FRI-UW-8206
May 1982

FISHERIES RESEARCH INSTITUTE
School of Fisheries
University of Washington
Seattle, Washington 98195

Complexing Kinetics of the Chehalis River Water

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FINAL REPORT

Washington Public Power Supply System
Contract No. C-0253

Approved

Submitted_____ _____

Director

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Introduction

Discharges of trace metals via cooling waters from thermal generating power plants are of environmental concern. The fate of the metals stripped from the cooling coils upon entering the river systems has been addressed in past literature as total metal. However, with improvement in detection methodology such as ion specific electrodes (ISE), pulse polarography and gel filtration, new approaches are now being used to understanding the fate of these metals. Pulse polarography has gained considerable attention since it discriminates between forms of metals based upon electrochemical properties.

Organics such as humic and fulvic acids are found in the Chehalis River water and previous work by this laboratory demonstrated the affinity of these substances for copper and zinc. Based on these findings, the Washington Public Power Supply System (WPPSS) determined a need to investigate the kinetics of these reactions. Are the metals instantaneously bound to the natural-occurring organics or is the rate a factor in considering the potential toxicity of the metals in question? These are some of the questions WPPSS is addressing in terms of the future discharge into the Chehalis River system.

Considerable controversy has attended the question of the best technique for describing the biologically available forms of metals in natural waters. A titrimetric anodic stripping procedure was described by Shuman and Cromer (1979) in which a kinetic correction is necessary for correct endpoints. Wilson, et al. (1980), utilizing anodic stripping voltammetry (ASV) and differential pulse polarography (DPP) for the determination of metal binding by fulvic acid (FA), observed that FA caused a cathodic shift in the Hg oxidation wave and the appearance

of a secondary peak about 15 mV anodic of the Cu^{2+}/Cu^{0} potential. They also found substantial discrepancies in Zn stability constant which they attributed to fulvic acid adsorption on the mercury.

Buffle, et al. (1980), in a very detailed study of the effects of FA on polarographic measurements,demonstrated that FA effect on the mercury electrodes does not result in irregularities of the measured currents. Concentrations above 10 mg/L can cause interferences. Hence, in the case of the Chehalis River system where the humics and fulvics are not too heavily concentrated (2-4 mg/L), interferences at the electrode surface are not considered a problem. However, cognizance is taken of the fact that there is a great variety of humics and fulvics found in natural water systems.

McCrady and Chapman (1979) employed the ion specific electrode to determine copper complexing capacity and others consider this to be the best of techniques (Giessy, et al., 1978). However, Sekerka and Lechner (1978) observed that the Cu^{2+} ISE responded to humic materials in the absence of Cu^{2+}. Doubt is also cast on the use of calibration curves in distilled water for ISE when Cu^{2+} analysis in natural waters are being determined.

A very recent comparison between polarographic and ion specific electrode measurements of free copper in the presence of soil-derived FA has been performed by Bhat, et al. (1981). This team's conclusion was in favor of the polarographic method with appropriate corrections for FA's presence, i.e., in cases where fulvics are very concentrated, dilution of the water or current corrections are necessary. They also concluded that estimation of free (Cu^{2+}) by ISE in presence of FA needed more research in order to establish reliability of the technique.

European researchers involved in metal speciation studies seem to concur in the use of Chau's (1974) method for studying binding capacities of natural waters for heavy metals. In light of this and other information cited above, the method we used in this study appears to be the best alternative at this time. However, one improvement to the Chau method would be to eliminate the acetate buffer for maintaining pH and substitute an isoxic degassing apparatus as suggested by Lecomte, et al. (1981). Their apparatus will maintain the ambient pH at $\pm$0.02 pH unit as well as serve as an O_2 eliminator. This method works by maintaining a constant partial pressure of CO_2-NO_2 in the cell. It is time-consuming since each experimental cell has to be optimized as to CO_2 and N_2 gas flow.

Purpose and Scope

The purpose of this project was to measure the binding rates of the Chehalis River water for copper and zinc at different seasons of the year. A polarographic technique, differential pulse anodic stripping, was the method of choice. The method was an adaptation of Chau, et al. (1974).

Materials and Methods

1. Sampling Objective. Objective of the sampling procedure was to obtain the Chehalis River samples that would represent as closely as possible the state and condition of the water at moment of collection.
2. Pre-Sampling Preparation
   a. Polyethylene bottles were washed thoroughly with detergent, then rinsed three times with tapwater and three times with de-ionized water. The de-ionized water used for rinsing has

a specific conductance of 0.1 μmho/cm. Bottles were then rinsed with 10% Ultrex nitric acid followed by three rinses with de-ionized water. The last water wash is tested for copper and zinc by graphite AA. If background metal concentrations are greater than the 10% HNO_3 wash, the acid wash is repeated until background levels are lower than that of acid wash. Then 100 ml of 10% HNO_3 is added to the sampling bottles for transport to the field for final rinsing.

3. Collection Site Protocol--Chehalis

   a. Location and Frequency of Sampling. Sampling location was at the discharge site midway between the north and south river banks. Sampling was done on the last Wednesday of the months of August, November, February, and May, beginning 27 August 1980 and ending 27 May 1981. Envirosphere Co. provided boat transportation to the site.

   b. The two grab sample bottles were emptied of 10% HNO_3 solution.

   c. Bottles were then rinsed three times with the river water.

   d. The two sample bottles were then immersed simultaneously and filled to the very top of the bottles, capped and immediately placed in transport cooler for transport to the laboratory.

   e. Time and date of sampling were recorded on the bottles.

   f. Temperature of water was recorded.

   g. The pH of water was taken and recorded at the time of sampling.

   h. River Collection. The samples collected at the river were as follows:

      Sample A: One 2-L bottle sample.

      Sample B: One 2-L duplicate sample.

Sample C: One 0.5-L sample spiked on site with 10 ppb each of copper and zinc.

Sample D: Field-spiked distilled water with the same concentration as in Sample C.

Sample E: One 100-ml sample in a polyethylene bottle was made acid with 0.1 ml of HNO_3 for total metal analysis.

Samples C and D were repeated for two sampling periods in order to establish the loss, if any, to the container wall in transit.

i. Sample Transport. Immediately after sampling, the samples were placed in an insulated cooler surrounded by ice. The samples were then transported to the University of Washington laboratory. Travel time from Chehalis site to the laboratory was about two hours. Samples were transported by auto.

4. Laboratory Handling of Water Sample

a. Samples were immediately refrigerated at 4°C upon receiving them at the laboratory.

b. Aliquots of the river water in duplicate were analyzed for total copper and zinc by graphite AA. Samples were compared with distilled water NBS standards. Internal standards of Cu and Zn were added to river water to assess any matrix effects on the total determination.

5. Laboratory Analysis for Total Metals

   a. Standard curves were run on each metal with at least five concentration levels.

   b. Analysis of the blank and midpoint standard was performed before assaying the samples. If results were unsatisfactory, i.e., if the blank or standard had changed more than 10% in absorbance since previous reading, the reason for the change was determined.

   c. For percent recovery, C and D field sample was compared with a C and D sample spiked in the laboratory. This allowed determination of loss to vessel wall during transit and percent recovery.

6. Laboratory Analysis for Complexing Kinetics of Chehalis River Water

   a. Fourteen 150-ml flaskseach with 100 ml of Chehalis River water were placed in a shaking water bath and allowed to equilibrate to ambient temperature of the Chehalis River water at time of sampling and pH buffered at ambient Chehalis River water pH. This step was tried at the outset but was soon modified because the time factor established in Attachment A of the contract could not be met, particularly the one-minute reading as requested in the description of work. Also, to moderate effects of temperature change the following modification was made. It was not feasible to work at the ambient river temperature since no temperature regulated cuvette was available. The river temperature ranges from 7°C to 12°C, and as soon as the water was removed from the 150-ml flask

of 7°-12°C and placed under the electrodes, the regulation of temperature would be lost and the variable of temperature change on the kinetics would be encountered. In view of this situation the reaction vessel was maintained at room temperature of about 19°-20°C. Therefore, the blank would be allowed to equilibrate to room temperature before any concentrations of copper were added or the blank scan made on the polarograph. Once the blank was scanned the first aliquot of copper or zinc was added and the reading made as soon as possible thereafter. The earliest reading possible was at two minutes. (This change was noted in the March 1981 report.)

b. Chehalis River complexation kinetics test format. In each of four samples the following levels of toxicants were tested (i.e., added in the ionic form to river water):

Copper, ppb: 250, 125, 60, 30, 15, 10, blank.

Zinc, ppb: 300, 150, 75, 40, 20, 10, blank.

Copper/zinc, ppb: 300/300, 150/150, 75/75, 30/30, 15/15, 10/10, blank

The details of each test are as follows:

(1) Measured the pH of the sample using a glass electrode.

(2) Sample was purged for 15 min with pure N_2.

(3) The toxicant to be tested was added in a small constant volume of 10 µl to bring the total toxicant concentration in the sample to the test level. This was consistant for each level of toxicant. Sample was stirred constantly.

(4) Using differential pulse anodic stripping voltammetry

(DPASV), we analyzed aliquots of the sample for toxicant in the labile form at the following times after toxicant addition: 2, 5, 10, 15, 30, and 60 minutes and 2, 7, 15, 30, and 60 minutes when both metals were added at once. Deposition times of 30 seconds were used. Voltage sweep was from -1.2 to 0.10 volts. Measurements were made at medium sensitivity. Buffer concentration in the cuvette was 0.06 M.

c. After labile metal determination, each concentration tested in b was assayed for total metal content by graphite furnace AAS.

d. Each ambient river sample was assayed for total and labile copper and zinc by DPASV and graphite furnace AAS before complexing capacities were performed.

7. Equipment and Materials Used

a. Graphite furnace atomic absorption spectrophotometer, Hitachi Model 180-70.

b. Differential pulse anodic stripping polarograph, Princeton Applied Research Model 374.

c. A controlled temperature shaking apparatus.

d. Insulated cooler for water transport.

e. Ultra pure hydrochloric acid and nitric acid.

f. Polyethylene water bottles.

g. Graduated beakers.

h. Volumetric flask.

i. National Bureau of Standards comparative metal standards of Cu and Zn and EPA Quality Control Standard #346.

j. Automatic pipettes and disposable tips.

Results and Discussion

When working with ambient natural waters such as the Chehalis River water, the researcher must minimize the effects of the buffer system on instrument response so that the blank river water measurement may be meaningful. The following effort was made to accomplish this end.

Table 1 (6-19-81) illustrates some typical blanks obtained in distilled water and Chehalis River water in the early stages of the binding kinetic study. The river water and distilled water blanks for copper were not as different as one might have expected; therefore, it was suspected that the buffer was contributing to producing the copper blank and not the river water. To determine if this was true, the buffer system was examined more closely.

The acetate buffer was made by neutralizing a 3-molar concentration of ammonium hydroxide with reagent grade acetic acid. This solution was then passed through a water washed chelex 100 column in order to collect any free copper or zinc as well as other metals. A second attempt to rid the buffer of endogenous copper or zinc was made by electro-purification of the buffer solution. The 3-molar pH 7.3 buffer was placed on the polarograph and subjected to a 15-min deposition at -1.2 volts, then removed from the electrodes and the copper or zinc plated on the mercury drop was discarded with the mercury. This served as the buffer for the ensuing kinetic studies (see Table 2).

A test was performed to demonstrate the contributions of metals to the system from the buffer solution. This was carried out on the electro-purified buffer. Table 3 (8-14-81) illustrates the buffer's contributions to the water (using de-ionized water) of zinc, cadmium, lead, and copper (see June 19 Report). There does not appear to be any

significant contribution to water blank from the buffer. The standard deviations for copper and zinc are essentially the same.

Information about Table 3:

(a) The potentials for lead and cadmium were not identifiable by peaks. The listed potentials were assumed and recorded from baseline readings. A copper and zinc potential was evident in increased electrolyte concentrations because of slight contamination of the electrolyte.

(b) The peak potentials shifted slightly negative as in the river sample with increasing electrolyte concentration.

(c) There were very small fluctuations in copper current readings over the entire concentration range.

A comparable experiment was performed using a river water sample (Table 4, 8-14-81) with following results:

(a) Peak potentials shift slightly negative with increase in electrolyte concentration.

(b) The 200 µl or 60 mM electrolyte concentration used in all our binding studies appears optimal.

(c) Current readings at the copper potential seem unaffected by electrolyte concentration changes.

(d) Starting current or baseline currents increase with increased electrolyte concentrations. This is shown in a separate table, No. 5.

(e) The cause of the decrease in current readings for zinc in Table 4 is unknown. As seen in Table 5, the starting base line increases with increasing buffer concentration in de-ionized water which may be attributed to slope changes. Slope changes occur with increasing salt concentrations, and likewise the current readings are affected.

A second problem to be solved was that of a double peak occurring in the potential range of copper, and high blanks occurring at this same potential. It was found that upon aspiration of a sample for 10 min with a water aspirator, the double peak disappeared. It was further found that if we increased the nitrogen degassing of the sample from the recommended 10 min purge to 15 min, the copper potential baseline area would decrease substantially. Upon optimizing the purge time, we found that the 15 min time period was satisfactory.

The concern for blank readings and their meaning continued throughout the study. Therefore, at this point the discussion of blanks and their meaning seems appropriate. The subject of natural water blanks is conspicuously missing or vague in publications concerning DPASV determinations of metal bindings. However, from phone conversations with K. Chau and John Montgomery, and from literature survey, we extracted the following information:

1. Chau made direct comparisons of lake water with de-ionized water in the labile metal determinations. He felt that the blank was of little consequence in the apparent complexing capacity measurement (Chau 1981).

2. Florence (1977) considered the blank to have a negligible influence on the measurement. The blank was obtained by halving and doubling the concentration of electrolyte used.

3. Young, et al. (1979), in employing DPASV measurements, used a standard addition procedure for estimating their blank.

4. John Montgomery (pers. commun.) of Harbor Branch Foundation in Florida, used the following method for blank determination: A river

sample and de-ionized water sample were spiked with at least five different concentrations of electrolyte, then scanned from -1,250 to +0.000 volts and peak currents were recorded. These points were plotted with the intercept as the blank determination.

The other choices of blank determination when using the model 374 are as follows.

1. The model 374 has a blank subtract mode which automatically enters into memory the background current readings and any peak current readings of the water blank.

2. A visual reading of the current at any potential may be recorded as blank information even though no peaks are evident--in other words, elevations of the base line without a discrete peak, where the instrument does not record a peak.

3. A blank may be determined by standard additions of metal to a given water sample where there is no binding evident--i.e., at zero metal additions on the X axis and current readings on the Y axis, or the Y intercept at zero additions may be used as the blank current reading.

4. The method suggested previously by J. Montgomery.

Discussion of the four blank methods:

1. The blank subtract mode. In our experience this method is only useful when we are determining total metals on the polarograph at pH 2-4. When using the subtract mode at ambient river pH of 7.2-7.5, the potentials shift with increasing metal additions. This shift will result in negative peaks on the polarograph and make the interpretation difficult.

2. Assumed peak potentials with current readings from the digital display method. This method is not very quantifiable because one is assuming a potential which may or may not be accurate since it is not evident where the peak will occur until after the binding capacity of the sample is exceeded. Also, the peak will continually shift negatively as concentrations of metals increase. Current readings at the copper potential are due in part to non-purgeable oxygen. Lastly, as will be seen in Table 5, the background current readings are dependent on concentration of electrolytes used in sample.

3. The standard additions method. This method seems very applicable if no binding is measurable in the water, i.e., the background current reading is primarily arising from the electrolyte component--such is the case in de-ionized water blanks. However, it is feasible to subtract the de-ionized water blank from the river blank and use this as the blank for the natural water sample which may or may not be due to a metal component.

4. Blank as determined by an electrolyte concentration curve. This method was tried and the results are shown in Tables 3 and 4. Table 4 shows data obtained from a river sample, assuming a potential for copper of -0.200 volts and read from the digital display. The zinc, lead, and cadmium peaks are derived from the ambient river levels since they are almost non-detectable in the corresponding de-ionized water. It is obvious that a plot of these current readings vs. electrolyte concentration as J. Montgomery suggested would be to no avail in establishing a blank reading. There seems to be no concentration

effect except in the zinc peak area of the river sample, and there the current reading has an inverse relationship. This inverse relationship may be caused by a possible complexation of the ambient river zinc by the increase in electrolyte concentration.

Table 3 also indicates that with increasing buffer concentration, contribution to the background current reading from the buffer is almost negligible. This is also seen in Table 4 showing results from a similar experiment using river water. The difference between the copper average of 208 in the de-ionized water and the 370 in river water could be due to the ambient copper contribution of the river water.

Discussion of Data on First Two River Samples

Tables 6-9 summarize the data obtained from the binding kinetics on the first two river samples. The first striking finding was that the binding had occurred during the first two minutes. Two minutes was the earliest possible time to take repeatable readings because of deposition time (when kinetics would play a part, not during the scan), purging time after metal addition, and equilibration time allowed. It is also important to note that the readings do not change significantly over time. A plus or minus 5% change in current readings is considered normal. Hence, it is assumed that the binding occurs at such a rapid rate that the polarograph offers little assistance in this elucidation. It would appear that a technique such as a stopped-flow spectrophotometer technique, suggested earlier, would be appropriate.

It is interesting to note that when establishing binding capacity curves, the peak currents for concentrations of metals after linearity is reached are not identical to metals in deionized water. Comparing Cu^{++} at 300 ppb in Figure 1 with copper at 300 ppb in Figure 3, one

finds a difference of about 1,000 n amp in peak current readings. Also, the slopes of the two curves differ slightly, which some reports indicate could be due to the increase in resistance in river water caused by natural ligands in the water, or the presence of additional complexation or equilibrium not being reached.

Figures 3-6 are plots of the average columns found in Tables 6-9. The average column represents an average of the timed readings of 2 through 60 minutes. Since there is no change in current over time, a plot of these readings should essentially give a binding capacity when the linear portion of the curve is extrapolated to the X axis. This indeed does happen. If these readings were representing the kinetics of the binding phenomenon, one would expect to see a decrease in readings over time, i.e., the 2-min reading would be a larger reading than the 60-min reading. This is not the case; the variability observed is no greater than fluctuations in instrument sensitivity.

In Figures 1, 3, 4, and 6, the non-linearity exhibited in copper at the low concentration end of the curve seems to be characteristic of binding curves. Chau, et al. (1974), and Shuman and Cromer (1979) found similar non-linearity in their complexing studies. However, the zinc curves do not demonstrate the same non-linearity as seen in Figures 2, 3, 5, and 6, nor do they indicate any sort of binding characteristics.

A plot of the labile metal versus time originally requested would be only an exercise since the readings are essentially constant from 2 min through 60 min. The only fluctuation is due to instrument not to kinetics changes (see quality control data, Table 12, below). A 10% fluctuation is considered normal for the instrument which seems to hold for each of these metals.

Polarograph precision and accuracy data relative to first and second water samples are shown below in Tables 10, 11, and 12. Table 10 illustrates the precision of the method and that it falls within the 10% fluctuation as described by the manufacturer. Table 11 illustrates the sensitivity of the method for the four metals at the concentration of 2×10^{-7} g/L. Table 12 indicates the accuracy of the method using the EPA quality control metal standard #476.

Discussion of Data on the Third and Fourth River Samples

In a discussion with Dave Pratt in March 1981, new approaches to the kinetics study were mentioned. The following approaches were used in the study of the third and fourth river samples: (1) The ion-specific electrode (ISE) in combination with the atomic absorption for ionic and total metal determinations was used on the fourth sample. (2) The separation of the humic and fulvic acids by reverse osmosis technique and the subsequent ultrafiltration separation of molecular weight fractions was used on the third river sample. The ultimate use of the molecular fractions was to determine binding capacities for each fraction and possibly the use of the molecular fractions in a stopped flow spectrophotometer for an assessment of the binding kinetics. (3) A third approach was to establish a standard binding capacity measurement with the use of a commercial humic acid.

The third river sample was collected on 14 February 1981. A 250-gallon sample was collected in the College of Fisheries portable water tank and transported to the College where it was processed through a B-10 DuPont polyamide holofibre (E.I. DuPont, Wilmington, Del.) on a reverse osmosis apparatus. The organics were concentrated about 125 times. This concentrate was analyzed for binding capacity and separated into five molecular weight fractions. An Amicon Model 402 ultrafiltration system was employed using XM-100, XM-50, PM-10, UM-2 and UM-05 ultrafilters. The corresponding molecular weight cut-offs are 100,000, 50,000, 10,000, 1,000, and 500 mw. The primary information obtained in this experiment was used by Terry Northstrom for his postdoctoral thesis. The details and findings will be in a thesis in the near future.

Routine copper complexing capacity was determined for both the ambient river water and the concentrate. The concentrate gave a binding capacity of about 500 µg/L which is questionable in view of Buffle's (1980) work with concentrated fulvic and humic acids. Calculating to ambient would indicate a BC of about 4 ppb of copper. The ambient BC for copper was indeterminable and the BC for zinc was 12 µg/L.

The binding capacities of the various molecular weight fractions will be described by Terry Northstrom. Available information on the third water sample at this time is given in Tables 13 and 14. Zinc and copper concentrations were determined on each molecular weight fraction separated by Amicon filters. The ambient water levels of

zinc and copper were measured before concentration and levels in the concentrate are shown in Table 14.

The fourth sample was collected on 21 May 1981 and used in the preliminary ISE assessment. The equipment used in this portion of the study was an Orion Model 9429 cupric electrode, and an Orion double junction reference electrode Model 90-02. The electrodes were connected to a battery-operated Kiethly Model 602 electrometer with an output into a Kiethly Model 370 milliampere recorder. This is an extremely stable electronic system, capable of measuring in the nA and nV range. The electrometer will amplify the signal to the output range of 1-10 milliamperes.

The buffer used was that of potassium acetate as described by McCrady and Chapman (1979) at a strength of 10 mM. The sample size used was 100 ml. A typical standard curve of cupric activity in de-ionized water from the raw data in Table 15 is seen in Figure 7. Optimum pH for operation of the ISE is 5.2. We determined complexing capacities for the Chehalis River water at 5.2 and 7.2. The electrode gave no current measurement at pH 7.2.

The data presented in Figure 7 were performed at pH 5.2 and are plotted as direct current measurements of Cu^{++} activity versus concentration. For comparison, Figure 8 is a graph of data collected on the polarograph. If one assumes the dotted line intercept, it would indicate binding of 12.6 ppb of copper, which is reasonable. By linear regression it calculates to be 12.4 ppb with an r^2 of 0.99.

The final experiment before expiration of the contract was that of the repeatability of the binding capacity utilizing a standard humic

substance. The humic standard used in this case was an Aldrich Chemical Co. reagent (H1, 675-2), a humic concentrate of natural origin. The standard concentration used was 10 mg/L.

Over a four-day period, four separate binding capacities were performed as described by Chau, et al. (1974). The results of these four BCs are shown in Table 16. These data simulate a DOC of 10 mg/L and a BC similar to that found in the Chehalis River during the summer--from 15 ppb to 30 ppb.

Concluding Remarks

The data presented in this final report, although not definitive as far as the binding kinetics are concerned, do offer some guidance to future work in this area. They offer a data base for better understanding of blank data obtainable by the DPASV technique. Our study demonstrated that the kinetics of the binding phenomenon are too fast for this technique. However, with the use of reverse osmosis and molecular filtration for obtaining the organic concentrates, the preliminary data suggest that the kinetics may possibly be established using these substances in a stopped-flow spectrophotometer following fluorescent changes. A similar method is now being researched by Chau (pers. commun.).

Table 1. Some representative blank readings. Note the dramatic shift of E_v for copper in distilled water as compared with river water. Polarographic conditions:

1. Purge time, 4 min
2. Sense setting, medium
3. Drop size, medium
4. Scan, -1.2 to +0.100
5. Dep. time, 30 sec
6. Scan rate, fast
7. Buffer, ammacetate, pH 7.2, 0.06 molar

Sample	Zn		Cu	
	E_v	n amp	E_v	n amp
Ch. River water				
1	-1.006	345	-0.138	601
2	-0.998	251	-0.130	464
3	-0.996	251	-0.110	430
4	-0.996	222	-0.116	408
Dist. H_2O				
1	-1.014	466	0.062	862
2	-1.012	333	0.060	691
3	-0.996	251	0.056	637
River water				
1	-1.010	320	-0.132	598
2	-1.008	275	-0.124	484
3	-1.006	255	-0.116	431
4	-1.004	229	-0.122	429
Dist. H_2O				
1	-0.988	283	0.056	287
2	-0.988	289	0.054	273
3	-0.986	280	0.054	285
River water				
1	-1.000	405	-0.122	663
2	-1.010	374	-0.134	686
3	-1.010	334	-0.130	645
4	-1.010	322	-0.128	605

Table 2. Blanks of Chehalis River water*.

Metal	Peak potential before EP	N-amp before EP	Peak potential after EP	N-amp after EP
Zn^{++}	-0.996	1472	-0.984	259
Cu^{++}	-0.070	2754	-0.103	399

*Averages of four blank readings at the assumed peak potential do not represent actual peaks. EP = electro-purification.

Table 3. Effects of different buffer concentrations on de-ionized water blanks.

Vol. of acetate	M	Zn	Cd	Pb	Cu
50 µl	0.02	160	64	55	201
		176	60	57	198
		187	67	50	234
(avg)		(174)			(211)
100 µl	0.04	145	70	64	218
		155	74	67	223
		150	70	64	204
(avg)		(150)			(215)
150 µl	0.06	131	55	50	188
		142	74	68	205
		142	76	72	196
(avg)		(138)			(196)
200 µl	0.08	126	70	72	184
		130	70	72	185
		126	70	72	180
(avg)		(127)			(183)
300 µl	0.12	124	83	83	212
		122	83	84	220
		120	83	85	218
(avg)		(122)			(217)
400 µl	0.16	114	80	83	227
		117	88	93	233
		120	84	92	233
(avg)		(117)			(231)
$\bar{X}$		138	73.4	71.3	208
SD		± 20.8	± 8.9	± 13.4	± 18.4
% Error		15	12	19	9

Table 4. Effects of differing buffer concentration on river sample blank determinations. Current readings are in nano-amperes.

Vol. of acetate	Zn	Cd	Pb	Cu
Potential	-1.520	-0.740	-0.510	-0.190
50 µl	2979	342	197	380
	3092	347	173	375
	3220	359	169	385
$\overline{\text{avg}}$	(3097)	(349)	(180)	(380)
100 µl	2768	363	179	365
	2542	354	166	340
	2868	382	199	388
$\overline{\text{avg}}$	(2726)	(366)	(181)	(364)
150 µl	2463	382	185	404
	2552	384	178	396
	2475	375	188	372
$\overline{\text{avg}}$	(2497)	(380)	(184)	(391)
200 µl	2041	375	199	354
	2055	386	197	361
	2036*	374*	197*	400*
$\overline{\text{avg}}$	(2044)	(378)	(198)	(372)
300 µl	1408	375	207	360
	1415	368	207	330
	1441	375	211	363
$\overline{\text{avg}}$	(1421)	(373)	(208)	(351)
400 µl	1062	382	231	365
	1047	358	222	359
	1067	370	220	367
$\overline{\text{avg}}$	(1059)	(370)	(224)	(364)
$\overline{x}$		369.5	195.8	370
SD		$\pm$ 13.02	$\pm$ 18.66	$\pm$ 19.67
% Error		4	9	5

*Run was a little unsteady.

Table 5. Effects on starting base line by differing buffer concentrations.

Acetate buffer concentration		Current measurement starting potential of -1.250 volts			
M	Vol.	1	2	3	Avg
0.02	50 µl	280	275	283	279
0.04	100	327	339	449	371
0.06	150	416	422	473	437
0.08	200	485	468	431	461
0.12	300	527	535	527	530
0.16	400	583	534	552	556

Table 6. Water sample, 8/27/80, kinetic data.

Metal added	Conc. µg/L	Blank current n-amps	Time 2'	5'	10'	15'	30'	60'	Avg ←	Total metal AAS, µg/ℓ
										1.0
Cu^{++}	Blk	195								
	10	--	264	266	257	249	256	252	257	16.0
	Blk	184								
	20	--	--	--	--	--	--	331	331	17.0
	Blk	201								
	40	--	647	630	619	617	613	649	629	29.0
	Blk	194								
	75	--	1089	1064	1064	1069	1080	1089	1076	81.0
	Blk	179								
	150	--	2697	2657	2669	2640	2629	2617	2652	140.0
	Blk	186								
	300	--	6400	6490	6440	6540	6480	6560	6485	289.0
										2.0
Zn^{++}	Blk	151								
	10	--	537	538	538	533	523	526	533	7.0
	Blk	144								
	20	--	875	934	834	945	958	958	917	24.0
	Blk	140								
	40	--	1682	1671	1714	1723	1767	1761	1720	45.0
	Blk	154								
	75	--	2450	3389	3379	3198	3198	3414	3171	81.0
	Blk	176								
	150	--	6240	5660	5670	6310	5740	5480	5850	140.0
	Blk	162								
	300	--	9370	9080	10720	10900	11330	10950	10392	281.0

Table 7. Water sample, 8/27/80, kinetic data.

Metal added	Conc. µg/L	Blank current n-amps	Time 2'	7'	15'	20'	30'	60'	Avg ←	Total metal AAS, µg/ℓ Cu	Zn
(Cu + Zn)											
	Blk	255								3.0	
Zn	10		853	875	871	850	872	842	860	7.4	
	Blk	--									
Cu	10	--	--	--	--	509	540	508	519		13.0
	Blk	188									
Zn	15	--	811	796	797		794	794	798	16	
	Blk	--									
Cu	15	--	--	--	--	--	--	--			23
	Blk	142									
Zn	30	--	1427	1436	1425		1435	1483	1432	32	
	Blk	249									
Cu	30	--	808	743	761		734	722	754		40
	Blk	115									
Zn	75	--	3286	3342	3407		3410	3441	3377	74	
	Blk	214									
Cu	75	--	2059	2248	2258		2283	2295	2229		80
	Blk	138									
Zn	150	--	6140	6280	6350		6320	6250	6268	150	
	Blk	237									
Cu	150	--	5020	5060	5140		5270	5250	5148		156
	Blk	122									
Zn	300	--	10860	11580	11550		11900	11940	11566	288	
	Blk	198									
Cu	300	--	10000	10890	11150		11180	11310	10906		280

Table 8. Water sample, 12/21/80, kinetic data.

Metal added	Conc. µg/L	Blank current n-amps	Time 2'	5'	10'	15'	30'	60'	Avg ←	Total metal AAS, µg/ℓ
Cu^{++}	Blk	206								1.5
	10		388	391	382	376	373	337	374	8.0
	Blk	211								
	15		402	410	396	396	393	378	395	11.0
	Blk	189								
	30		546	565	532	556	562	572	555	30
	Blk	219								
	60		831	802	830	816	808	775	810	57
	Blk	189								
	125		2181	2161	2197	2022	2079	2033	2112	123
	Blk	208								
	250		4150	4100	4110	4040	3928	3969	4049	246
Zn	Blk	151								2.4
	10		537	538	538	533	523	526	532	8
	Blk	144								
	20		875	934	834	945	958	958	917	23
	Blk	140								
	40		1682	1671	1714	1723	1767	1761	1719	32
	Blk	154								
	75		2450	3389	3379	3198	3198	3414	3171	72
	Blk	176								
	150		6240	5660	5670	6310	5740	5480	5850	150
	Blk	162								
	300		9370	9080	10720	10900	11330	10950	10392	250

Table 9. Water sample, 12/21/80, kinetic data.

Metal added	Conc. µg/L	Blank current n-amps	Time 2'	7'	15'	30'	60'	Avg ←	Total metal AAS, µg/ℓ
(Cu + Zn)									
Zn	Blk	194							0.9
	10		646	645	644	646	656	647	13.0
Cu	Blk	204							0.5
	10		429	426	428	428	430	428	12.2
Zn	Blk	150							
	15		763	777	806	794	812	790	13.0
Cu	Blk	186							
	15		460	478	475	486	491	478	15.4
Zn	Blk	151							
	30		1321	1347	1234	1361	1451	1343	35.0
Cu	Blk	221							
	30		711	704	676	724	748	713	30.0
Zn	Blk	168							
	75		2869	2730	2272	2878	3190	2788	69.0
Cu	Blk	198							
	75		1780	1768	2043	1933	1938	1892	72.0
Zn	Blk	177							
	150		6780	6920	7000	6980	7000	6936	150.0
Cu	Blk	203							
	150		5090	5210	5180	5070	5030	5116	152.0
Zn	Blk	184							
	300		12600	12510	12920	13300	12920	12850	310.0
Cu	Blk	194							
	300		10820	11040	11440	11670	11090	11212	302.0

Table 10. Current data for a river blank repeated seven times.

	Zn	Cd	Pb	Cu
1	2123	90	114	300
2	2662	119	140	345
3	2666	115	130	325
4	2268	110	123	312
5	2784	105	127	285
6	2775	102	120	299
7	2807	100	115	295
$\overline{X}$	2584	106	124	309
SD	$\pm$ 274	$\pm$ 9.8	$\pm$ 9.1	$\pm$ 20.5
%	10.6	9.2	7.4	6.6

Table 11. Polarographic information measuring 200 ppt of each metal.

Metal	SD	CV	n
Zn	4.79	9%	5
Cd	2.22	3%	5
Pb	4.36	10%	5
Cu	3.20	3%	%

Table 12. Accuracy of measurement using EPA standard solution #476 in a water sample.

	Zinc	Cadmium	Lead	Copper
Current in nanoamps	N.D.	262	640	481
	N.D.	266	646	496
	N.D.	267	655	501
Concentration in µg/L in ambient water sample	N.D.	1.48	5.78	3.60
Less concentration in ambient water	N.D.	0.17	0.65	1.37
Net concentration for EPA standard found	N.D.	1.31	5.13	2.23
Concentration in original EPA standard	N.D.	1.35	5.65	1.85
% Recovery	N.D.	97	91	120

Table 13. Zinc and copper content of various molecular weight fractions.

Molecular Wt. fraction	Zinc µg/L	Copper µg/L
500-1,000	0.11	N.D.
1,000-5,000	0.29	0.16
5,000-10,000	0.19	0.20
10,000-50,000	0.04	0.04
50,000-100,000	0.05	0.11
100,000-300,000	0.03	0.08
Over 300,000	0.62	0.25

Table 14. Concentration of metals in ambient and humic concentrate.

Ambient		Humic concentrate	
Metal	Conc. µg/L	Metal	Conc. µg/L
Zn	< 10.0	Zn	563
Cd	< 0.2		
Pb	< 1.0		
Cu	2.5	Cu	191

Table 15. Raw data for Cu^{++} in deionized water. The n amp readings are taken from the recorder, allowing 10 min for stabilization.

Cu Std 1 x 10^{-4} M	DI-H_2O	Buffer	Cu^{++} Conc. (ppb)	Kiethly Reading (mamp)
0 µl	99.0	1.0	0.0	0.2
50	98.95	1.0	3.2	1.4
100	98.90	1.0	6.4	2.7
250	98.75	1.0	15.9	5.5
500	98.50	1.0	32.0	13.0
1,000	98.00	1.0	64.0	22.0

Table 16. Four determinations of binding capacities on four separate days. Parentheses indicate blank readings. Conditions:
Binding substance = humic acid, Aldrich Chem. Co. H1,675-2 at 10 mg/L, metal is copper
Sens = Med.
Rate = Fast
Scan = -1.2 to +0.1 volts
Purge time = 15 min
Dep. time = 60 sec
Buffer = Sod. Ac. pH 7.3 at 0.02 molar

Day 1			Day 2		
Conc ppb	E_v Pot.	n amps -blank	Conc 1	E_v Pot.	n amps -blank
0		(290)	0		(287)
20	-0.158	210	20	-0.148	192
40	-0.150	493	40	-0.148	572
60	-0.124	1019	60	-0.112	1237
80	-0.114	1695	80	-0.107	2053
100	-0.110	2724	100	-0.104	2740
120	-0.106	3237	120	-0.104	3550
140	-0.104	4040	140	-0.102	4300
			160	-0.102	4499
			180	-0.102	6217
Day 3			Day 4		
0		(208)	0		(228)
20	-0.184	297	20	-0.245	109
40	-0.170	567	40	-0.236	243
60	-0.148	897	60	-0.234	363
80	-0.124	1383	80	-0.214	564
100	-0.116	2177	100	-0.174	793
120	-0.116	2632	120	-0.150	1055
140	-0.114	3326	140	-0.141	1378
			160	-0.134	1793

Calculated BC

Day	BC, µg/L	r^2
1	34.6	0.999
2	32.5	0.995
3	32.3	0.997
4	34.6	0.996

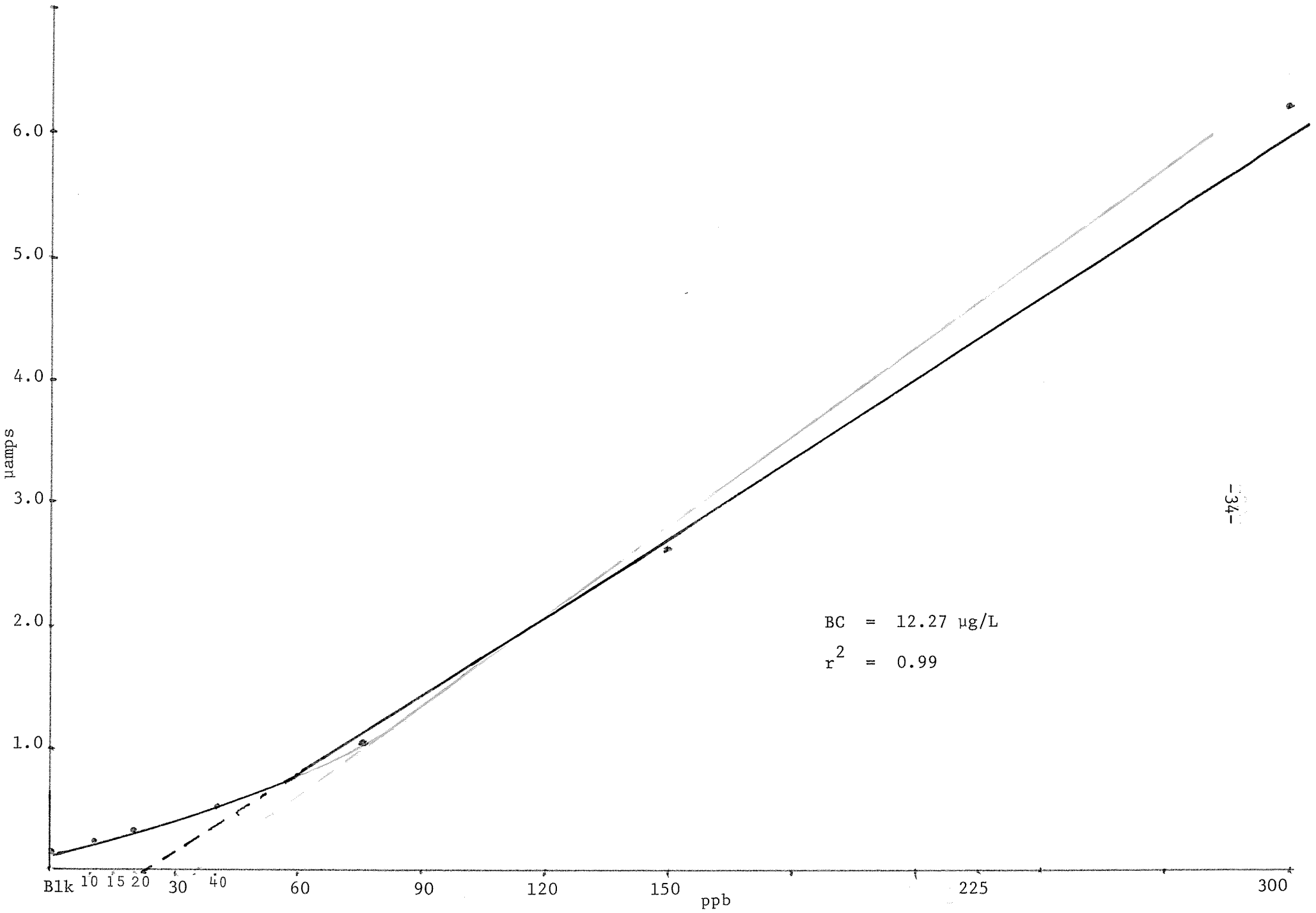

Fig. 1. Plot of copper alone, 8/27/80 water.

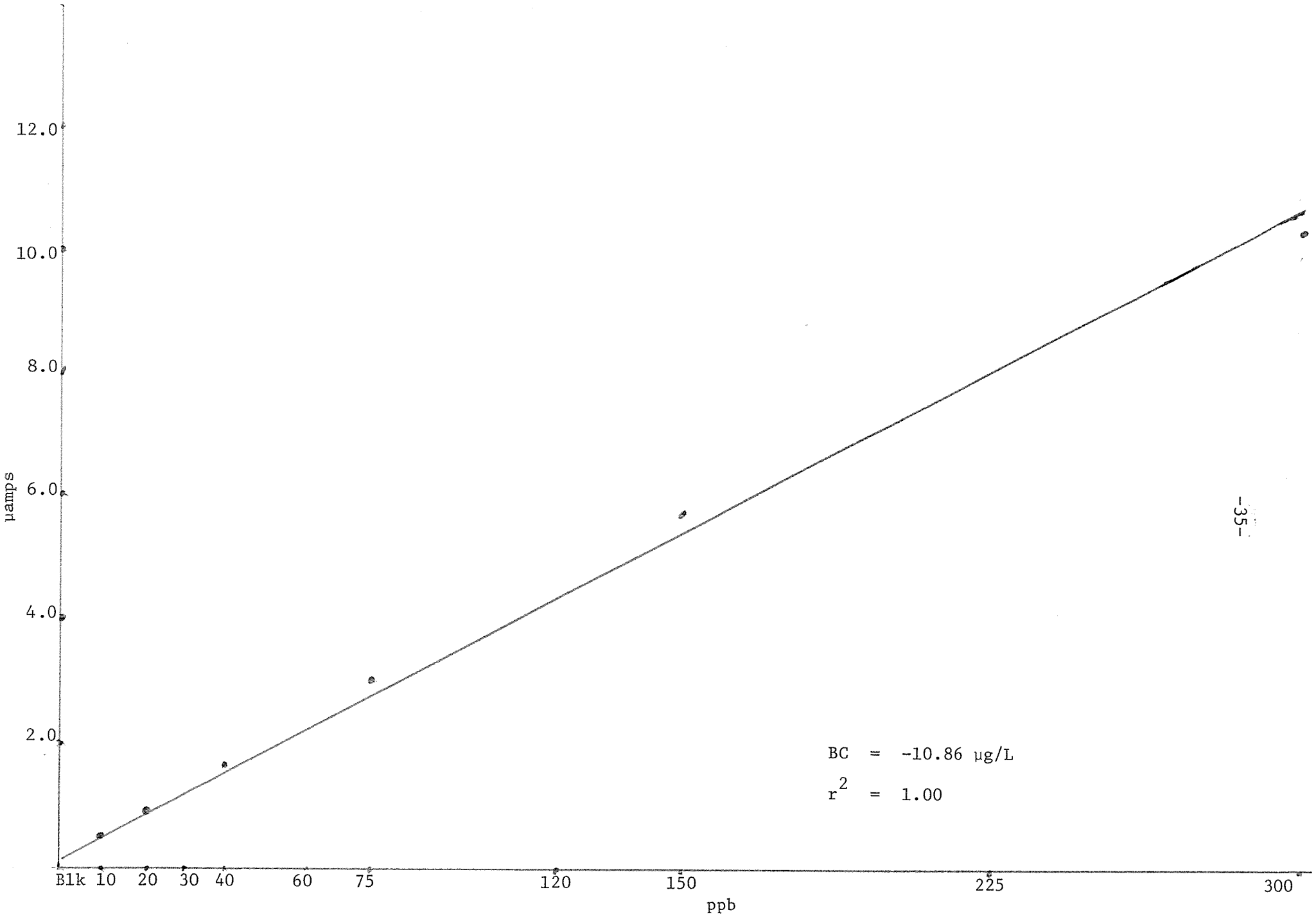

Fig. 2. Plot of zinc alone, 8/27/80.

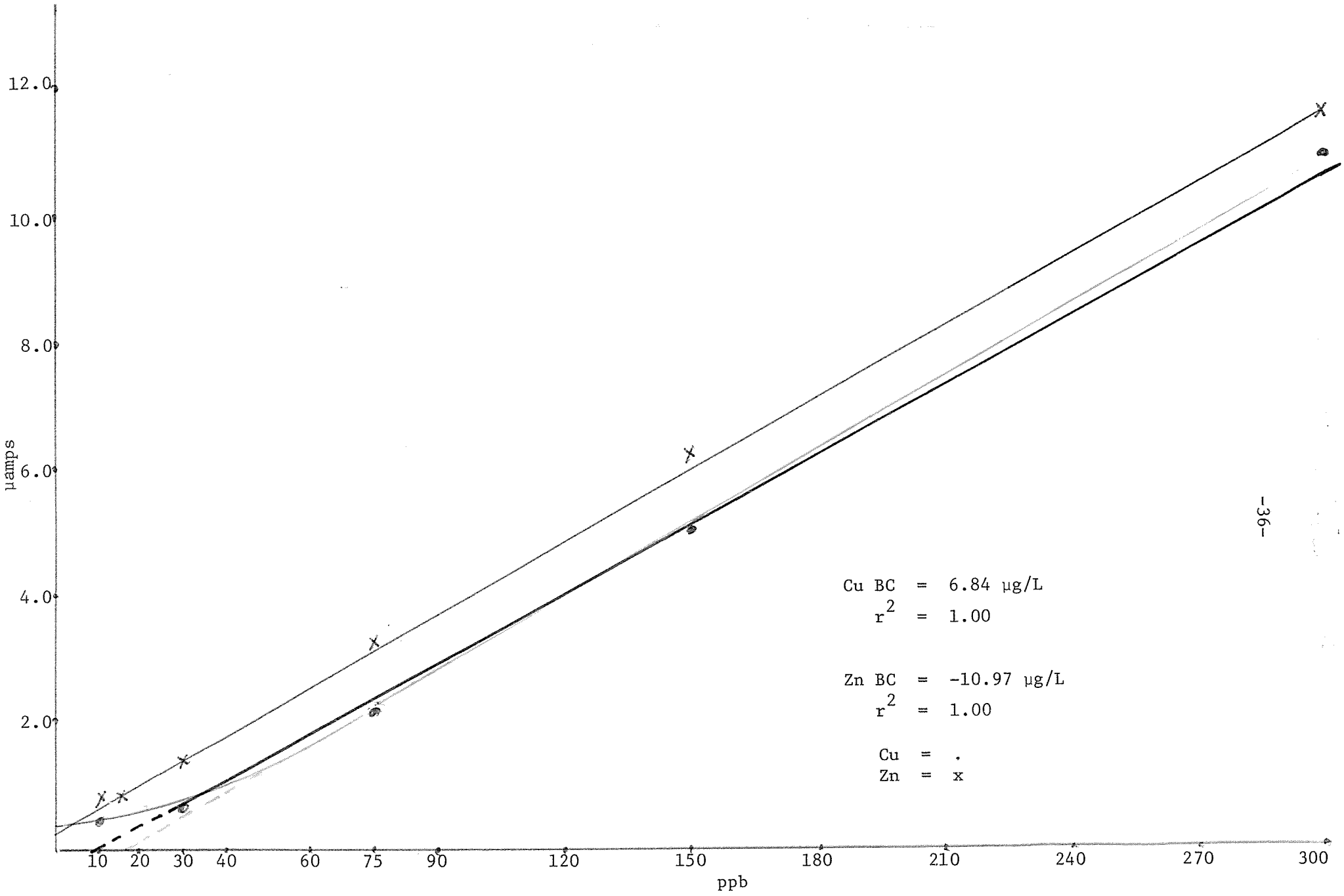

Fig. 3. Plot of Cu + Zn additions, water, 8-27-80.

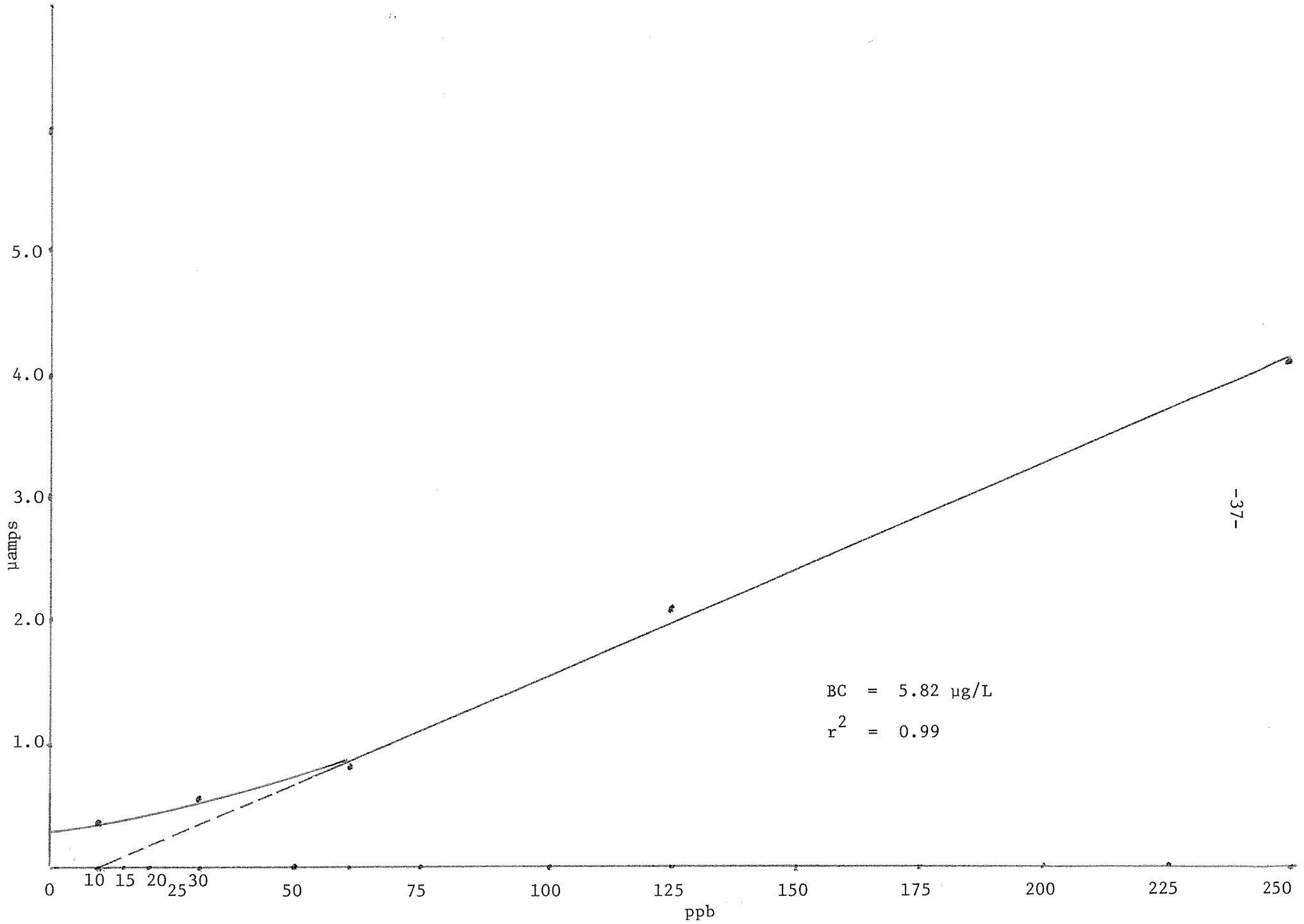

Fig. 4. Copper alone, 12/21/80.

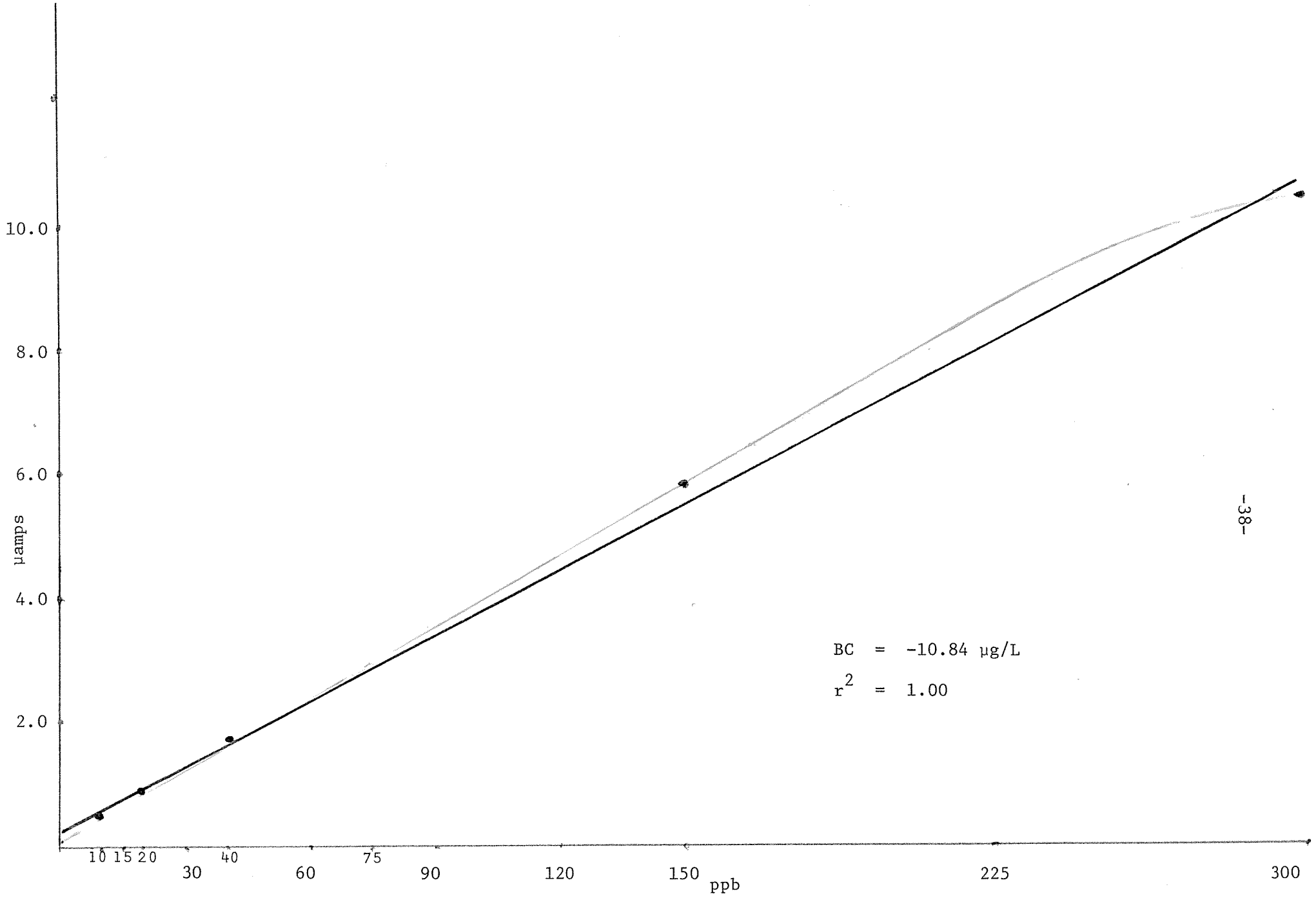

Fig. 5. Zinc alone, 12/21/80.

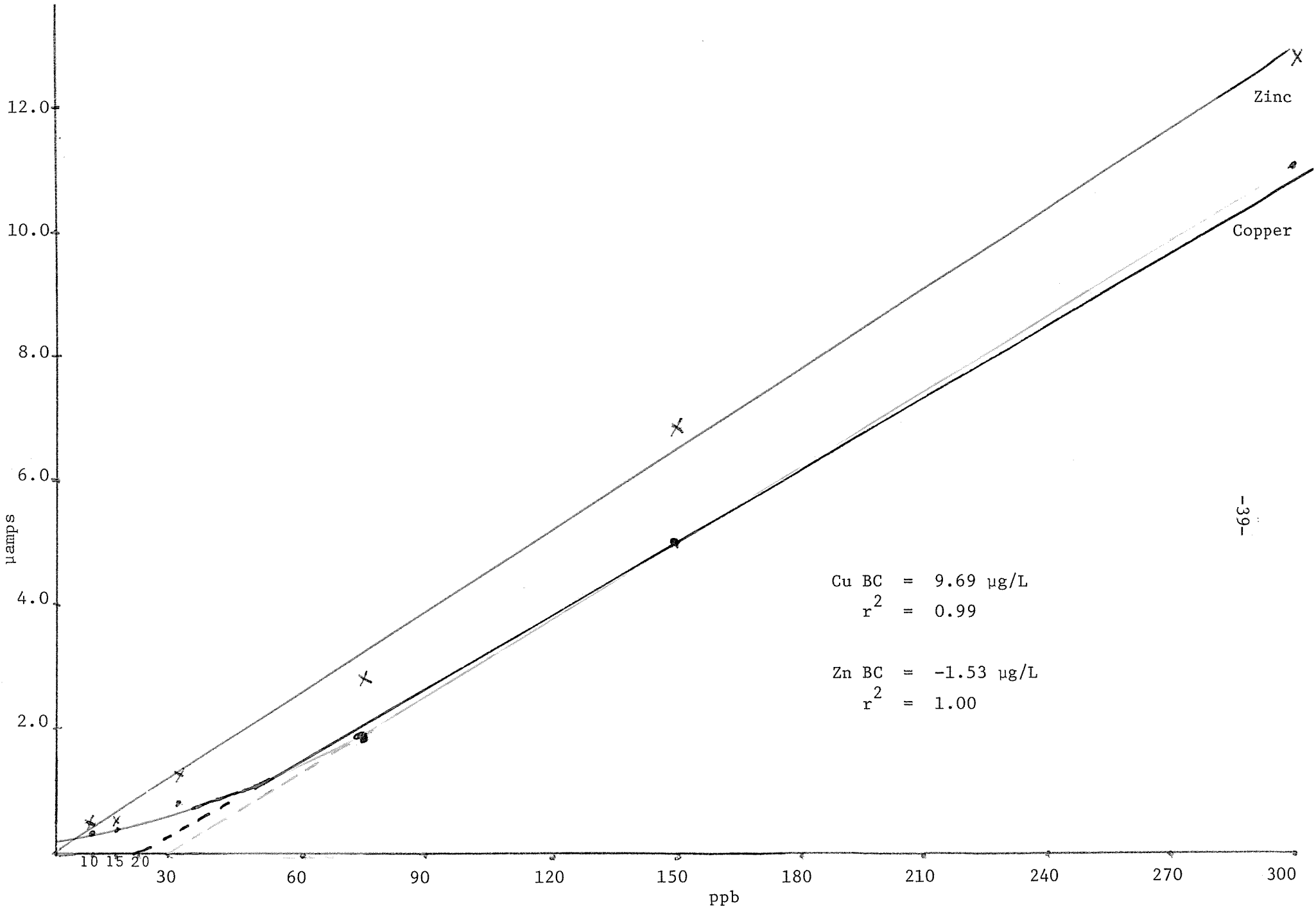

Fig. 6. Copper (•) + Zinc (x), 12/21/80.

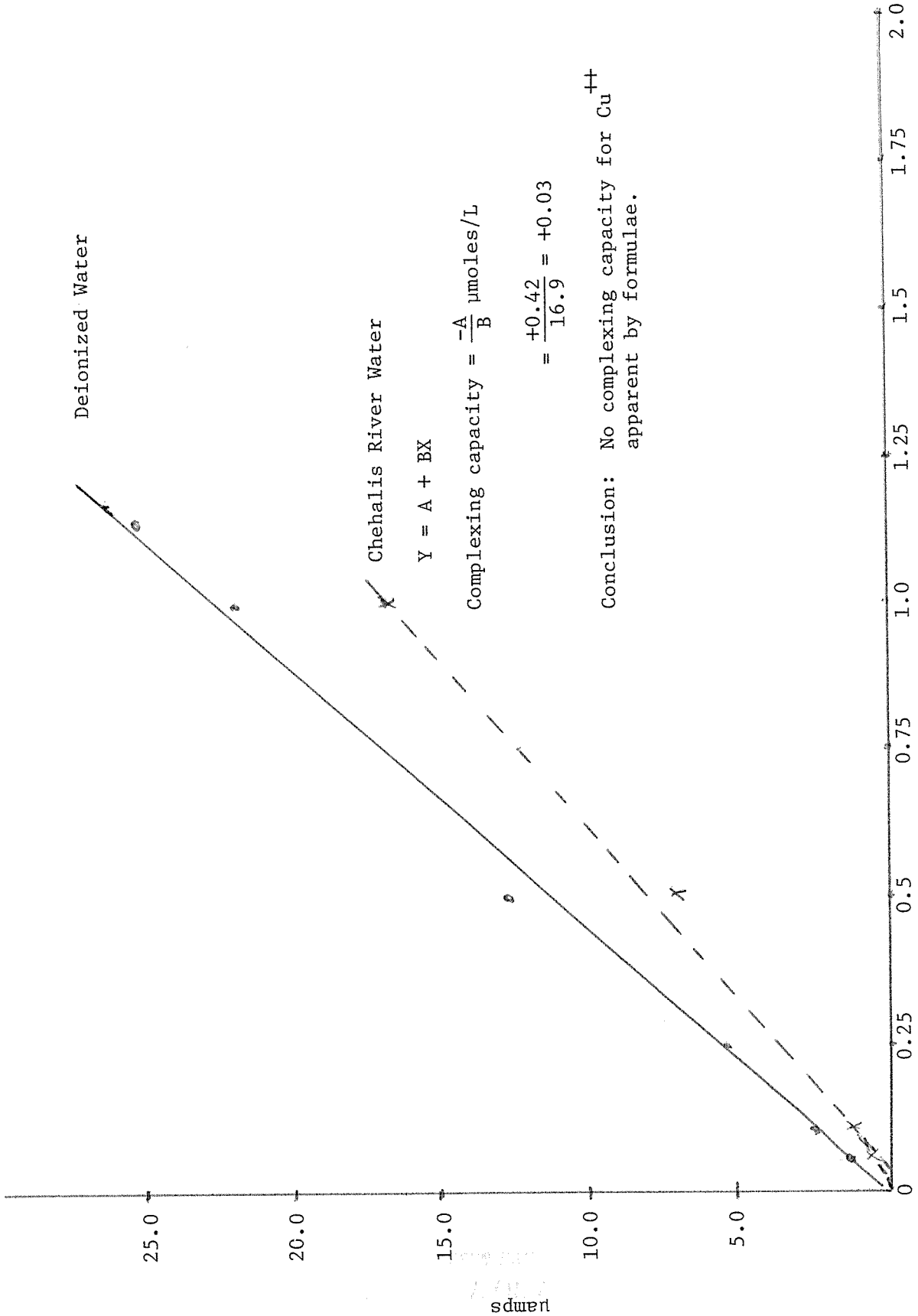

Fig. 7. Standard curve for copper in deionized water and complexing capacity of Chehalis River water determined by ion specific electrode. Data points not corrected for probable cupric ion background in the acetate buffer, pH = 5.2.

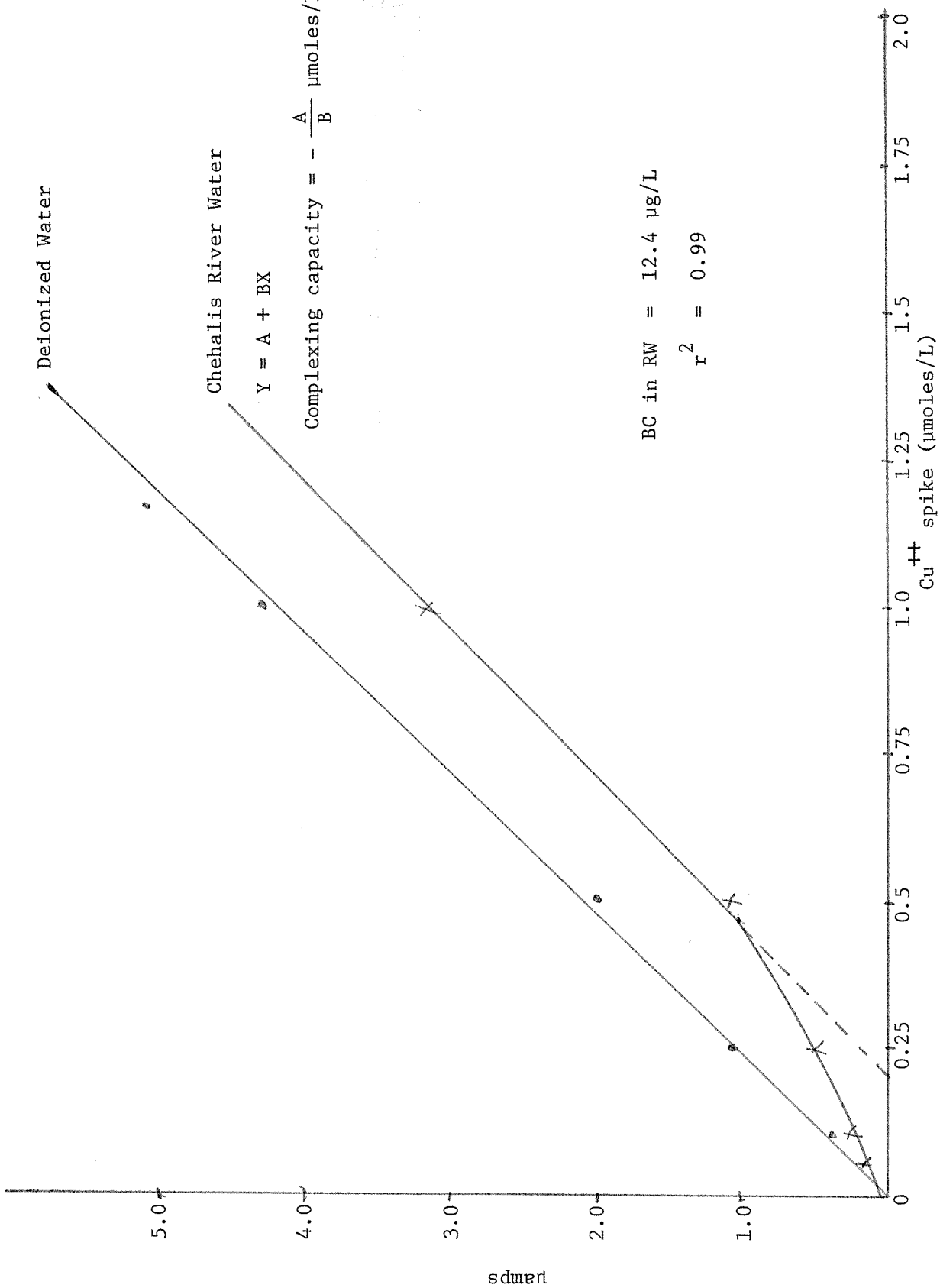

Fig. 8. Standard curve for copper in deionized water and complexing capacity of Chehalis River water by diff. pulse anodic stripping voltammetry.

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