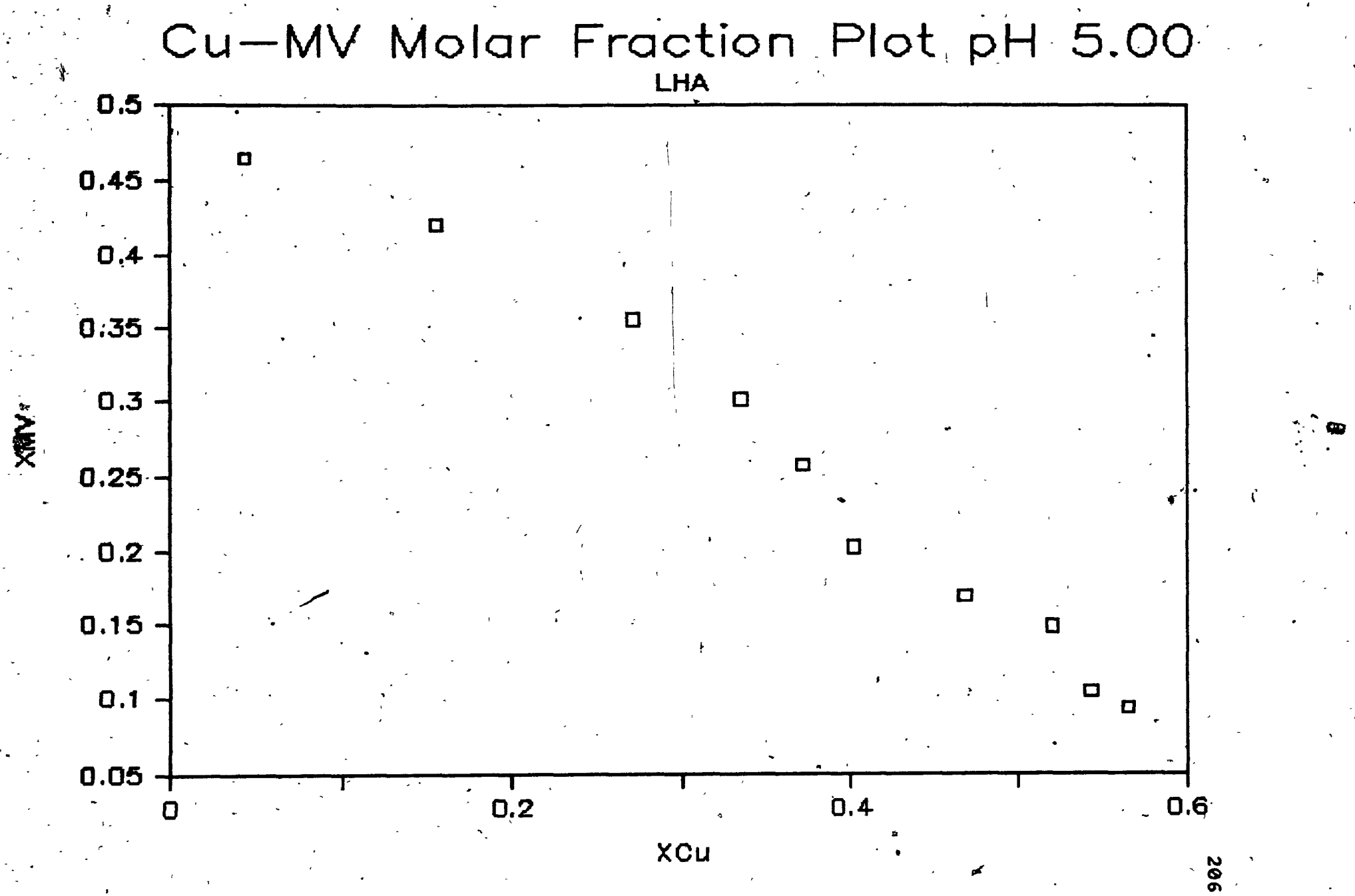

Cu—MV Molar Fraction Plot pH 5.00
LHA
0.5
0.45
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
XMV
0
0.2
0.4
0.6
XCu

Figure 69

If the structure of humic acid is such that the concentration of dicarboxyl sites is small, most of the copper will bind to salicylic sites. This does not seem to be the case in the sample studied. Addition of copper to humic acid suspensions at pH 5.00 produced an almost instantaneous aggregation of humic acid molecules, which suggests a large concentration of dicarboxyl sites with carboxyl groups located in different humic acid molecules.

The expected binding capacity for a divalent cation interacting only with already ionized carboxyl groups only should be about 0.51 millimole per gram at pH 5.00. Experimental estimates of the binding capacity for copper at pH 5 are much higher than this value. They range between 1.3 and 1.4 millimoles of copper per gram of humic acid. These values coincide with half the total amount of carboxyl group per gram of humic acid.

Comparison of the release of magnesium by copper with that of paraquat by copper shows that the removal of magnesium is complete, indicating a total competition for binding sites between copper and magnesium (Figure 70). This is corroborated by the reverse experiment as shown in Figure 71. The sites covered by copper include those with which magnesium interacts, which in turn are the same as those with which paraquat interacts.

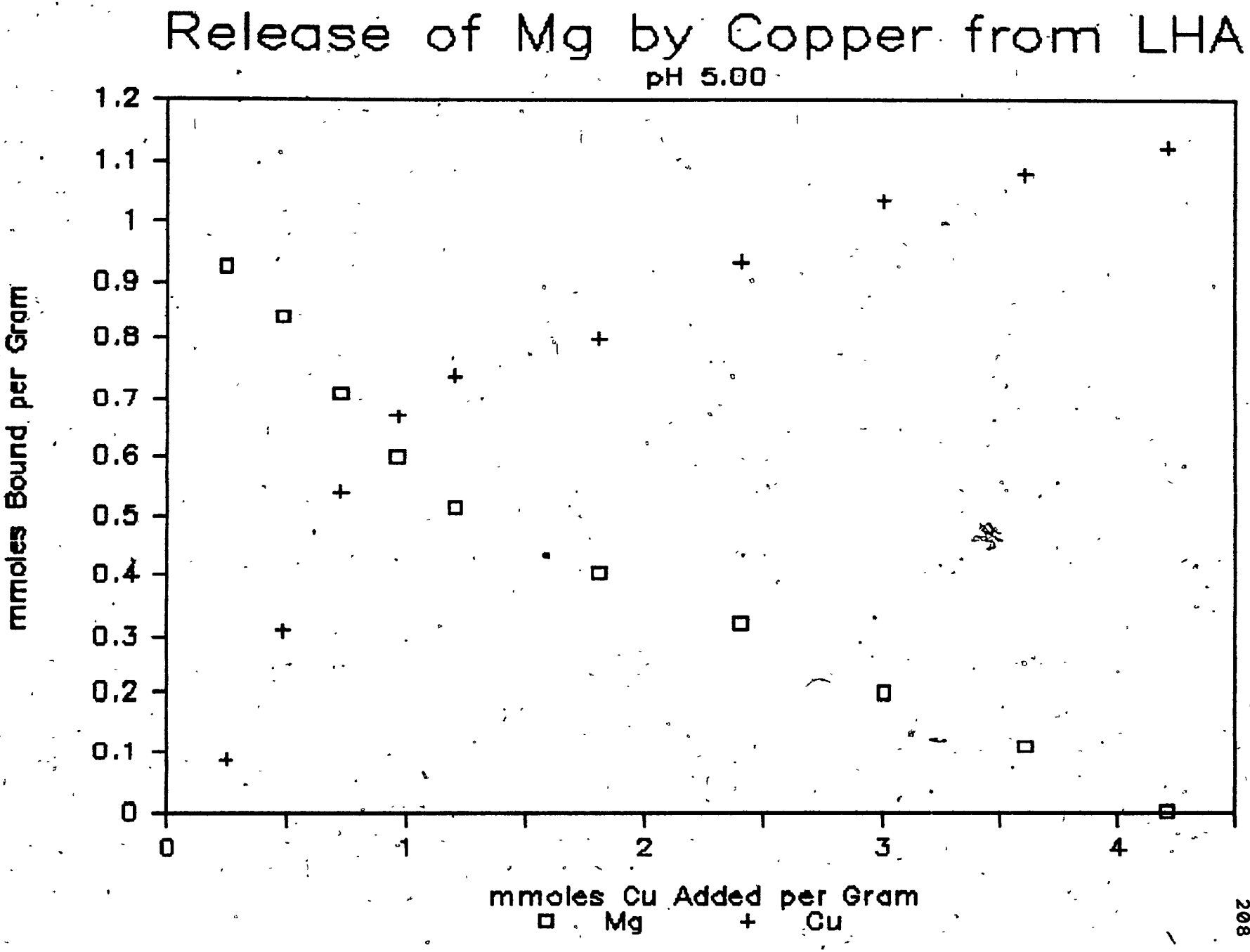

Release of Mg by Copper from LHA
pH 5.00
mmoles Bound per Gram
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
1
2
3
4
mmoles Cu Added per Gram
Mg
Cu

Figure 70

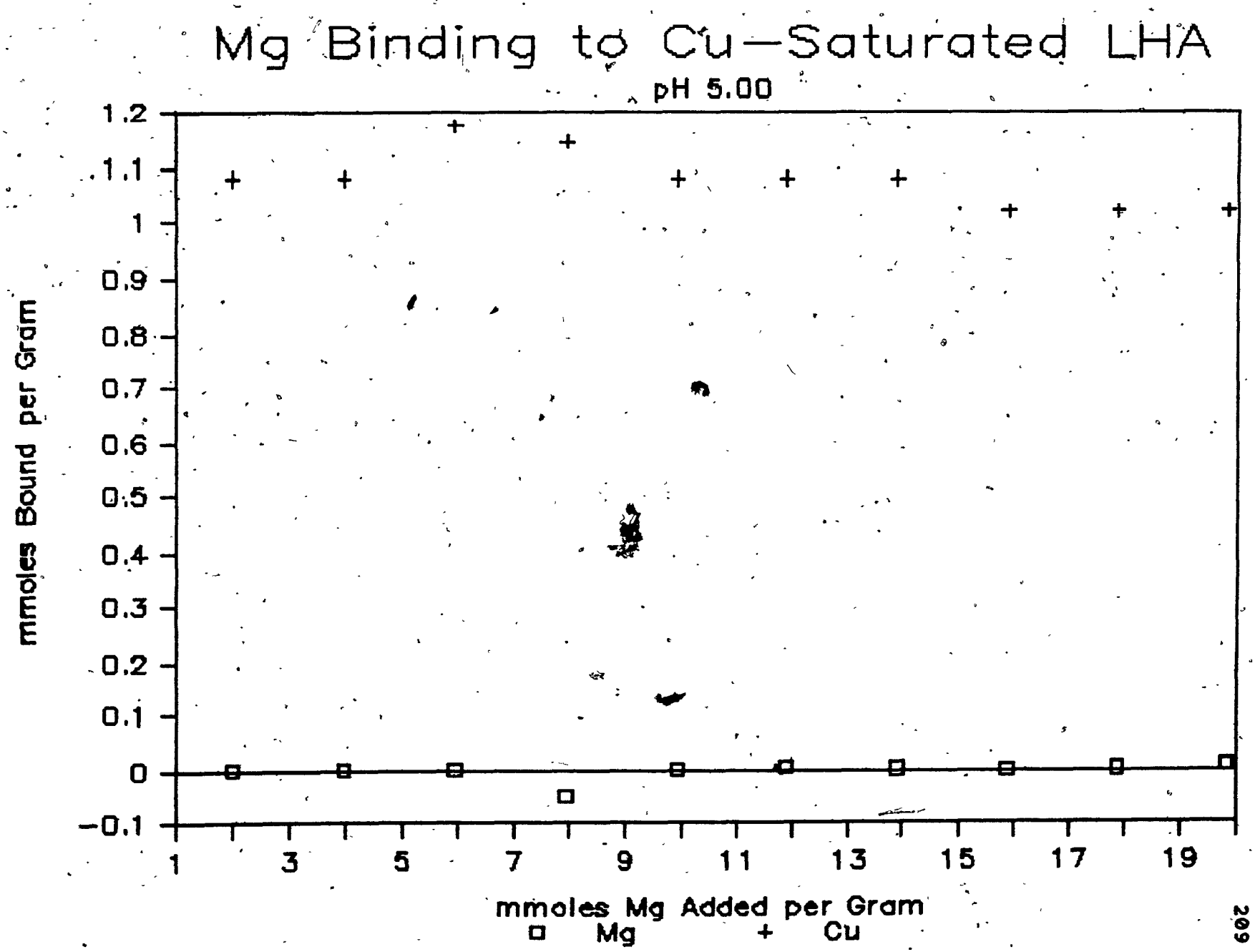

Mg Binding to Cu—Saturated LHA
pH 5.00
mmoles Bound per Gram
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
1
3
5
7
9
11
13
15
17
19
mmoles Mg Added per Gram
Mg
Cu
209

Figure 71

The picture emerging from the above results is that copper is able to remove most but not all of the paraquat initially bound to humic acid. There is still an amount bound to humic acid which cannot be displaced by copper. The binding of copper may be taking place via both salicylic and dicarbolxylic sites, although based on the experimental results, the formation of dicarboxylic complexes between copper and carboxyl groups in different humic acid molecules seems to predominate. The formation of salicylic and dicarboxylic complexes must be accompanied by the release of protons from the hydroxyl part of the sites and from the remaining protonated carboxyl groups leading to a decrease in pH. In experiments with copper at an initial pH of 5 the pH at equilibrium was about 1 pH unit lower, but correlation with copper bound was not attempted because of large scatter of experimental data. A detailed study of this situation is needed, using greater humic acid concentrations in order to detect changes in pH with more confidence.

The reverse experiment, in which humic acid saturated with copper is titrated with paraquat, is shown in Figures 72 and 73. The most noticeable feature is that little copper is released from humic acid by paraquat. This situation is similar to the one at pH 3.00. Paraquat cannot displace copper once it is bound to humic acid. If copper is blocking the carboxyl groups available to paraquat, as suggested before, there should be a total reduction of paraquat binding this was not the case.

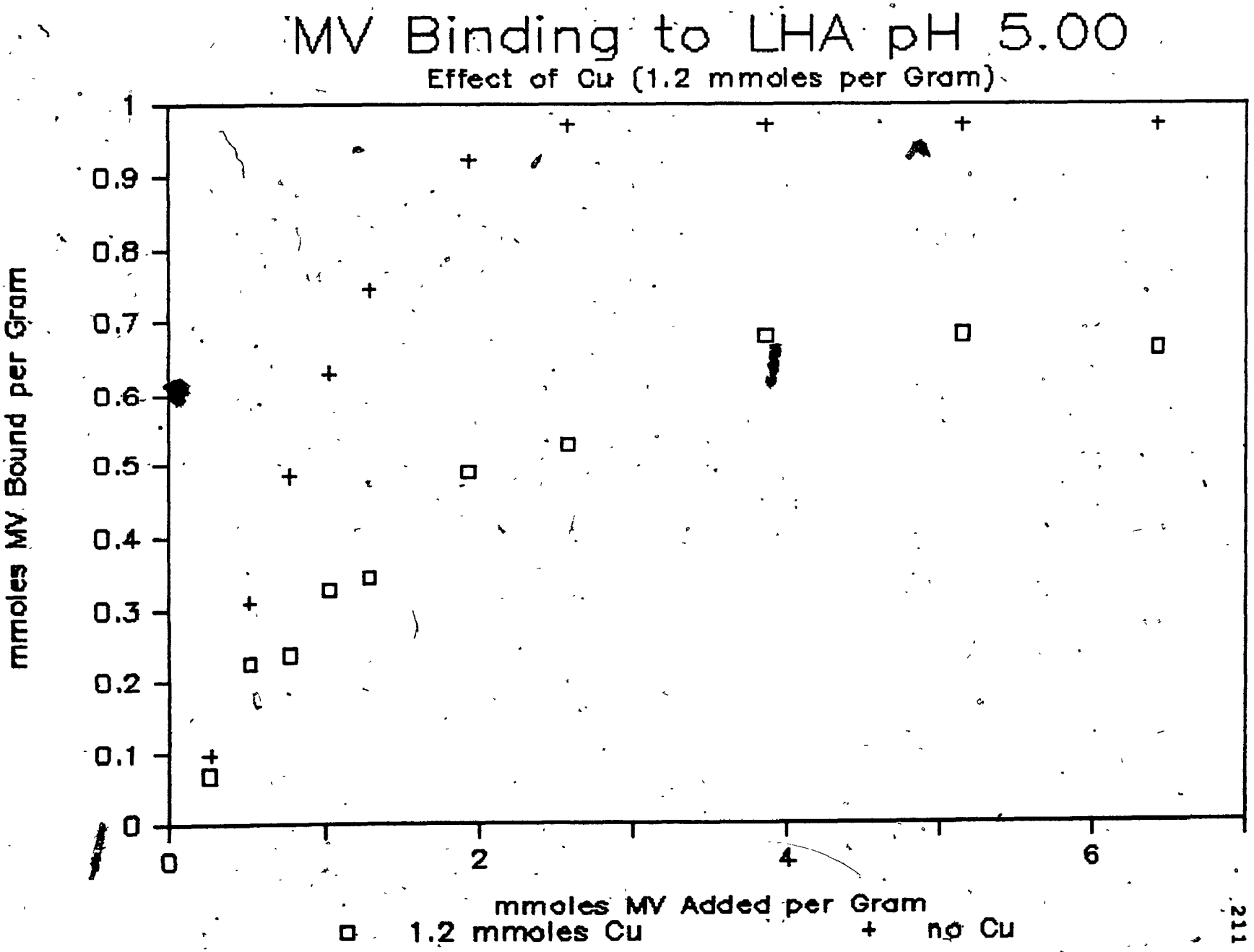

MV Binding to LHA pH 5.00
Effect of Cu (1.2 mmoles per Gram)
mmoles MV Bound per Gram
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
mmoles MV Added per Gram
1.2 mmoles Cu
no Cu
211

Figure 72

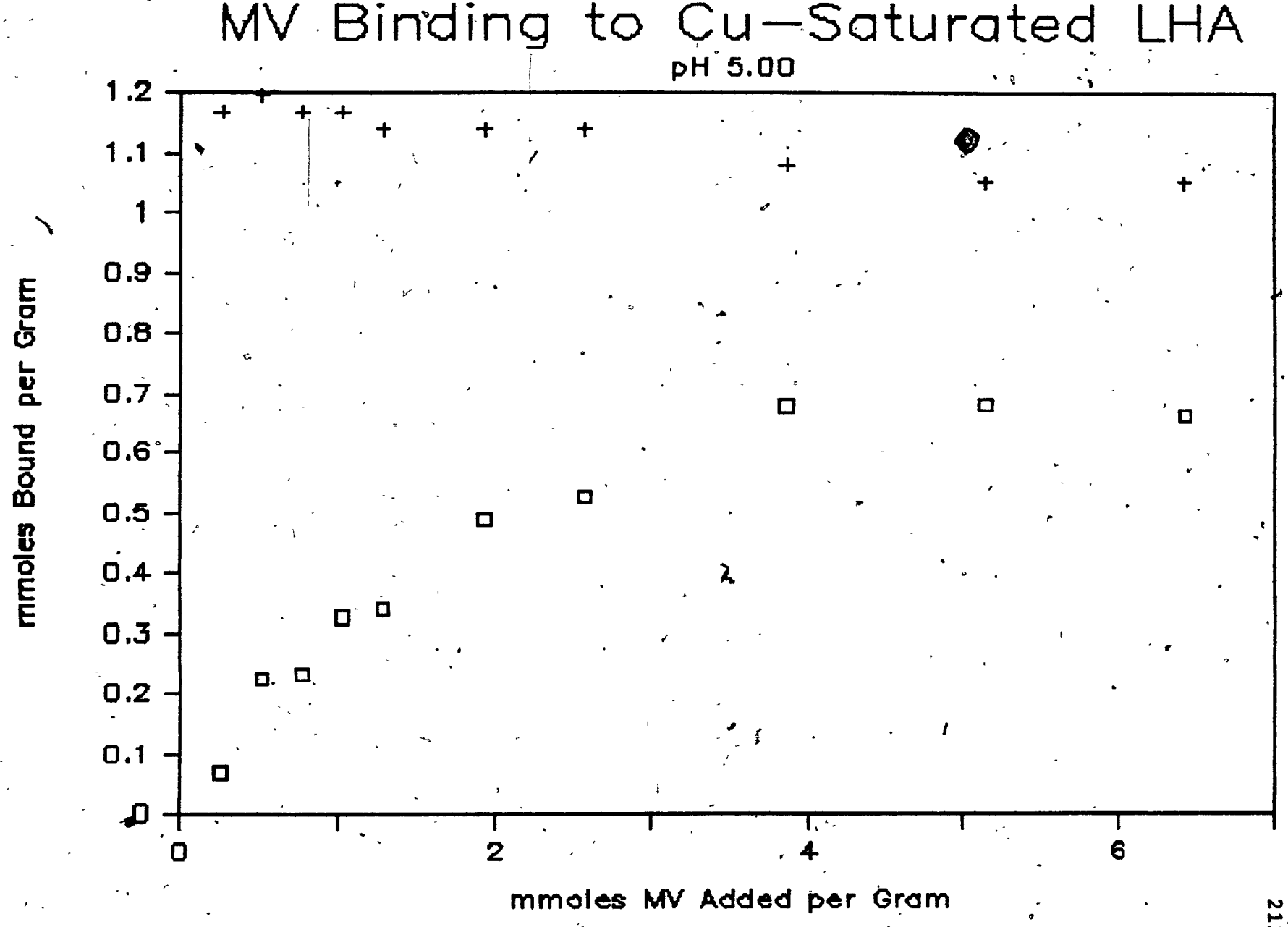

MV Binding to Cu—Saturated LHA
pH 5.00
mmoles Bound per Gram
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
2
4
6
mmoles MV Added per Gram

Figure 73

What is implied here is that paraquat may be binding to sites which are not involved in ion exchange reactions. This behaviour must be compared to the case of copper saturated humic acid titrated with magnesium as shown in Figure 71. The binding of magnesium is zero in the presence of copper; ie., copper effectively blocks the carboxyl group sites to which magnesium binds.

The reduction in the apparent binding capacity of paraquat in the presence of copper is about 0.45 millimoles per gram which is quite similar to the reduction in the presence of magnesium ions. The main difference is that copper is not displaced. This result is not an experimental artifact. At the paraquat saturation level, 0.7 mmoles of copper per gram would have been released if paraquat had displaced copper, and this would have been detected by the atomic absorption technique used for the analysis of copper. In fact none was detected.

Two main conclusions can be drawn from the present results. First, the exchange reaction between copper and paraquat on humic acid is not reversible within the concentration ranges considered in the sense that removal of copper by paraquat does not take place to the same extent as the removal of paraquat by copper. Second, the binding of paraquat is not affected by copper as much as might be expected based on the blocking of ion exchange sites by copper ions. Therefore, the reduction in the binding capacity

of paraquat in the presence of copper as in the case of magnesium cannot be attributed totally to direct site blocking the metal ions since the amount of metal ion bound does not correspond to the decrease in the apparent binding capacity.

At constant paraquat concentration and increasing copper added to humic acid, the reduction in the binding of copper corresponds to site blocking by paraquat, although it could also be the result of conformational changes. Similar effects result with calcium and magnesium. The apparent binding capacity of calcium in the presence of magnesium is below its value in the absence of magnesium. This cannot however be attributed to cation site blocking since no magnesium remains in the humic acid exchanger.

5.1.12.1. Equilibrium functions.

The information obtained in the experiments discussed above allows formulation of the equilibria taking place between each metal ion and humic acid at pH 5.00.

Equilibrium functions as defined by Equation 47 were calculated for the various experiments.

Differential equilibrium functions are shown in Figure 74. The important feature in this Figure is that, while the differential functions for calcium and magnesium show little variation with site loading, the differential function for paraquat increases greatly with increase in free sites.

In the experiments involving two cations simultaneously, the equilibrium functions take a different meaning. For example, in the case of magnesium-saturated humic acid titrated with calcium, one is looking at an ion exchange reaction between magnesium and calcium.

Figure 75 shows the average equilibrium functions for magnesium and paraquat for magnesium-saturated humic acid titrated with paraquat at pH 5. The calculations were done assuming a total of 2 mmoles/g of potential sites. This includes most of the carboxyl groups already deprotonated. The equilibrium functions are almost constant, the small decrease with increased site loading perhaps being due to electrostatic effects. This result permits better identification of the ion exchange path followed. As was shown earlier, paraquat effectively replaces magnesium in a 1:1 ratio and both cations compete for the same sites. Therefore, the equilibrium can be defined in terms of a Mg-LHA exchanger. The selectivity function as defined by Helfferich (67) is plotted in Figure 76. It can be seen that it is almost constant and shows a slight preference for paraquat throughout.

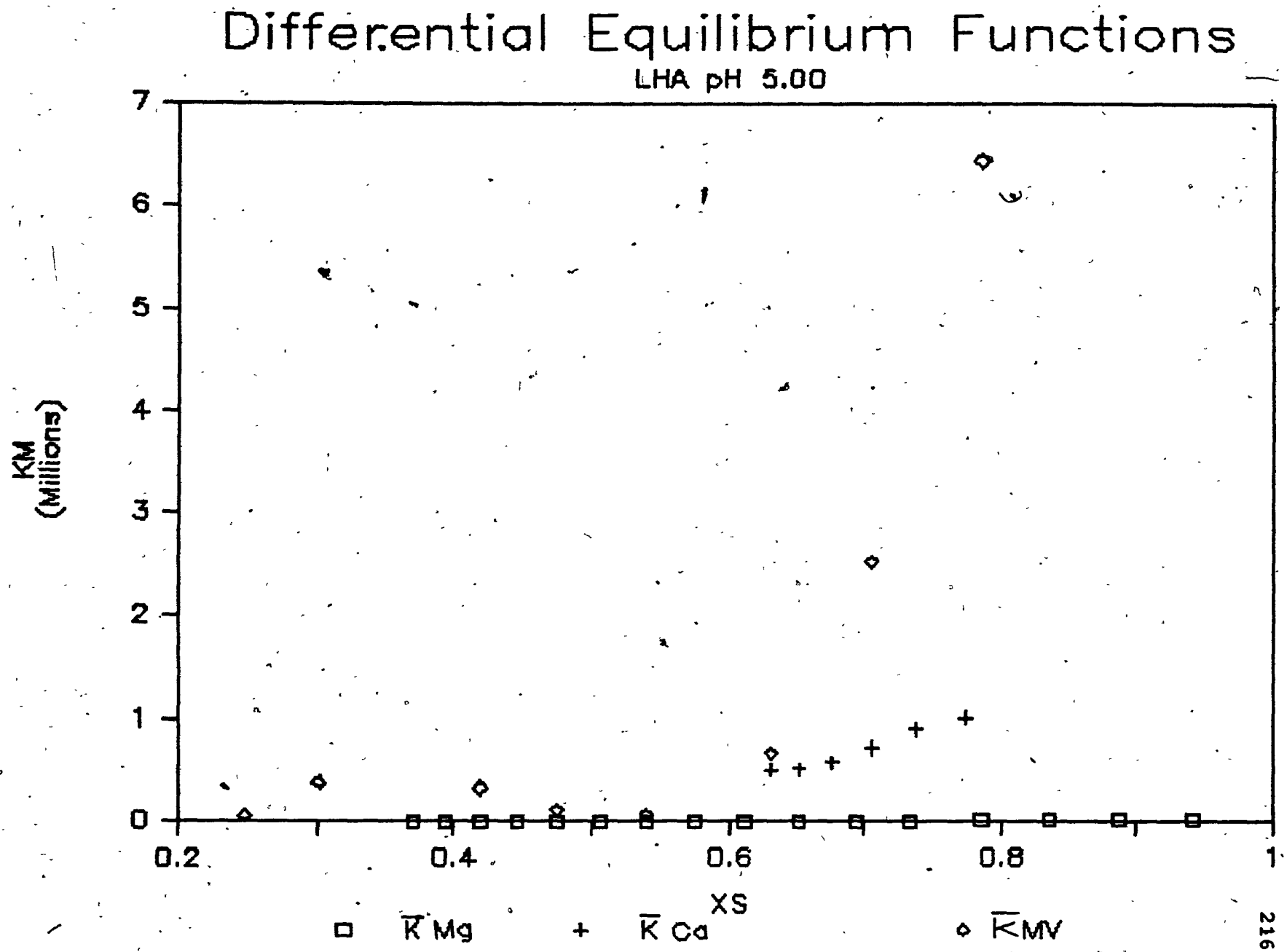

Differential Equilibrium Functions
LHA pH 5.00
KM (Millions)
7
6
5
4
3
2
1
0
0.2
0.4
0.6
0.8
1
XS
K Mg
K Ca
KMV

Figure 74

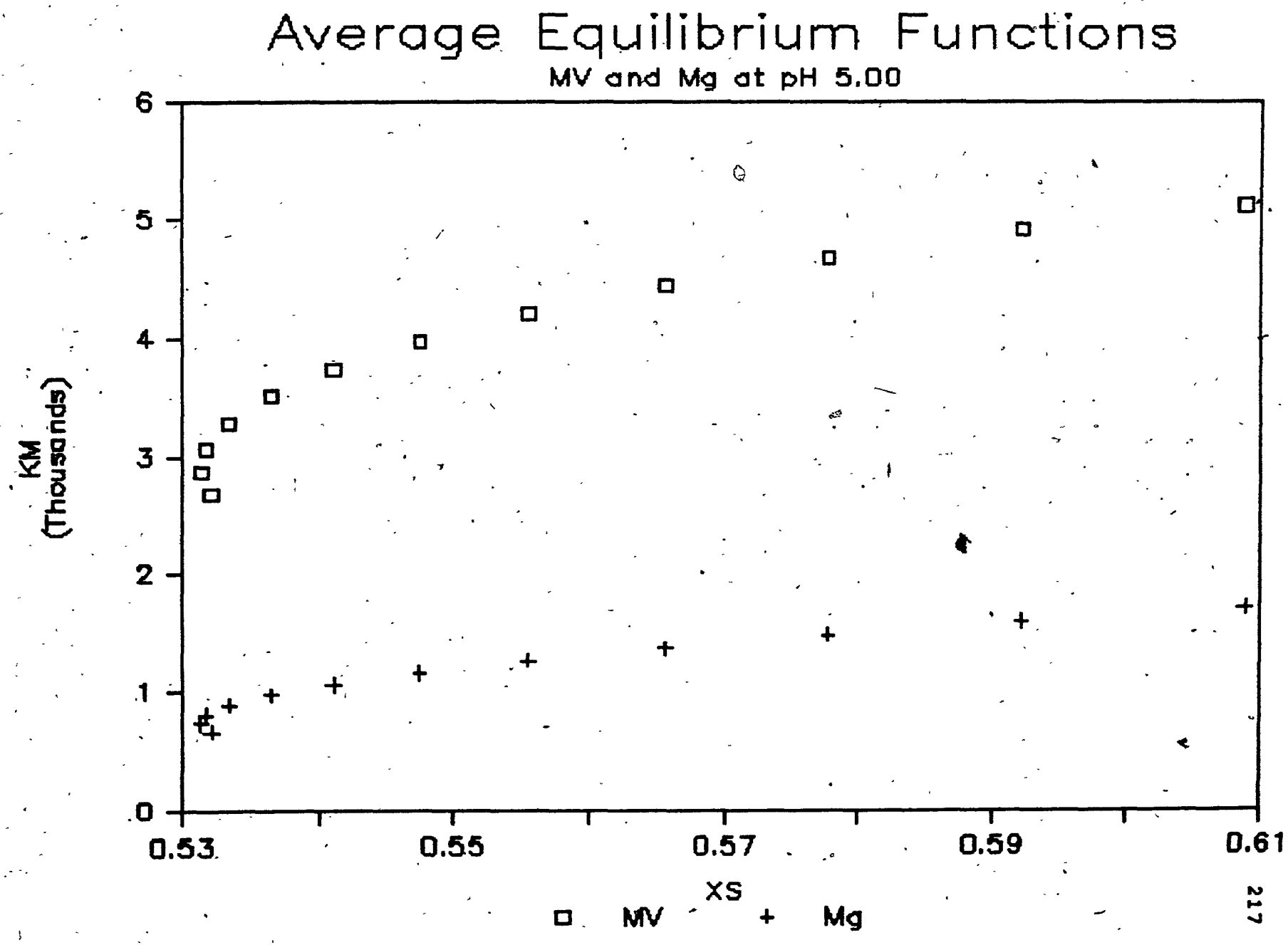

Average Equilibrium Functions
MV and Mg at pH 5.00
KM
(Thousands)
6
5
4
3
2
1
0
0.53
0.55
0.57
0.59
0.61
XS
MV
Mg

Figure 75

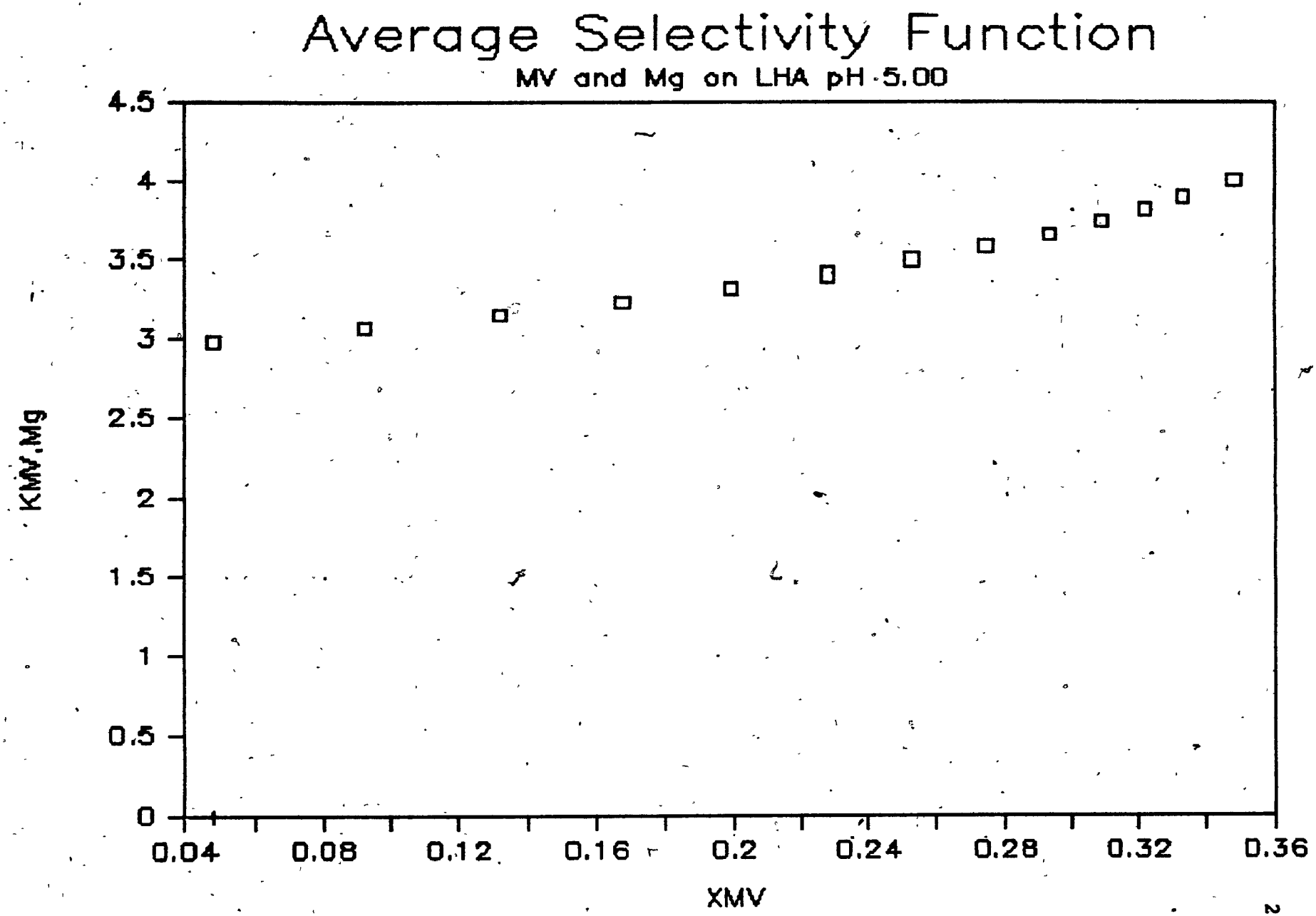

Average Selectivity Function
MV and Mg on LHA pH 5.00
KMV,Mg
4.5
4
3.5
3
2.5
2
1.5
1
0.5
0
0.04
0.08
0.12
0.16
0.2
0.24
0.28
0.32
0.36
XMV

Figure 76

Using arguments similar to those above, the selectivity function for the case of magnesium-saturated humic acid titrated with calcium was plotted in Figure 61. There is a dramatic change in the preference for calcium compared to magnesium.

5.1.13. The calcium-magnesium-paraquat system at pH 5.

Experiments in which humic acid at pH 5 was titrated simultaneously with calcium, magnesium and paraquat were carried out. The total level of cations was kept well below saturation levels. The calcium level was such that little precipitation was visible. Results for some of these experiments are shown in Figures 77,78 and 79, for calcium, magnesium and paraquat respectively. The calculated average equilibrium functions for paraquat, calcium and magnesium are shown in Figure 80. It can be seen that there is little change with respect to the single cation experiments.

Calculated values for the average differential equilibrium functions and mole fractions are shown in Tables 26 and 27 on Pages 224 and 225.

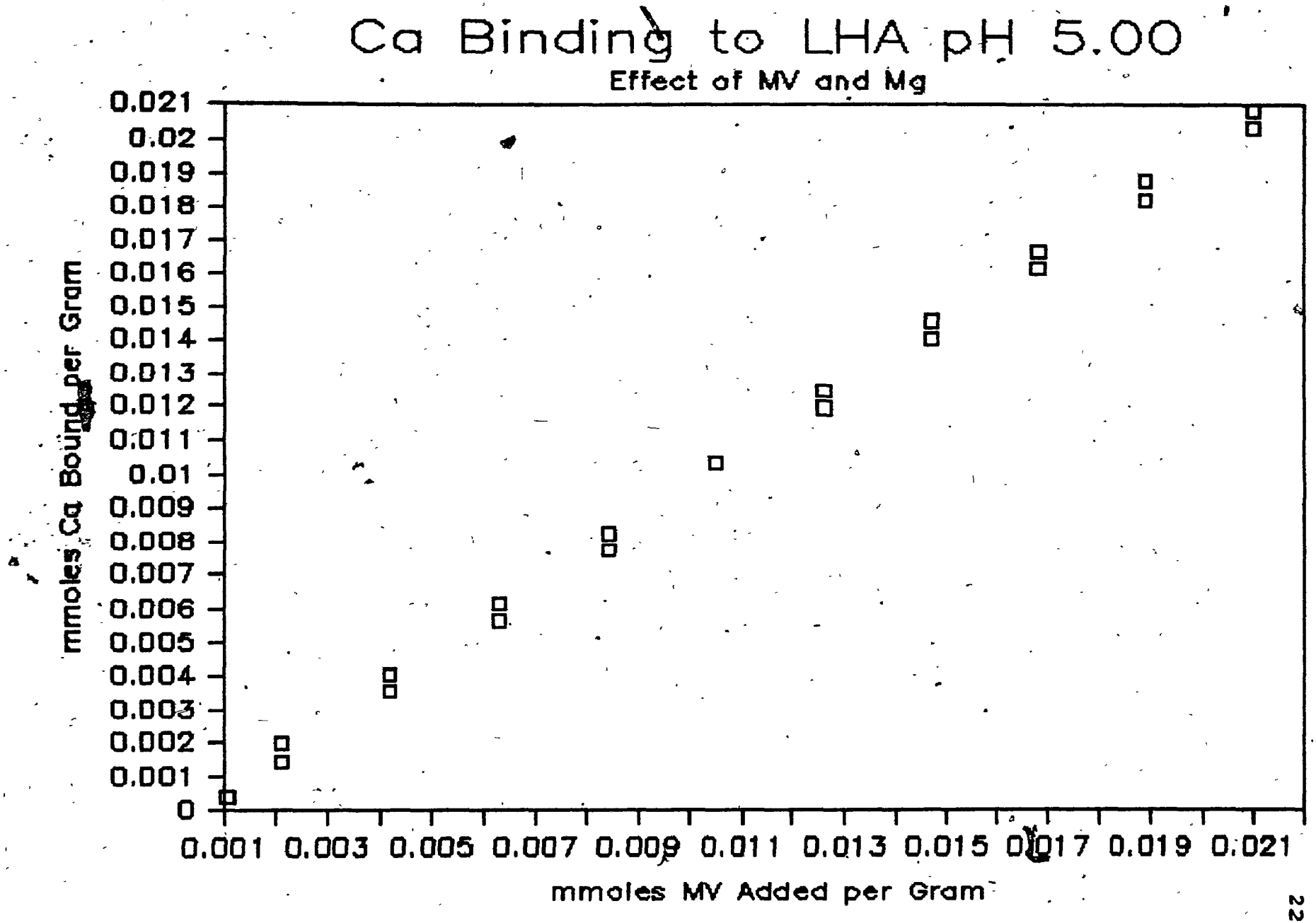

Ca Binding to LHA pH 5.00
Effect of MV and Mg
mmoles Ca Bound per Gram
0.021
0.02
0.019
0.018
0.017
0.016
0.015
0.014
0.013
0.012
0.011
0.01
0.009
0.008
0.007
0.006
0.005
0.004
0.003
0.002
0.001
0
0.001 0.003 0.005 0.007 0.009 0.011 0.013 0.015 0.017 0.019 0.021
mmoles MV Added per Gram

Figure 77

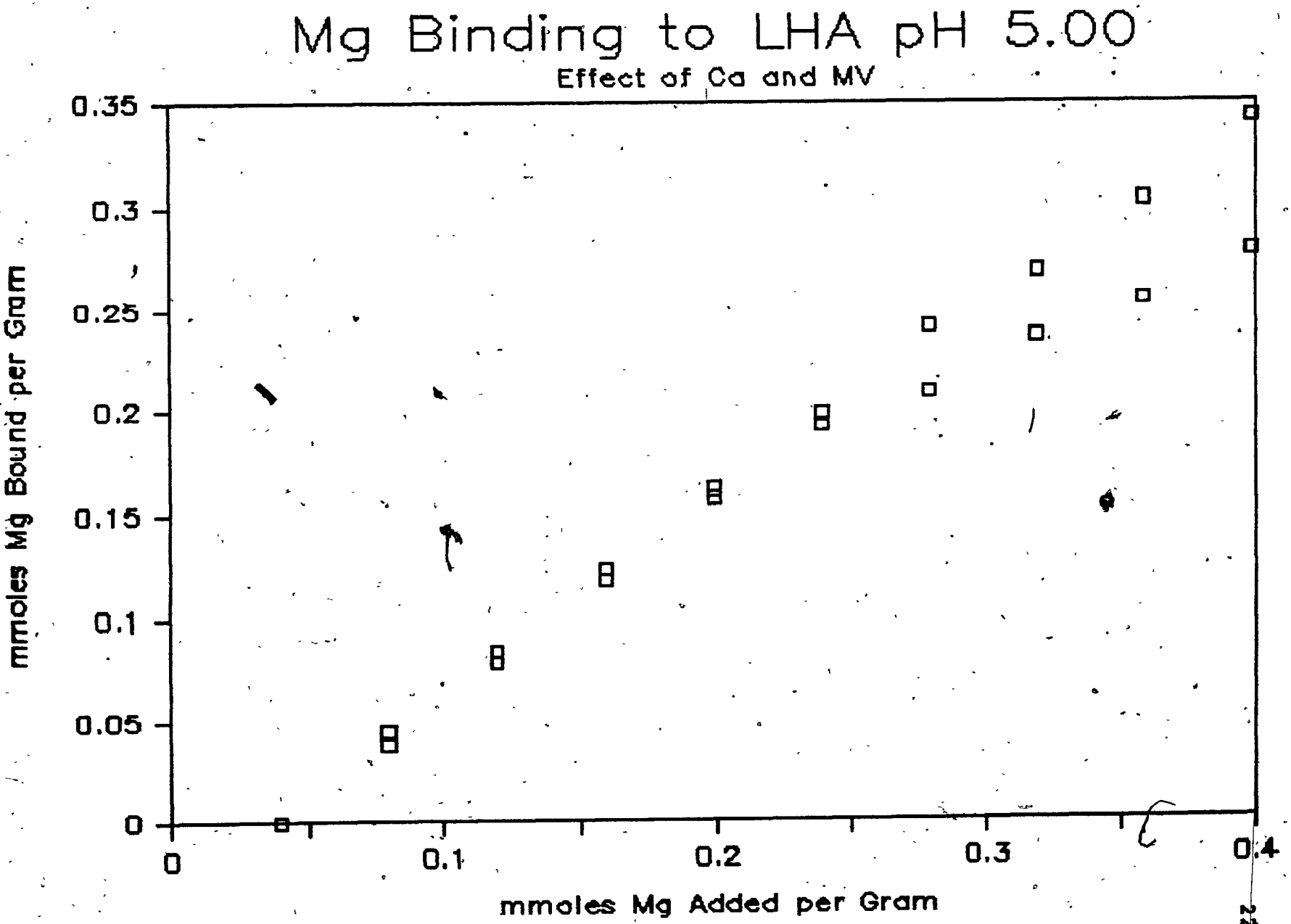

Mg Binding to LHA pH 5.00
Effect of Ca and MV
mmoles Mg Bound per Gram
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
0.1
0.2
0.3
0.4
mmoles Mg Added per Gram

Figure 78

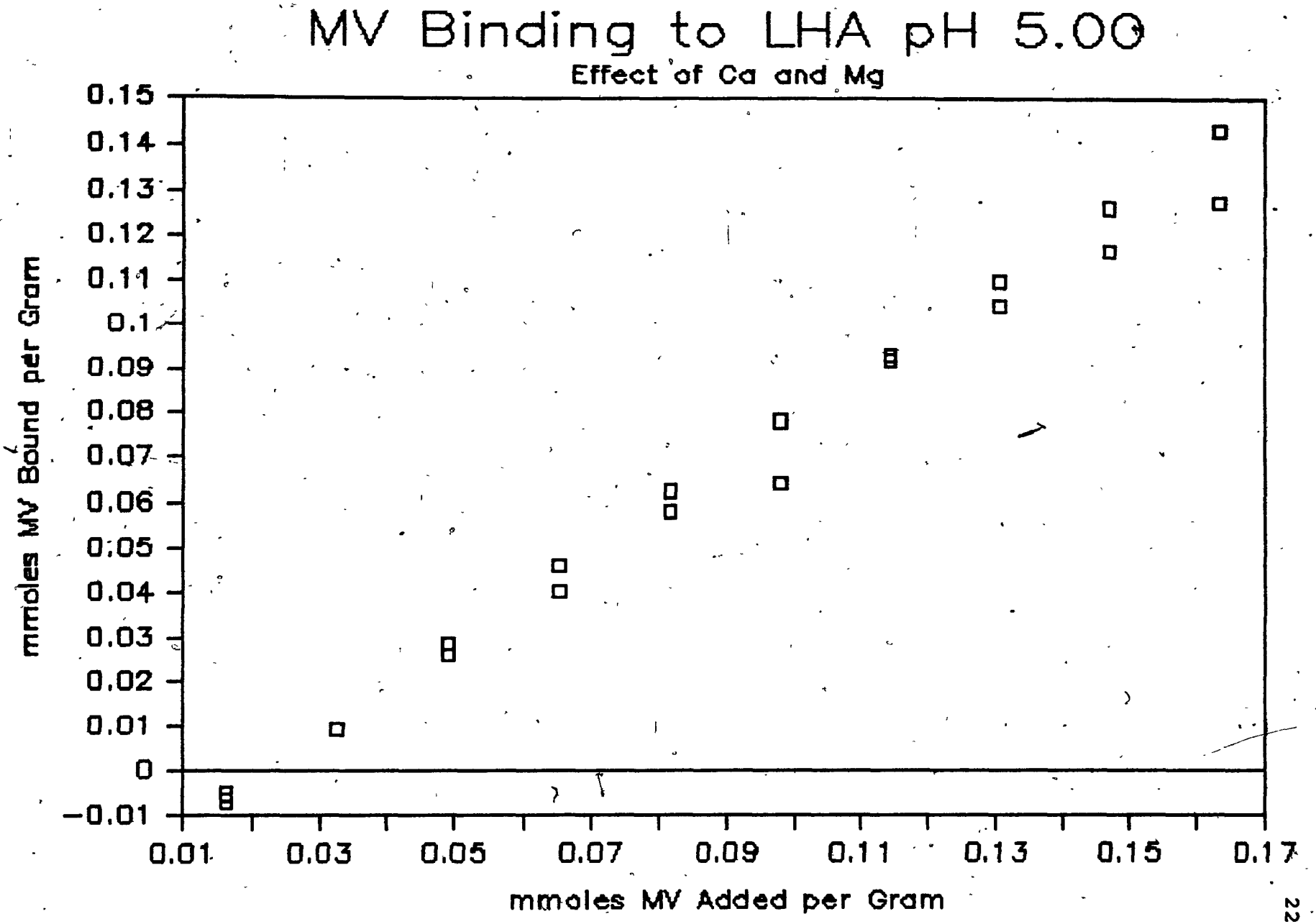

MV Binding to LHA pH 5.00
Effect of Ca and Mg
mmoles MV Bound per Gram
0.15
0.14
0.13
0.12
0.11
0.1
0.09
0.08
0.07
0.06
0.05
0.04
0.03
0.02
0.01
0
-0.01
0.01
0.03
0.05
0.07
0.09
0.11
0.13
0.15
0.17
mmoles MV Added per Gram

Figure 79

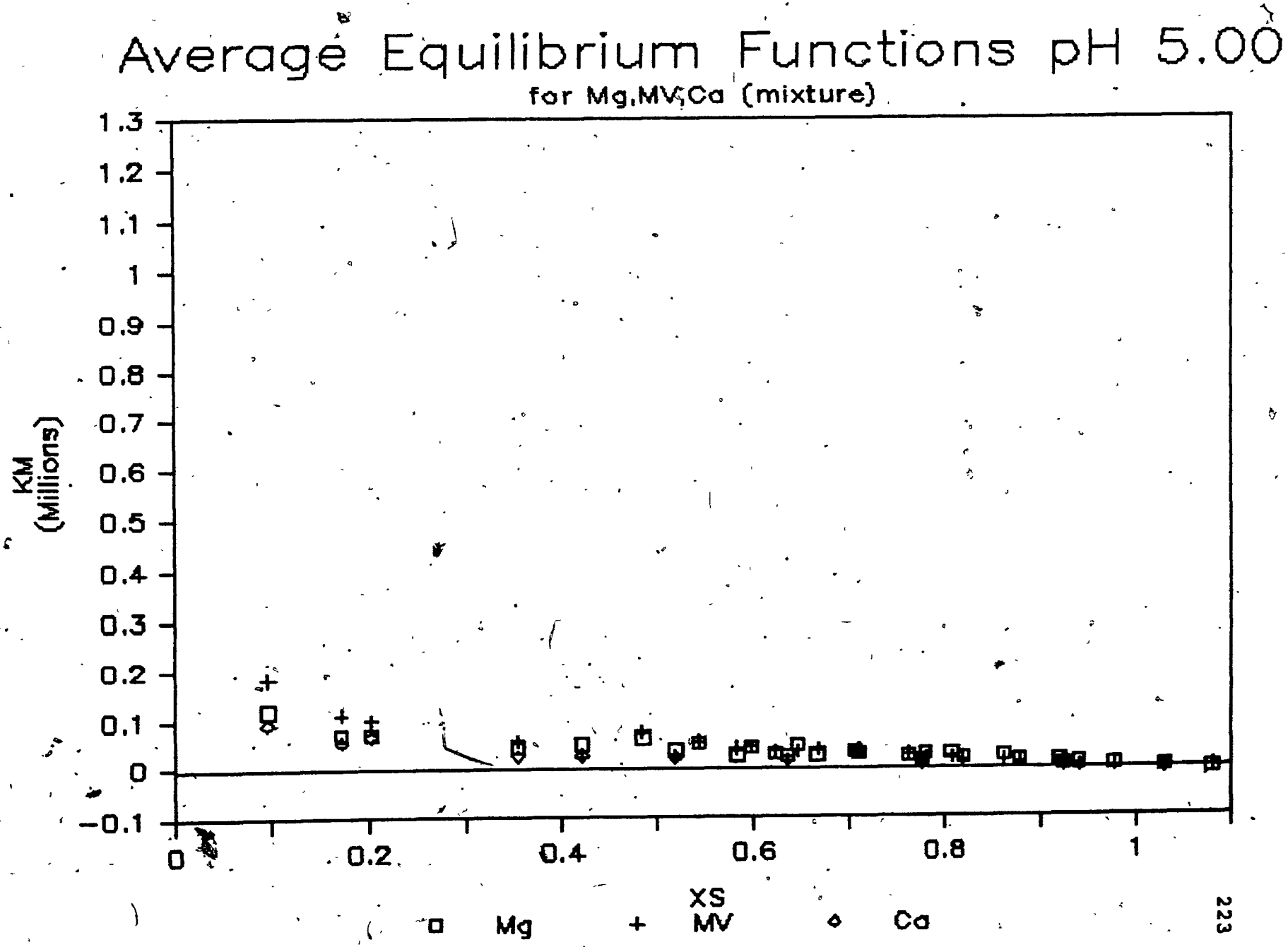

Average Equilibrium Functions pH 5.00
for Mg,MV,Ca (mixture)
KM (Millions)
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
-0.1
0
0.2
0.4
0.6
0.8
1
XS
Mg
MV
Ca
223

Figure 80

Table 26

Average Equilibrium Functions

Ca, Mg, MV at pH 5.00

X_S (±%8)	X_{Ca} (±%6)	X_{Mg} (±%2)	X_{MV} (±%3)	$\overline{K}_{Mg}$ (±%12) $x10^{+3}$	$\overline{K}_{Ca}$ (±%10) $x10^{+4}$	$\overline{K}_{MV}$ (%10) $x10^{+3}$
0.978	0.002	0.018	0.002	4.35	7.56	0.168
0.920	0.004	0.056	0.017	1.33	16.61	5.69
0.861	0.006	0.094	0.033	23.24	26.89	11.96
0.807	0.008	0.128	0.049	27.75	38.46	19.04
0.762	0.010	0.153	0.065	23.22	51.07	26.81
0.709	0.012	0.187	0.080	27.06	66.06	35.84
0.666	0.014	0.212	0.094	25.08	82.08	37.46
0.622	0.016	0.242	0.104	26.84	100.62	33.82
0.582	0.018	0.263	0.118	24.92	121.07	38.87

Humic acid concentration 0.1 gr/Lt. Concentration ranges for each metal ion: Ca from 2.1 umole/gr to 21 umole/gr; Mg from 40 umole/gr to 358 umoles/gr; MV from 16.3 umole/gr to 150 umole/gr.

Table 27

Average Equilibrium Functions

Ca, Mg, MV at pH 5.00

X_S (±%8)	X_{Ca} (±%6)	X_{Mg} (±%2)	X_{MV} (±%3)	$\overline{K}_{Mg}$ (±%12) x10+3	$\overline{K}_{Ca}$ (±%10) x10+4	$\overline{K}_{MV}$ (%10) x10+3
0.924	0.015	0.037	0.009	4.87	0.120	2.14
0.776	0.061	0.077	0.026	11.87	0.670	7.30
0.635	0.105	0.116	0.039	21.91	1.53	12.17
0.517	0.136	0.155	0.057	35.97	2.07	23.06
0.420	0.164	0.189	0.063	48.90	2.59	22.21
0.354	0.176	0.205	0.090	41.40	2.40	56.65
0.203	0.231	0.232	0.102	69.65	65.60	96.67

Humic Acid concentration 0.1 gr/Lt. Concentration ranges for each metal ion: Ca from 40 umole/gr to 403 umole/gr, Mg from 39 umole/gr to 398 umole/gr and MV from 16.3 umole/gr to 163 umole/gr.

5.1.14. Interaction of Paraquat with Montmorillonite.

Titrations of Montomorillonite with paraquat at pH 5.00 is shown as a binding curve in Figures 81. A plateau at about 0.9 milliequivalents per gram indicates that paraquat cations were bound up to approximately the exchange capacity of the clay which, as measured by sodium and magnesium uptake is 0.950 milliequivalents per gram. The difference in the exchange capacity and the amount of paraquat bound at saturation falls within experimental error. It has been recognized that the adsorption of paraquat on montmorillonite is an irreversible process, that is the removal of paraquat from the clay by other cations does not take place readily. Experiments with a variety of cations, including copper confirm this result. The displacement of cations from the negatively charged sites in the inter-layer spaces of montmorillonite can be seen in Figures 82 to 84. That the release of sodium by paraquat, from a sodium-saturated clay sample takes place corroborates the ion exchange mechanism proposed by Weber et al (45). Substitution of sodium by other cations produced similar results.

The reverse experiment, in which clay particles are saturated with paraquat and titrated with increasing amounts of copper ions , showed that the paraquat-clay interaction is in fact irreversible (Figure 85).

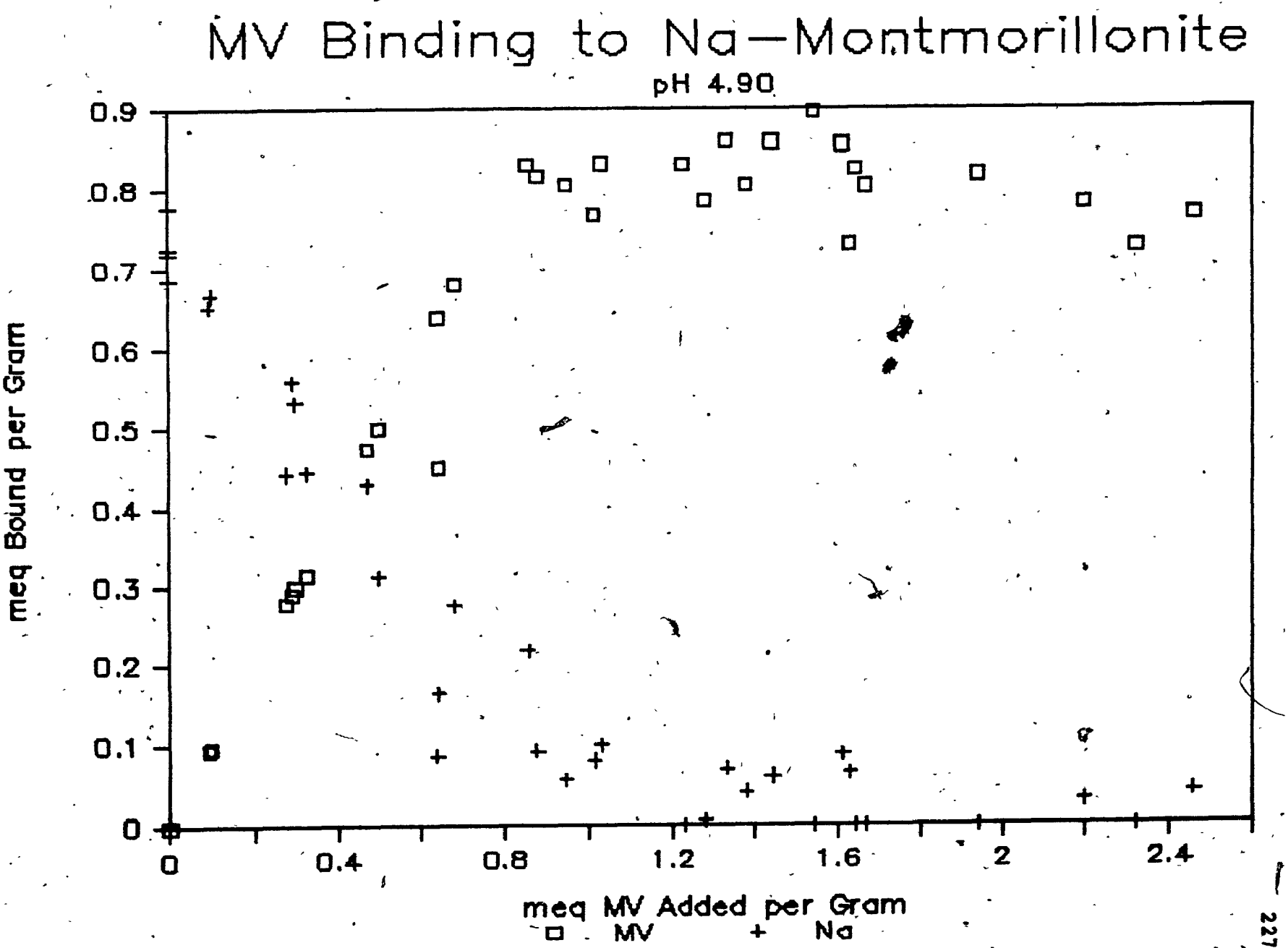

MV Binding to Na—Montmorillonite
pH 4.90
meq Bound per Gram
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.4
0.8
1.2
1.6
2
2.4
meq MV Added per Gram
MV
Na

Figure 81

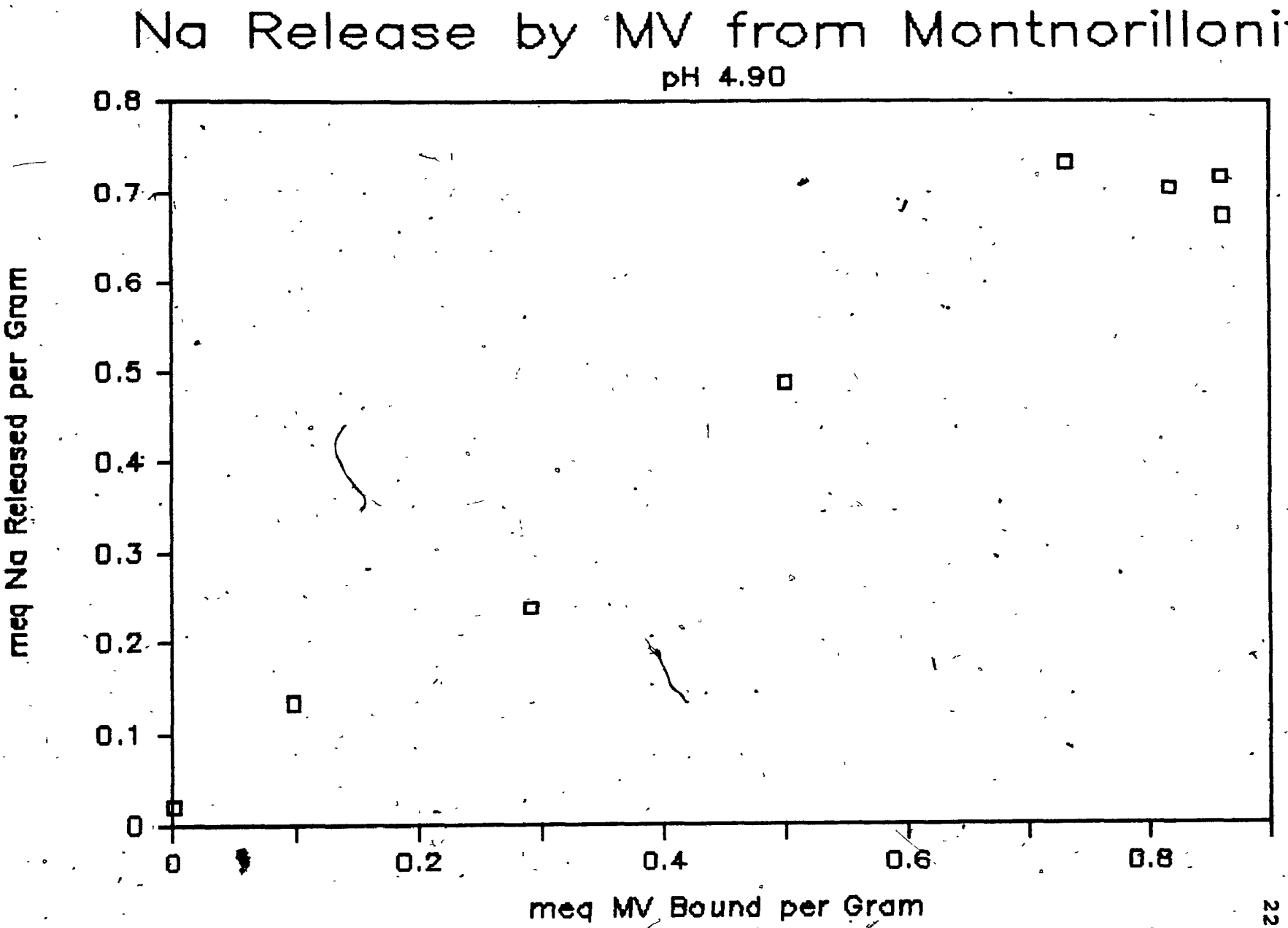

Na Release by MV from Montnorillonite
pH 4.90
meq Na Released per Gram
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
meq MV Bound per Gram

Figure 82

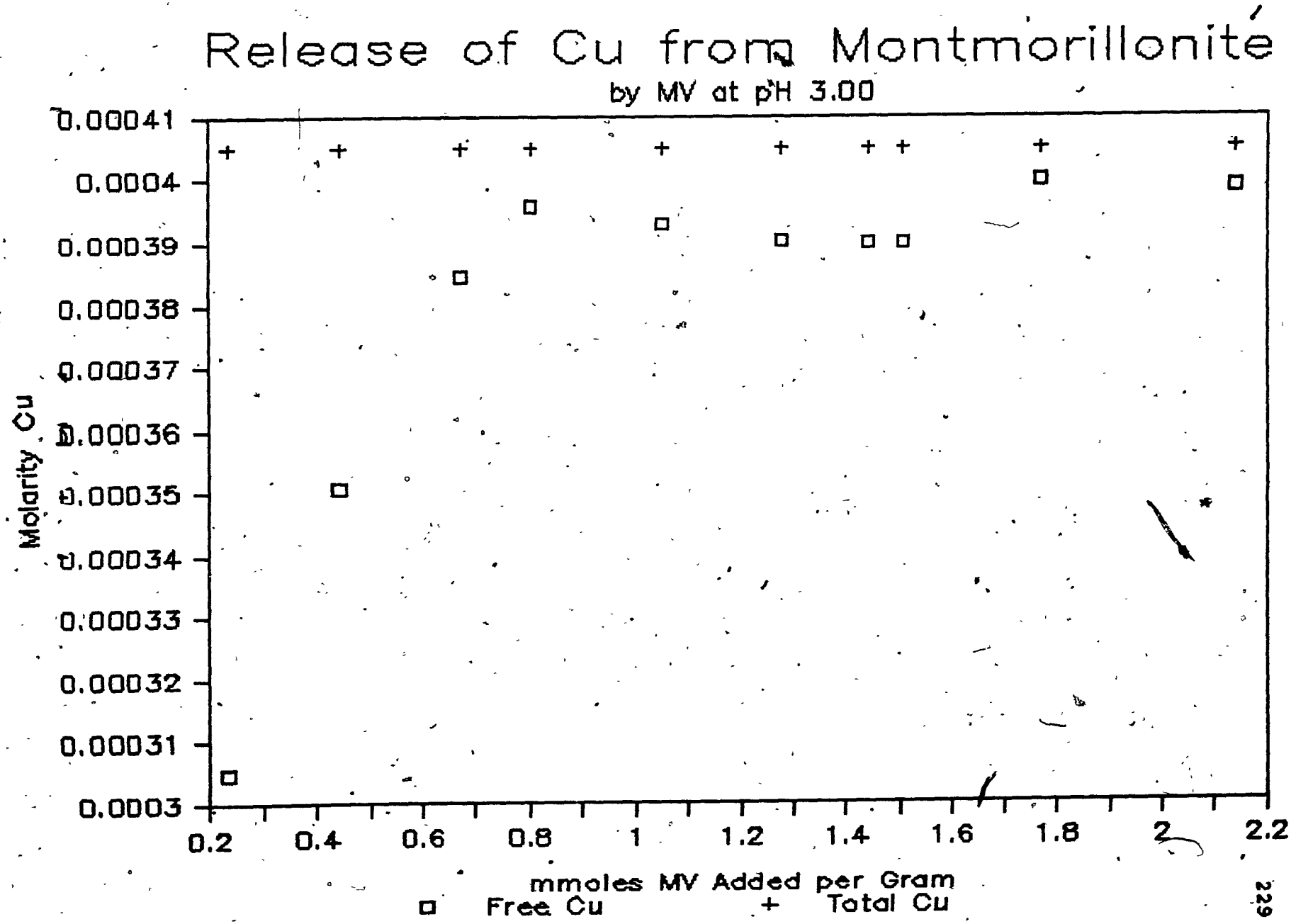

Release of Cu from Montmorillonite
by MV at pH 3.00
0.00041
0.0004
0.00039
0.00038
0.00037
0.00036
0.00035
0.00034
0.00033
0.00032
0.00031
0.0003
Molarity Cu
0.2
0.4
0.6
0.8
1
1.2
1.4
1.6
1.8
2
2.2
mmoles MV Added per Gram
Free Cu
Total Cu

Figure 83

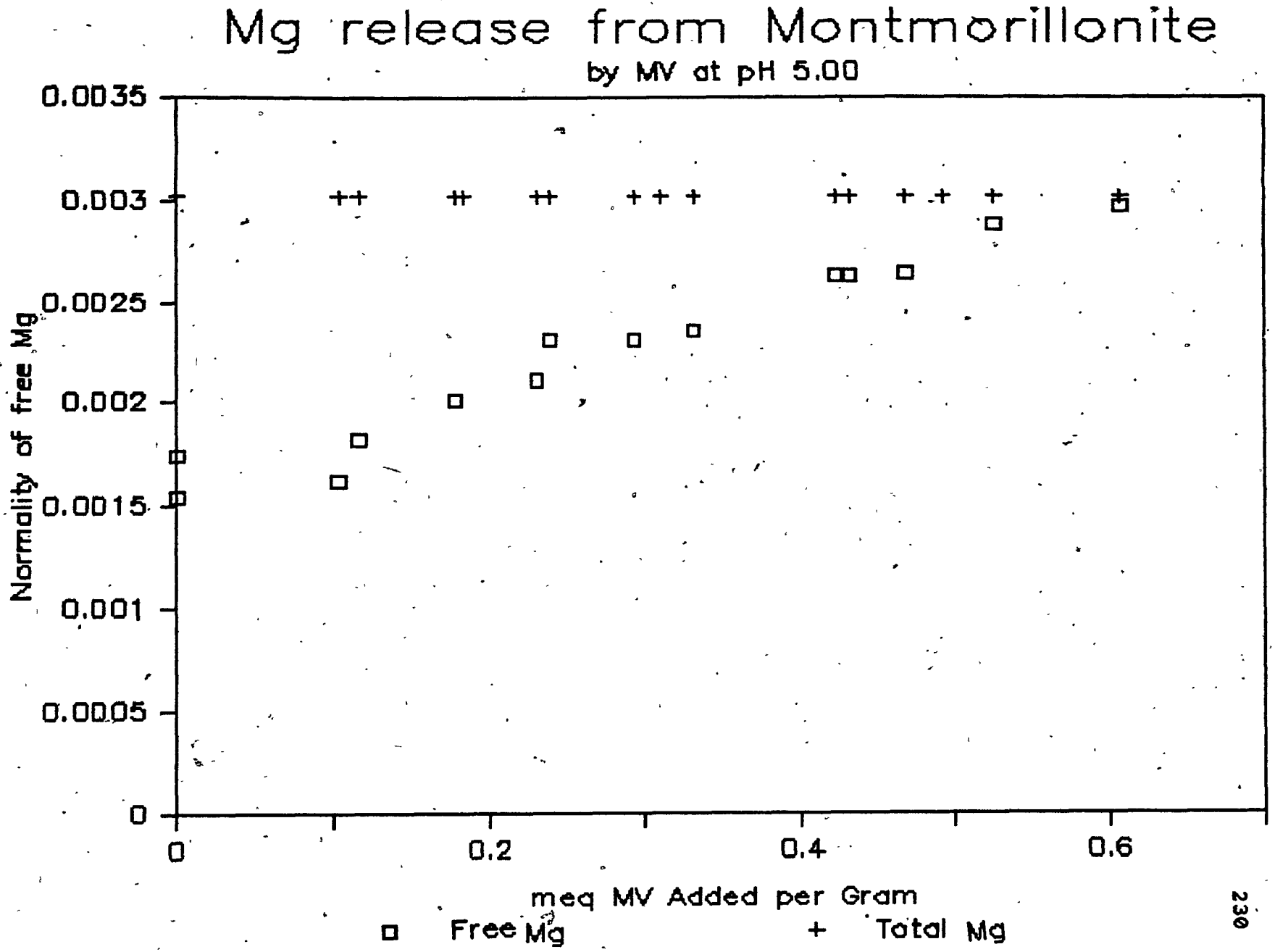

Mg release from Montmorillonite
by MV at pH 5.00
0.0035
0.003
0.0025
0.002
0.0015
0.001
0.0005
0
Normality of free Mg
0
0.2
0.4
0.6
meq MV Added per Gram
Free Mg
Total Mg

Figure 84

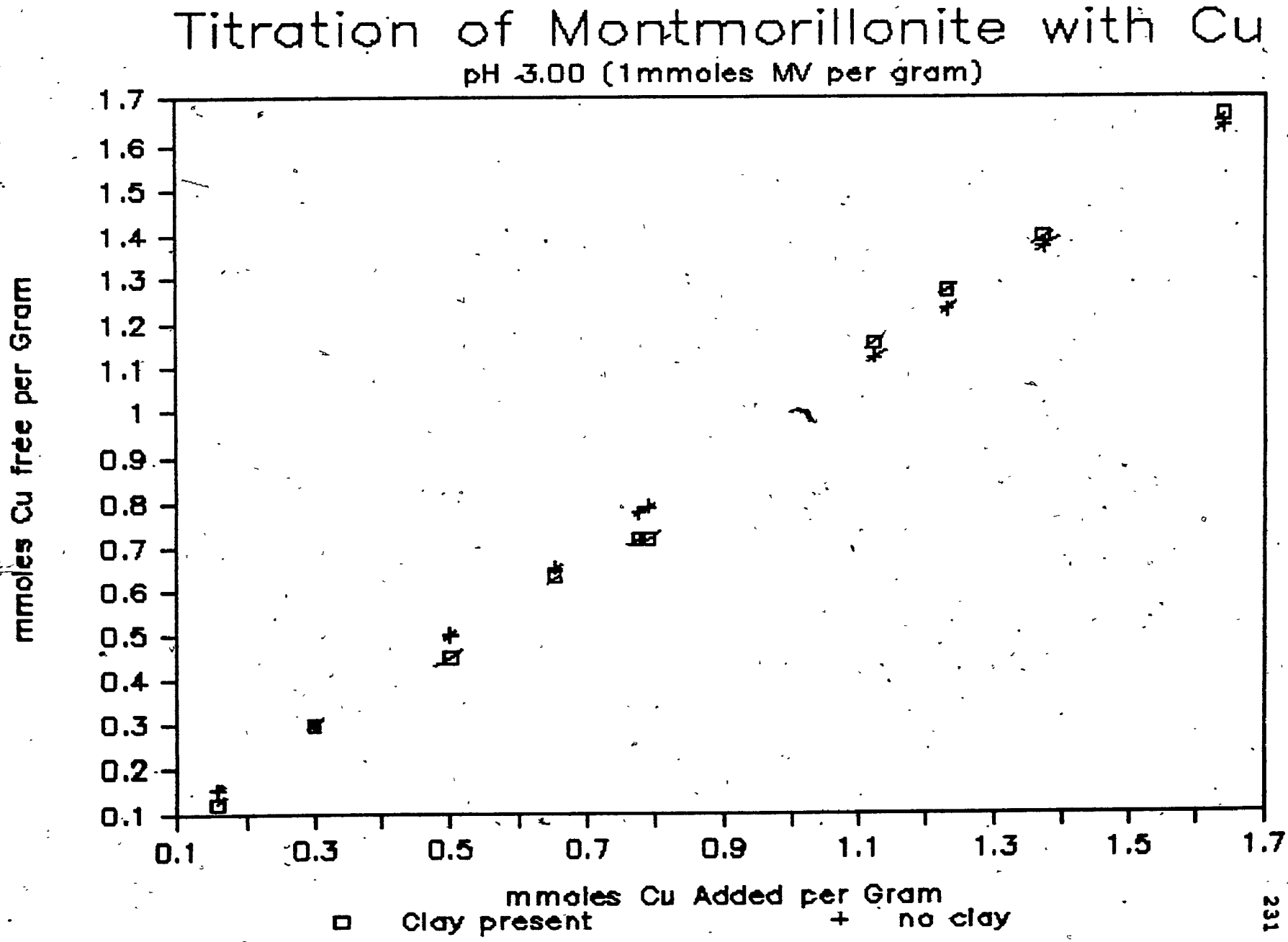
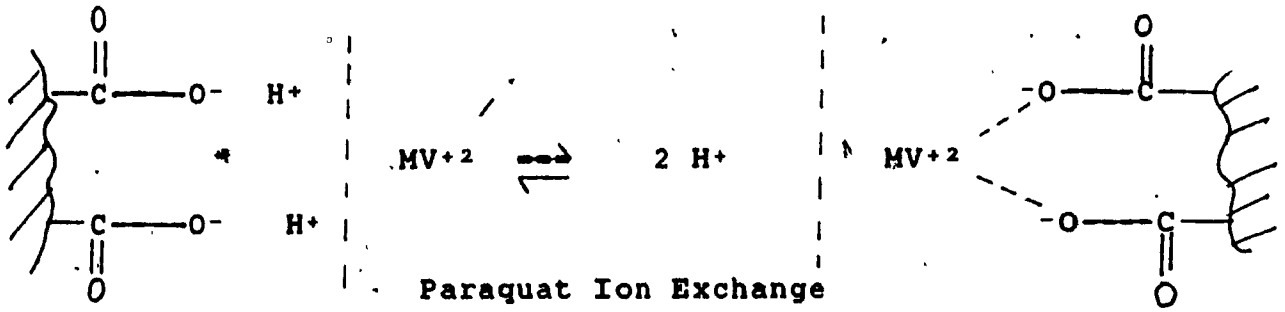

Titration of Montmorillonite with Cu
pH 3.00 (1mmoles MV per gram)
mmoles Cu free per Gram
1.7
1.6
1.5
1.4
1.3
1.2
1.1
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0.1
0.3
0.5
0.7
0.9
1.1
1.3
1.5
1.7
mmoles Cu Added per Gram
Clay present
+ no clay

Figure 85

5.1.15. Paraquat interaction with LHA at pH 3.00.

It has been recognized (4,6,7,37,32,41) that paraquat engages in ion exchange reactions with humic substances. At low pH values the exchange reaction taking place must involved the proton as the exchanging species. The binding of paraquat occurs via displacement of the strongest acidic protons, ie. the carboxylic acid sites in humic acid inside the internal gel solution. This implies that paraquat is mainly interacting with only one type of site since all the carboxyl groups in LHA can be considered chemically identical for this humic acid sample. Ion exchange of paraquat in LHA can de illustrated as follows;



Paraquat Ion Exchange

Figure 86

The carboxyl groups in humic acid make up the main anionic sites. The penetration of paraquat into the gel solution is controlled by the Donnan potential. The two groups making up the bidentate site must have the necessary geometrical disposition in order to match the charge distribution in paraquat, This requirement will certainly reduce the number of sites accessible

to paraquat compared to those available to other cations.

The use of the term "bidentate site" is not an appropriate one since is has the connotation of chelation which is not believed to be the case here. It also suggests the existence of specific interactions. The use of terms like "anionic divalent site" and "bidentate site" merely provides a convenient way of defining the ion exchange reaction.

The ion exchange equilibrium can be expressed as:

$$\overline{K}_{MV} = \frac{X_{MV} \ [H^+]^2}{X_{SH2} \ [MV^{+2}]}$$

The possibility of paraquat binding to humic acid by means of forces other than electrostatic interactions cannot be ruled out. Neutral salts such as $NaNO_3$ and NaCl reduce the amount of paraquat bound as the concentration or ionic strength is increased. This is an indication of the importance of the electrostatic interaction since sodium ions can compete with paraquat for ion exchange sites. If another type of interaction is taking place it must also be sensitive to changes in ionic strength. Herbicides such as atrazine, which do not participate in ion exchange reactions with humic substances also show binding which is sensitive to changes in ionic strength(5). Charge transfer complexation and hydrogen bond sorption are examples of possible interactions sensitive to ionic strength. Based on the

survey of the literature of paraquat interaction with a variety of compounds (29,30,38) charge transfer seems to be a common occurrence. For example Ledwith (29) suspected charge transfer complexation between paraquat and phenolic materials. One requirement for charge transfer complexation is that the paraquat cation and the charge transfer "complexing agent" must have favorable overlap of electron deficient and electron rich regions, respectively. For this to happen, there must be a favorable distance between the two members of the complex. In this context the electrostatic attraction between paraquat and the deprotonated carboxyl groups is a favorable situation. If charge transfer were to take place between paraquat and carboxyl groups, then this mechanism would be intimately linked to the main mechanism of ion exchange. This hypothesis does not exclude the formation of charge transfer complexes involving "sites", particularly phenolic moieties, not engaged in ion exchange.

5.1.15.1. Effect of other Cations.

There is ample evidence in the literature which points at ion exchange involving carboxyl groups in humic acids as the main mechanism in paraquat binding (4,6,7,38). Best et al(40) and Kahn (37) considered this in a rather simplistic way. Factors such as "site definition", "site loading", and the like were vaguely discussed. It is in fact important to compare the

behaviour of other cations interacting with humic acid, taking into consideration the sterochemical and electrostatic differences between paraquat and other simple metal ions.

At pH 3.00 the values for the average equilibrium functions for cations follow the order: Cu > Ca> MV> Mg. The values for calcium are rather uncertain since larger errors were involved. With the exception of paraquat this sequence can be explained by simple electrostatic effects. The hydration radii of calcium and copper being smaller than that of magnesium implies that these cations shall be preferred over magnesium by humic acid. With respect to calcium and copper it is the possible that part of the hydration shell for both cations is lost when interacting with humic acid, implying an even stronger interaction. The preference of calcium over magnesium by carboxyl ion exchangers has been documented recently by Kwak et al.(66).

Humic acid's total acidic capacity as determined by titration with barium hydroxide is 7.60 mmoles per gram, copper covers about 2.4 millimoles per gram or about 32 % at pH 5, whereas other cations cover about 12 %. The total acidity includes 2.4 mmoles per gram of carboxyl groups, the rest has been assumed to be phenolic protons. The possibility of even weaker acidic sites cannot be ruled out, but it is believed that these will not interact significantly with metal ions under the

pH range in this study. Each cation will interact with a collection of sites. However, similar cations are expected to interact with the same or similar sites. This is the case for calcium and magnesium. Both cations compete for the same collection of sites, as has been shown earlier.

The effect of each cation on the equilibrium of paraquat and humic acid is shown in Table 28.

Table 28

Effect of similar loadings of various cations on the paraquat-humic acid interaction

Average Equilibrium Function at pH 3

	X_{MV}	X_C	X_{SH2}	$\bar{K}_{MV}$
--	0.074	----	----	9.72×10^{-3}
Cu	0.066	0.057	0.877	6.61×10^{-3}
Mg	0.052	0.063	0.886	4.90×10^{-4}
Ca	0.063	0.068	0.869	2.61×10^{-4}
Cu	0.062	0.128	0.800	8.84×10^{-4}

It can be seen that both calcium and magnesium decrease the paraquat equilibrium function to the same extent. Copper does not affect it to as great an extent. This is a clear indication that sites with which calcium and magnesium can interact also interact with paraquat to a larger extent than those sites interacting with copper. A larger copper loading is needed in order for copper to reduce the average equilibrium function for paraquat to the same degree as did calcium or magnesium. The last entry in Table 28 corroborates this observation. This may be a consequence of the order in which cations, particularly copper bind to different sites. If copper prefers salicylic-like sites and calcium and magnesium bind to carboxylic sites, then copper will interact with the salicylic-like sites available then with carboxyl sites. The compression of humic acid molecules into a macro-gel structure at low pH means that the flexibility of the molecules is much less than at pH values higher than 5. This means that cations such as calcium and magnesium are attracted to the charge developed in the gel internal solution regardless of the geometry of the "sites". These cations are expected to be territorialy bound. Copper ions will show the same effect, but may also interact specifically with salicylic and dicarboxylic sites.

Despite the similarities between the sites interacting with magnesium and calcium and those interacting with paraquat, about 50 % of the paraquat binding sites are not shared with these

cations. With copper, only about 25% of the sites are not being shared. A simple diagram can show this clearly.

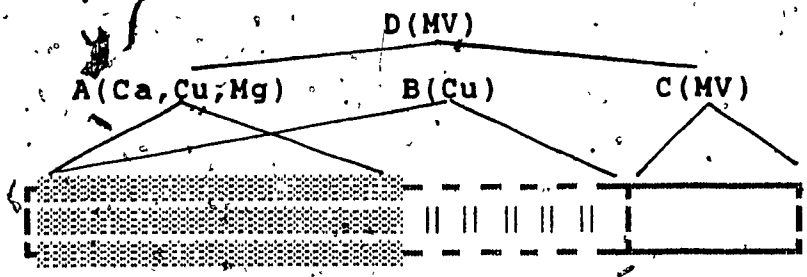


Figure 87

Diagram for sites shared by paraquat, copper, calcium and magnesium on LHA

Sites A are common to all cations. It is very likely that these are carboxyl groups which are ion-paired to relatively free protons in the interior of the gel solution. Sites B could be either weaker carboxyl acids or salicylic-like sites or both, to which paraquat interact but not necessarily via ion exchange. Copper interacts with sites B. Sites C, sites with which only paraquat interacts are probably phenolic moieties inside and outside the gel structure. D represents the total number of sites interacting with paraquat. Saturation of

carboxyl groups in humic acid with copper ions at pH 3.00 does not exclude paraquat from binding to humic acid. As has been shown earlier paraquat binding occurs without displacement of copper. The level of copper loadings used ensured that all carboxyl group sites were covered by copper. This leads to the idea that this situation is a particular one in which paraquat is sorbed by a non-ion exchange mechanism.

5.1.16. Interactions of cations with humic acid at pH 5.00.

The interactions of cations with humic acid under pH conditions greater than 4.5 will be quite similar to the interactions with a "dissolved" fulvic acid. The macroscopic gel structure of humic acid which prevailed at low pH is almost non existent at pH 5.00. The destruction of the gel structure carries an important consequence. The mechanism controlling the binding of cations is no longer dependent on a Donnan potential at the macroscopic level, since the internal gel solution has been reduced to a minimum. In fact the results obtained by Marinsky et al. (15,16,17) for various fulvic acids showed that the molecules are impermeable to electrolytes, which means that binding reactions take place at the surface of the polyelectrolyte. This, on the other hand, does not exclude the possibility that a microscopic-gel system is operating. Nevertheless, macroscopic Donnan effects are minimum.

Although no similar study has been done for soil humic

acids, it is reasonable to expect that a similar.

At pH 5.00, the character of the interactions between cations and humic acid will be mainly electrostatic between the already ionized carboxyl groups present in humic acid and cations in solution. This electrostatic interaction may result, depending on the cation involved, in a specific binding, such as may be the case of copper which form complexes with dicarboxyl and salicylic sites.

In studying the complexation of manganese by a soil fulvic acid, Gamble et al (68a) made the distinction between inner sphere and outer-sphere complexes. NMR measurements (68) provided evidence for the conclusion that cations such as manganese are held electrostaticaly in the vicinity of the anionic groups in fulvic acid molecules and that the cation retained its hydration shell. This is clear evidence that no ligand exchange occurred in the binding mechanism. The energy involved is purely electrostatic. In fact, the binding energy for manganese to fulvic acid is almost twice that for potassium ions. Manning (69,70) have used the term "territorialy bound cations" to define cations bound as described above. In this context the term outer-sphere complex is synonymous with "territorialy bound cation". On the other hand, cations such as copper are able to form very strong complexes with carboxyl and salicylic groups, requiring the displacement of relatively tightly bound protons from the phenolic portion of salicylic

sites. The energy involved is larger than in the case of purely electrostatic binding. In the case of copper the complexing mechanism also involves the loss of water making up the hydration shell and can be visualized as a ligand substitution reaction. These types of complexes are typical "inner-sphere complexes".

At pH 5.00 and zero ionic strength, some of the carboxyl groups in humic aid are ionized. Acid base titration results show that about 39.3 % of the original carboxyl acid content has been neutralized. The amount of carboxyl groups ionized per gram at pH 5.00 can then be estimated to be about 1.02 millimoles per gram. In the case of cations interacting with ionized carboxyl groups only, the apparent binding capacity should be about 0.51 millimoles per gram. This represents an upper limit, assuming that all sites are available to cations and are located in the polyelectrolyte in such a way that no steric hindrance exists. The saturation level attained depends also on the binding constant for that particular cation.

5.1.17. Paraquat-Magnesium system.

The proposed stoichiometry for the binding of paraquat to humic acid at pH 5.00 suggests that paraquat must form complexes similar to those between magnesium and humic acid. Based on the paraquat-magnesium experimental results, both cations share common sites. Nevertheless, the equilibrium function for paraquat implies that its interaction with humic acid is

stronger than that for magnesium. This is confirmed by the fact that experiments in which paraquat-saturated humic acid was titrated with magnesium did not show any displacement of paraquat.

The charge distribution in the paraquat cation is quite different from that of a sphere cation such as magnesium. Figure 88 shows schematically the location within the cation where positively charged centres are most likely to occur.

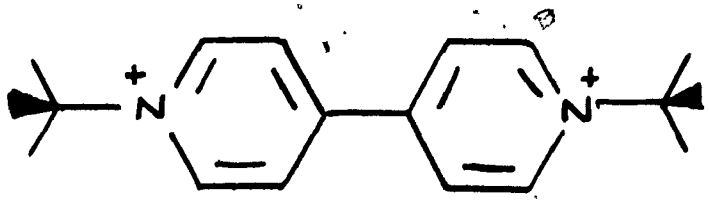


Figure 88

Positive charge distribution

This charge distribution in paraquat may be a crucial factor in binding to carboxyl groups in humic acids. A distribution of charge throughout the surface of the molecule will permit interactions with carboxyl groups which may not be adjacent to each other.

The order of binding intensities is: $MV^{+2} > Ca^{+2} > Mg^{+2}$ for the same cation loading. The differential equilibrium functions (Figure 74) for each cation indicate the same trend. The calcium humic acid equilibrium, as mentioned before, is different from the other two because the formation of precipitate introduces a second physical phase. It has been included, however, for comparative purposes. The greater binding of paraquat over the other two cations may be due to the charge stabilization present in paraquat.

5.1.18. Copper-paraquat system:

The main feature of this system is that paraquat binds with little displacement of copper ions when introduced into a copper saturated humic acid system. In the reverse situation, copper does displace paraquat but not completely.

Two pieces of information must be considered to interpret these results. First, copper binding to humic acid at pH 5.00 results in almost immediate precipitation of humic acid. As mentioned before, this is an indication of the formation of copper dicarboxylic complexes with carboxyl groups present in

different humic acid molecules. The fact that this takes place very early in the titration implies that this type of complex formation predominates. If this is actually correct, then the apparent binding capacity for copper at pH 5.00 reflects the total number of carboxyl groups present in the humic acid sample. Second, given that the value for the apparent binding capacity for copper is 1.25 %5 millimoles per gram, compared to the total number of carboxyl groups, which is 2.43 %4 millimoles per gram, this accounts for about 1.2 millimoles of "bidentate sites", copper must be binding to all of the carboxyl groups present in humic acid including the rather weak acid sites not ionized at pH 5.00.

The blocking of these sites by copper at pH 5.00 is evident from both the copper-magnesium and the paraquat-copper experiments. If paraquat were to bind with the same strength as does magnesium, which it does not, no binding would take place. The fact that binding occurs, and that most of the carboxyl groups are binding copper indicates that in the presence of copper paraquat binds to other sites. It is quite possible that the precipitated copper-humates provide a surface onto which paraquat can attached itself in physical and possibly chemical interactions. In this context it is important to consider the results obtained by Ledwith (29) for the interactions of paraquat with phenolic compounds indicating possible charge transfer complexes.

5.1.19. Internal and External Variables.

The correlation of cation binding with external variables such as pH, ionic strength, concentration of cations, etc, provides only a qualitative picture when dealing with colloidal systems as complicated as humic acid suspensions. It is true that knowledge of these variable is needed to describe the chemical equilibrium, but they usually reflect poorly the chemistry at the site of the reactions; i.e. the interior of the humic gel.

An example of this can be seen in the study of the pH effect on the apparent binding capacity of paraquat on humic acid. The results of this study are shown in Figure 89. They provide little information other than lowering the pH produces a decrease in the apparent binding capacity. As has already been pointed out, the existence of an internal gel solution in humic acid particles implies that the pH inside the gel, as well as the concentration of cations, is quite different from that in the external solution. Unpublished results on the binding of paraquat to Laurentide Fulvic Acid (72) indicate that fulvic acid binds much less paraquat than humic acid under similar conditions. Fulvic acid-paraquat interactions are less sensitive to changes in the pH of the external solution, and in fact remain almost constant in the 3 to 4 pH range. A similar situation was found by Guy et al (4), for the binding of paraquat to polysteryne sulfonic acid. In addition, changes in ionic

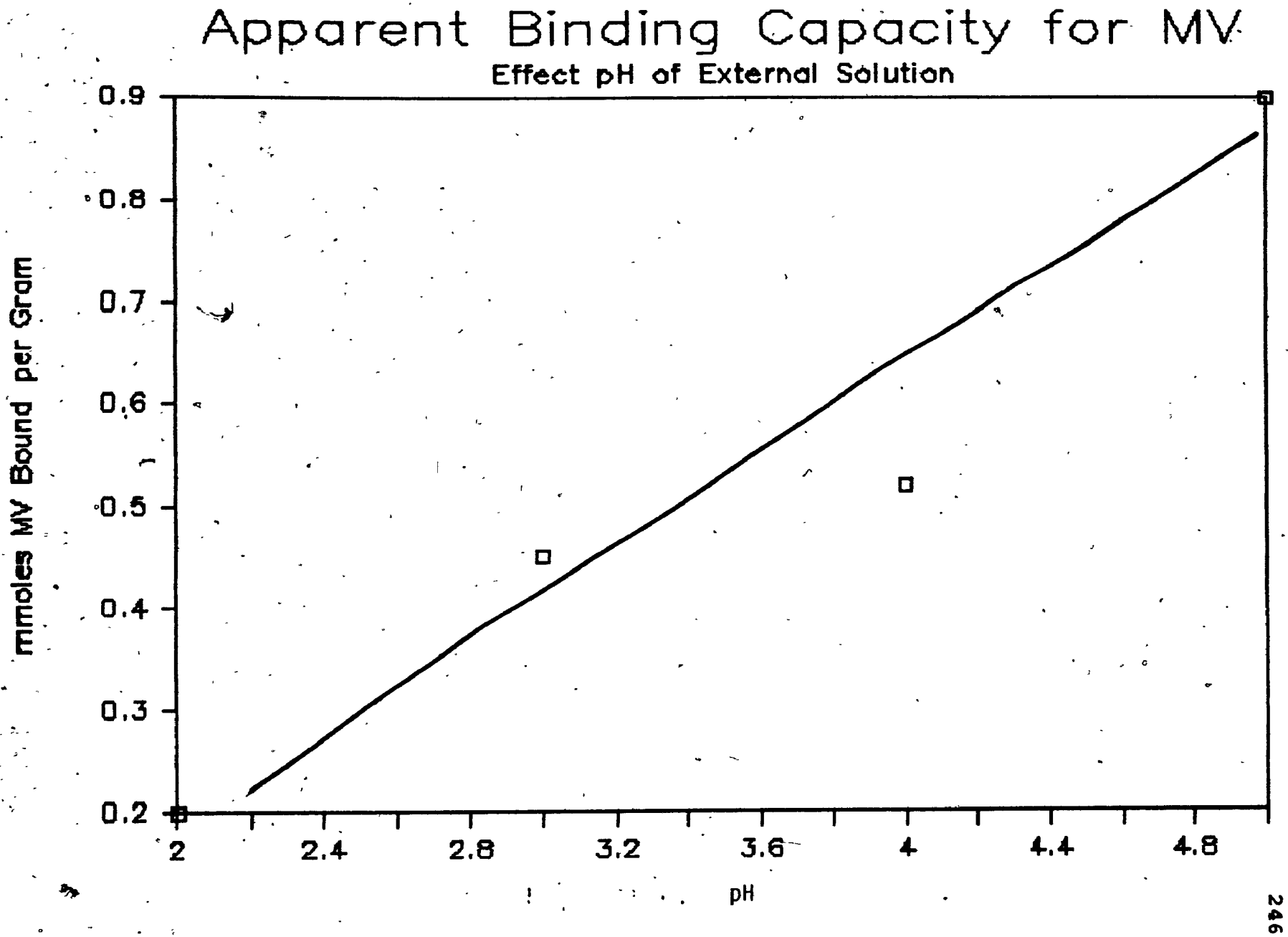

Apparent Binding Capacity for MV
Effect pH of External Solution
mmoles MV Bound per Gram
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
2
2.4
2.8
3.2
3.6
4
4.4
4.8
pH

Figure 89

strength did not change binding properties. Differences in the pH behaviour of humic acid are a consequence of the macro-gel-like nature. Humic acid particles have an "internal solution" with a high concentration of carboxyl groups.

Further information can be obtained if one chooses more appropriate variables as was done in the present work. Evidence has been obtained to confirm the hypothesis that the main agents involved in the binding of paraquat to humic acid are the carboxyl groups. Based on titration data for LHA the fraction of acid remaining in the gel can be calculated. This fraction consists of "free" protons, but ion-paired to carboxyl groups, and bound protons. In Figure 90 the apparent binding capacity for paraquat has been plotted against the percentage of acid remaining in the gel. This plot provides more information than the previous plot (Figure 89). The intercept gives an estimate of the total potential binding capacity, assuming only paraquat-carboxyl interactions. The value of 1.9 millimole per gram is quite reasonable, based on the total carboxyl content.

The effect of cations can be described by plots including inner variables as well (Figure 92). Figure 91 shows the effect of copper ions on the apparent banding capacity for paraquat at various pH values. The decrease at pH 3 and 4 follows a linear relationship.

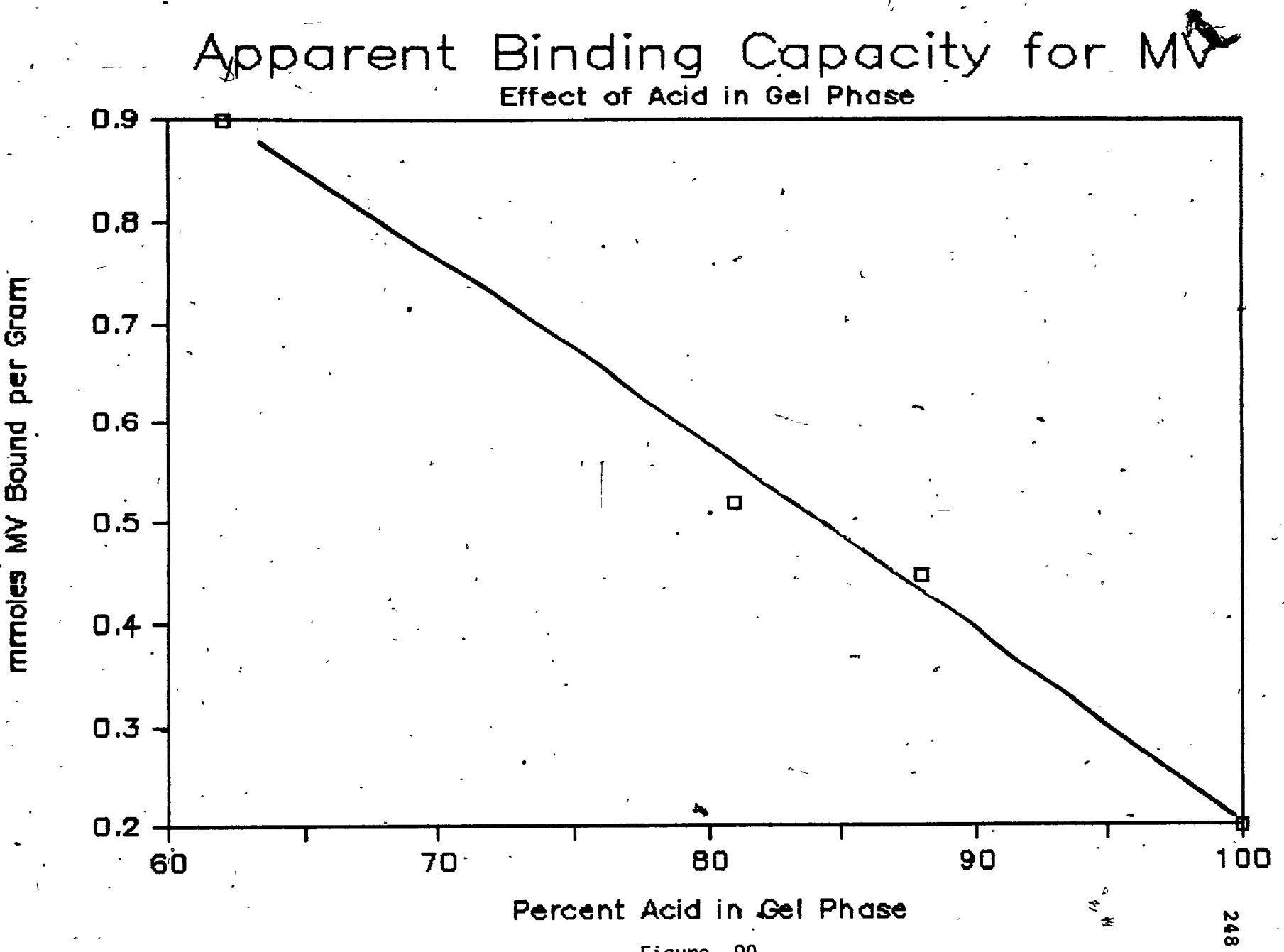

Apparent Binding Capacity for MV
Effect of Acid in Gel Phase
mmoles MV Bound per Gram
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
60
70
80
90
100
Percent Acid in Gel Phase

Figure 90

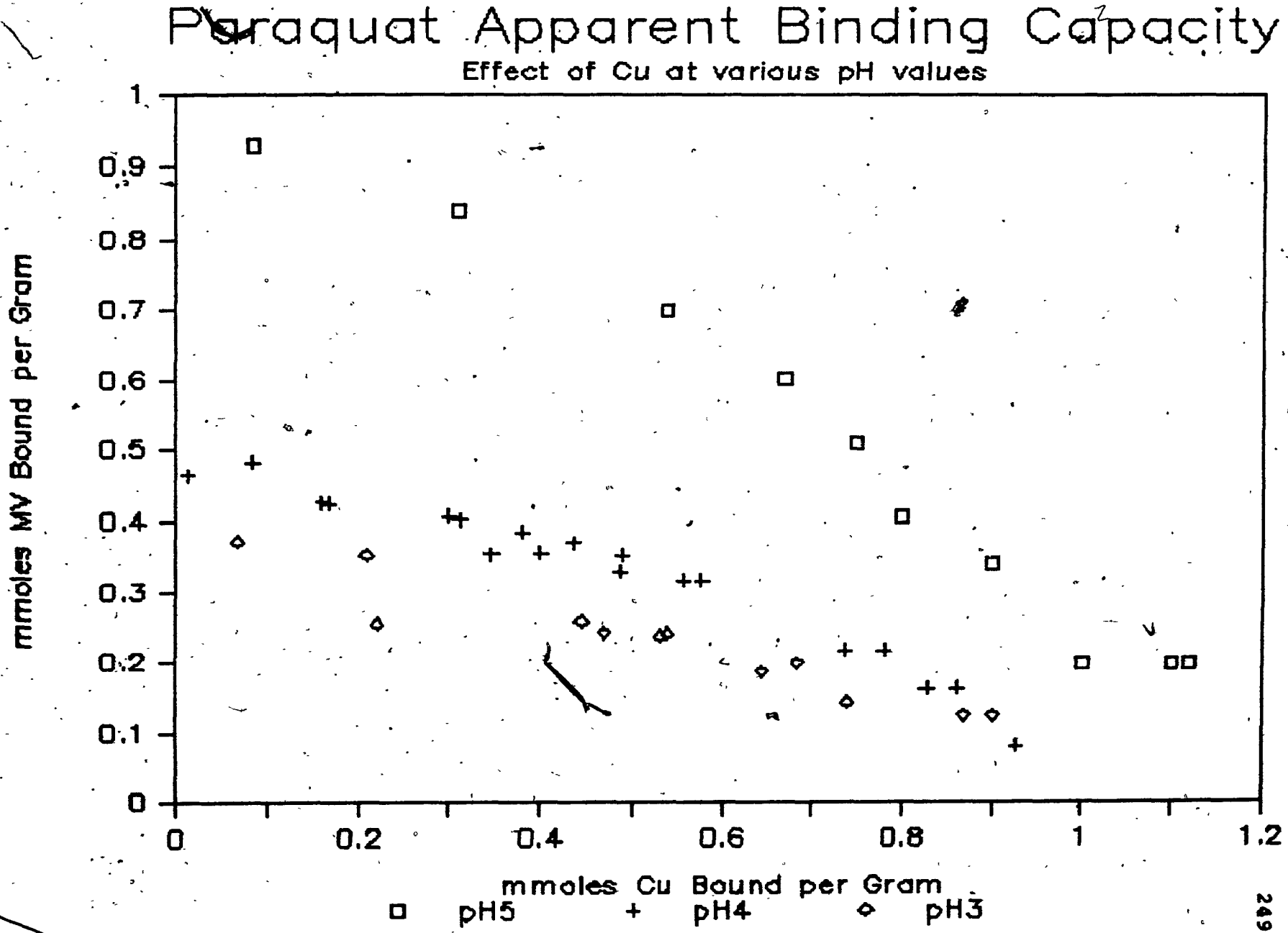

Paraquat Apparent Binding Capacity
Effect of Cu at various pH values
mmoles MV Bound per Gram
1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
0
0.2
0.4
0.6
0.8
1
1.2
mmoles Cu Bound per Gram
pH5
pH4
pH3

Figure 91

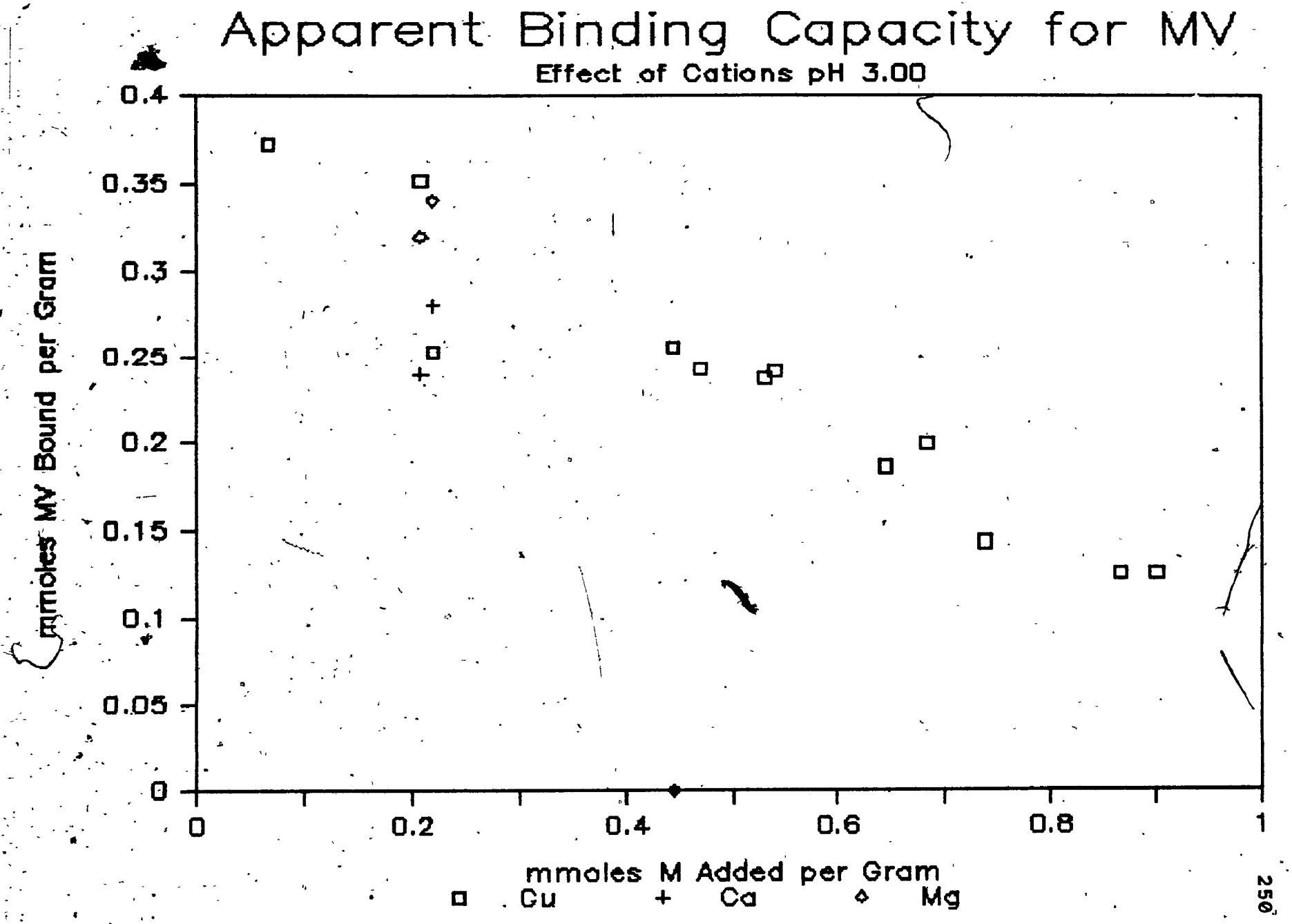

Apparent Binding Capacity for MV
Effect of Cations pH 3.00
mmoles MV Bound per Gram
0.4
0.35
0.3
0.25
0.2
0.15
0.1
0.05
0
0
0.2
0.4
0.6
0.8
1
mmoles M Added per Gram
Cu
Ca
Mg
250

Figure 92

5.1.20. Summary of results.

5.1.20.1. At pH 3.00 titration of humic acid with magnesium causes some of the humic acid to go into solution as can be detected by visual inspection of the supernatant solution. This effect is not seen with ions such as copper, calcium, paraquat and sodium.

5.1.20.2. At pH 5.00 titration of dissolved humic acid with copper or calcium result in precipitation of humic acid, leaving a clear supernatant. The extent of the precipitation depends on the amount of the metal ion added.

5.1.20.3. At pH 5.00 titration of humic acid with paraquat or magnesium does not cause precipitation of humic material.

5.1.20.4. Titration of humic acid at pH 5.00 with paraquat in the presence of magnesium caused some aggregation of humic material and partial precipitation.

5.1.20.5. Titration of humic acid at pH 5 with paraquat in the presence of copper, and vice versa, caused precipitation of humic material.

5.1.20.6. Titration of humic acid at pH 5 with calcium in the presence of excess magnesium caused precipitation of humic material.

5.1.20.7. Equilibrium functions for paraquat, magnesium and calcium, at pH 3.00, are quite constant within experimental error. Average values of average were in the order; MV > Ca > Mg.

5.1.19.8. Equilibrium functions for copper-humic acid showed variations with sites being loaded which were outside the limits of experimental error.

5.1.19.9. The apparent binding capacity for the cations investigated followed the sequence: Cu > MV > Mg = Ca, at pH 3 and Cu > MV = Mg > Ca at pH 5.

5.1.19.10. Binding of paraquat and copper to humic acid but of calcium or magnesium was detectable at pH 2.

5.1.19.11. Approximately 0.1 mmoles/g of paraquat cannot be displaced from humic acid by cations such as copper, calcium and magnesium under conditions where the Donnan mechanism is controlling the degree of metal ion binding (low ionic strength).

5.1.19.12. In the presence of sufficient copper to saturate the ion exchange site on LHA, paraquat binds with release of very little copper.

Chapter 6

6.1. Conclusions

6.1.1. The acidity function of the carboxyl groups present in LHA can be represented by a single site model with an intrinsic pK_a of 3.70. The variation of pK_{app} with degree of dissociation can be attributed to electrostatic effects.

6.1.2. To study the interaction of herbicides with soil colloids, such as humic acid, it is important to understand the physical nature of the adsorbing material. This is particularly critical when dealing with humic acids. The pH dependent solubility of humic acid must be taken into consideration when postulating binding mechanisms for metal ions and cationic herbicides. The existence of a macro-gel structure in humic acid at low pH values defines the type of mechanism controlling the sorption of ions. Under these conditions, Donnan potentials control metal and organic ion uptake.

6.1.3. The interaction of paraquat with Laurentide Humic Acid at pH 3.00 can be modeled as being an ion exchange reaction involving the carboxyl groups that make up some of the ion exchange sites in this humic acid sample. At low ionic strength, when Donnan potentials are operating, the ion exchange reaction of paraquat with humic acid is not totally reversible. Removal of paraquat by cations such as calcium, magnesium and copper is not complete. This hysteresis effect may be due to a secondary

interaction. Charge transfer between electron rich regions in the humic acid moieties and the electron deficient paraquat ring system could be a possibility as has been suggested by previous researchers. High ionic strength solutions totally exclude paraquat from interacting with humic acid particles.

6.1.4. Evidence is presented for the formation of 1:1 "complexes" of paraquat with monovalent carboxyl sites in Laurentide Humic Acid at pH 5.00. This may take place between ion-paired paraquat and an ionized carboxyl group or divalent paraquat and an ionized carboxyl group followed by partial or total neutralization of the remaining positive charge by electron rich moieties in the humic acid molecule.

6.1.5. The removal of paraquat from humic acid by calcium, magnesium or copper is not complete at pH 5.00. Copper ions are able to displace about 70 % of the total paraquat bound to a paraquat saturated humic acid.

6.1.6. The interaction of copper with Laurentide Humic Acid, at pH 5.00, seems to take place via dicarboxylic site " pseudo-chelation"; ie. with carboxyl groups located in separate humic acid molecules. The saturation of sites with copper at this pH indicates that copper can interact with almost 100% of the carboxyl groups present in the sample.

6.1.7. Calcium ions interact with Laurentide Humic Acid in a similar fashion as does copper at pH 5.00. The extent of site coverage by calcium is much less than that by copper. This may

be due to the fact that calcium may not be able to displace protons from the remaining protonated carboxyl groups.

6.1.8. Magnesium interaction with Laurentide Humic acid at pH 5.00 is very similar to the interaction of paraquat with the same humic acid: The main difference is in the intensity of the interaction, which is weaker for magnesium.

6.1.9. The binding capacities for paraquat, calcium, and magnesium at pH 5.00 can be correlated to the fraction of ionized carboxyl sites in LHA. Values of about 0.90 millimoles per gram for paraquat and magnesium, and of 0.45 millimoles per gram for calcium fall within the estimated fraction of ionized sites available at this pH.

6.1.10. Average ion exchange equilibrium functions for paraquat, calcium and magnesium at pH 3.00 are almost constant considering the experimental. This is believed to be due to the narrow range of types of sites with which each of these cations interacts, and the constant value for the dissociation function for the carboxyl groups in LHA.

6.1.11. At pH 3.00 the competition between paraquat and any of the cations studied, namely calcium, magnesium and copper, for the ion exchange sites introduces a discontinuity in the $K_M X_{SH2}$ versus X_{SH2} plots. The nature of this discontinuity is still open for discussion, one possibility could be a change in the structure or configuration of the humic acid gel resulting from cation binding.

Chapter 7

7.1. Suggestions for further research.

7.1.1. A study of the dependence of the solubility of humic acid with pH. This may involve the collection of aliquots of humic acid suspension at every point during titration with base followed by an appropriate chromatographic analysis in order to detect the possible presence of small monomeric acidic moieties.

7.1.2. Florescence quenching studies of dissolved LHA at pH 5, using copper and paraquat as quenchers. This may provide information concerning the degree of quenching brought about by each cation, for similar loadings. Comparison of these results could permit a better assessment of the overlap of sites shared by both cations.

7.1.3. Light Scattering studies in the course of copper and calcium titrations of humic acid at pH 5. The information obtained by these studies would allow one to distinguish between chelation and "pseudo-chelation" as well as providing a better idea of the concentration thresholds at which precipitation occur.

7.1.4. Use of an ion-specific electrode to monitor "free" paraquat in humic acid suspension. A recently developed ISE

for paraquat could be used to monitor titrations of humic acid with this herbicide. Comparison with ultrafiltration results would be useful.

7.1.5. Total analysis of cationic and anionic species in filtrates from humic acid suspensions. This is needed in order to check for electroneutrality and possible passage of organic anions through ultrafiltration membranes.

References.

1.- Ashton F. and Craft A., Chapter 11 in Mode of Action of Herbicides., John Wiley and Sons, 2nd edition, 1975.

2.- New Scientist, May edition, 1986.

3.- Rose, M. S., The Research for an Effective Treatment of Paraquat Poisoning. Chemistry and Industry, 10, 413, 1975.

4.- Guy, R. D., Narine, D. R. and deSilva, S., Canadian Journal of Chemistry, 58(8), 547, 1980.

5.- Haniff, M. I., Ph.D. Thesis, Concordia University, 1984.

6.- Burns, I. G., Hayes, M. H. B. and Stacey, M., Weed Research, 13, 67, 1973.

7.- Burns, I. G., Hayes, M. H. B. and Stacey, M., Ibid, 13, 79, 1973.

8.- Katchalsky, A., Progress in Biophysics, 4, 1, 1954.

9.- Gamble, D. S., Schnitzer, M., Kendorff, H., and Langford, C. H., Geochimica et Cosmochimica Acta, 47, 1311, 1983.

10.- Collins, M. R., Gary, L. A. and Steelink, C,. Environmental Science and Technology, 20, 1028, 1986.

11.-Dzombak, D. A., Fish, W. and Morel, F. M. M., Environmental Science and Technology, 20(7), 669, 1986.

12.- Fish, W., Dzombak, D. A. and Morel, F. M. M., Environmental Science and Technology, 20, 676, 1986.

13.- Underdown, A. W., Langford, C. H. and Gamble, D. S., Environmental Science and Technology, 16, 132, 1985.

14.- Marinsky, J. A. and Ephraim J., Environmental Science and

Technology, 20, 349, 1986., 20, 354, 1986.

15.- Marinsky, J. A. and Ephraim J., Ibid, 20, 367, 1986.

16.- Marinsky, J. A. and Ephraim J., Ibid, 20, 349, 1986.

17.- Merle, Y. and Marinsky, J. A., Talanta, 31, 199, 1984.

18.- Calderbank A and Slade P., in Chapter 11 in Herbicides: Chemistry, Degradation and Mode of Action., Kearney P. C. and Kaufman D. D., Vol 2, 2nd edition, Marcel Dekker.

19.- Lewin, R. Science 229, 257, 1985.

20.- Calderbank A and Slade P., in Chapter 11 in Herbicides: Chemistry, Degradation and Mode of Action., Kearney P. C. and Kaufman D. D., Vol 2, Marcel Dekker.

21.- Bullivant, C. M., British Medical Journal, 1, 1272, 1966.

22.- Smith, D. C. and Heath, D., CRC Critical Reviews in Toxicology, 4, 411, 1976.

23.- Lewin, R., Science, 229,257, 1985.

24.- Seiber, J. N. and Woodrow, J. E., Archives of Environmental Contamination and Toxicology, 10, 133, 1981.

25.- Lott, P. F. and Lott, W. J., Journal of Chromatographic Science, 16, 390, 1978.

26.- Franke, G., Pietrulla, W. and Preussner, K., Z. Analytical Chemistry, 298, 38, 1979.

27.- Van Emon, J., Hammock, B. and Seiber, J. N., Analytical Chemistry, 58, 1873, 1986.

28.- Stevenson, F. J., Humus Chemistry, 1982.

29.-Ledwith, A. and Woods, H. J., Journal of Chemical Society

(C), 1422, 1970.

30.- White, B. G., Journal of Chemical Society, Part II, 2001, 1968.

31.- Ebbesen, T. W. and Ferraudi, G., Journal of Physical Chemistry, 87, 3717, 1983.

32.- Burns, I. G. and Hayes, M. H. B. Residue Reviews, 52, 117, 1973.

33.- Barnett, J. R., Hopkins, A. S. and Ledwith, A., Journal of the Chemical Society (Perkin II), 80, 1972.

34.- Kuczynsky, J. P., Milocavljevic, B. H., Lappin, A. G. and Thomas, J. K., Chemical Physics Letters, 104, 1984.

35.- Baumgartner, E., Bertolotti, S. G., Cosa, J. J., Gasponer, H. E., Hamity, M and Previtali, C. M., Journal of Colloid and Interfacial Science, 115, 417, 1987.

36.- Kobayashi, K. and Niki, K., Chemical Letters, 829, 1982.

37.- Khan, S. U., Residue Reviews, 52, 1, 1073.

38.- Khan, S. U., Journal of Environmental Quality, 3(3), 202, 1974.

39.- Van Dijk, H. Geoderma, 5, 53, 1971.

40.- Best, J. A., Weber, J. W., Soil Science, 114, 444, 1972.

41.- Narine, R. D., and Guy, R. D., Soil Science, 133(6),356, 1982.

42.- Sojo, L., Zienius, R. H., Langford, C. H. and Gamble, D. S., Environmental and Technology Letters, 8, 159, 1987.

43.- McCall, H. G., Bovey, R. W., McCully, M. C. and Merkle, M.

G., Weed Science, 20(3), 250, 1972.

44.- Weber, J. B. and Weed, S. B., Proceedings of the Soil Science Society of America, 32. 485, 1968.

45.- Weber, J. B., Ward, T. M. and Weed, S. B., Ibid, 32, 197, 1968.

46.- Weed, S. B. and Weber, J. B., Proceeding of the Soil Science Society of America, 33, 380, 1969.

47.- Hayes, M. H., Pick, M. and Thomas, B., Journal of Colloid and Interfacial Science, 65(2), 254, 1978.

48.- Schnitzer, M. and Skin, S. I., Soil Science, 105, 392, 1968.

49.- Gill, R., Qua, S. C., Moffat, A. C., Journal of Chromatography, 255, 483, 1983.

50.- Buffle, J., Greter, F. L., and Haerdi, W., Analytical Chemistry, 49, 877, 1977.

51.- Perdue, E. M. and Lytle, C. R., Environmental Science and Technology, 17, 654, 1983.

52.- Sposito, G., CRC Critical Reviews in Environmental Control, 16(2), 193, 1986.

53.- Marinsky, J. A., Gupta, S. and Schindler, P., Journal of Colloid and Interfacial Science, 89(2), 401, 1982.

54.- Marinsky, J. A., Gupta, S. and Schindler, P., Journal of Colloid and Interfacial Science, 89(2), 412, 1982.

55.- Khan, S. U., Journal of Soil Science, 24(2), 244, 2973.

56.- Staub, C., Buffle, J. and Haerdi, W., Analytical Chemistry, 56, 2843, 1984.

57.- Buffle, J. and Staub, C., Analytical Chemistry, 56, 2837, 1984.

58.- Gamble, D. S., Haniff, M. I. and Zienius, R. H., Analytical Chemistry, 54, 732, 1986.

59.- Gamble, D. S., Haniff, M. I. and Zienius, R. H., Ibid., 54, 727, 1986.

60.- Guy, R. D., and Chakrabarti, C. L., Canadian Journal of Chemistry, 54, 2600, 1976.

61.- Ruzic, I., in Complexation of Trace Metals in Natural Waters, Kramer, C. J. M. and Dunker, J. C. (eds), Martinus Nihoff/Dr W. Junk Publishers, The Hague/Boston/Lancaster,1984.13

62.- Ruzic, I and Nikolic, S., Analytica Chimica Acta, 140, 331, 1982.

63.- Ruzic, I., Analytica Chimica Acta, 140, 99, 1982.

63a.- Morel, F. M. M., Dzombak, D. A. and Fish, W., Environmental Science and Technology, 21, 1135, 1987.

64.- Perdue, E. M. Reuter, J. H., and Ghosal, M., Geochimica and Cosmochimica Acta, 44, 1841, 1980.

65.- Saar, R. A., and Weber, J. H., Environmental Science and Technology, 14, 877, 1980.

66.- Kwak, C. T. and Mattai, J., Macromolecules, 19, 1663, 1986.

67.- Helfferich, F., Ion Exchange, sec 5-4, Page 157, McGraw Hill Book Company Inc., 1962.

68.- Gamble, D. S., Langford, C. H. and Tong, J. P. K., Canadian Journal of Chemistry, 54, 1239, 1976.

68a.- Deczky, K. and Langford, C. H., Canadian Journal of Chemistry, 56, 1947, 1978.

69.- Manning, G., Accounts of Chemical Research, 12, 443, 1979.

70.- Manning, G., Reviews of Biophysics, 8, 179, 1978.

71.- Hayes, M. H. B., Residues Review 57, 19, 1975.

72.- Chamlian, R. and Sojo, L., Unpublished Results, 1987.

Appendix 1

1.1. Calculations.

1.1.1. Binding curves

The amount of bound of a particular cation was determined by subtracting the amount recovered or "free" from the initial amount added. Triplicate results at least were secured for all titrations curves. In some cases up to six replicate were obtained. The batch titration curves obtained were fitted to polynomials by a least squares BASIC routine written by the authors. In a few cases the titration curves were split into two straight line sections. The experimental error was determined by taking the fitted titration curve as the average and subtracting experimental values from it. Table 29 shows the results of such a data treatment for the titration of humic acid with paraquat at pH 4.00

1.1.2. Equilibrium Functions.

Average equilibrium functions for single cation experiments were calculated by Equations 16 on Page 16
A fitted titration curve was generated for the experimental range covered. This provided averaged values for the free cations in solution, as well as amounts bound. The whole calculation was done using BASIC routines KM.BAS and KSM.BAS written by the author. These programs provided K and K X_{SH2} values. The

plots of $\bar{K} X_{SH2}$ versus X_{SH2} were fitted to polynomials and their derivatives gave the differential equilibrium functions scans. The relative errors in $\bar{K}$ and K are similar to those for the binding curves, ranging from 1 to 15 % approximately.

For the cases with more than one cation, the average equilibrium function was determined directly from the averaged experimental results.

Table 29

Paraquat Titration of LHA at pH 4

mmoles/gr total	mmoles/gr free	mmoles/gr calculated	Relative Error
0.04992	0.0550	0.0547	0.51
0.10346	0.0460	0.0506	-9.3
0.10750	0.0560	0.0507	10.5
0.14536	0.0545	0.0534	2.0
0.17021	0.0499	0.0573	-13.00
0.19244	0.0589	0.0622	-5.2
0.22822	0.0664	0.0726	-8.5
0.29866	0.0693	0.0901	-23.1
0.31833	0.1077	0.1014	6.13
0.49174	0.2410	0.2248	-4.12

Appendix 2

2.1 Laurentide Humic Acid Titration Data

Table 30

Laurentide Humic Acid Titration
0.100 gram in 100 mLs double distilled H_2O
0.1 M NaOH

mLs	H^+ Molarity	Gel Phase Acid moles
0.000	2.907×10^{-4}	2.190×10^{-4}
0.100	1.654×10^{-4}	2.213×10^{-4}
0.200	1.516×10^{-4}	2.125×10^{-4}
0.300	9.468×10^{-5}	2.080×10^{-4}
0.400	5.264×10^{-5}	2.021×10^{-4}
0.500	3.127×10^{-5}	1.941×10^{-4}
0.600	1.917×10^{-5}	1.853×10^{-4}
0.700	1.155×10^{-5}	1.758×10^{-4}
0.900	1.008×10^{-5}	1.557×10^{-4}
1.000	9.829×10^{-6}	1.456×10^{-4}
1.100	1.083×10^{-5}	1.352×10^{-4}
1.200	9.834×10^{-6}	1.252×10^{-4}
1.300	9.862×10^{-6}	1.150×10^{-4}
1.500	9.907×10^{-6}	9.468×10^{-5}
1.600	9.428×10^{-6}	8.457×10^{-5}
1.700	8.568×10^{-6}	7.450×10^{-5}
1.800	7.722×10^{-6}	6.442×10^{-5}
1.900	6.624×10^{-6}	5.438×10^{-5}
2.000	4.270×10^{-6}	3.939×10^{-5}
2.100	3.943×10^{-6}	2.434×10^{-5}
2.200	2.647×10^{-6}	1.423×10^{-5}
2.300	1.596×10^{-6}	4.123×10^{-6}
2.400	1.470×10^{-6}	1.504×10^{-7}

Table 31

Laurentide Humic Acid Titration
0.100 gram in 100 mLs double distilled H_2O
0.1 M NaOH

mLs	H^+ Molarity	Gel Phase Acid moles
0.000	6.778×10^{-4}	1.870×10^{-4}
0.100	6.175×10^{-4}	1.826×10^{-4}
0.200	5.693×10^{-4}	1.770×10^{-4}
0.300	5.297×10^{-4}	1.706×10^{-4}
0.400	4.796×10^{-4}	1.652×10^{-4}
0.500	4.518×10^{-4}	1.576×10^{-4}
0.600	4.125×10^{-4}	1.512×10^{-4}
0.700	3.706×10^{-4}	1.450×10^{-4}
0.800	3.340×10^{-4}	1.383×10^{-4}
0.900	3.189×10^{-4}	1.295×10^{-4}
1.000	2.823×10^{-4}	1.142×10^{-4}
1.100	2.649×10^{-4}	1.142×10^{-4}
1.350	1.954×10^{-4}	9.531×10^{-5}
1.400	1.808×10^{-4}	9.161×10^{-5}
1.500	1.681×10^{-4}	8.253×10^{-5}
1.600	1.323×10^{-4}	7.581×10^{-5}
1.700	1.196×10^{-4}	6.675×10^{-5}
1.800	1.033×10^{-4}	5.805×10^{-5}
1.900	8.749×10^{-5}	4.931×10^{-5}
2.000	7.060×10^{-5}	4.078×10^{-5}
2.100	6.485×10^{-5}	2.968×10^{-5}

Appendix 3

3.1. Redox Properties of Laurentide Humic Acid

Table 32

Redox Properties of Laurentide Humic Acid

No background electrolyte

ALPHA	pH	pK_{app}
0.117	3.537	4.413
0.108	3.781	4.700
0.143	3.820	4.597
0.161	4.024	4.740
0.185	4,279	4.922
0.253	4.505	4.974
0.291	4.717	5.103
0.373	4.937	5.164
0.413	5.008	5.159
0.455	4.965	5.044
0.495	5.007	5.015
0.536	5.006	4.927
0.618	5.004	4.795
0.659	5.026	4.739
0.740	5.112	4.658
0.781	5.179	4.627
0.841	5.370	4.645
0.862	5.404	4.610

Table 33

Redox Properties of Laurentide Humic Acid

0.1 M NaCl background electrolyte

ALPHA	pH	pK_{app}
0.274	3.209	3.632
0.296	3.245	3.620
0.322	3.276	3.600
0.343	3.329	3.600
0.375	3.345	3.570
0.399	3.385	3.562
0.424	3.431	3.565
0.450	3.476	3.563
0.485	3.496	3.522
0.511	3.550	3.529
0.546	3.577	3.496
0.621	3.709	3.494
0.636	3.743	3.500
0.672	3.774	3.463
0.699	3.878	3.513
0.735	3.922	3.480
0.769	3.986	3.463
0.804	4.058	3.445
0.838	4.151	3.437
0.882	4.113	3.240
0.909	4.387	3.389

Appendix 4

4.1. Carboxyl acid content in gel phase.

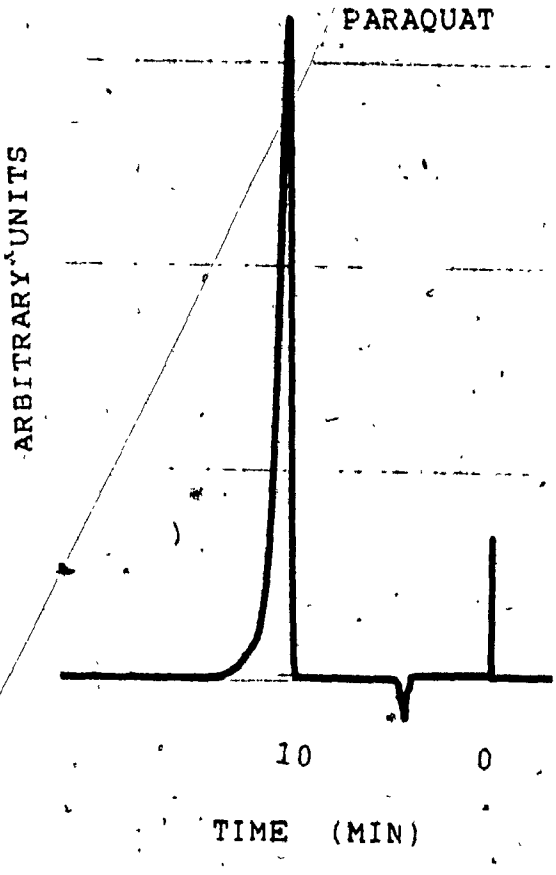
Table 34

Gel Phase Acid as a function of volume of base added to 0.100 g in 100 mLs of d.d H_2O. 0.1 M NaOH

$$Q_{GH} = C_0 + C_1 V_b + C^2 V_b^2 + C_3 V_b^3 + C_4 V_b^4$$

Coefficient	Calculated value
C_0	2.206×10^{-4}
C_1	-1.560×10^{-5}
C_2	-9.691×10^{-5}
C_3	4.524×10^{-5}
C_4	-7.440×10^{-6}

Appendix 5



HPLC Chromatogram of paraquat in humic acid suspension after filtration through a YM2 membrane.