Polarographic investigation of an unusual contaminant in trichlorobiphenyl

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Polarographic Investigation of an Unusual Contaminant in Trichlorobiphenyl

A thesis presented to the Committee on Graduate Studies and the Department of Chemistry of Union College, Schenectady, New York, in partial fulfillment of the requirements for the degree of Master of Science.

by Henry M. Stahr 1961

Approved by

Robert W. Schaefer

Approved by George H. Reed

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I. INTRODUCTION

An interest in polarography of organic compounds developed because of the need for an instrumental technique to determine unstable chlorine compounds in askarels used in the electrical industry for dielectric fluids. A chance contamination of trichlorobiphenyl used to impregnate capacitors caused the electrical industry untimely failures in their devices in 1956. These compounds break down under the influence of heat and electrical stress to form a buildup of conducting species which ultimately cause capacitors to fail.\(^1\) Several test methods have been developed,\(^2\) all of which involve anionic hydrolysis of the unstable compounds and a potentiometric titration of the resulting chloride ion. One of these tests has become the tentative standard of the ASTM.\(^3\) Westinghouse workers have done work of a similar nature, and one of their tests was published in 1958.\(^1\) Since polarity of a chlorine atom on an organic molecule correlates with its susceptibility to anionic attack and this further correlates with the relative ease of polarographic reduction, it was of interest to study this means as a possible test for detection of these reactive compounds.
II. THEORY

The analytical technique known as polarography was originated by Professor Jaroslav Heyrovsky at Charles University, Prague, Czechoslovakia about 1926. The principle involved is based on the unique properties displayed by an electrolytic cell consisting of a nonpolarizable reference electrode, a readily polarized electrode (such as the mercury drop) and an electrolytic solution containing small amounts of electro-reducible or electro-oxidizable material.

When an increasing electromotive force is impressed across such a cell and the resulting current is plotted as a function of the applied voltage, a curve is obtained whose extension along the current axis is directly related to the concentration of the trace material and whose inflection point is located at a voltage characteristic of that material.

Polarization curves:

It is understood that the oxidation of a particle or substance consists of the loss of electrons:

\[ \text{Fe}^{+++} \rightarrow \text{Fe}^{++++} + e \]

Conversely any reduction is effected by the addition of electrons originating either from an electron supplier (sufficiently reducing particle)

\[ 2\text{Fe}^{++++} + \text{Sn}^{++} \rightarrow 2\text{Fe}^{++++} + \text{Sn}^{+4} \]
or from a current source where the electron transferring electrode is brought to a sufficiently negative potential. It is this latter process that is of interest here.

The reduction of organic compounds is often effected by fixation of hydrogen which can only originate from protons present in the medium.

\[
\text{QUINONE} + 2H^+ + 2e^- \rightarrow \text{HYDROQUINONE}
\]

There are at least two ways of explanation of this mechanism. One method is by the transfer of electrons onto the protons.

\[
H^+ + e^- \rightarrow \text{H}^0
\]

The \( \text{H}^0 \) thus formed is in an active state which allows it to react with the electro-reducible substance. This may be a direct reaction, or the \( \text{H} \) may be catalytically activated by adsorption on the electrode and then reacted. The latter may account for the nature of the electrode affecting the reaction of the resulting compounds.

The second manner of reaction may be a transfer of electrons onto the electro-reducible species, yielding a negative ion which will eventually become a radical.
and in another stage will trap the $H^+$ and yield a neutral molecule (or radical).

\[
\text{\textcircled{1}} - \text{H}^+ + \text{H}^+ \rightarrow \text{\textcircled{2}} - \text{O-H}
\]

Eventually this radical may be reacted to a more stable compound through a free radical mechanism or may become a stable compound through interaction by a chain stopping mechanism.

The reduction of organic compounds can also be effected by breaking of a sufficiently polar bond (carbon-chlorine). In this first stage there will be a successive transfer of two electrons:

\[
\begin{align*}
R & - \text{C}_H^+ - \text{X} + e^- \rightarrow R - \text{C}_H^+ + \text{X}^- \\
R & - \text{C}_H^+ + e^- \rightarrow R - \text{C}_H^+
\end{align*}
\]

Then in the second reaction the negative ion thus formed collects the protons to yield the final compound.

\[
R - \text{C}_H^- + \text{H}^+ \rightarrow R - \text{C}_H^-
\]

In order to reduce a reducible species it is electrolyzed by two electrodes between which a variable potential $E$ is applied. One electrode (the easily polarizable one)
is immersed in the solution, the other (reference electrode) is kept at a well defined potential. In this manner $E$ indicates directly the potential of the electrode under investigation with respect to the reference electrode.

For each value of $E$ there is a corresponding electrolysis current $i_d$, which according to Faraday's law is proportional to the quantity of the reducible species reduced per second (stated another way the rate of electron exchange between the electrode and the reducible substance). When the negative value of $E$ is too low, the reduction is not possible ($i = 0$). When $E$ reaches a sufficient value the reduction begins and increases in an exponential manner as shown in the diagram.\(^{(a)}\)

Actually reduction occurs only in the narrow layer of the solution next to the electrode with the reducible species being replenished by diffusion.

Eventually $i$ (the current) becomes relatively flat,\(^{(b)}\) and the reduction is now independent of $E$ and depends only on the diffusion of the reducible species to the electrode surface. This is called the diffusion plateau and the current
here (minus the background current) is called \( i_d \), the diffusion current.

If the electrode surface is agitated the replenishment of the electrode layer will be easier and \( i_d \) will be higher. This replenishment also depends on size of the electrode and temperature.

Theoretically the shape of the polarization curve can be expressed in mathematical form. Since the reducible species \( (X) \) yields a reduction compound \( (Y) \) we can write

\[
E = E_0 + \frac{RT}{nF} \ln \left( \frac{X}{Y} \right)
\]

According to Faraday's law \( Y \) is proportional to \( i_d \). At the half wave potential \( (E^{1/2}_0) \) for which \( i = i_d/2 \), half of \( X \) is reduced and \( \frac{X}{Y} = 1 \). Hence, \( E^{1/2}_0 = E_0 \); \( E \) is then a constant, the redox normal potential.

Quite frequently, the equilibrium of the electronic exchange electrode-solution is not achieved instantaneously, and for equal \( i \), the potential to be applied has a higher value than that expected. This difference with respect to the reversible value is called overvoltage (distance \( mm' \) and \( mm'' \) in the accompanying diagram).

\[
\begin{matrix}
\text{m} & \text{m'} & \text{m''} \\
\end{matrix}
\]
This overvoltage increases with $i$; hence, the slope of the curve is lower than when reversibility is maintained. It is possible that the overvoltage is so high that the curve for one species disappears (e.g. reduction of aldehydes to alcohols can be observed but oxidation of alcohols to aldehydes is shifted towards excessive positive potentials).

An excellent example here is the overvoltage of $H^+$ on mercury. While discharge of $H_2$ occurs as expected for polished platinum the potential required for mercury is 600 mv more negative.

Ilkovic(5) has derived the relation between $i_d$ and the characteristics of the substance and of the capillary

$$i_d (ua) = 607 \, n \, c \, D^{5/6} m^{2/3} t^{1/6}$$

where $n =$ number electrons in reaction
$c =$ concentration of reducible species
$D =$ diffusion constant of reducible species in cm$^2$/sec
$m =$ output of capillary in mg/sec
$t =$ period of drop in seconds

A mercury electrode of the quiet pool(6,7) or a stirred pool(8) can also be used. Using the pool electrode the process
is not the same. Instead of measuring $i_d$, the current measured is the current developed in polarizing an electrode.
III. APPARATUS AND CHEMICALS USED

1) A Sargent Model XV Polarograph shown in figures I and II was used throughout these studies.

2) A Sargent Cell #S29381 (figure III) was used with the dropping mercury electrode.

3) A cell after Ullman et al(6) made by Fisher Scientific Company in figure IV was used with the pool studies.

4) Tetrabutyl ammonium iodide used in early studies was obtained from Matheson Coleman and Bell. It was necessary to twice crystallize this material from ethanol. Later Eastman white label reagent was obtained and was used without further purification.

5) Other chemicals as follows were obtained from Eastman and did not need purification: tetrabutyl ammonium bromide, tetraethyl ammonium iodide and bromide, lithium chloride, and ethanolamine.

6) Mercury-cathodic grade was obtained from F. W. Berk and Company.

7) A galvanized steel pan was used to contain the cell and accessories to prevent Hg spillage. The pan was coated with an epoxide resin to prevent any amalgamation or loss of Hg.

8) Nitrogen was obtained from Pittsfield General Electric gas works.
9) Pure gum rubber tubing was used throughout where necessary.

10) Commercial Solvents Corporation 190 proof undenatured alcohol was used as a solvent until the supply was exhausted. Then Baker Chemical Company 3A alcohol was used after distillation.
IV. EXPERIMENTAL

A. Preliminary Studies with the Dropping Mercury Electrode

Using the Sargent Model XV Polarograph (figure I) and the Sargent cell (figure III) and an electrolyte composed of 95% ethanol as a solvent and purified tetrabutyl ammonium iodide at a 0.1 molar concentration, preliminary runs were made on 1242 Aroclor* samples. Aroclor samples which gave high chloride values when reacted with methanolic sodium hydroxide, and samples which gave low chloride values when so reacted were run. In each run the electrolyte was degassed until no appearance of oxygen subsisted - usually 7-10 minutes. The nitrogen was directed through two gas scrubbing tubes before entering the cell, one with pure ethanol and one with a sample of the electrolyte used in the analysis.

After a suitable blank was obtained (figure V) a sample of the Aroclor was introduced into the cell and the solution was degassed an additional ten minutes.

"Normal" Aroclor samples gave no wave but did decrease the potential where hydrogen reduction started. A similar effect is seen in figure VI where o, p, dichlorobenzene does not shift the potential to a more positive value but m,

* Trade-mark Monsanto Chemical Company.
dichlorobenzene does. These samples were run at 0.8 g. sample per 25 ml. electrolyte. The wave obtained from the sample of contaminated Aroclor is shown in figure V also. The sensitivity setting of the Polarograph is shown on the figures.

In figures VII and VIII waves obtained from the polarographic reduction of carbon tetrachloride and benzene hexachloride (14% $\gamma$-isomer) are shown. Figure XII shows a curve of $\gamma$-phenyl-n-propylchloride - a very unstable aliphatic chlorine compound. These runs were made at reduced sensitivity to facilitate their presentation, and all figures are idealized curves. The bottom of the oscillation due to mercury drop fluctuation was used to draw the curve.

At this point it may be well to explain that the intent at the outset was to separate the known mixture of isomers which make up the commercial Aroclor product so that a characterization of the isomers with respect to the ease of polarographic reduction might be made. Specialized gas chromatographic equipment is necessary for separation of the Aroclor's components. The extremely long capillary column and ultra sensitive detection equipment was not available from stock but had to be specially built at considerable expense. The lack of this equipment caused the postponement of this work. The wave obtained with a high level of hydrolyzable chlorine sample was found to be reproducible.
B. DROPPING MERCURY ELECTRODE STUDIES

To ascertain if this wave was caused by a hydrolyzable species, the electrolyte was changed by adding ethanolamine. Five ml. of ethanolamine solution, which was made by dilution of 20 g. of ethanolamine with 80 g. of 95% ethanol, was added to 20 ml. of the tetrabutyl ammonium iodide electrolyte. The results are shown in figure IX. The sample size was 0.20 g. of lot 510 Aroclor in 25 ml. of electrolyte. This shows that the wave produced by the unknown species is reduced as the compound undergoes hydrolysis. A sample without ethanolamine in the electrolyte shows no change after standing in the cell. It should be pointed out here that the sample had the mercury pool anode removed when it was allowed to stand and the whole cell was covered with aluminum foil to prevent any reaction of the electrolyte or cell contents with ultra violet light; and, of course, a blanket of nitrogen was kept over the cell and its contents throughout the experiment. A rate study of the dehalogenation of 1-benzene hexachloride also was made but the concentration was so high that the time intervals chosen did not allow the reaction to go to completion. The results are shown in figure X and it can be seen that the same type of reaction takes place here.

It was of interest to see what the effect would be of adding "normal" Aroclor to a cell containing a sample of the
FIGURE V

"GOOD" AROCLOR AND "BAD" AROCLOR WITH DROPPING MERCURY ELECTRODE AND TETRABUTYL AMMONIUM IODIDE ELECTROLYTE
FIGURE VI
DICHLOROBENZENE WITH DROPPING MERCURY ELECTRODE
IN TETRAFUTYL AMMONIUM IODIDE

150 mm.

100 mm.

50 mm.

I (0.003 ua.)

APPLIED VOLTAGE
FIGURE VII
BENZENE HEXACHLORIDE IN TETRABUTYL AMMONIUM IODIDE
WITH DROPPING MERCURY ELECTRODE

APPLIED VOLTAGE
FIGURE VIII
CARBON TETRACHLORIDE WITH DROPPING MERCURY ELECTRODE IN TETRABUTYL AMMONIUM IODIDE
FIGURE IX

RATE OF HYDROLYSIS "BAD" AROCLOR SAMPLE
WITH DROPPING MERCURY ELECTRODE
FIGURE X
RATE OF HYDROLYSIS OF BENZENE HEXACHLORIDE
IN AROCLOR WITH DROPPING MERCURY ELECTRODE

APPLIED VOLTAGE
FIGURE XI

THE ADDITION OF "GOOD" AROCLOR TO "BAD" AROCLOR

WITH DROPPING MERCURY ELECTRODE

APPLIED VOLTAGE

(0.002 ua./mm.)

(0.006 ua./mm.)
FIGURE XII
γ-Phenyl-n-propyl chloride in tetraethyl ammonium iodide
with dropping mercury electrode

γ-phenyl-n-propyl chloride (.02 ua./mm.)

δ-phenyl-n-propyl chloride in lot 883 (.01 ua./mm.)

APPLIED VOLTAGE
FIGURE XIII
MERCURY POOL WAVES OF "BAD" AROCLOR IN TETRABUTYL AMMONIUM IODIDE

Blank

"Bad" Aroclor

APPLIED VOLTAGE
FIGURE XIV

MERCURY POOL WAVES OF DILUTIONS OF MONSANTO SYNTHETIC "BAD" AROCLOR IN NORMAL AROCLOR

- 100 ppm.
- 30 ppm.
- Blank

APPLIED VOLTAGE
FIGURE XV

MERCURY POOL WAVES OF BENZENE HEXACHLORIDE

IN NORMAL AROCLOR
FIGURE XVI

RATE OF REACTION OF ETHANOLAMINE WITH "BAD" AROCLOR IN TETRABUTYL AMMONIUM IODIDE WITH THE MERCURY POOL

ELAPSED HOURS
FIGURE XVII

CALIBRATION CURVE MONSANTO SYNTHETIC "BAD" AROCLOR
WITH MERCURY POOL IN TETRAETHYL AMMONIUM IODIDE ELECTROLYTE

PPM. CHLORIDE AS INDICATED BY HYDROLYSIS TEST
FIGURE XVIII

CALIBRATION CURVE "BAD" AROCLOR WITH MERCURY POOL IN TETRAETHYL AMMONIUM BROMIDE

PPM. CHLORIDE AS INDICATED BY HYDROLYSIS TEST
"bad" Aroclor. Four samples of 0.2 g. each of "good" Aroclor were added to the cell containing 0.2 g. of "bad" Aroclor. It can be seen that the maximum wave height is only slightly diminished even when 0.8 g. of "good" Aroclor is added. The diminution is probably a viscosity effect since there is an increase in viscosity with concentration of Aroclor.

Finally a lot sample of "bad" Aroclor (lot 510) was distilled. The cuts were as follows: first 10% was 13.7 ppm. by hydrolysis test, second cut 80% of the total was 1 ppm. by the hydrolysis test, third cut last 10% was 2670 ppm. by the hydrolysis test.

A sample 20 ppm. by the hydrolysis test was made by dilution of the lot 510 Aroclor sample with normal Aroclor. It gave such a small increase in the wave over the normal Aroclor that it was judged that the highest sensitivity of the Polarograph and the micro range extender would be necessary for normal samples. Using the micro range extender did increase the difference between low level samples of Aroclor; however, the background current at these sensitivities is so high that the differences in sample are a small percentage of the total wave.

This would make the use of this procedure unwieldy. Hence, it was of interest to investigate the quiet mercury pool.
C. The Quiet Mercury Pool Electrode

The quiet pool electrode has been used for analysis for some time. It was mentioned above that Ullman et al.,(6) used this device with water waste samples. Cooke et al., at Cornell (7) have used the pool for an analogous study; they have determined the 6-isomer content of hexachlorocyclohexane.

The first runs were made using a makeshift cell put together out of a glass tube, a dispersion tube, a piece of tungsten wire, a ball and socket joint and a filter tube. This cell was soon found to be inadequate since the size of the pool was not reproducible.

It was also soon found that it was necessary to clean up traces of oxygen in the nitrogen for pool work. This was done by using a Sargent micro-combustion tube furnace. A quartz tube was filled with copper turnings, and this furnace was added in the gas stream between the nitrogen source and the scrubbing tubes. This provided a low oxygen background and enabled some flat blanks to be obtained.

Ullman's cell (figure 4) was adopted to give a more reproducible pool size. Lithium chloride, tetrabutyl ammonium iodide and tetrabutyl ammonium bromide all gave too high a background (blank) and hence were not used. Finally by
degassing under -0.2 v. a solution of tetraethyl ammonium bromide a blank which was of a consistent small level was obtained.

It was soon discovered that at this type of electrode the sensitivity for the impurity was so high that microgram quantities had to be used. Difficulties in successfully transferring these quantities from syringes to the electrolytic cell showed up as variations of large order.

This left one recourse - to dilute the sample in the electrolyte and then add a portion of the diluted Aroclor to the cell. In practice the system was degassed at -0.2 v. for 5-10 minutes. A blank was run, a sample of the electrolyte was removed, a sample of the diluted Aroclor was added, the system was again degassed for five minutes, and the run was made.

Complete procedures are given on pages 19 to 24 for both the dropping mercury electrode and the mercury pool electrode.

During the experimental work the supply of 95% pure grain ethanol was exhausted, and the solvent system had to be changed to Baker Chemical Company 3A denatured ethanol. By distilling off the first cut (stopping when first signs of temperature rise was noted) about 80% of this material was
usable. Successful runs were obtained using this material in all but three cases where no amount of distilling did any good.

A few samples using tetraethyl ammonium bromide and dimethyl formamide as a solvent were run to see if this would result in extending the workable range of the voltage scan. No such extension was accomplished but the same waves were obtained.

Samples of the results obtained with the mercury pool are shown in figures XIII, XIV and XV.

After development of the method a sample of Aroclor which contained addition chlorine compounds purposely synthesized by Monsanto Central Research Laboratory became available. Runs were made on dilutions of it. The results are shown in figure XIV.

Next a sample of the "bad" Aroclor (300 ppm.) was placed in a solution containing ethanolamine as a dehalogenation reagent and tetraethyl ammonium bromide as an electrolyte. (Thirty g. of 20% ethanolamine in ethanol was added to 70 g. 0.1 m. tetraethyl ammonium bromide in ethanol.) Then 0.05 g. of the "bad" Aroclor was added, and the solution was allowed to stand. Samples of the mixture were removed and run at 0, 2, 3½, 4½ hours. The results are shown in figure XVI. Here again the hydrolytic reaction of the contaminant is demonstrated.
Finally the sensitivity of the pool electrode toward both contaminated Aroclor and the synthetic Aroclor was determined with dilutions of each in normal Aroclor. The results are shown in figures XVII and XVIII.
D. Dropping Mercury Electrode Procedure

1) The Sargent cell #S-2931 is used for polarographic analyses with the dropping mercury electrode.

2) The dropping mercury electrode is assembled and adjusted so the drop time is 5-7 seconds.

3) Mercury is introduced into the side arm to make a connection with the Polarograph and the platinum electrode sealed through the glass side tube.

4) After introducing 25 ml. of electrolyte into the cell 0.3 ml. of mercury is added as a pool anode so that it makes a good connection with the platinum wire.

5) The solution is degassed for 5-10 minutes and a blank is run.

6) Tetraethyl ammonium bromide and tetrabutyl ammonium iodide have both been used in the cell with Aroclor samples. The blank should be flat until -1.5 v. at 0.003 ua/mm. or at 0.002 ua/mm. should show some background rise. Hydrogen reduction in either case starts at about 1.5 v.

7) The Aroclor sample to be analyzed can be introduced directly into the cell chamber. A sample of 0.8 ml. to 25 ml. of electrolyte is the limit of solubility.

8) The sample is then degassed for about 5 minutes to remove any O₂.
9) The sample is run at 0.003 ua./mm. or higher sensitivity. At a sensitivity above 0.003 ua./mm. the micro range extender has to be used. In this case the micro range extender is added between the cell and Polarograph and a resistance is added on the micro range extender so that a suitable blank curve is obtained.

10) Either a calibration curve is prepared for a series of synthetically diluted samples to give a range of hydrolysis values or a "good" sample is run and the experimental sample is compared with it and the difference between the samples is noted.

About 0.002 ua./ppm. has been observed at a concentration of 0.8 ml./25 ml. of electrolyte.
B. Mercury Pool Procedure

1) The salt bridge and silver-silver chloride electrode are constructed as outlined below.

2) The electrolyte (0.1 molar tetraethyl ammonium bromide) is introduced into the cell chamber. This is degassed for 5-7 minutes with purified N₂.

3) The mercury (cathodic grade) is introduced by means of a buret under the solution's surface (about 0.4 ml. of Hg is added).

4) The solution is now degassed at -0.2 v. scale setting on the 0-1 v. range until the background is negligible.

5) A blank is then run on the electrolyte. If all is well it should be flat until around 1.5 v. at 0.02 ua./mm. and it will probably show background at 0.01 ua./mm.

6) The sample to be run (Aroclor) is diluted in the electrolyte 1 ml./25 ml.

7) Then 5 ml. of this diluted solution is introduced into the cell after removing 5 ml. of electrolyte.

8) The sample is then degassed again 3-5 minutes and scanned for 0-1; 1-2 v. with the Polarograph.

9) A measure of the peak height minus blank current should be proportional to the hydrolytic level of reactive chlorine in the sample. The peak should occur at approximately -0.8 v. on the 0-1 v. scale.
10) Either a calibration curve is made up with prepared samples at various levels of hydrolytic contamination or a direct difference from a standard "good" sample may be noted. About 0.02 ua./ppm. has been observed at concentration specified above.
F. Salt Bridge for Polarographic Cell

A salt bridge may be prepared in the following way for the polarographic cell.

1) Two g. of agar-agar and 2 g. lithium chloride are weighed into a suitable container.

2) Twenty-five ml. of water is heated in a beaker to around the boiling point.

3) Agar and salt are stirred into the water.

4) Further heating of this mixture for 2-3 minutes should produce a viscous soft gel.

5) The soft gel is introduced into the electrode side of the cell by means of a syringe (25 ml. size does nicely), allowed to cool and the bridge is ready for use.

Ag-AgCl Electrode

1) Part of the agar bridge is removed from the outer end of the salt bridge tube to form a cavity for the electrode.

2) In this space an acidified saturated solution of KCl is placed and a few crystals of AgNO₃ are added.

3) The silver wire is anodized in an acidified KCl solution for a short period each day. It is best formed into a helix to give as much surface area as possible for a short length.
4) The helix of Ag wire (chloridized) is introduced to make the electrode complete and serve as a connection to the Polarograph.
V. DISCUSSION AND CONCLUSIONS

The first work was done with the dropping mercury cell of the E. H. Sargent Company; hence, the half wave potentials were somewhat variable (+50 mv). The half wave potential was apparently at about -0.25 v. for the contaminant. Benzene hexachloride half wave was at about -0.25 v. and carbon tetrachloride -0.35 v., 1-phenyl n propyl chloride -0.17 v. These values shifted to more negative potentials with the addition of ethanolamine. The half peak potentials of the pool samples versus the Ag-AgCl electrode were -0.40 v. for the contaminant and -0.6 v. for benzene hexachloride. This agrees with Cooke's (7) values in the more aqueous solvent.

The sensitivity of the dropping mercury procedure is not sufficient to use the test as a control technique for normal Aroclors of which the hydrolysis values are less than 1.0 ppm chloride.

Even with the mercury pool the extrapolated values for sensitivity are higher than the normal levels of Aroclor samples.

Hence, it would be necessary to resort to increasing the concentration of the Aroclor sample. This could be done simply by adding a larger aliquot of the dilute sample or making a more concentrated solution and at a higher temperature.
and diluting this in the cell compartment. It is not desirable to expose the mercury pool in the cell by removing too much of the electrolyte so adding more sample to the cell would require care.

A better means of increasing the sensitivity would be to use a larger pool surface area, or since the reduction product is soluble in the electrolyte a stirred pool could be used. This has the advantage of a fairly compact system with a renewable surface area.

Another interesting area to investigate would be the use of a microelectrode and a more concentrated solution of the organic compound as used in the dropping mercury studies. This should give a higher sensitivity than the dropping mercury electrode and still lower than the mercury pool.

The inordinate sensitivity for these unknown compounds observed here with the pool is amazing. A down scan is flat and a rescan on the system is much lower than the starting sample. In fact two scans seem to reduce the reactive species almost quantitatively.

This study has shown that the contaminant in Aroclor is reducible, and the Polarograph can be used as a tool to detect low levels of these hydrolyzable chlorine compounds.
Further efforts should be made to extend this preliminary effort to the isolated isomers of the chlorinated biphenyls. The greatest value can be derived by the use of the Polarograph to help characterize activity of micro samples available from a chromatographic separation. Early efforts of Hudson Falls Laboratory workers Guiles, Kozoriz, et al., have shown that this commercial product is a large number of separable isomers. Their work is to be published soon.
VI. LITERATURE CITED


VII. APPENDIX