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A CASE EXAMINATION OF THE STANDARD
ELUTRIATE TEST

by

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A case examination of the standard elutriate
test, a screening procedure for dredging regulatory
criteria. Discussion based on observed water quality
parameters = complexing capacity, stability, heavy
metals, phosphorus and others.

by

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INTRODUCTION

The impact of dredging activities on the Great Lakes environment has recently received a great deal of attention as evidenced by the recent report of the International Working Group[1]. As yet no one can say for certain what can or cannot be dumped in open water or on land. On the other hand, it is necessary to provide dredging criteria which are as fair and sound as possible. In this light, the present working rules need to be improved, as can be illustrated by a recent statement of the Working Group[2].

" The Working Group concluded that the unqualified acceptance of the numerical system, currently employed as the sole basis for characterizing sediments, was not supportable. A preferred approach is based upon a case-by-case evaluation. How-ever, it was recommended that some form of a numerical system be employed in order to define clearly uncontaminated sediments. Dredging operations associated with such sediments would not be subject to the more rigorous evaluation anticipated for other materials. "

The criteria of the U.S. Environmental Protection Agency (EPA), which are based on bulk-sediment composition, are also known to be lacking in some respects[3]. To better determine the

pollution status of dredged materials prior to open water disposal,
EPA and U.S. Corps of Engineers have proposed a screening procedure
-- the standard elutriate test -- essentially to determine the
"solubility of pollutants". Although this is an improvement over
the EPA criteria, further realistic examination of the test is
necessary. This report relates to water quality parameters which
were considered in a series of tests designed to appraise the
elutriate technique. It is hoped that the discussion will shed
some new light on this important approach.

An attempt was made to create a situation which closely
reflected a real occurrence. Suppose that a company wants a permit
to carry out the following dredging project:

Dredging site = Hamilton Harbour - near Dofasco

Steel Co. (Fig. 1, location 1)

(The sediment is believed to be polluted)

Dumping site = Lake Ontario (Fig. 1, location 2)

(The water is believed to be relatively

clean)

The question is whether or not a permit should be granted.
Obviously many aspects have to be taken into consideration before
the final decision can be made, but the chemical aspects form the
focus of attention in this report.

EXPERIMENTAL

Preparation of solutions and chemicals

The standard elutriate was obtained following the procedures which are described by Keely and Engler[3]. Two liters of sediment were mixed in situ with eight liters of unfiltered water from the disposal site in a polyethylene container. This mixture, having 1:4 volume ratio of sediment:water, was then manually shaken for one hour, as vigourously as possible. (Note that the original procedures recommend using a shaker and a half hour shaking time; since at the time we didn't have a shaker big enough to handle the 5-gallon container, we assumed that one hour manual shaking would produce comparable effects.) After shaking, the mixture was allowed to settle for one hour; then, the supernatant was decanted and filtered once with glass-filter and thrice with 0.45 μ membrane filter in order to obtain the clear filtrate. (Here we assumed that filtering once through a glass-filter and twice through a 0.45 μ membrane filter would replace the centrifugation step as stated in the original procedures.) The clear filtrate, called standard elutriate and designated by X, was then subdivided for analyses of constituents concerned. X will also represent a certain parameter--say mercury concentration--in the standard elutriate. In the same fashion, X_o refers to filtered disposal site water or a certain parameter in it.

We also prepared other solutions (Y_o, Y, Z_o and Z) in the same manner as X_o and X:

Y_o = dredging site water

Y = 1:4 volume ratio of sediment:dredging site water

Z_o = 50-50 mixture of X_o and Y_o

Z = 4:1:4 volume ratio of dredging site water:sediment: disposal site water.

All mixing was done aboard ship right after the samples were collected. A shipek grab was used to obtain the sediment samples, (Sly[4]).

Reagent grade chemicals or better were used without further purification. The preparation of fulvic acid has been described elsewhere[5].

Methods

Most of the analyses were made by Water Quality Branch, CCIW, using the methods described by Traversy[6], except for com -plexing capacity (C_x C_y) and conditional stability constant (K). C_x C_y was measured by anodic stripping voltammetry[7], and was tentatively used in the K measuring processes[8,9]. The titration cell, designed and built in our laboratory and described elsewhere[8,10] , is schematically shown in Fig. 2. K was determined at $25^{\circ}C$;the concentration of background electrolyte, $NaNO_3$, which was needed to help stabilize the electrode response, was 0.03 M.

It has been observed (Chau, personal communication) that the complexing capacity of a water sample from Lake Ontario, stored at room temperature, decreases with time and may even -tually reach zero within 1-2 months. To prepare the background solution for potentiometric titrations we collected a water sample from Hamilton Harbour (Fig. 1, location 3), the sample was twice filtered through 0.45 μ membrane filter and stored at room temperature for three months. The complexing capacity was then measured, in duplicate as in other cases. A small value of 0.75 μ M was obtained and since this was not zero, K values measured were not quite absolute. In spite of this relative character of the stability constant, it may be readily seen that it is clearly indicative of the class of reacting materials.

The titration experiment with ethylenediamine tetraacetic acid (EDTA) was restricted to pH below 4 as at higher pH the EMF readings were out of calibration range. The reported log K values for CuEDTA at pH 3, 4, 5, 6 and 7 are respectively 8.3, 10.2, 12.2, 14.0 and 15.4[11]. The calibration for the prepared solutions was made at pH 5.5, whilst that for fulvic acid (FA) was conveniently made at pH 3-4, which should be rigourously valid up to at least pH 5.5[9]. The same calibration was used for the titration at higher pH, and according to Orion instruction manual (form IM94-291869) this should be satisfactory, especially when working with low concentrations of cupric ions.

RESULTS AND DISCUSSION

Complexing capacity and conditional stability constant

The complexing capacity values of different solutions are reported in Table 1. As can be seen, $C_x C_y$ clearly increases in X and Z cases, indicating that some exchange processes occurred during the mixing-shaking actions and apparently in favor of the release mechanism. Although it isn't so obvious in Y case--which could mean that the sediment and water at dredging site are in an equilibrium state--we will see that the evaluation of conditional stability constant helps decide whether or not some exchange took place.

In order to obtain K, we needed to know the total concentration of ligands, T_L, available for reaction with cupric ions. For that we have tentatively set $C_x C_y$ equal to T_L, assumed that complexation is the most important mechanism, and proceeded to measure K as previously done[9]. The resulting log K values are shown in Table 1 and plotted as X, Y, Z and Y_o in Fig. 3. An interesting feature of the plot is that Y is significantly higher than Y_o (even though $C_x C_y$ (Y) $\sim C_x C_y$ (Y_o), thus apparently in-dicating that some exchange occurred and that the released material can form stronger complexes. Another point is that log K values for X, Y and Z are about the same, which means that the complexing material released in all three cases is basically the same. (All of the sediment was from the same location.)

To gain some insight regarding these released materials, two comparative studies with fulvic acid (FA) and ethylenediamine tetraacetic acid (EDTA), were made. The complexing capacity of both acids were determined and also set equal to T_L. Log K's for FA (triangles) and EDTA (circles and stars) are plotted in Fig. 3, in which several points can be discussed. But the feature of interest here is that log K's of X, Y and Z are relatively much closer to FA's than to EDTA's, implying that the released material is a) a weaker complexing material than EDTA, and b) it could possess some characteristics of fulvic material.

The effect of equating C_x C_y and T_L on fulvic acid is that two distinct behaviors of log K were produced, depending on the mole fraction of copper, x_{cu} (see Fig. 3). (x_{cu} is defined as $T_{cu}/(T_{cu} + T_L)$ where T represents total concentration; thus T_{cu} is total concentration of copper). For clarity, two smooth curves were drawn to represent the open triangles and the solid ones, having $x_{cu} = 0.6$ - 0.8 and 0.42 respectively. The first curve rises so rapidly with pH that, at pH higher than about 5.3, the concentration of the complexes exceed T_L, thereby making the evaluation of K impossible. This means that the amount of complexes formed increases rapidly with pH and it seems to imply that the actual total concentration of ligands or com- plexing sites is really greater than the C_x C_y value itself. Similarly with X, Y and Z cases at pH 5.5, we could not evaluate K at $x_{cu} > 0.5$, hence X, Y and Z in Fig. 3 represent the data points having x_{cu} smaller than

0.5. The cu-EDTA experiment was also carried out at $x_{cu} < 0.5$; the open circles refer to experimental data, and the two stars joined by a line to the literature values[11] (at 20° C and ionic strength 0.1). The second curve represented by the solid triangles, on the other hand, behaves more normally--that is the change in log K with pH is not as drastic, and also we were able to evaluate K at higher pH. Futhermore, the curve could easily be made up of X, Y and Z points also, which led us to speculate that the released material from sediment and fulvic material have similar reacting properties.

We have seen that by setting the value of $C_x C_y$ equal to total concentration of ligands, some difficulty arose when we tried to evaluate K at $x_{cu} > 0.5$. It should be noted that for EDTA, Chau et al[12] observed $C_x C_y$ = molar concentration based on molecular weight. We found $C_x C_y$ = 0.255 times molar concentration of bidentate chelating sites (b.c.s.) for fulvic acid. In order to appreciate the change in K with ways of expressing the concentration of ligands, let us analyse FA data in terms of b.c.s., and similarly treat the data on X, Y, Z and Y_o as if the reacting materials in these solutions had the same complexing sites as fulvic acid. The resulting constants are plotted in Fig. 4, whose symbols refer to the same data as in Fig. 3. The main features of interest in Fig. 4, as compared to Fig. 3, are a) the general lowering of log K, and b) the more "normal" behavior of log K associated with the

open triangles. Except for the region of pH > 4.75 for the open

triangles, the net lowering effect in all log K's is about one

unit. All these changes in log K, however, still indicate that

whatever was released from the sediment is a weaker complexing

material than EDTA, it is about as strong as FA, and the value

of $C_x C_y$ (as measured by voltammetry) may well be lower than the

actual total concentration of available reacting sites.

Heavy metals, other parameters, and ocean dumping criteria

Table 1 provides some experimental water quality

parameters together with their standard. Note that for complexing

capacity, X is equal to 2.25 X_0, that is X > 1.5 X_0--the present

upper limit of ocean dumping criteria, and therefore it would be

a "no-go" case. But does it really mean that a value of X = 124

ppb is a hazard to concerned species? To appreciate this dilemma

further, let us take Zn as another example where X = 7.5 X_0--an

apparent "no-go" case. In this, X is only 60 ppb and is way below

the acceptable limit of drinking water standard (DW) [13a], 5000

ppb (Table 1). Furthermore, it is even smaller than the standards

for marine (MW) or freshwater (FW) aquatic life [13b, 13c] (see also

Table 1). As these standards are realistically related to environ-

ment, it would seem most sensible to compare X and X_0 to them

(rather than comparing X and 1.5 X_0). Finally as Z solution is

prepared from both waters, it should be more representative than X,

which is prepared from disposal site water alone; then, it might even be better to use Z value in lieu of X for comparison with the standards.

The concentration of Hg, Cd and Pb in the standard elutriate is about equal to that in the original disposal site water, and is smaller than the standard for drinking water and marine or freshwater aquatic life. For Hg, however, FW is only slightly greater than X_o, meaning that the Hg level in this part of Lake Ontario is nearly critical for aquatic life. Is this a fact? (The local smelts which we caught in buckets and buckets looked healthy and were delicious!)

For phosphorus, however, it looks as though there may be some concerns. But firstly note the different units expressed, in Table 1, for DW, FW and in all the solutions, it is impossible to rigourously compare them as expressed. One can multiply FW by 3.066 and have it expressed as inorganic phosphates (306.6 ppb), which is higher than the acceptable limit for drinking water standard (200 ppb). Furthermore, according to Canadian drinking water standards[13a], the maximum permissible limit is more than an order of magnitude greater than the acceptable limit. For a further example, consider Arsenic where the latter limit is 10 ppb and the former is 50 ppb. For Cyanide it is even more, 10 ppb vs. 200 ppb. Thus it appears that the phosphorus concentrations in X_o, ..., Z solutions are not as critical as they look. Nevertheless, our results do indicate

that the release of phosphorus in one form or another is rather large: $X = 3 X_0$, $Y = 1.8 Y_0$ and $Z = 4.7 Z_0$. Also, the total concentration of phosphorus in unfiltered samples (bracketed values in Table 1) are considerably higher than X, Y, and Z. The biological significance of such particulates remains, as yet, incompletely understood.

As for DDT, oil and grease, and total dissolved solids, the concentrations in all the solutions are definitely below the standards. E_h values were measured before filtration steps and are also reported in Table 1. For X_0 and Y_0 solutions, measurements were made in situ at 7° C and 9° C respectively, whereas for X, Y and Z they were done after the shaking steps. From the change in E_h (Table 1), it looks as if some oxidation processes might have occurred during the mixing of sediment and water.

Finally, it is interesting to note that the concentration of Zn, Hg, Pb, Cd and P in interstitial waters (IW)[14] are no higher than the corresponding standards. In fact, they are generally lower, and the high limits of IW are exceptions rather than rules. (The values on Pilot Island are those from December 1973 - July 1974; those of Chemex were taken before and after dredging at Port Stanley, Lake St. Clair and Bronte Harbour in the latter part of 1973).

CONCLUSION AND SUGGESTIONS

The following conclusion and suggestions pertain mainly to the study as described above. Some could be valid generalizations however.

1. Although the concentration of the standard elutriate can be greater than 1.5 times the original concentration for the four heavy metals considered, it is still less than the standards for drinking water and freshwater or marine aquatic life. Thus these releases themselves do not significantly affect the water quality.

2. The mixing - shaking processes of the water-sediment mixtures result in: a) large release of total phosphorus into the water column (>1.5 times the original concentration); b) a decrease in the E_h values of the water; and c) an increase in the conditional stability constant value.

3. In these theoretical dredging activities, some complexing material is released to the water column, and its re-acting strength is similar to fulvic acid. The complexing capacity in general increases after settling. As this parameter is necessary for stability constant evaluation, supplementary studies on it are highly desirable--in particular by specific ion electrode and by Gran's functions[15].

4. For potentionmetric titrations, one needs to prepare the "zero" complexing capacity solution, which is relevant to the solution concerned, say S, whose complexing capacity is known. For this we suggest dividing S into two parts, one for actual titrations and the other passed through the XAD-2 column (which extracts complexing materials) for background solution.

5. The unfiltered samples from water-sediment mixtures (as compared to the filtered ones) contain very high concentration of phosphorus and most probably other pollutants as well.

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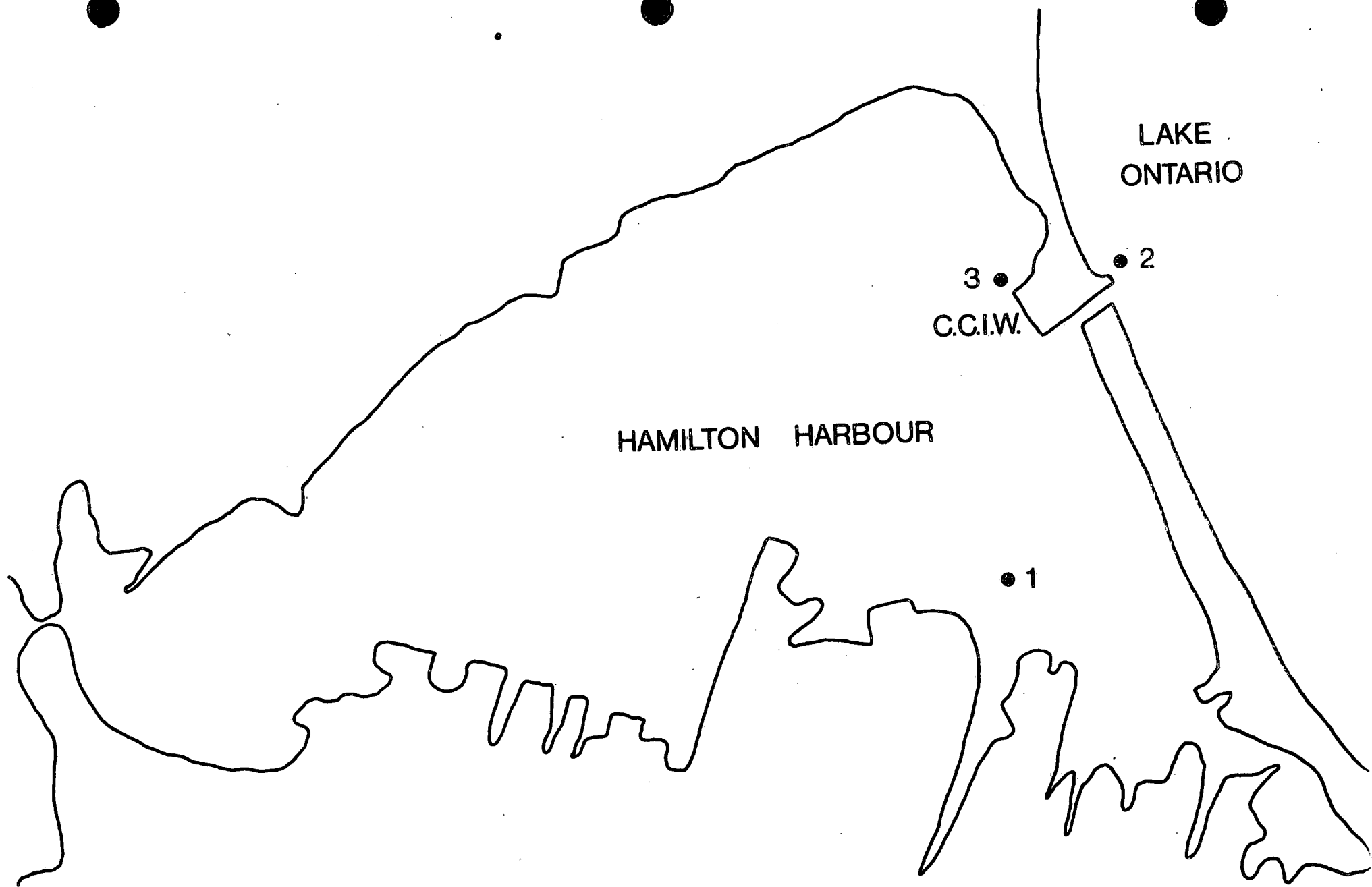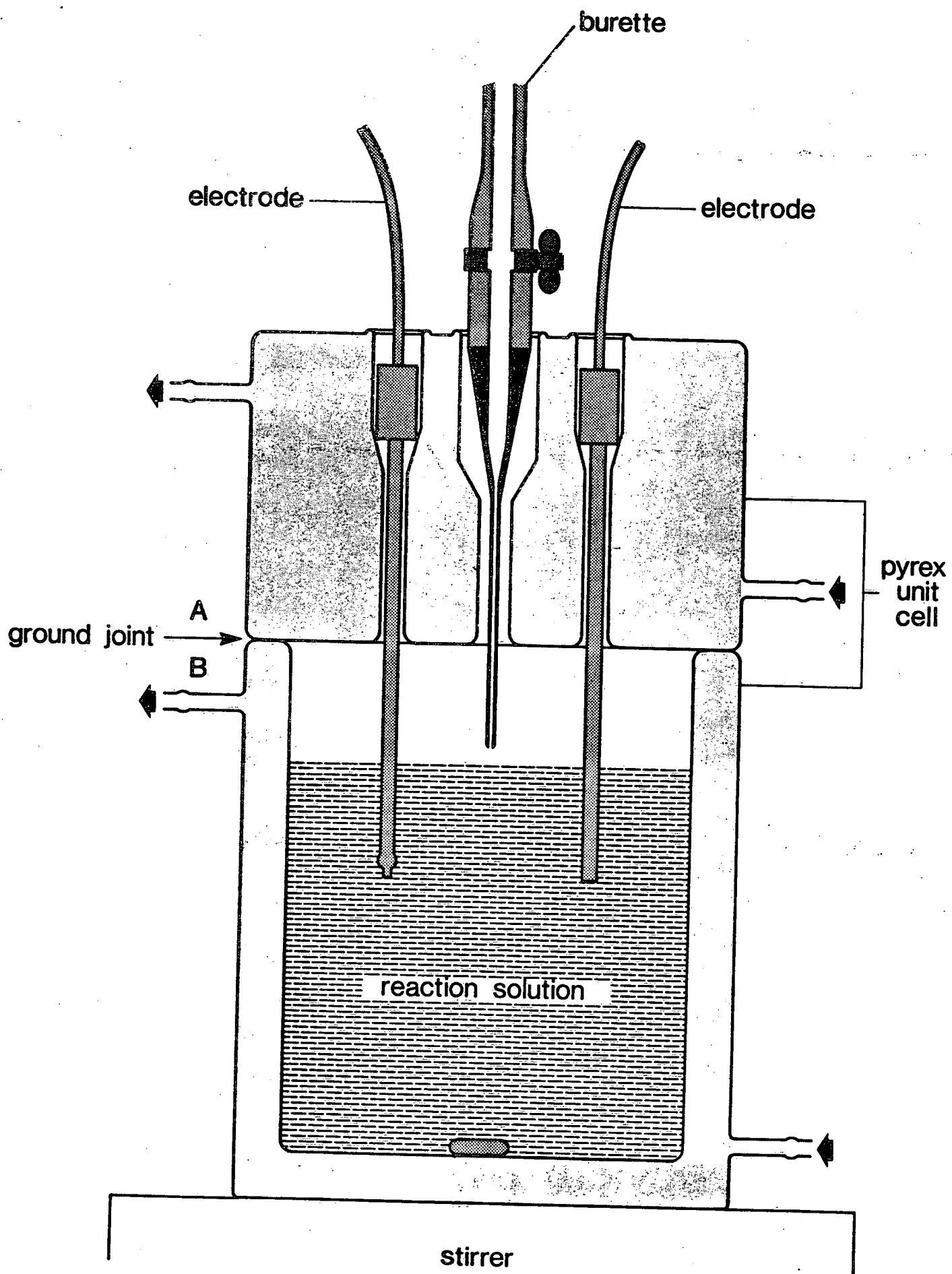15. D. S. Gamble, Can. J. Chem., 50, 2680 (1972).

LAKE
ONTARIO

LAKE
ONTARIO

3 ●

● 2

C.C.I.W.

HAMILTON   HARBOUR

● 1

FIG. 1   SAMPLING LOCATIONS

burette

electrode — electrode

pyrex
unit
cell

ground joint → A

B

reaction solution

stirrer

FIG. 2   TITRATION CELL

FIG. 3   LOG K $(C_x C_y)$ and pH

Legend (inside plot):
- ○ Cu EDTA
- ☆ Cu EDTA (ref. 11)
- ▲ Cu FA $\alpha C_{Cu} = 0.16$
- △ Cu FA $\alpha C_{Cu} = 0.27 - 0.52$
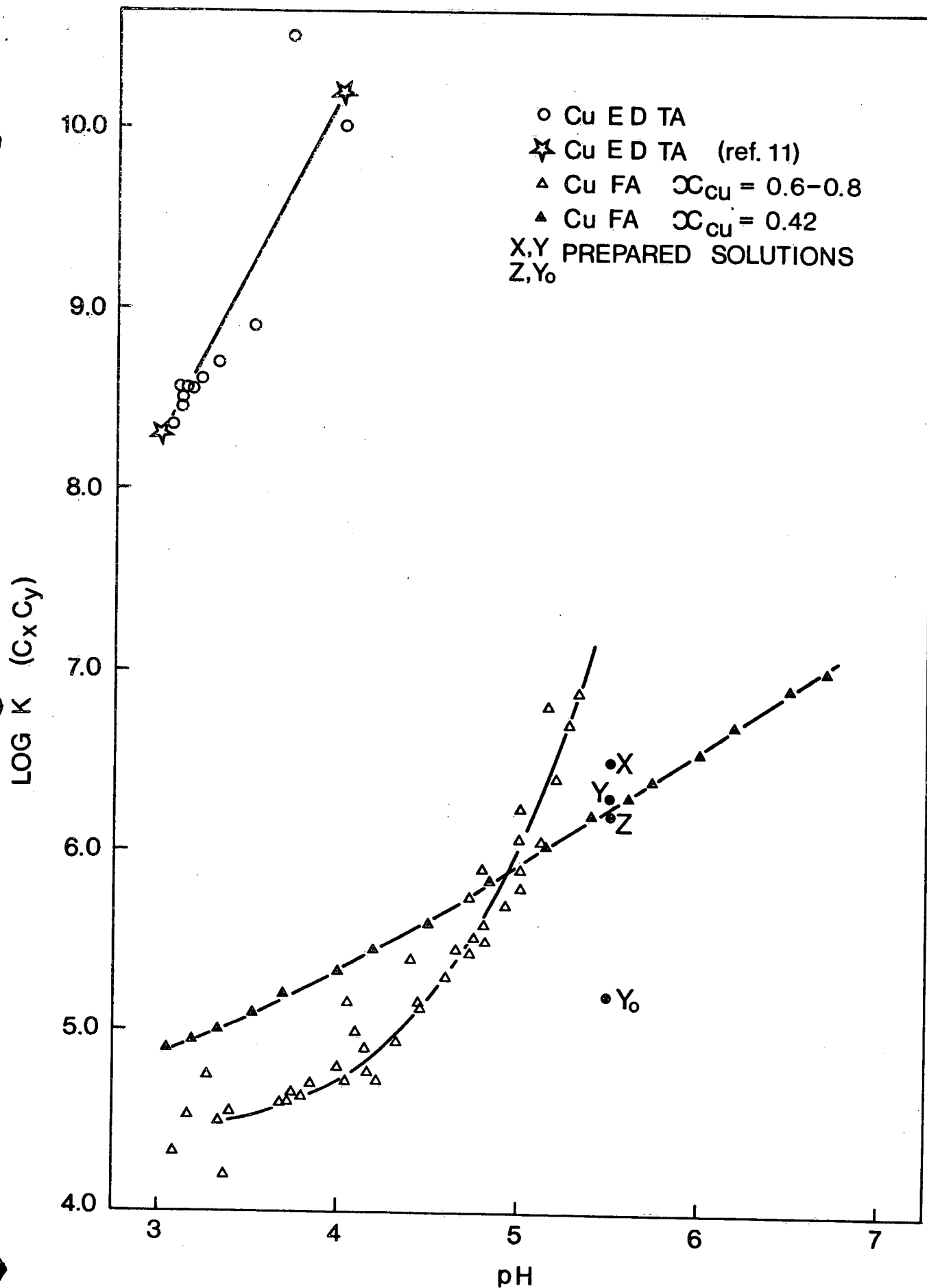- X,Y PREPARED SOLUTIONS
- Z,Y$_o$

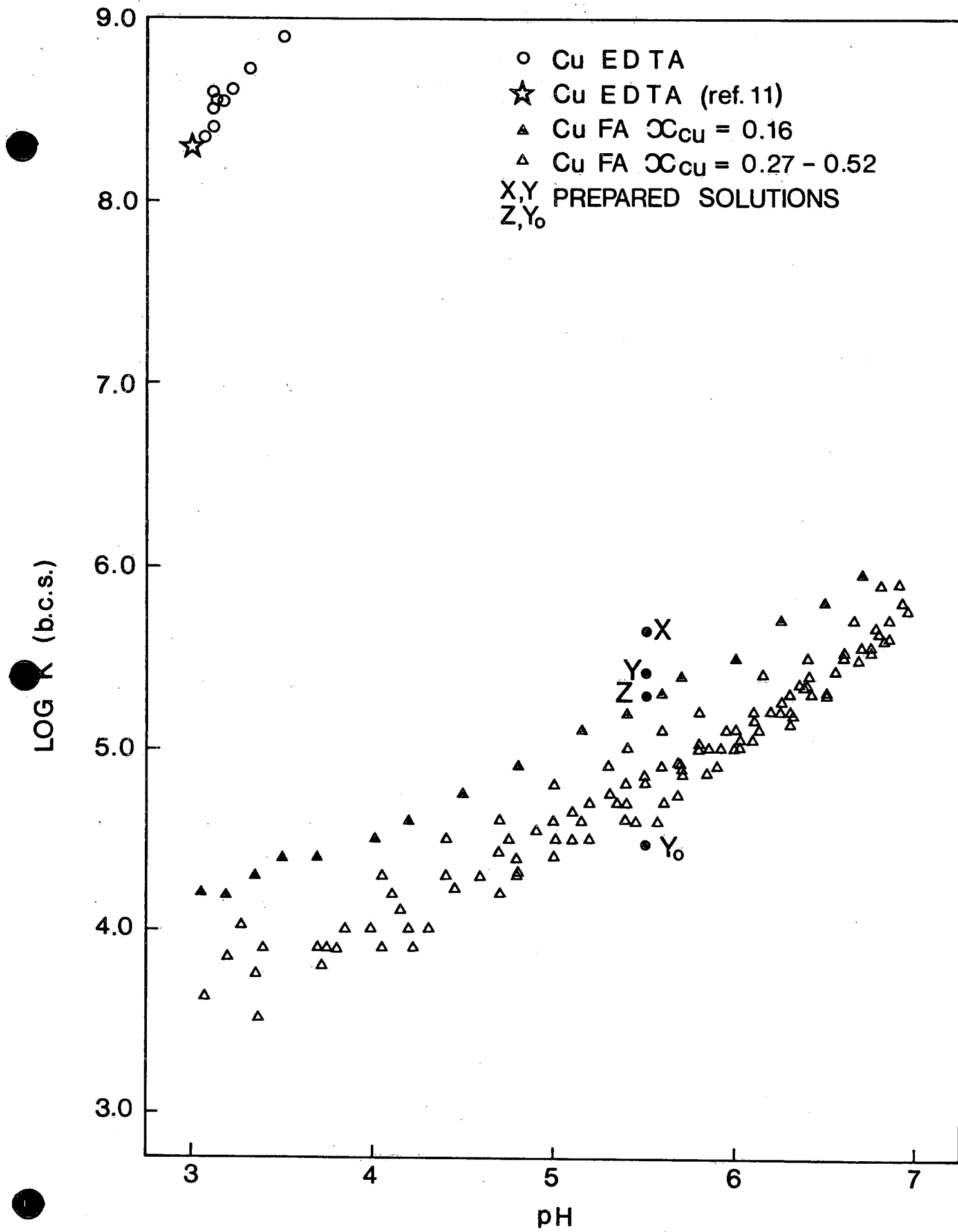Y-axis: LOG K (b.c.s.)
X-axis: pH

FIG. 4 LOG K (b.c.s.) and pH

Table 1. Some experimental water quality parameters and their standard

Constituents	DW* (Drinking Water)	FW* (Fresh Water)	MW* (Marine Water)	X_o (Disposal Site Water)	X (Standard Elutriate)	Y_o (Dredging Site Water)	Y (Sediment-Dredging Site Water)	Z_o (Mixture of both waters)	Z (Sediment-both waters)	Pilot Island	IW* Chemex Report
Complexing Capacity (in terms of Cu/ppb)	---	---	---	55	124	200	207	95	168	---	---
$\log K_{(cx\ cy)}$ at pH 5.5 25°C	---	---	---	---	6.5 ± 1.7%	5.2 ± 10.7%	6.3 ± 2.6%	---	6.2 ± 5.2%	---	---
Zn, ppb	5000+	75	100	8[12]**	60	32[60]	60	12	10	10 - 1100	1 - 56
Hg, ppb	5|3d	0.2	1.0	0.17[0.13]	0.17	0.18[0.22]	0.15	0.17	0.18	0.1<-0.54	<0.1-0.7
Pb, ppb	50	100	50	<0.5[2]	<0.5	<0.5[2]	<0.5	<0.5	<0.5	50<-<100	<2-60
Cd, ppb	10	0.4 - 3	10	<0.2[<0.2]	<0.2	<0.2[<0.2]	<0.5	<0.2	<0.2	10<- 30	<1- 3
P, ppb	200+ (as inorg. phosphates)	100 (total inorg. as P)	---	92[153] (tot. as P)	276[6750] (tot. as P)	153[400] (tot. as P)	275[9200] (tot. as P)	92 (tot. as P)	430[5200] (tot. as P)	100-3000 (tot. as P)	25-740 (tot. as P)
DDT, ppb	42	---	---	<0.005	<0.005	<0.005	<0.005	<0.005	<0.005	---	---
PCB, ppb	---	---	---	0.1	<0.1	<0.1	<0.1	<0.1	0.2	---	---
Oil & Grease, ppm	---	invisible,	---	[1.0]	[1.0]	[1.0]	[1.0]	2.0	[2.0]	---	---
Total dissolved Solids, ppm	1000+	~15	---	[226]	[205]	[369]	[337]	289	[297]	---	---
E_h, mv(E_h for dredge site sediment= -160)	---	---	---	250(7°C)	-20	340	-30	---	0.0	200-475	---

* DW = Drinking water standards (maximum permissible limit), ref. 13a except for Hg where it is 13d.
  FW = Fresh water aquatic life objectives (maximum limit), ref. 13b.
  MW = Marine water aquatic life standards (maximum limit), ref. 13c.
  IW = Interstitial water, ref. 14.
  X_o, X, ... Z = see detailed definitions in experimental section.

+ Acceptable or objective, ref. 13a and 13b.
** Values in brackets [ ] are those for unfiltered samples.

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