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HEAVY METAL REMOVAL WITH STARCH XANTHATE AND STARCH WITH POTASSIUM HYDROXIDE

by

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A Research Report
Presented to the Graduate Committee
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Master of Science

in

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5/17/76
(date)

Gary Poehlein
Professor in Charge

Chairman of the Department
of Chemical Engineering

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S. K. B.

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Abstract

Starch xanthate has been found to be very effective in the removal of heavy metals from waste water. The goals of this report are to: 1. Find the best method to make starch xanthate. 2. Discover how to achieve a high degree of substitution in starch xanthate. 3. Define the conditions under which the removal of metals is most complete.

There are two methods to make starch xanthate--
1. One-Step Crosslinking and Xanthation of Starch
2.Xanthation of previously crosslinked starch. The following modifications in the above methods are beneficial-- 1. Run the xanthation reaction at 32 F rather than room temperature to increase the degree of substitution. 2. Add some magnesium sulfate during the xanthation phase to decrease washing time and to increase the stability of the product. 3. Run the xanthation reaction for one or two hours instead of 16 hours. 4. Use potassium hydroxide instead of sodium hydroxide to produce the xanthate group. 5. Discontinue washing the product with ether. 6. Discontinue the intermediate heating step in the One-Step Crosslinking and Xanthation procedure. 7. Increase the ratios of hydroxide/starch and carbon disulfide/starch

to increase the degree of substitution.

While modifications 1, 4, and 7 increased the degree of substitution, the increase did not produce the desired effect on neutralizing ability. Neutralizing ability (gram starch needed to neutralize one mole of metal) showed little correlation with the amount of sulfur present. However, neutralizing ability decreased as the amount of sodium and potassium in the starch xanthate increased. This indicates that some or all of starch xanthate's neutralizing ability is due to the presence of bound sodium hydroxide and/or potassium hydroxide.

Final pH was an important factor in the removal of heavy metals. Fe^2 was removed effectively (less than 50 PPB) from pH 7.0 to 8.5 by both starch xanthate and starch with KOH. Mn^2 was removed effectively at pH 8.0 or greater by starch with KOH. Ni^2 was removed effectively by starch with KOH at pH 10.0 or greater. Zn^2 was removed effectively by starch with KOH in the pH range 9.0-10.0. Cr^3 was removed effectively in the pH range 7.0-8.0 by starch with KOH.and in the pH range 6.5-7.5 by starch xanthate. Cu^2 was removed effectively in the pH range 7.5-8.5 by starch xanthate and at pH 7.5 or above by starch with KOH.

Heavy Metal Removal with Starch Xanthate and Starch with Potassium Hydroxide

I. Introduction

Recent pollution control legislation passed by Congress has set stringent water pollution standards for 1977 and mandated zero discharge by 1985. Even though these standards may be eased to lessen the economic impact of environmental control on industry and the economy in general, the standards agreed upon will still be a severe challenge to available technology. This report concentrates on removing heavy metals from waste waters.

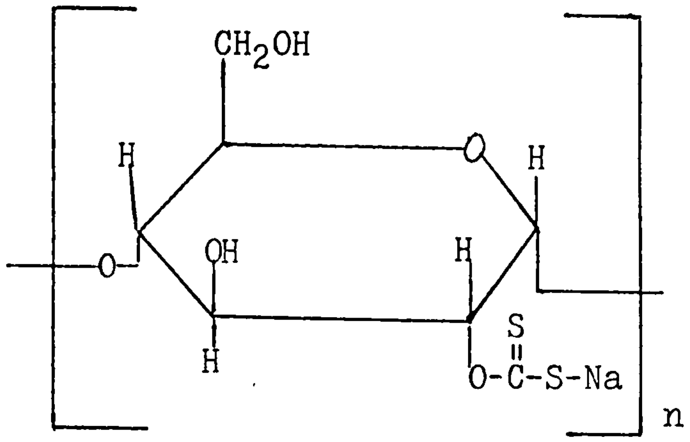
Dr. R. E. Wing and associates[14] have found that crosslinked starch xanthate can remove some heavy metals (Cu^2, Ni^2, Cd^2, Pb^2, Cr^3, Zn^2, Fe^2) well below Illinois discharge limits. Since starch xanthate reacts quickly and is easily filtered from waste water, it represents a promising solution to the presence of heavy metals.

The goals of this report are to: 1. Find the best method to make Starch xanthate. 2. Discover how to achieve a high degree of substitution in starch xanthate. 3. Define the conditions under which the removal of heavy metals is the most complete.

II Discription of Starch Xanthate

The structure of starch xanthate is believed to be:

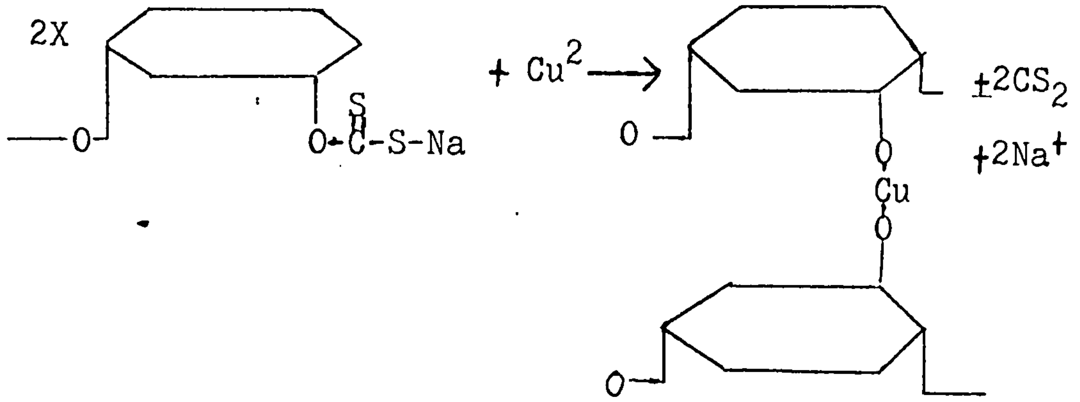
Figure 1



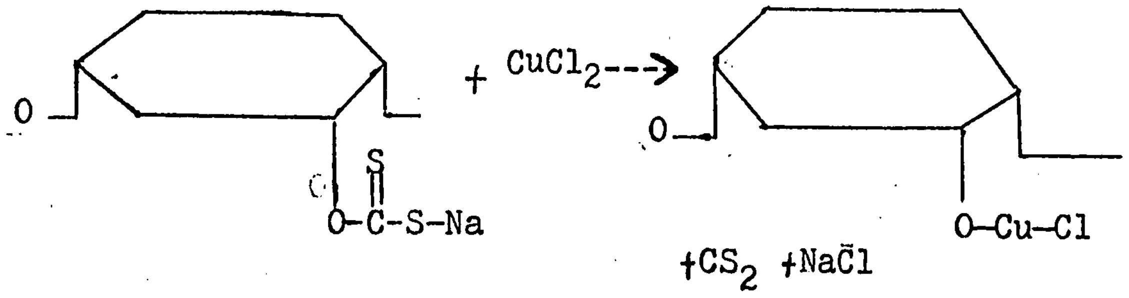
The xanthate group may be substituted at the other two hydroxide positions. Since degree of substitution numbers above 1 have been obtained[3], apparently more than one of these positions may contain the xanthate group at the same time. However, in most cases numerous anhydroglucose units in the starch chain are not substituted with the xanthate group. The starch is crosslinked during preparation of starch xanthate or previously crosslinked starch is used to make the starch xanthate insoluble in water. This eliminates the need for a cationic polymer to aid in removal.[15]

Starch xanthate is a yellow powder that frequently has a noxious odor (due to sulfur by-products). It is easily suspended in water although it is not soluble. If left at room temperature, starch xanthate will deteriorate and become more noxious. It will remain stable if stored at 0°C.

Although the exact method by which starch xanthate removes heavy metals from waste waters has not been determined, two reaction mechanisms have been proposed. One proposed reaction mechanism[7] is--



However, the amount of starch xanthate required for neutralization in my experiments consistently refuted this mechanism. I was able to neutralize one mole of metal with less than two moles of the xanthate group. A second proposed mechanism is--



A U. S. patent has been approved for the removal of mercury by this mechanism. Some CS_2 is evolved during the neutralization reaction. However, CS_2 is also evolved when starch xanthate is suspended in water. Therefore, my experiments neither confirm nor refute this mechanism.

Starch xanthate also contains some moisture (10%-14%[14]) and a considerable amount of bound hydroxide, NaOH and KOH. This bound hydroxide accounts for the basic character of starch xanthate. Its effect on metal removal will be discussed below.

III. Preparation of Starch Xanthate

One of the primary goals of this research effort was to find an easy method to produce a good quality starch xanthate with a high degree of substitution. After producing many poor quality batches with low degrees of substitution I eventually produced a starch xanthate with a degree of substitution of 0.4. A good quality xanthate has little odor, is easily suspended in water, has few by-products, and is easily washed (washing agents filter through it quickly).

There are two different procedures for making starch xanthate. In the first method a highly crosslinked starch is reacted with sodium hydroxide (or potassium hydroxide) and carbon disulfide.

> "A highly crosslinked starch (53-91E, Vulca 100, 10136-1) (35.4 g) was slurried in water (225 ml), sodium hydroxide (8 g) in water (100 ml) was added, and the mixture was stirred 30 min. Then carbon disulfide (5ml) was added and the mixture was stirred 16 hr. at 25°C. The slurry was filtered through a coarse fritted-glass funnel and the solid was washed successively with water (75 ml), several portions of acetone (500 ml total), and ether (100 ml). After drying in a vacuum oven at 25°C for 2 hr., the pale-yellow solid was stored at 0°C in a closed container."[14]

The second method has been called the One-Step Crosslinking and Xanthation of Starch. After commercial corn starch has been crosslinked, it is reacted with sodium hydroxide (or potassium hydroxide) and carbon disulfide.

> "Commercial corn starch (100g, 10% H_2O) was slurried in water (150 ml) containing sodium chloride (1.5 g) and epichlorohydrin (5.5 ml). To this slurry was added potassium hydroxide (6 g) in water (40 ml) slowly over 30 min. The slurry was warmed to 50°C and then cooled to room temperature. Water (50 ml) and epichlorohydrin (2 ml) were added and the mixture was stirred for 16 hr. The suspension, now containing highly crosslinked starch, was treated with sodium hydroxide (48 g) in water (250 ml). Carbon disulfide (15 ml) was added near the bottom of the beaker and the mixture was stirred for 16 hr. The mixture was filtered and was washed with water (100 ml), acetone (750 ml), and ether (200 ml). After drying for 2 hr. under vacuum, the product was analyzed."[14]

Several modifications of the above procedures were tried in order to improve the degree of substitution in the starch xanthate. The first modification, as suggusted by Swanson[8], was the application of heat during the final mixing phase in order to increase the rate of reaction. This was done in an erlenmeyer flask with a cooling jacket at the top. The cooling jacket was added to the flask to condense water and especially carbon disulfide. When high heat was applied, the rate of evaporation and condensation was noticeably vigorous. However, the resulting product had a poor degree of substitution (see Table 1, batch #11). When a moderate heat was used, the rates of evaporation and condensation were correspondingly lower. The degrees of substitution with moderate heat (see Table 1, batch #12) were good, but inferior to results obtained at room temperature (see Table 1, batch #16).

As mentioned above reaction at 32°F was found to promote a good degree of substitution. This modification was suggested by the poor results at high temperatures and by the results of Adamek and Purves[1]. They found that the maximum degree of substitution was obtained at 5°C (41°F), as compared to 23°C(73.4°F), and at a reaction time of 24 hours. To obtain the

Table 1

Batch Preparation Data

Batch #	Hydroxide	Intermediate Warming?	Stirring Time(hr)	Amount of Extra Water Added(ml)
1	NaOH	Yes	1	2000
2	NaOH	Yes	15	200
3	NaOH	-	-	-
4	NaOH	Yes	15	400
5	NaOH	-	-	-
6	NaOH	Yes	17	500
7	NaOH	-	-	-
8	NaOH	No	17	250
9	KOH	No	17	500
10	KOH	-	-	-
11	KOH	-	-	-
12	KOH	-	-	-
13	KOH	-	-	-
14	NaOH	-	-	-
15	KOH	-	-	-

Table 1 (cont.)

Batch Preparation Data

Batch #	Procedure	Grams Starch	Moles Alkali / Mole Starch	Moles CS_2 / Mole Starch
1	A*	400	1.944	0.4148
2	A	100	1.944	0.4148
3	B**	35.4	0.915	0.3803
4	A	100	1.944	0.4148
5	B	177	0.7322	0.3803
6	A	200	1.944	0.7405
7	B	177	1.830	0.7606
8	A	100	1.944	0.4039
9	A	100	1.944	0.4039
10	B	177	0.915	0.3803
11	B	35.4	0.915	0.3803
12	B	35.4	0.915	0.3803
13	B	35.4	7.322	1.5212
14	B	35.4	7.322	1.5212
15	B	35.4	0.915	0.3803

*One-step Crosslinking and Xanthation of Corn Starch

**Xanthation of Previously Crosslinked Starch

Table 1 (cont.)

Batch Preparation Data

Batch#	Stirring Heat	Stirring Time(hr)	% Sulfur	D. S.	Neutralizing Ability*
1	No	16	0.25	0.006	6081
2	No	16	2.74	0.071	-
3	No	9	0.57	0.015	-
4	No	17	3.10	0.082	1409
5	No	17	1.30	0.034	16548
6	No	17	2.50	0.066	1865
7	No	17	3.40	0.091	1310
8	No	1	3.00	0.080	708
9	No	1	3.50	0.095	786
10	No	2	3.15	0.085	1568
11	Yes	3	0.17	0.004	-
12	Yes	2	1.90	0.050	3321
13	Yes	2	5.27	0.148	1377
14	Yes	1	4.80	0.132	1381
15	32°F	2	3.36	0.091	1894

*Grams Starch Required To Neutralize One Mole of Metal

Table 2

Batch Preparation Data

Batch #	Procedure	Extra Water Added	Grams Starch	Moles KOH / Mole Starch	Moles CS_2 / Mole Starch
16	B**	0	35.4	3.660	1.5212
17	A*	500	100	1.944	0.4039
18	A	?	100	7.776	1.6156
19	A	?	400	7.776	1.6156
20	A	0	100	Waste Liquor from #19	
21	B	100	100	4.05	0.5385
22	B	100	100	1.01	2.154
23	Hydroxide Only Added	0	35.4	3.66	0

*One-step Crosslinking and Xanthation of Corn Starch

**Xanthation of Previously Crosslinked Starch

All of the above batches were prepared with KOH and stirred for two hours after addition of CS_2

Table 2 (cont,)

Batch Preparation Data

Batch #	% Sulfur	Degree of Substitution	Neutralizing Ability	Wt. % K
16	10.95	0.345	722	12.9
17	5.95	0.169	589	17.4
18	12.40	0.404	655	11.3
19	-	-	-	-
20	0.11	0.003	2511	3.05
21	2.78	0.075	386	20.3
22	2.49	0.066	600	8.41
23	0	0	622	12.1

lower reaction temperature the reaction beaker was placed in a larger beaker containing ice water during the final mixing phase. This reaction at 32°F produced several batches of starch xanthate with good degrees of substitution (see Table 2, batch #s 16-18).

A troublesome experimental difficulty was the long time it took to wash the starch xanthate with water and acetone. The addition of magnesium sulfate (about 10 g) after the hydroxide has been added produces a starch xanthate which washes quickly. Dr. R. E. Wing, who suggested this addition in a private communication, also reports that the addition of magnesium sulfate increases the stablility of starch xanthate. He reports no deterioration after several months of storage at room temperature. It should also be noted that washing with ether was discontinued. It filtered through the starch xanthate too quickly and removed few, if any, of the undesireable by-products.

Another modification of the starch xanthate preparation procedure was shortening of the reaction time. Although Wing[14] suggested 16 hours as the reaction time, and Adamek[1] found 24 hours was the best reaction time, Lancaster[4] found that most of the xanthation occurs in the first hour. I have found that two hours is sufficient time for the carbon disulfide to react. (Note: The stirring time listed on the first page of Table 1 is the crosslinking reaction time.)

Adamek and Purves[1] tried xanthations of starch with several hydroxides. They found that the use of potassium hydroxide rather than sodium hydroxide more than doubled the degree of substitution obtained. Table 3 lists three groups of xanthations in which the method of preparation, the ratio of alkali to starch, and the ratio of carbon disulfide to starch are all the same. In each of these three groups the batch prepared with Potassium hydroxide had a higher degree of substitution.

Wing[14] suggested that the intermediate heating, the additional water, and the additional epichlorohydrin during crosslinking of the One-Step Crosslinking and Xanthation procedure were unnecessary. Batches 8, 9, 17, 18, 19, and 20 were produced without this step. Its elimination produced no notable effect. A peculiar difficulty of this procedure occurred with the addition of the sodium hydroxide solution. The mixture immediately became extremely viscous. It was

Table 3

Sulfur Content in Sodium S.X.

vs Potassium S.X.

Batch #	Hydroxide	Alkali/Starch	CS_2/Starch	%Sulfur	Degree of Substitution
13	KOH	7.322	1.5212	5.27	0.148
14	NaOH	7.322	1.5212	4.80	0.132
10	KOH	0.915	0.3803	3.15	0.085
3	NaOH	0.915	0.3803	0.57	0.015
9	KOH	1.944	0.4039	3.50	0.095
2	NaOH	1.944	0.4148	2.74	0.071
4	NaOH	1.944	0.4148	3.10	0.082

necessary to add additional water to the mixture to decrease its viscosity and allow it to be mechanically stirred again.

Two obvious modifications designed to increase the degree of substitution are increasing the amount of alkali and increasing the amount of carbon disulfide. Increasing both at the same time yields a higher degree of substitution (Table 1, batch #s 13 and 14, Table 2, batch #s 16 and 18). However, increasing only alkali or only carbon disulfide does not produce good results (Table 2, batch #s 21and22).

Therefore, the above modifications to the One-Step Crosslinking and Xanthation of Starch will make it look like this--

> Commercial corn starch (100 g) was slurried in water (150 ml) containing sodium chloride (1.5) and epichlorohydrin (5.5 ml). To this slurry was added potassium hydroxide (6 g) in water (40 ml) over a period of 30 minutes. The mixture was then stirred for two hours. The reaction vessel was then placed in an ice bath. Potassium hydroxide (268.8 g) in water (1500 ml), magnesium sulfate (10 g) in water (100 ml), and carbon disulfide (60 ml) were added. After being stirred

for two hours the mixture was filtered and washed with water (500 ml) and several portions of acetone (500 ml total). The starch xanthate was then dried at room temperature under vacuum.

The xanthation of previously crosslinked starch would be done like this--

A Highly crosslinked starch (35.4 g of the Hubinger Co.'s HPD 53-91E) was slurried in water (225 ml). Potassium hydroxide (45 g) in water (200 ml) was added and the mixture was stirred for 30 minutes. The reaction vessel was placed in an ice bath. Magnesium sulfate (5 g) in water (100 ml) and carbon disulfide (20 ml) were added and the mixture was stirred for 2 hours. The mixture was then filtered and washed with water (100 ml) and acetone (200 ml). The starch xanthate was dried at room temperature under vacuum.

IV. Degree of Substitution

Degree of substitution is a measure of the fraction of anhydroglucose units that have a xanthate chemical group substituted for an -OH group. Degree of substitution is calculated from the amount of sulfur present in the starch xanthate according to the formula--

$$D.S. = 162 \times (\%S) / (6400 - 98 \times (\%S))$$

for sodium starch xanthate. For potassium starch xanthate the formula is--

$$D.S. = 162 \times (\%S) / (6400 - 114 \times (\%S)).$$

These formulas neglect the presence of water and hydroxide in the starch xanthate. They also assume that all of the sulfur present is bound in the xanthate group.

Two methods of sulfur analysis were used. The first method was barium sulfate precipitation. This method gave low results for samples with more than 1% sulfur. Most of the sulfur analyses reported were done by the second method, the Schöniger determination of sulfur[13]. This method gave more reliable results.

I tried an indirect method of analysis. I mixed 1 g of starch xanthate in 100 ml of water and used the barium sulfate precipitation method of analysis on the mixture. Unfortunately, this method has two shortcomings. First, some of the sulfur is evolved as carbon disulfide when starch xanthate is mixed in water. Second, the starch xanthate is really suspended in the water. Therefore, a sample of the suspension that accurately represents its composition is difficult to obtain. I have come to the conclusion that this method of analysis is only worthwhile for an order of magnitude check on the other two methods of analysis above.

A high degree of substitution is desirable to decrease the amount of starch xanthate needed per mole of metal. If the second proposed reaction mechanism is indeed the correct one, then one mole of the xanthate group is needed to neutralize one mole of metal. However, my experiments did not confirm this ratio. I conducted tests on almost all of the starch xanthate batches to determine their neutralizing (metal-removing) ability. The results are shown in Table 1, Table 2, and in Figure 2. Figure 2 shows that there is little, if any, correlation between the sulfur content of starch xanthate and its neutralizing ability. A second order equation obtained from the LEAPS[5] program representing the data is $NA= 1475 - 2959S + 2192S^2$. This means that something else is responsible for most, if not all of starch xanthate's neutralizing ability.

Bound hydroxide is responsible for most of starch xanthate's neutralizing ability. Figure 3 is a graph of the neutralizing ability of starch xanthate vs. the amount of sodium and potassium present. The abscissa represents the neutralizing ability of any xanthate groups present plus the neutralizing ability of the bound hydroxide. This correlation is much better. A second order equation obtained from the LEAPS[5] program representing the data is $Y= 3319 - 13394X + 15391X^2$. These results raise the question--What is the xanthate group's role in metal removal?.

Direct methods of analysis for the xanthate group's presence are ineffective due to the bound hydroxide. It may be possible to wash out all of the hydroxide with water and acetone. However, it is unlikely that the xanthate group would remain stable. Washing with dilute acid would remove or destroy all of the hydroxide, but it would also destroy the xanthate group. Until starch xanthate can be prepared with little or no bound hydroxide, its neutralizing ability will be suspect.

Figure 2

Neutralizing Ability vs Sulfur Content

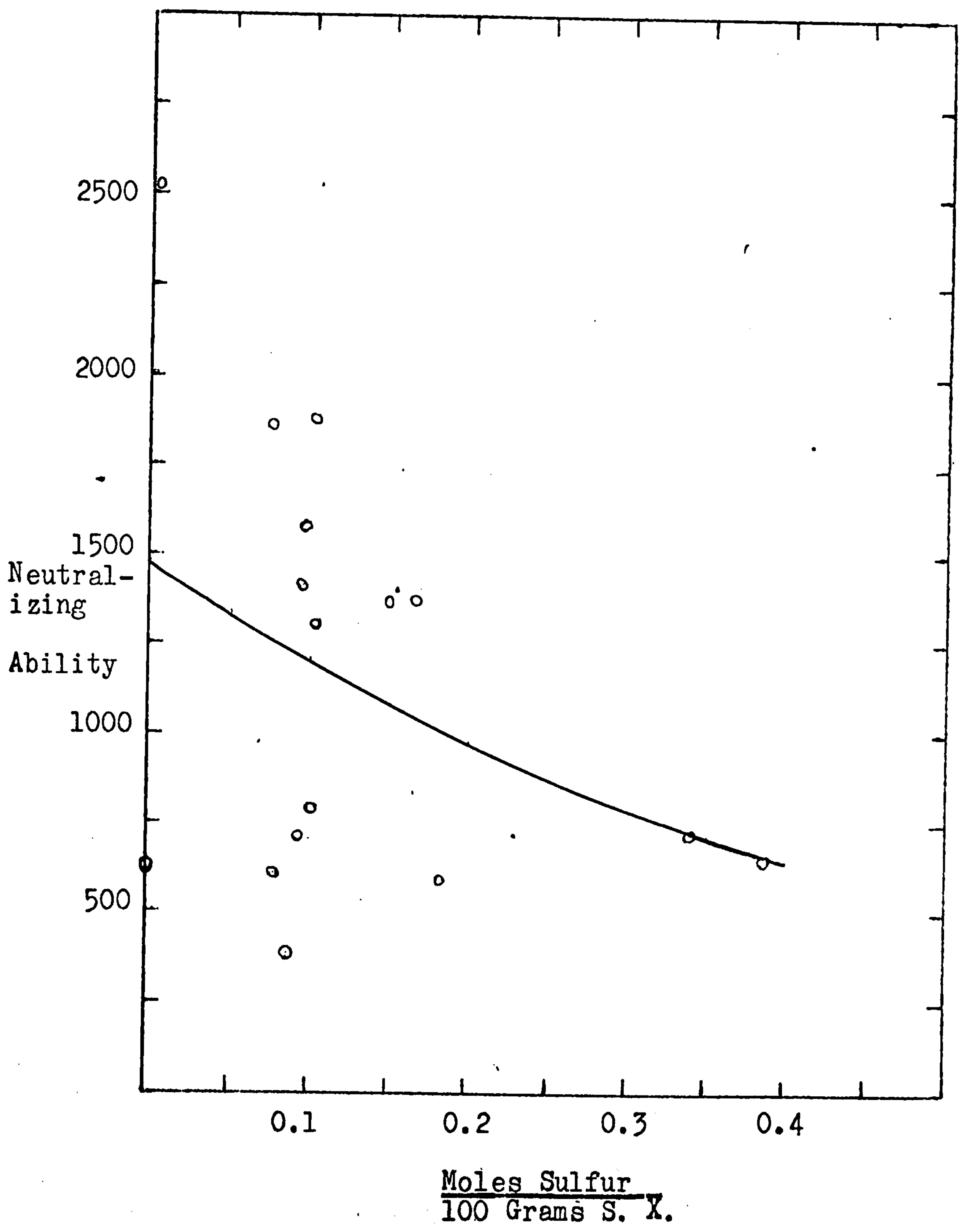
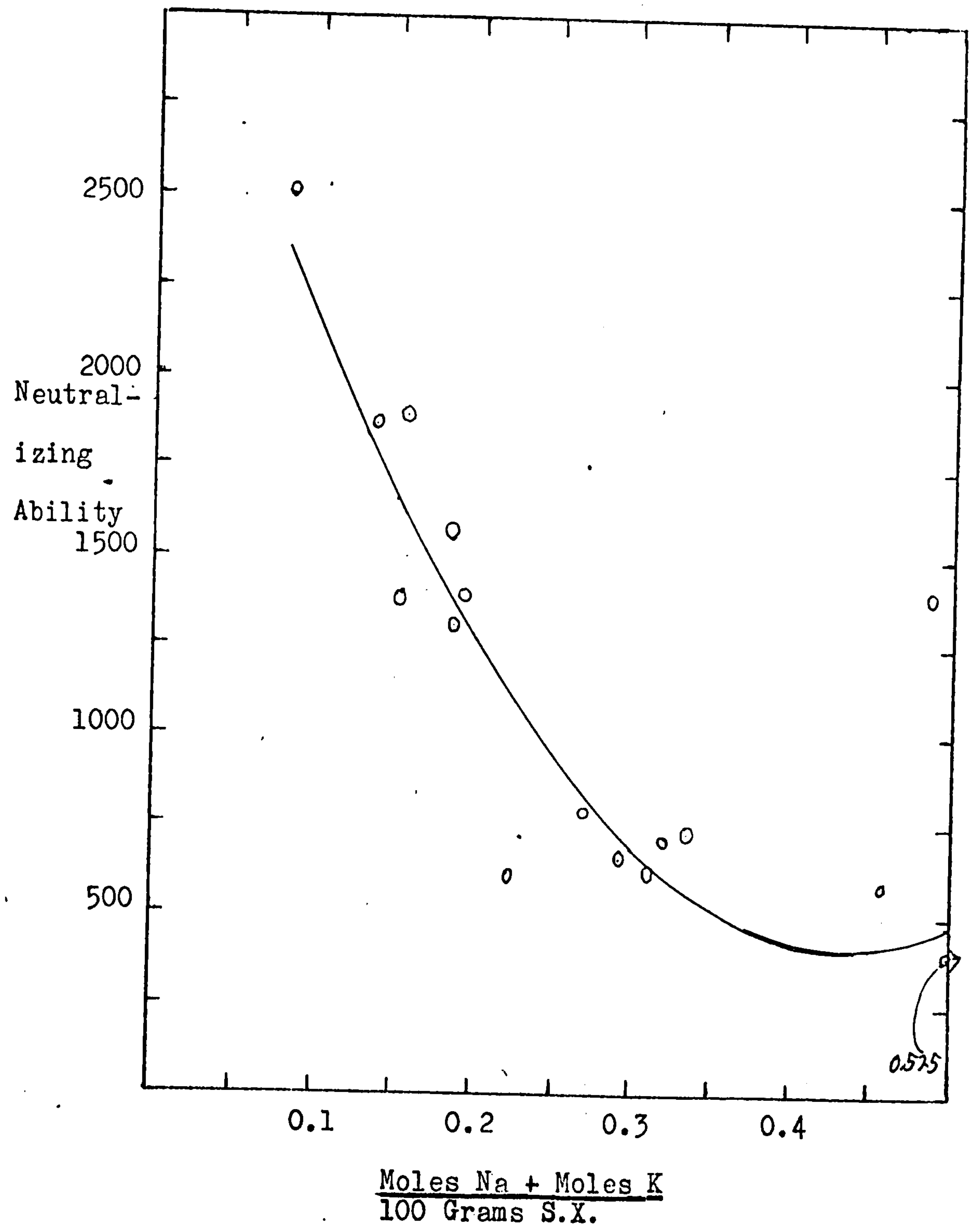


Figure 3

Neutralizing Ability vs Hydroxide Content



V. Removal of Heavy Metals

The most important characteristics of starch xanthate is its ability to remove heavy metals from waste waters. Swanson[9] and co-workers were successful in removing mercury with a starch xanthate-cationic polymer complex. Wing[15] and co-workers extended this method successfully to several other heavy metals. Wing[14] and co-workers claim to get good removal when using insoluble starch xaanthate (which eliminates the need for an expensive cationic polymer). The results of this study were not nearly as favorable as the results Dr. Wing[14] reported.

Although final pH was not considered to be an important factor by Dr. Wing[14,15], Weiner[12] and Dean[2] both cite pHs of precipitation for heavy metals. I found metal removal to be very pH dependent. Figures 4-9 graph metal removal vs. pH for Fe^2, Ni^2,Mn^2, Zn^2, Cr^3, and Cu^2 (initial concentration 25,000 PPB). Table 4 give the LEAPS[5] coefficients for the curves in these graphs which have the form $\log_{10}$(conc.)= B + A1 x pH + A2 xpH^2.

Ferrous iron is removed quite effectively in the pH range 7.0-8.5 by both starch xanthate and starch with potassium hydroxide. In this range it is removed

Figure 4

Concentration of Fe^2 vs pH

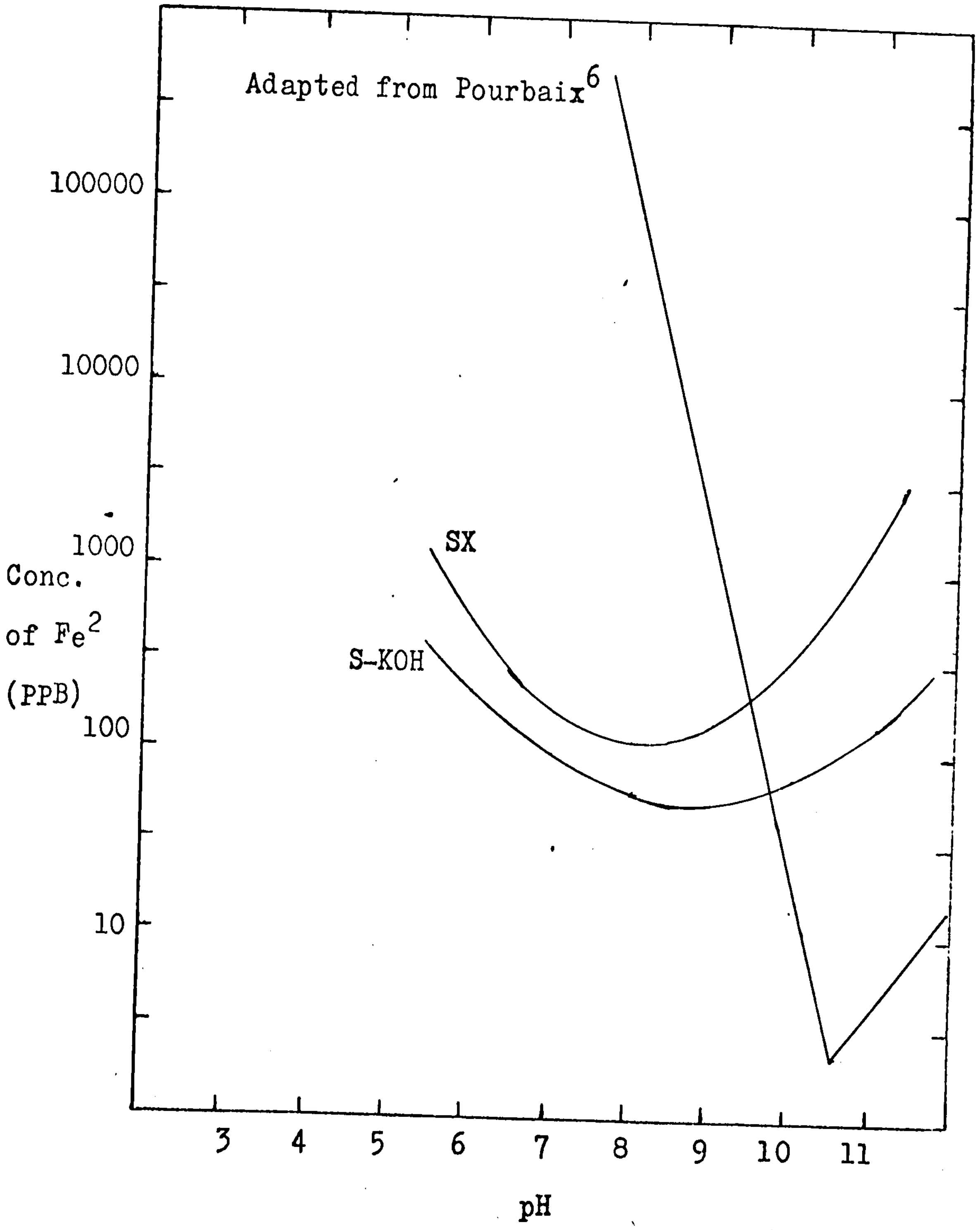


Figure 5

Concentration of Ni^2 vs pH

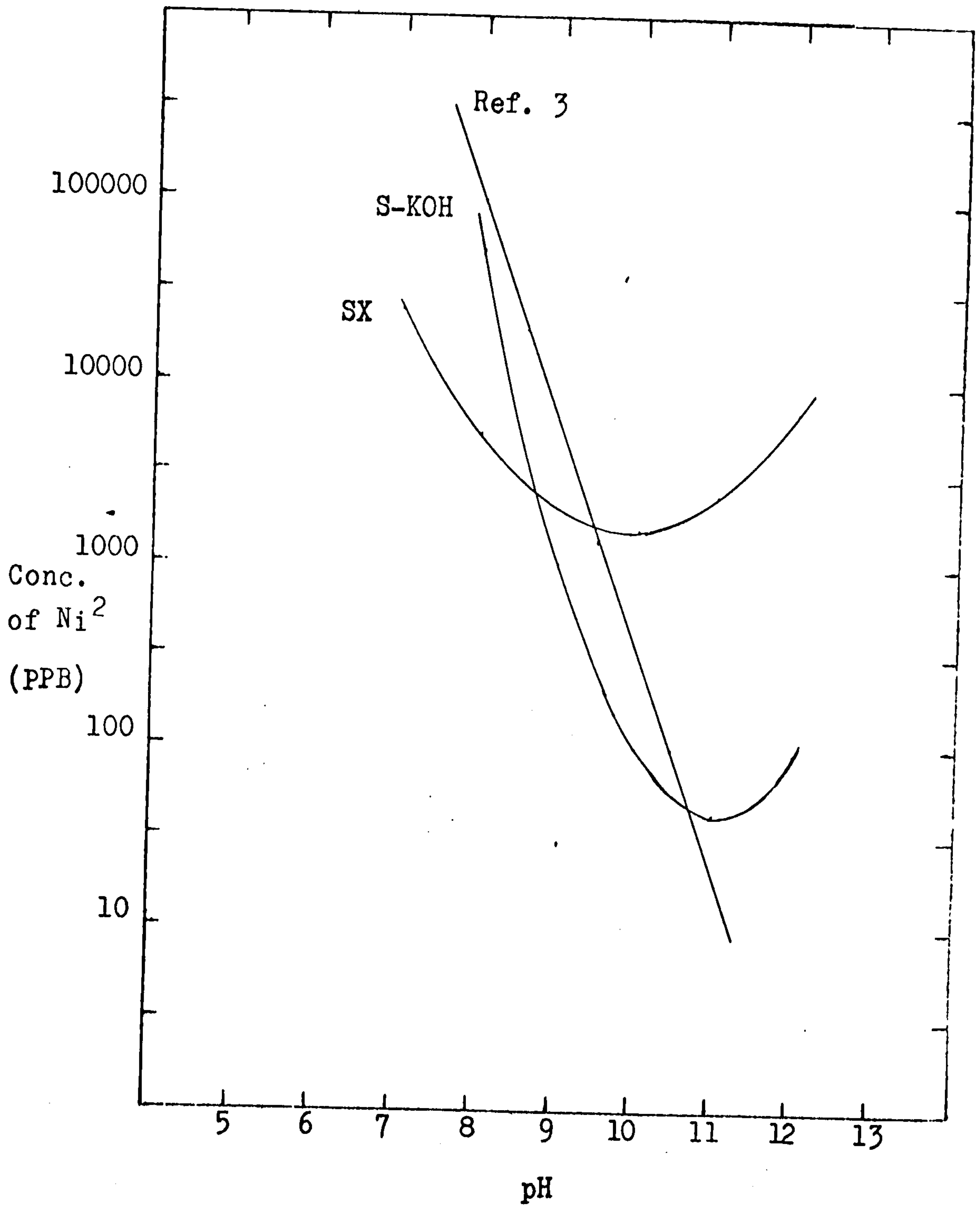


Figure 6

Concentration of Mn^2 vs pH

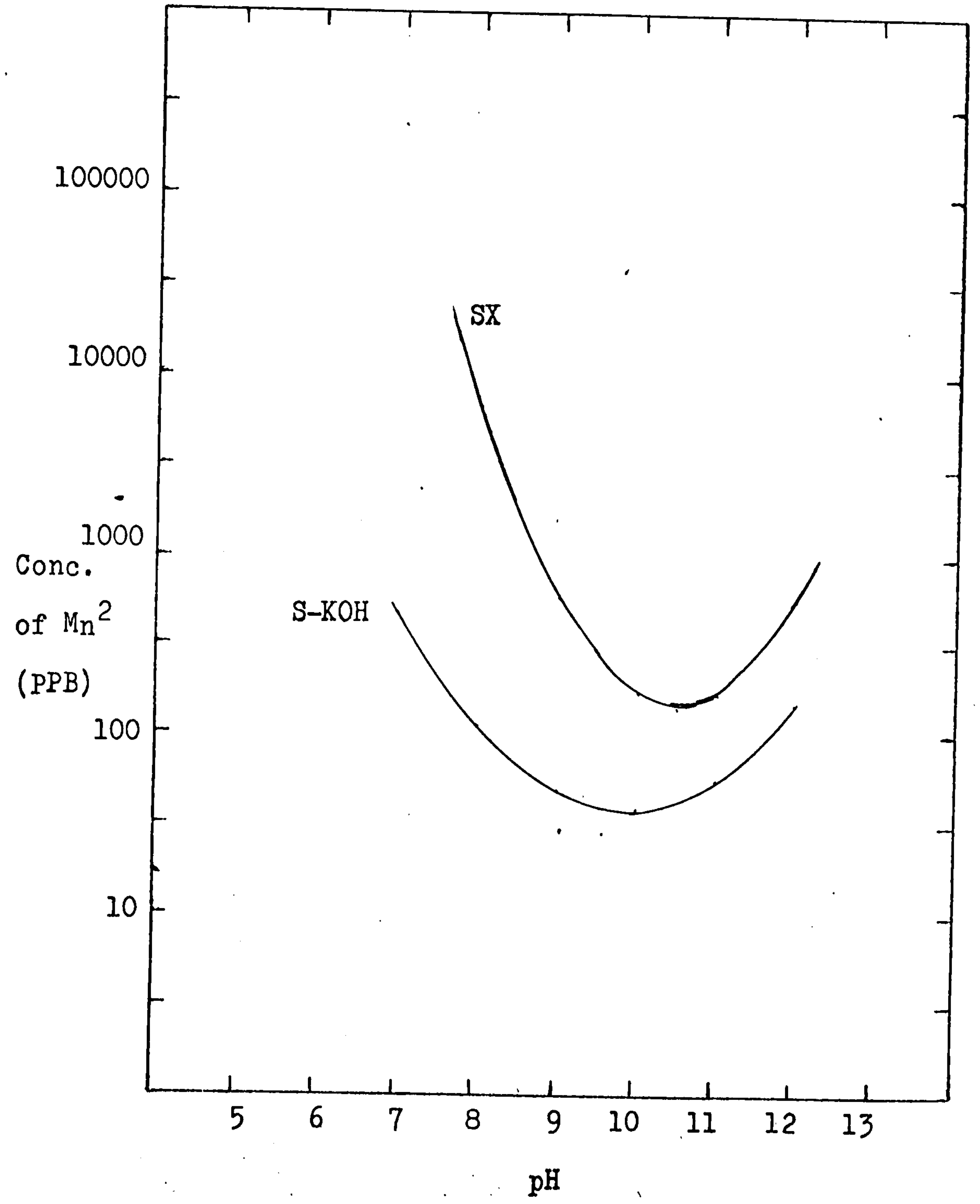


Figure 7

Concentration of Zn^2 vs pH

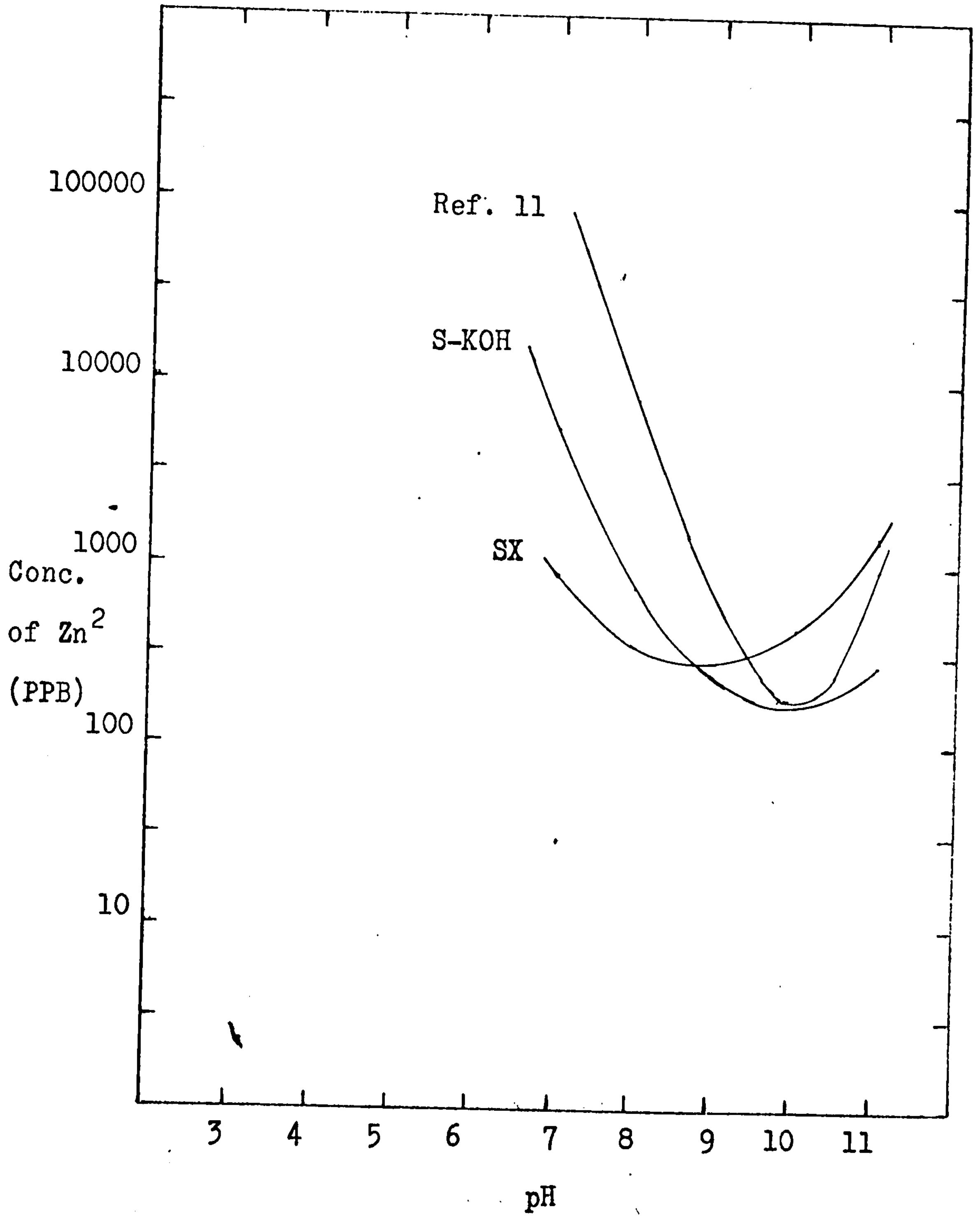


Figure 8

Concentration of Cr^3 vs pH

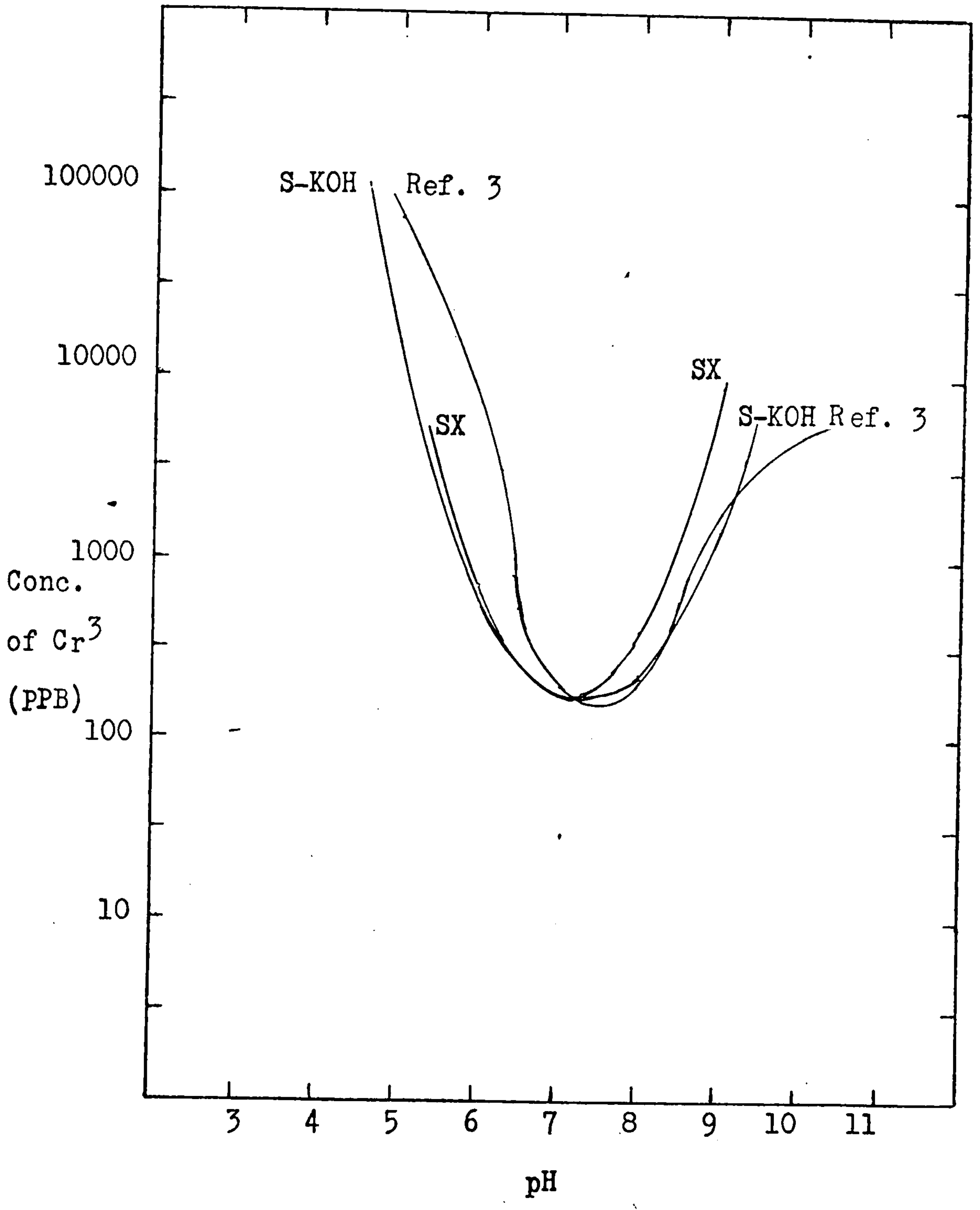


Figure 9

Concentration of Cu^2 vs pH

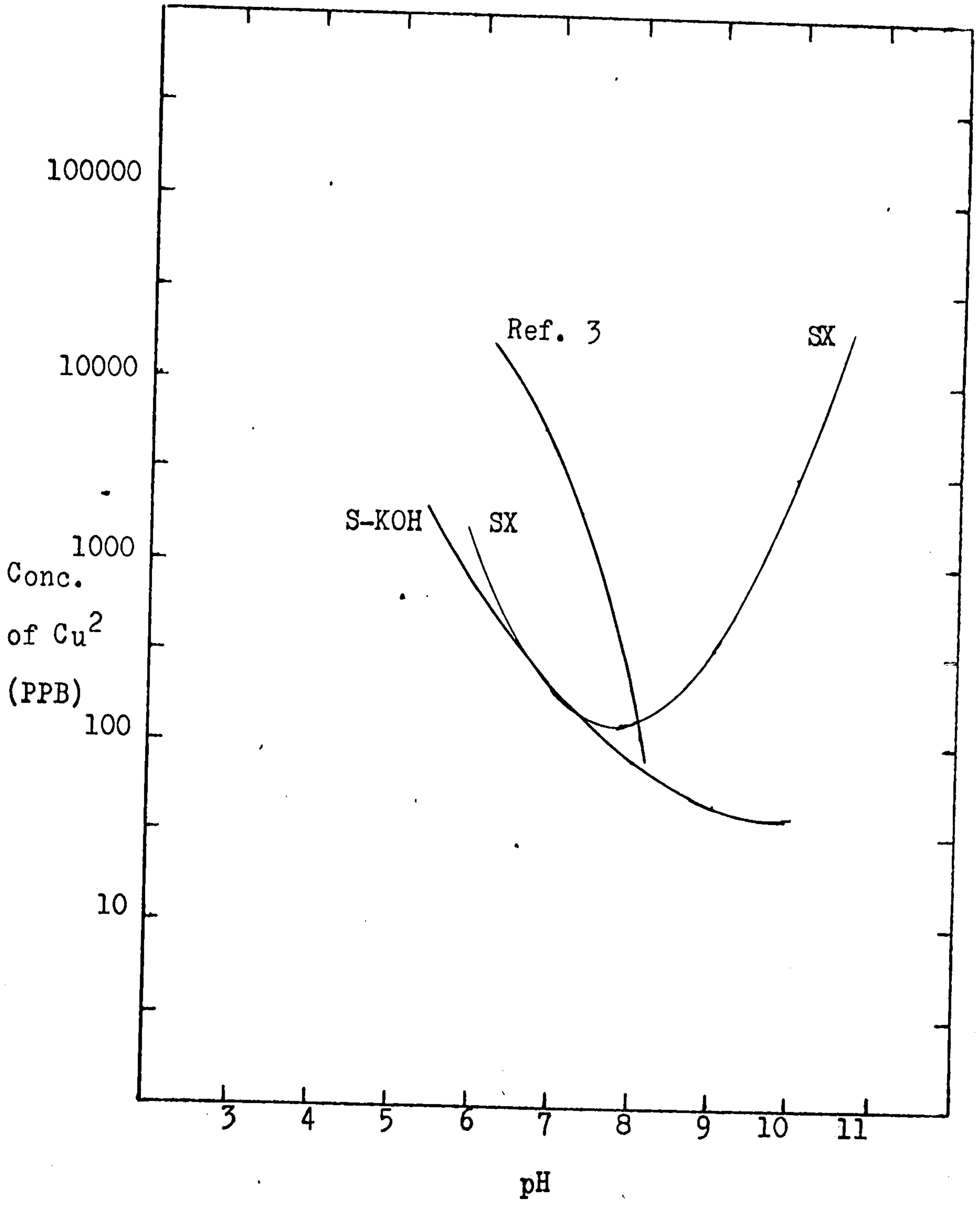


Table 4

LEAPS Coefficients

Metal	B	A1	A2
			Starch Xanthate
Fe^2	11.364	-2.283	0.140
Ni^2	17.132	-2.825	0.143
Zn^2	13.571	-2.523	0.143
Mn^2	31.296	-5.549	0.264
Cr^3	26.840	-6.903	0.484
Cu^2	19.029	-4.337	0.278
			Starch with KOH
Fe^2	7.720	-1.376	0.079
Ni^2	42.603	-7.443	0.338
Zn^2	20.213	-3.652	0.185
Mn^2	14.166	-2.548	0.129
Cr^3	21.852	-5.358	0.365
Cu^2	9.837	-1.673	0.085

to less than 50 PPB, my lower limit of analysis. Above 8.5 the iron begins to come back into solution.

Manganese is removed effectively by starch with potassium hydroxide above a pH of 8.0. Starch xanthate is not as effective, although the results are severely scattered (see Appendix 1.).

Nickel is removed effectively by starch with potassium hydroxide above a pH of about 10.0. Starch xanthate is not too effective in removing nickel.

Zinc is removed best by starch with potassium hydroxide in the pH range 9.0-10.0. The results with starch xanthate were too scattered to draw any conclusions about zinc and starch xanthate.

The removal of chromium by both starch with potassium hydroxide and starch xanthate followed the pattern predicted by the E.P.A.[3] The best removal occurred in the 6.5-8.0 pH range.

The removal of copper by starch with potassium hydroxide was at the lower limit of analysis when the pH was 7.5 or higher. Removal of copper by starch xanthate had a rather pronounced minimum at about 8.0. Although much of my data is scattered and some of it is inconsistent, there is one conclusion that I feel is valid. I believe that pH is a very important factor in heavy metal removal. Any method, including those noted above, that purports to remove metals independent of pH is very suspect in my eyes. In any event, there appears to be a set of conditions for each of the metals tested at which the residual is less than 50 PPB.

VI. Quality of the Effluent

As stated above, metal removal from waate waters can be very effective. However, in the process of removing metals some elements are added to the effluent. The addition of sodium starch xanthate to dilute solutions of metals (25 PPM) resulted in the presence of 20-100PPM of sodium in the effluent. The neutralized solutions contained from 0 to 50 PPM of sulfur. Total organic carbon levels were 0-20 PPM, but this amount would cause no BOD problems.

Another factor to consider is the final pH of the effluent. A pH above 9.0 would make the effluent unsuitable for discharge. Fe^2, Cr^3, Cu^2, Mn^2 can be removed at an acceptable pH. However, zinc and nickel pose a problem. Effective removal of zinc by starch with potassium hydroxide occurs from 9.0 to 10.0. Any removal process would have to be operated at the lower limit of this removal range. However, further work with starch xanthate could reveal an acceptable pH for removal.

Nickel poses a much more serious problem. It is removed effectively by starch with potassium hydroxide at pH 9.7 and above. Some form of pH lowering would have to be used after the starch with nickel was filtered out.

VII. Economic Considerations

An extensive economic analysis was not undertaken, but a number of factors can be pointed out. Wing[14] has estimated that starch xanthate could be produced for $.20-$.22 per pound. Assuming a neutralizing ability of 300 lb per lb-mole of metal, the cost of starch xanthate would be about $1.00 per pound of metal removed.

The removal process itself would be rather simple.

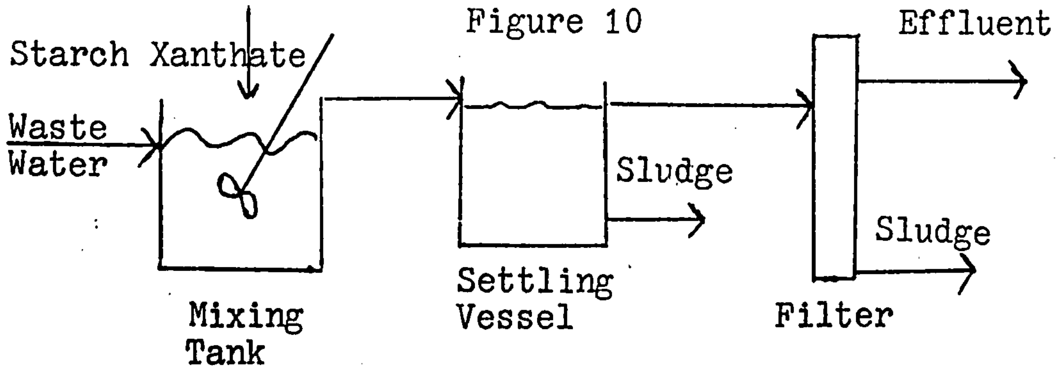


Figure 10

Due to the quick action of starch xanthate, the mixing tank might be replaced by 5-10 minutes of turbulent flow through a pipe.

Recovery of the metal from the sludge has been suggested. However, there must be many favorable factors present at the same time before this would be practical. First a starch xanthate or starch with potassium hydroxide must be used that has a low neutralizing ability (lb SX per lb-mole metal). Second, the sludge must have a high concentration of metal. Third, little acidity must be present in the waste water. If the pH is lowered to 2.0, twice as much starch xanthate is required. If the pH is lowered to 3.0, 10 times as much starch xanthate is necssary. Fourth, the presence of more than one metal would create very difficult separation problems. Moreover, Tripler[10] has found that few metals are recovered from metal finishing wastes. He points out the poor economics involved and the low unit value of most heavy metals.

Bibliography

1. Adamek, E.G., and Purves,C.B., "The Divergent Behavior of the Hydroxides of Lithium, Sodium, and of Potassium, Rubidium, and Cesium in the Xanthation of Cellulose and Starch." Canadian Journal of Chemistry, Vol. 35, P. 960, (1957)
2. Dean,J.G., Bosqui,F.L., and Lanouette,K.H., "Removing Heavy Metals from Waste Water." Environmental Science and Technology, Vol. 6, P. 518, (1972)
3. E.P.A. Technology Transfer Seminar Publication, "Waste Treatment, Upgrading Metal Facilities - to Reduce Pollution", P. 29, Jan. (1974), revised
4. Lancaster,E.B., Black,L.T., Conway,H.F., and Griffin,E.L. Jr., "Xanthation of Starch in Low-Concentration Pastes." Industrial and Engineering Chemistry Product Research and Development, Vol. 5, P. 354, (1966)
5. LEAPS, Lehigh Amalgamated Package for Statistics, users manual prepared by Hugh McFadden, Jr., Lehigh University Computing Center, 28 February 1976
6. Pourbaix,Marcel, "Atlas of Electrochemical Equilibria in Aqueous Solutions", P. 311, Pergamon

Press, New York (1966).

7. Russell,C.R., Buchanan,R.A., Rist,C.E., Hofreiter, B.T., and Ernst,A.J., "Cereal Pulps. 1. Preparation and Application of Cross-Linked Cereal Xanthates in Paper Procucts." Tappi, Vol. 45, No. 7, P. 59, (1962)

8. Swanson,C.L., Naffziger,T.R., Russell,C.R., Hofreiter,B.T., and Rist,C.E., "Xanthation of Starch by a Continuous Process." Industrial and Engineering Chemistry Product Research and Development, Vol. 3, No.1, P. 22, (1964)

9. Swanson,C.L., Wing,R.E., Doane,W.M., and Russell, C.R., "Mercury Removal from Waste Water with Starch Xanthate-Cationic Polymer Complex." Environmental Science and Technology, Vol. 7,

10. Tripler,Arch B. Jr., Cherry,R.H. Jr., Smithson, G. Ray, Jr., "Reclamation of Metal Values from Metal-Finishing Waste Treatment Sludges", National Environmental Research Center, Office of Research and Development, U.S. Environmental Protection Agency, EPA-670/2-75-018, April(1975)

11. United States Environmental Protection Asseciation, "Development Document for Advanced Notice of Proposed Rule Making for Effluent Limitations

Guidelines and New Source Performance Standards for the Hot Forming and Cold Finishing Segment of the Iron and Steel Manufacturing Point Source Category, August, (1975)

12. Weiner,Robert F., "Acute Problems in Effluent Treatment", *Plating*, Vol. 54, P. 1354, (1967)
13. White, D.C., *Mikrochim Acta*, P. 807, (1962)
14. Wing,R.E., Doane,W.M., and Russell,C.R., "Insoluble Starch Xanthate: Use in Heavy Metal Removal." *Journal of Applied Polymer Science*, Vol. 19, P. 847(1975)
15. Wing,R.E., Swanson,C.L., Doane,W.M., and Russell, c.R., "Heavy metal removal with starch xanthate-cationic polymer complex." *Journal Water Pollution Control Federation*, Vol. 46, No. 8, P. 2043, (1974)

Appendix 1

This appendix describes how the removal data were obtained and lists those data.

The waste water was prepared as follows--

1. 1000ml of distilled water was adjusted to pH 7.0.
2. The proper amount of a compound containing the metal (0.1243 g $FeSO_4 \cdot 7H_2O$, 0.1099 g $ZnSO_4 \cdot 7H_2O$, 0.1281 g $CrCl_3 \cdot H_2O$, 0.1119 g $NiSO_4 \cdot 6H_2O$, 0.0982 g $CuSO_4 \cdot 5H_2O$, 0.0770 g $MnSO_4 \cdot H_2O$) was dissolved in the distilled water.

The starch xanthate (batch #21)or starch with potassium hydroxide (batch #23) was then added to a beaker containing the metal compound solution. The mixture was stirred with a magnetic stirrer for one hour. The pH of the mixture was recorded. The mixture was then filtered on a milipore filter (0.45 micron), and the filtrate was measured for any volume loss. The filtrate was bottled and analyzed later.

Figure 11

Concentration of Fe^2 vs pH

(starch xanthate)

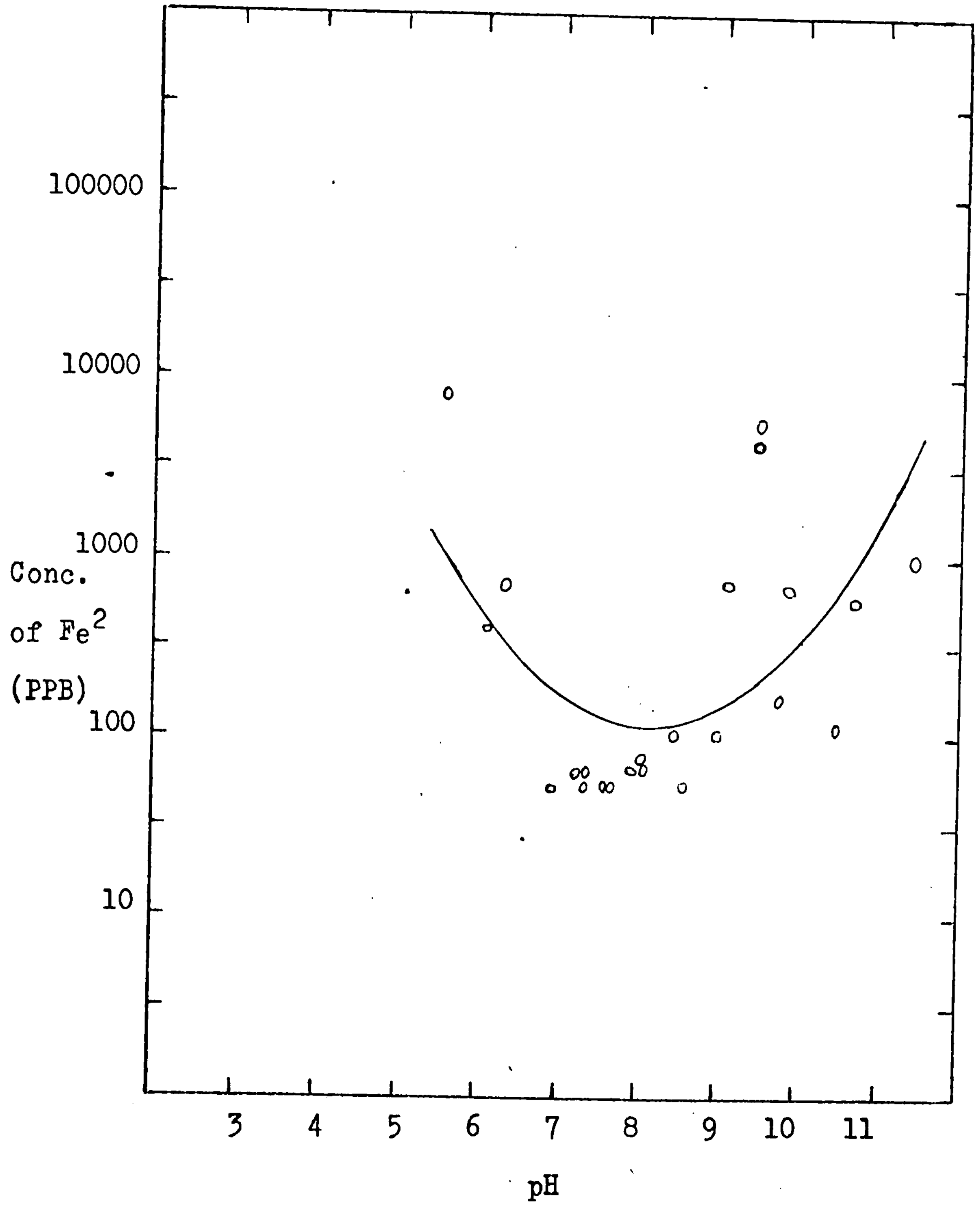


Figure 12

Concentration of Fe^2 vs pH

(starch with KOH)

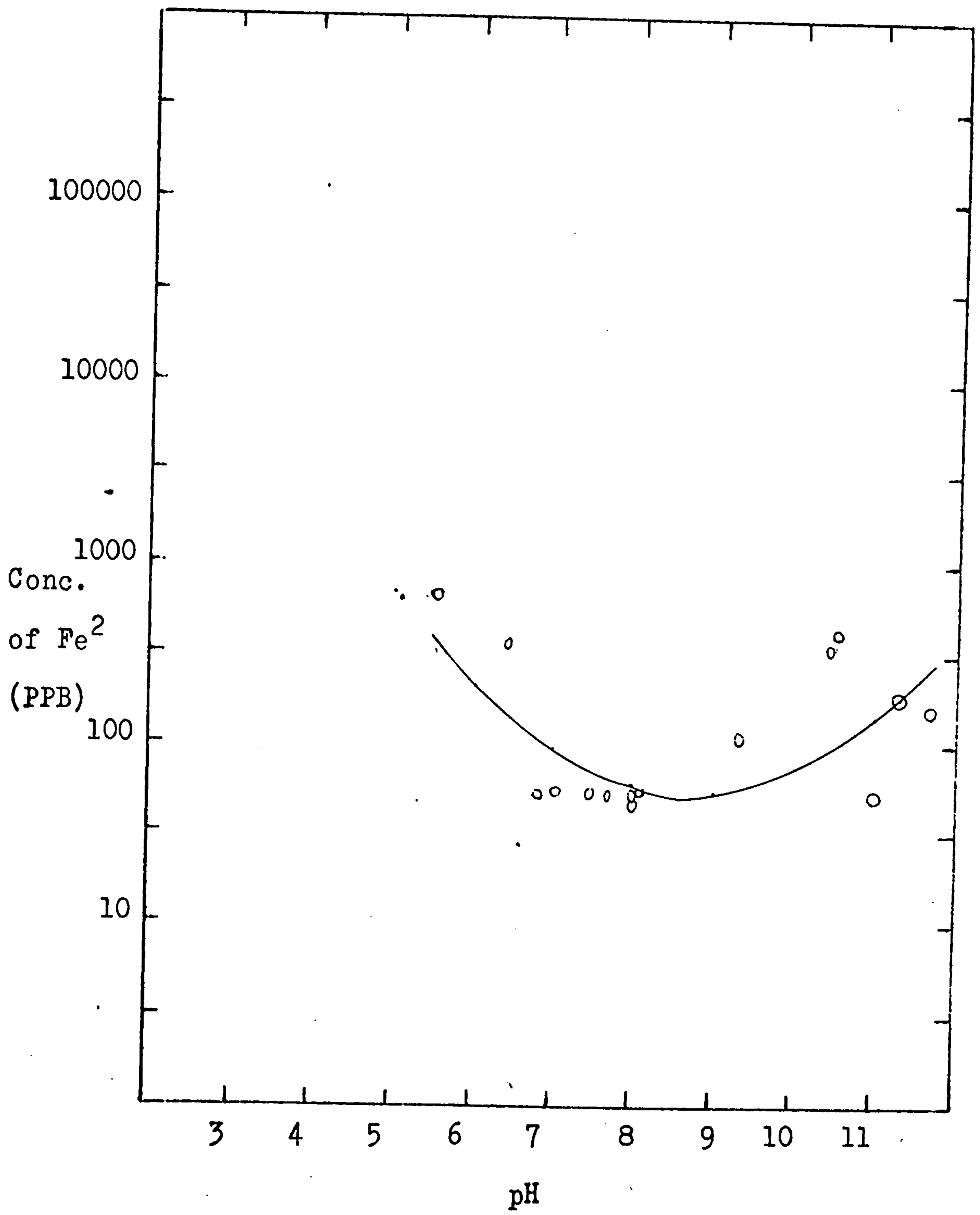


Figure 13

Concentration of Ni^2 vs pH

(starch xanthate)

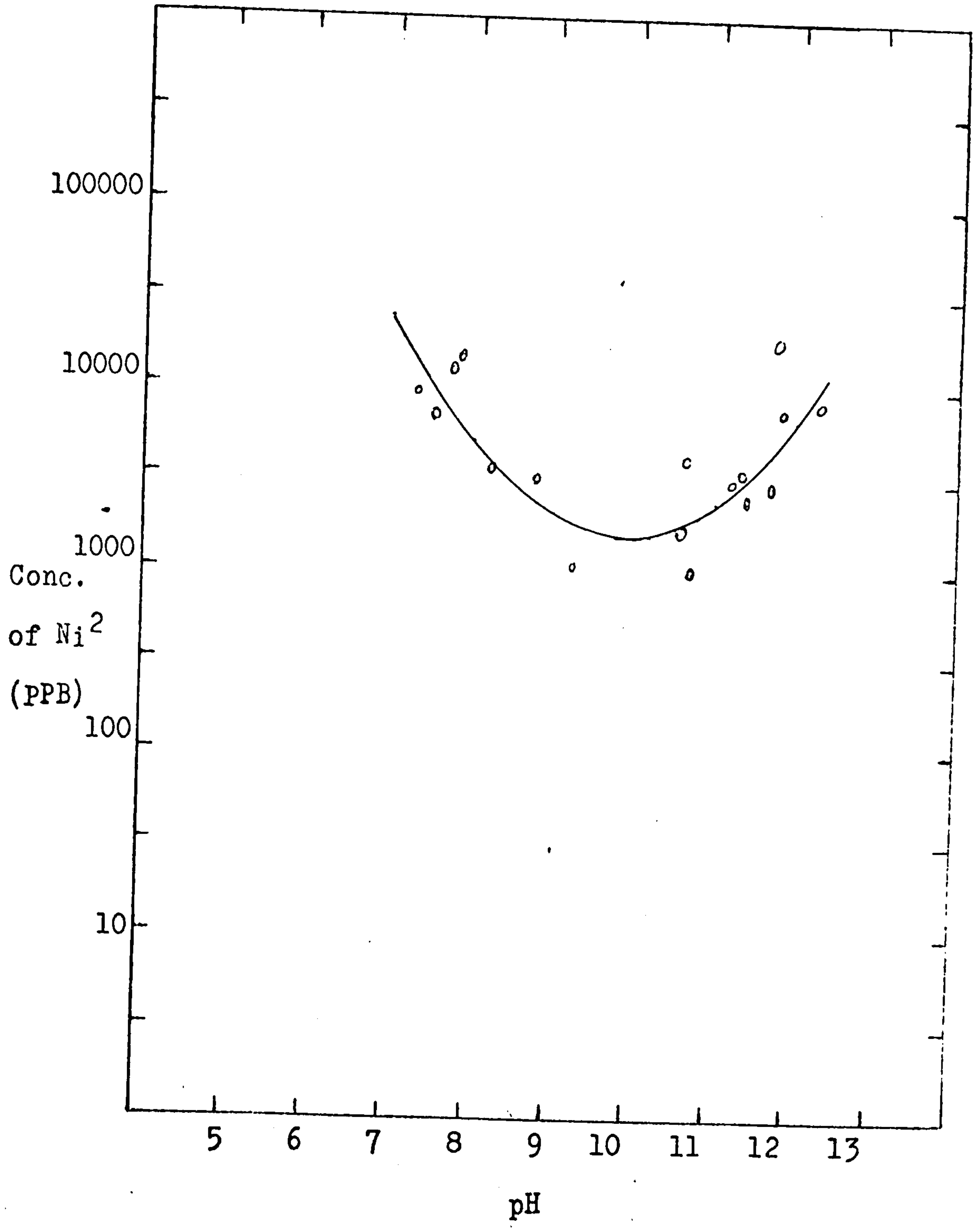


Figure 14

Concentration of Ni^2 vs pH

(starch with KOH)

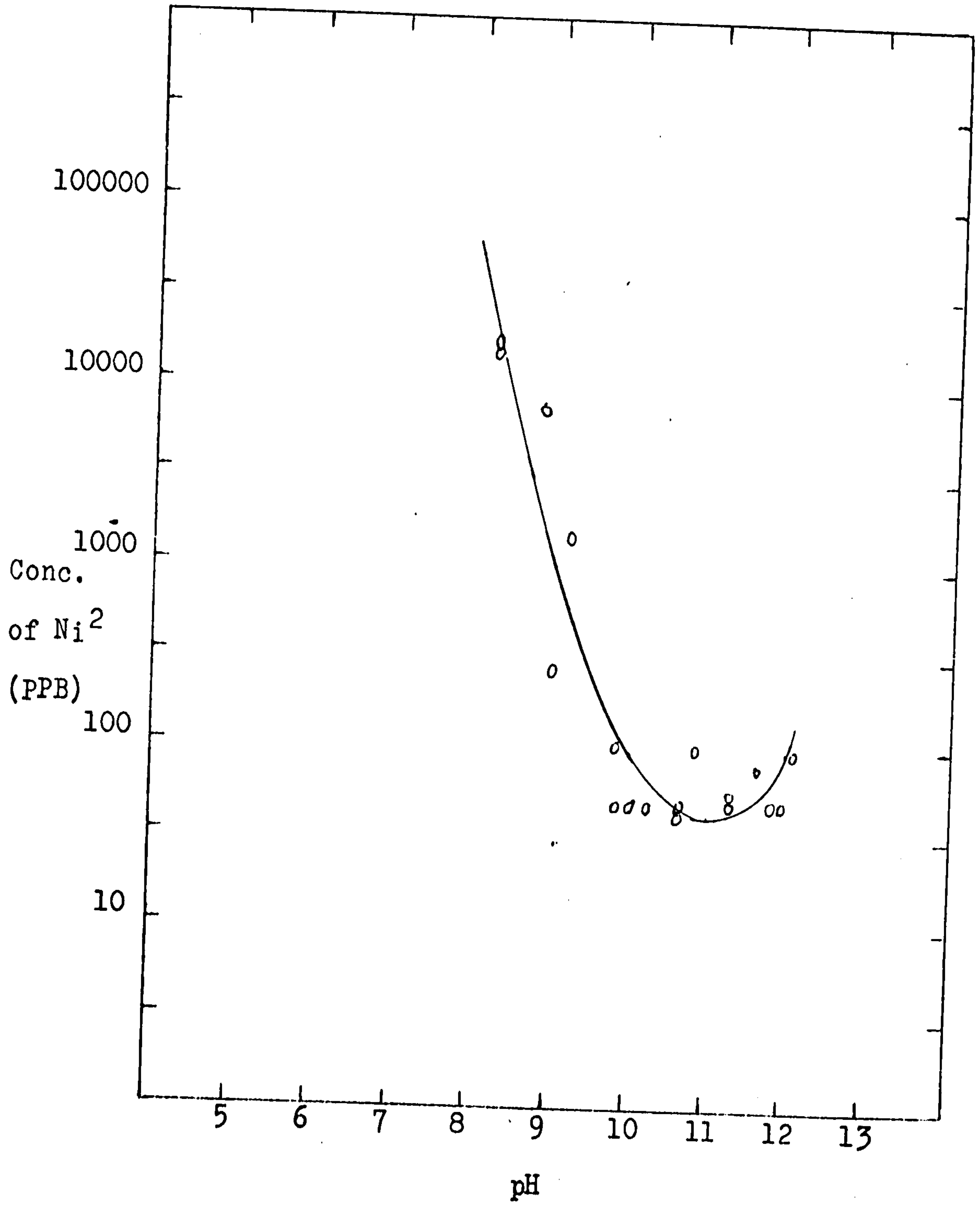


Figure 15

Concentration of Mn^{2} vs pH

(starch xanthate)

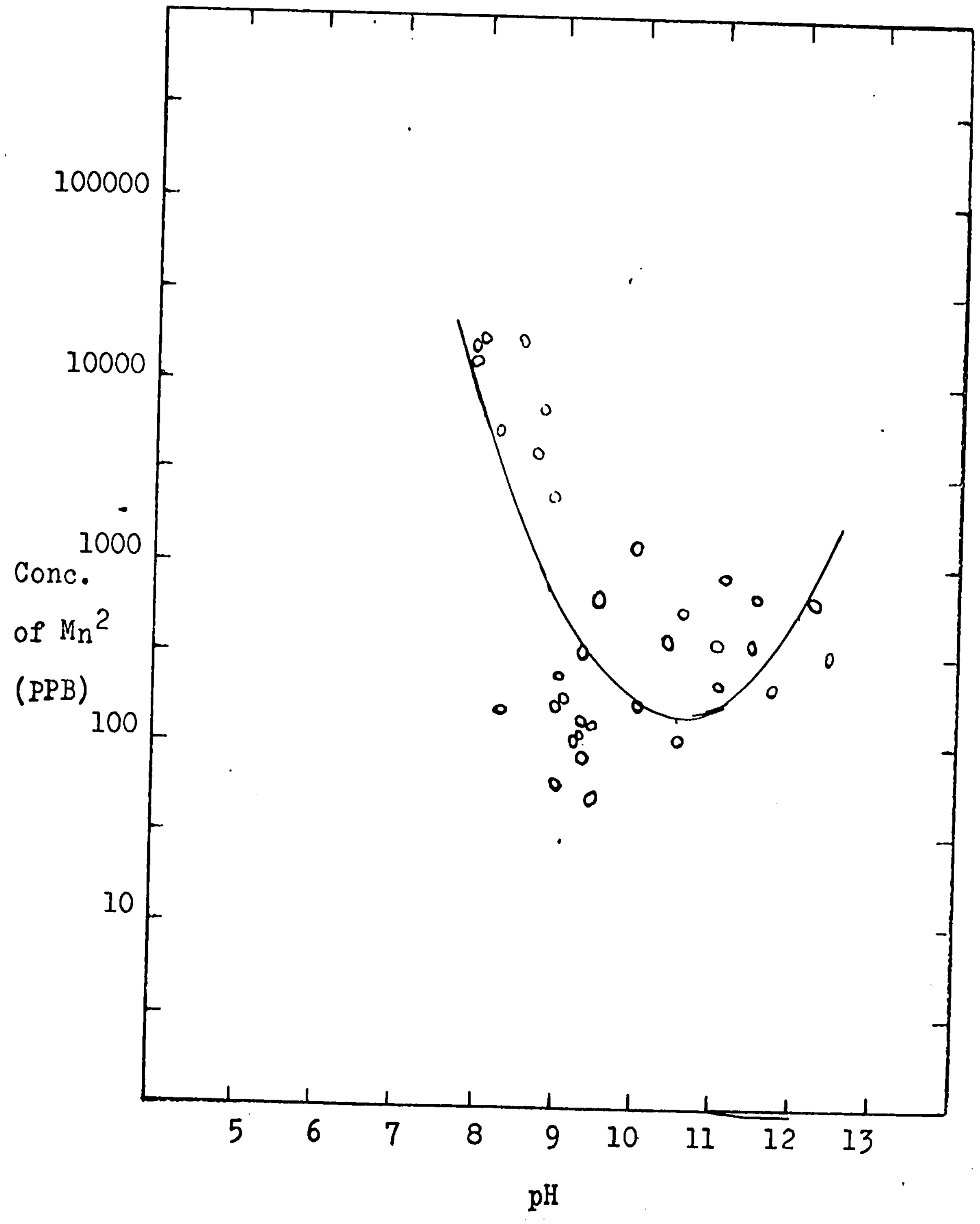


Figure 16

Concentration of Mn^2 vs pH

(starch with KOH)

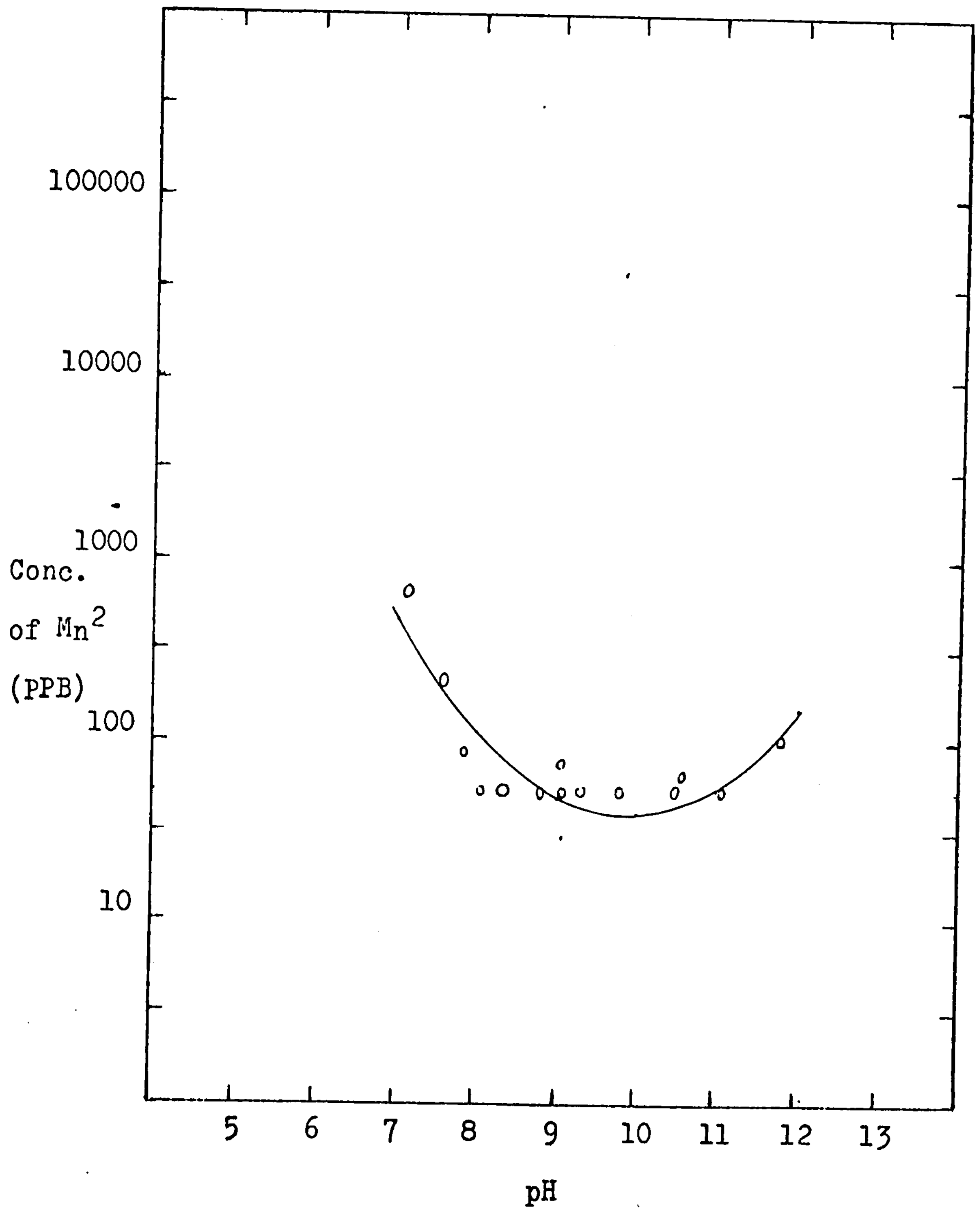


Figure 17

Concentration of Zn^2 vs pH

(starch xanthate)

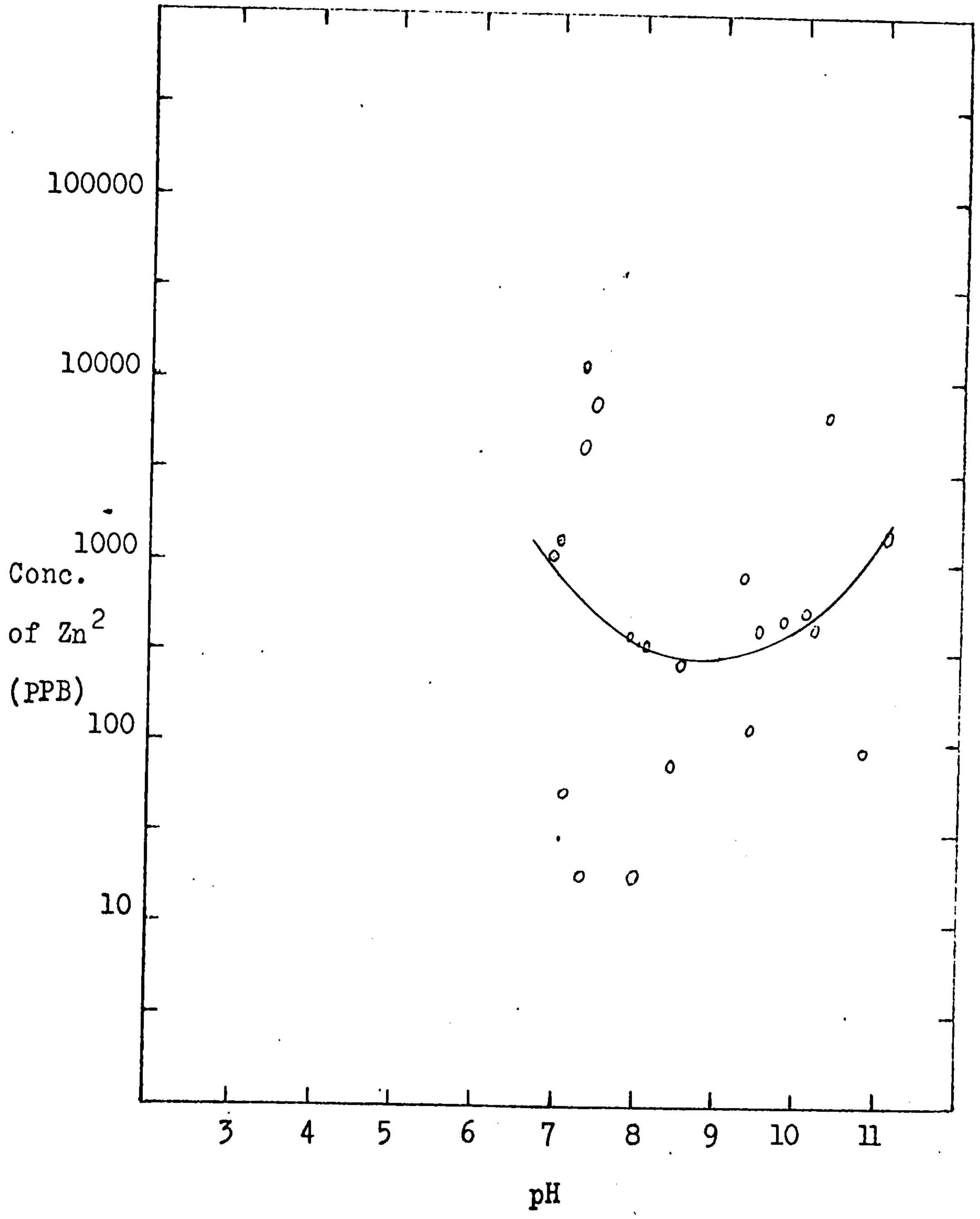


Figure 18

Concentration of Zn^2 vs pH

(starch with KOH)

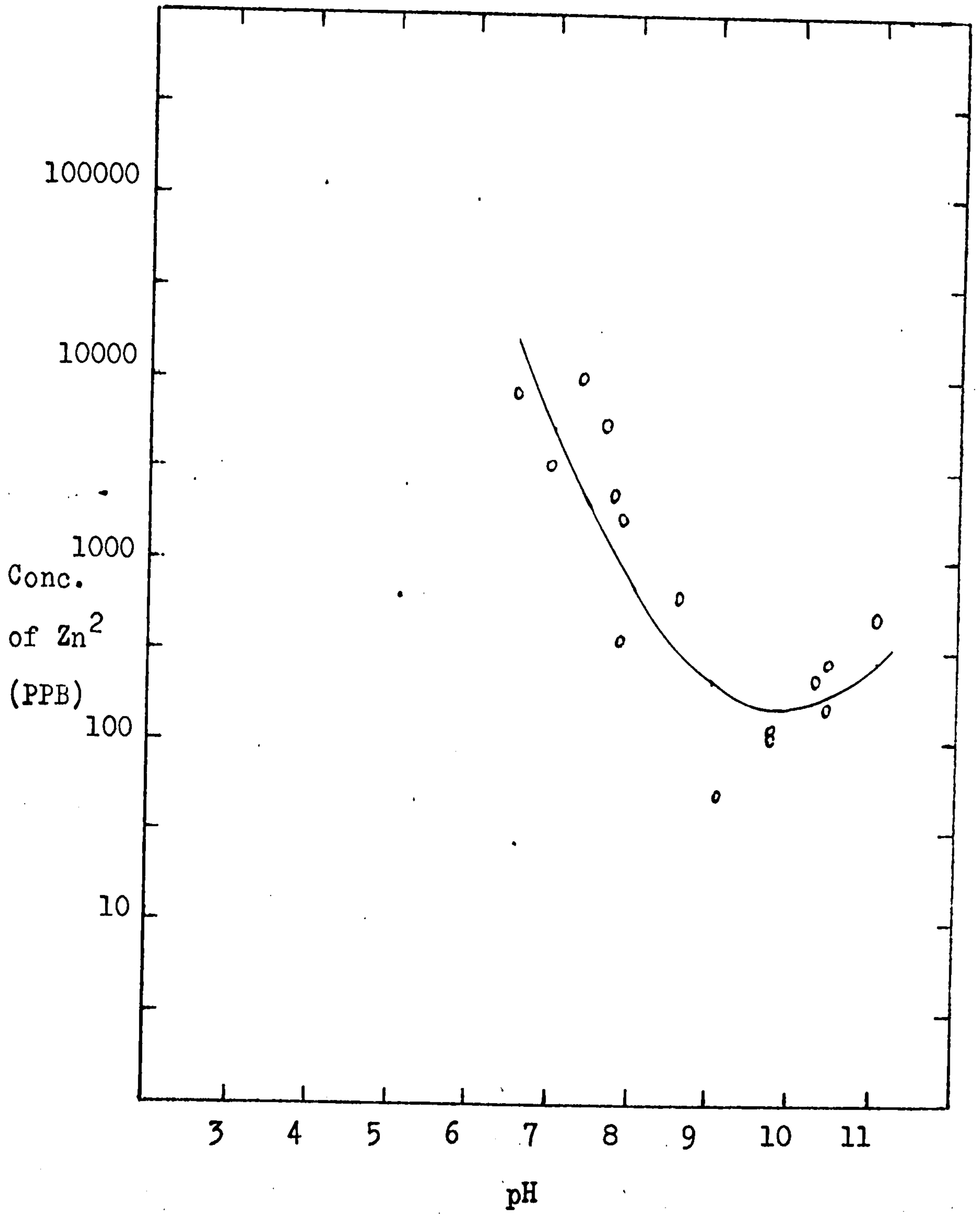


Figure 19

Concentration of Cr^3 vs pH

(starch xanthate)

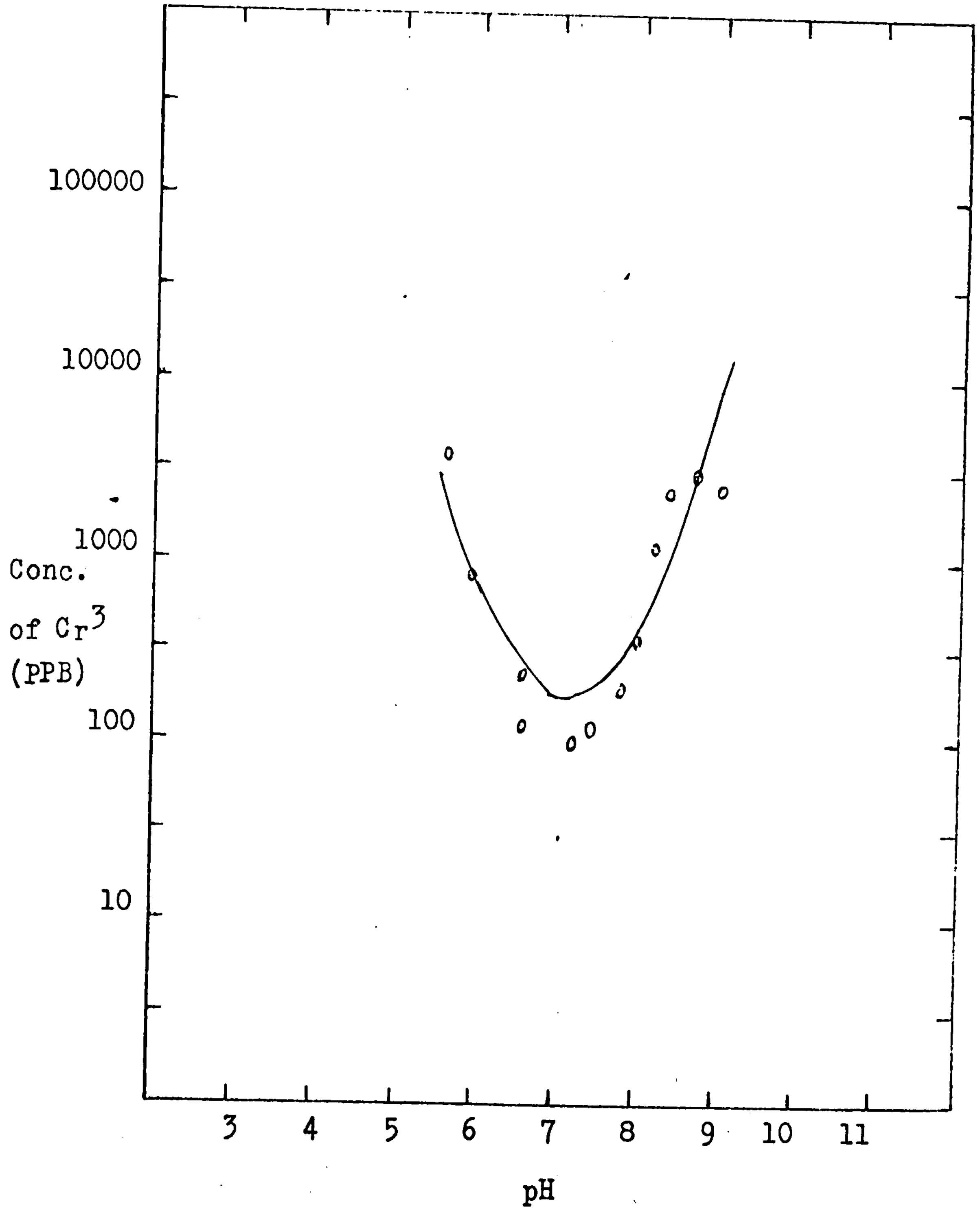


Figure 20

Concentration of Cr^3 vs pH

(starch with KOH)

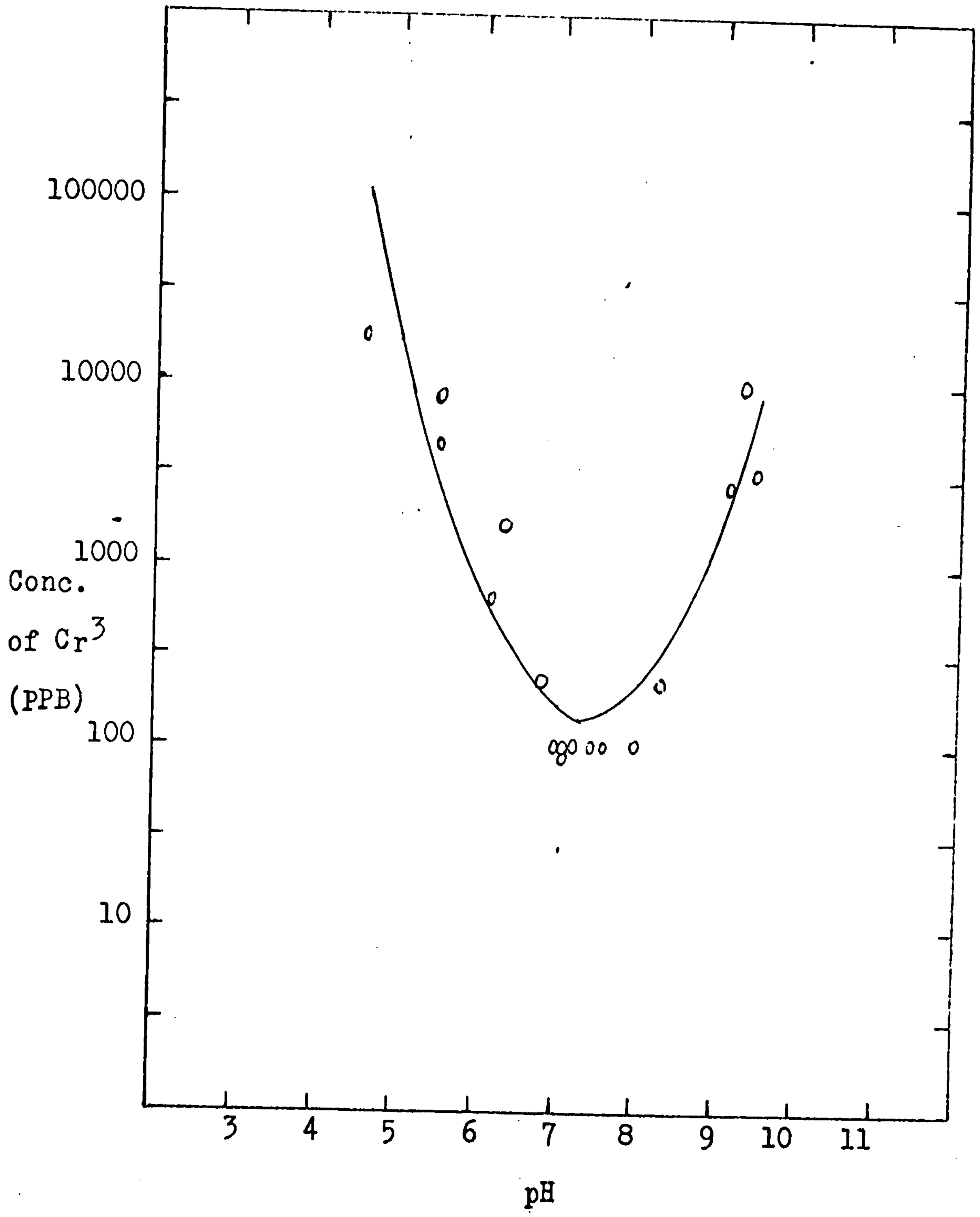


Figure 21

Concentration of Cu^2 vs pH

(starch xanthate)

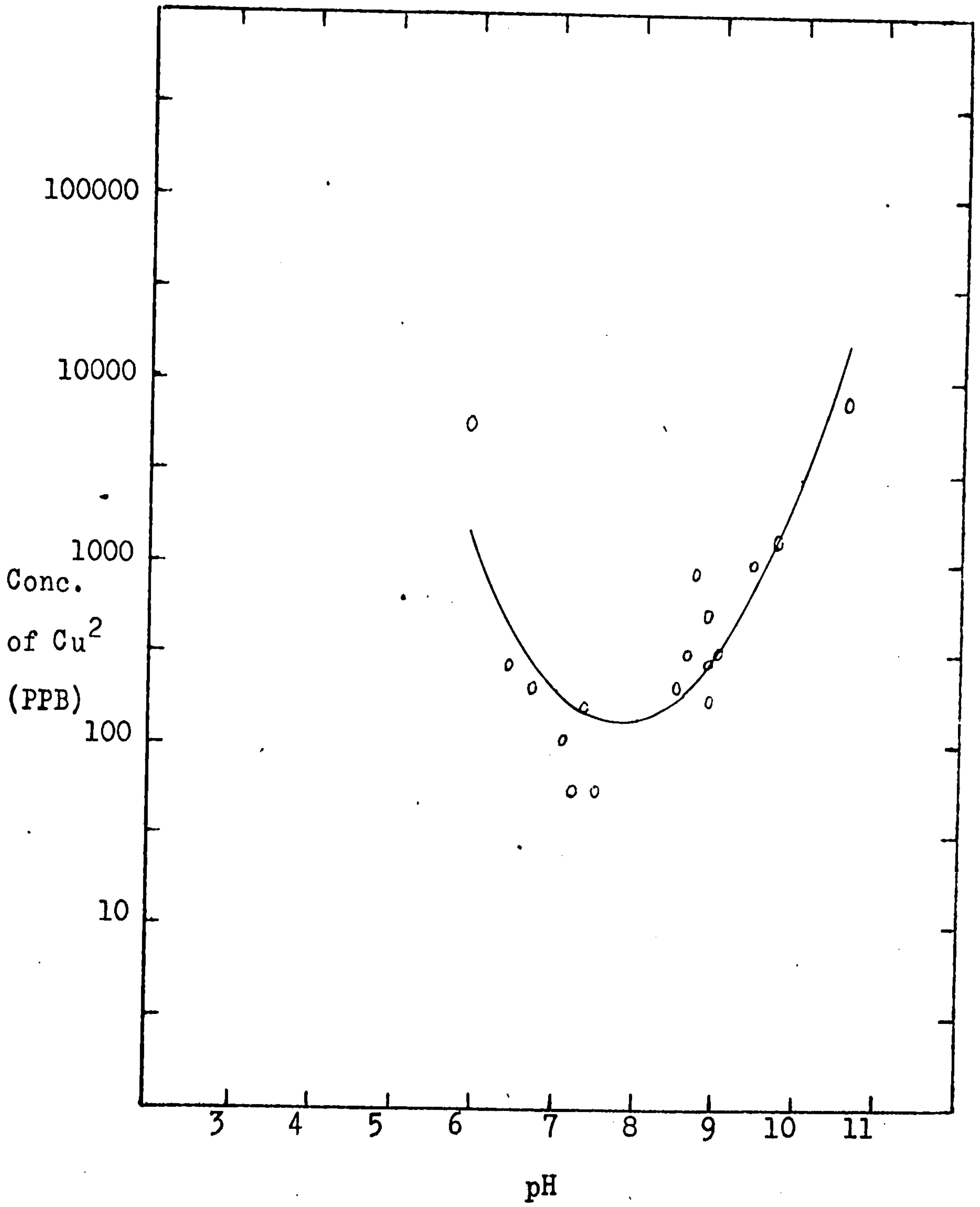
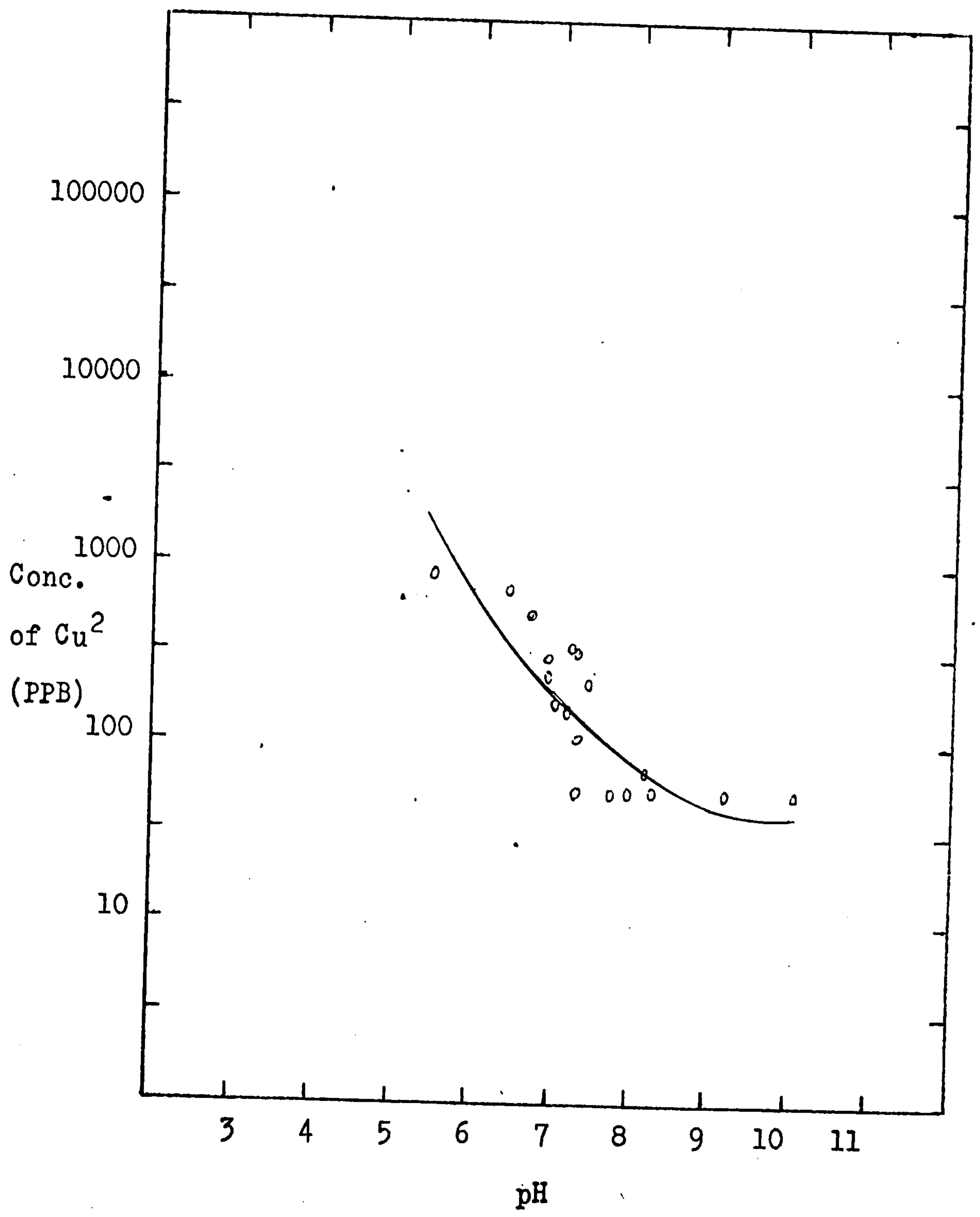


Figure 22

Concentration of Cu^2 vs pH

(starch with KOH)



Vita

I was born in Pen Argyl, Pa. on March 1, 1953 and grew up in Bangor, Pa. I graduated from Bangor Area Senior High School, Class of '71, and matriculated at Lehigh University. I was a member of Phi Kappa Theta social fraternity and Phi Eta Sigma honorary fraternity. I was President and Vice-President of the Lehigh University of the Society of American Military Engineers. I was a Distinguished Military Graduate from Lehigh with a B.S. in Chemical Engineering, Class of '75. I received a reserve commission in the United Stares Army on June 1, 1975. On June 14, 1975 I was married to the former Cathy Alice Vicario. Upon completion of my graduate studies I will receive a Regular Army commission in the United States Army and take a position as a second lieutenant in the Ordance Corps.