N90-24354

ANODE MATERIALS FOR ELECTROCHEMICAL WASTE DESTRUCTION

Peter M. Molton
Battelle
Pacific Northwest Laboratory

Clayton Clarke
Florida A & M University

SUMMARY

Electrochemical Oxidation (ECO) offers promise as a low-temperature, atmospheric pressure method for safe destruction of hazardous organic chemical wastes in water. Anode materials tend to suffer severe corrosion in the intensely oxidizing environment of the ECO cell. There is a need for cheaper, more resistant materials. In this experiment, a system is described for testing anode materials, with examples of several common anodes such as stainless steel, graphite, and platinized titanium. The ECO system is simple and safe to operate and the experiment can easily be expanded in scope to study the effects of different solutions, temperatures, and organic materials.

INTRODUCTION

Prerequisite Knowledge Required

The basic experiment can be performed by any technically minded high school student with elementary knowledge of electrical circuits and ionic conduction. The expanded experiment (use of different anolyte solutions, addition of organic "wastes", gas chromatography, etc.) should be performed only by students with a good knowledge of inorganic chemistry and beginning organic chemistry, and an ability to use instrumental methods of analysis. The experiment is based on research being performed at the Pacific Northwest Laboratory to develop ECO as a usable alternative to other waste disposal methods (ref. 1-3).

OBJECTIVES

The objective of the experiment is to demonstrate that any system which is capable of destroying waste materials in an oxidizing environment is itself subject to corrosion, and to find a material which can survive this environment for a long enough time to be commercially useful. Background information on this topic can be found in (ref. 4). After performing the experiment, the student should be encouraged to speculate on possible novel materials which might be more suitable than the expensive platinized titanium (such as conducting plastics, for instance).

EQUIPMENT AND SUPPLIES

Basic Experiment

The necessary equipment comprises:

A power supply capable of providing up to 6 amps at up to 9 volts.
Two pumps capable of pumping up to 300 ml/min. of dilute acids or alkalies.
An Electrochemical Cell (construction described below).
A sheet of selective anion-permeable membrane (e.g., Riapore 1035).
Anode and cathode electrodes made of stainless steel, graphite, and a resistant metal such as platinum or platinized titanium.
Two graduated cylinders (capacity $>$ 500 ml) with a liquid take-off at the bottom (for electrolyte recycle).
Plastic tubing to interconnect the above.
A red and a black insulated wire to connect the power supply to the ECO cell.

Expanded Experiment

In addition to the above, the apparatus (shown in Figure 1) can be set up for measuring the effect of temperature, measurement of gases evolved from the anode and cathode compartments, measurement of pH changes during the experiment, etc. For this, additional equipment includes:

Two hot-plate stirrers to heat the solutions to $<$80°C.
Tubing take-off from the tops of the graduated cylinders to inverted burettes to measure gas evolution rates.
A small metering pump for continuous addition of an organic (water-soluble) solvent (in the Figure, the example given is Hexone, or methyl isobutyl ketone).
Instrumentation as available: Gas chromatograph; pH meter; gas flow meter; gas analyzer (Oxygen and carbon dioxide).

The effect of oxidation conditions on anode materials can be determined visually, or measured with a micrometer gage.

For all experiments, the experimenter has a choice of electrolytes: A dilute acid (e.g., nitric or sulfuric, about 0.5 - 1 M), an alkali (e.g., sodium hydroxide, 1 M), or a salt solution to ensure good ionic conduction.

Cell Construction

ECO cells are available commercially but can be constructed easily for teaching purposes with the facilities of a small workshop. A cell comprises an approximately 7 x 7 cm area. An exploded view of a commercial cell is shown in Figure 2. It is made from laminated teflon sheets, ca. 3 mm thick. Stainless steel end-plates are used to bolt the whole assembly together (4 bolts, one at each corner) tightly enough to prevent leaks. Each electrode plate is held between two plastic plates, with holes drilled at the corners to permit electrolyte flow on <u>both</u> sides of the electrode. The ionic membrane which separates the anode <u>and</u> cathode compartments is held between two sheets of rigid plastic mesh (some pressure develops within the cell due to osmotic forces). Polypropylene may be used instead of teflon for most purposes, but will not last as long in use. Similarly, connecting tubes between the cell and the pumps and electrolyte reservoirs should preferably be made of teflon, but polypropylene can be substituted. Any design of cell can be used in this experiment, including wires suspended in liquid. Two essential features of any cell used for this experiment are (a) the ionic membrane used to separate the cathode and anode compartments, and (b) recycled electrolytes, or a way of removing gas generated in the cell.

PROCEDURE

An electrochemical flow cell is set up as shown in Figure 1. The flow cell is fitted with a stainless-steel cathode. The anode is made of (a) stainless steel, (b) graphite, or (c) platinum or platinum on titanium. A Riapore 1035 anionic membrane separates the anode and cathode compartments. The anode and cathode each have an available electrode surface area of 20 cm^2. The anolytes used in the experiment are generally N NaOH or N nitric acid (total volume of 300 - 500 ml). The catholyte has the same material (acid or alkali), concentration and total volume as the anolyte. If an above room temperature experiment is to be performed, the catholyte and the anolyte are heated and stirred. Burettes inverted over water can be used (optional) to measure gas evolution. Flow of anolyte and catholyte through the cell is started by turning on the two Teflon pumps (Saturn model SP 2000 with Minarik motor controllers). Direct current power is supplied by a Hewlett-Packard model 6281A DC power supply with a maximum capacity of 6 A. Teflon tubing is used to connect all of the system components and Galtek sample valves are used to take samples during system operation.

In a typical experimental run, 500 ml each of anolyte and catholyte are added to the cleaned and leak-checked system. The circulating pumps, heaters, and stirrers are turned on, and the system brought to the desired temperature (this step is omitted for room-temperature experiments). The power supply is then turned on and adjusted to provide 6 A to the cell; the time, voltage, and amperage are noted on the data sheet. The student will note the behavior of the cell, such as visible color changes in the recirculating solutions, which would indicate corrosion of the electrodes. If desired, this can be followed by a simple wet chemistry test or colorimetric measurement for iron (from stainless steel), or carbon dioxide production rate can be monitored to follow the dissolution of a graphite anode.

The experiment can be terminated at any time, preferably after 4-8 hr, and the cell disassembled carefully and cleaned. The degree of corrosion of the electrode can then be determined by direct measurement. As a rule of thumb, a stainless steel anode will show signs of corrosion within 1 hr, from the appearance of a brown insoluble suspension in the anolyte solution; graphite will be completely eaten through in about 6 hr; and platinized titanium will show no effect. Depending on the amount of laboratory time available, each electrode could be subjected to the oxidation conditions in a single experiment (with reassembly of the cell each time), or a single material can be examined in a day. The rate of corrosion can also be adjusted by varying the current through the cell, to suit the instructors convenience.

If an actual organic "waste" degradation is to be performed as well as a measurement of electrode corrosion, a suitable water-soluble compound can be added at a 1-2% concentration before the power is turned on (for safety reasons, to avoid a possible fire if leakage of pure solvent should occur). The anolyte solution is then recirculated for 5 min to mix the organic compound in completely. Hexone (5ml), acetone, diglyme, methanol, or any common solvent can be used. For safety reasons, flammable solvent additions should be monitored or performed by the instructor. Continuous addition can also be performed via a metering pump (as shown in Figure 1). Figures 3 and 4 show typical results of addition and oxidation of common organic substances in the cell.

SAMPLE DATA SHEETS

An example of the data obtained from a typical experiment is shown in Figure 5. The experiment included addition of hexone, and use of a Pt/Ti anode. In this experiment, the anode was inert. Data on the rate of organic destruction is shown in Figure 6.

INSTRUCTOR NOTES

The electrochemical oxidation experiment is widely adaptable in terms of materials studies (corrosion and chemistry), can be adjusted as to time required by simply varying the voltage across the cell, and is simple and safe to perform. Chemicals used are generally dilute acids and alkalies and are relatively nontoxic. Of course, safety glasses should be worn throughout or the experiment performed in a fume hood.

A battery can be substituted for the power supply. Tubing can be either teflon, as recommended, or a cheaper substitute plastic. Obviously, metal tubing will not work. If pumps are not available, a single pass-through, gravity feed of electrolyte can be used.

The electrochemical cell itself could be made in an engineering workshop class, from teflon or polypropylene sheet and stainless steel (for the end plates).

There is unfortunately no real substitute for the ion-permeable membrane or for using some form of platinum as a permanent (non-corrodible) anode. One exercise for the student could be to suggest and perhaps test a potential replacement!

Theory

A simplified theory of electrochemical oxidation is as follows: A hydroxyl ion gives up an electron at the anode, generating a hydroxyl radical (HO.), which can either undergo the normal water electrolysis reaction to form oxygen gas, or can react with an organic compound to hydroxylate it. Enough hydroxylations and even the most resistant organic compound will fall apart to form, eventually, carbon dioxide and water. Of course, hydroxyl radical can also attack the anode and convert a metal into its hydroxide.

Hazards

The experiment itself is remarkably hazard-free. The major problems in practice have been liquid spills of acid, alkali, or solvent, and consequent damage to clothing. Cell leakage has occasionally occurred when an anode plate became perforated and eaten away through the side of the cell. This spillage and leakage problem can be solved by placing a glass oven dish underneath the apparatus to catch spills. Cathode and anode gases should never be mixed, as water electrolysis is a side-reaction and this generates hydrogen (cathode) and oxygen (anode) in explosive proportions. Therefore, the evolved gases should be vented and not allowed near a spark. The pumps and power supply are located outside the hood or remote from the cell for this reason. No smoking should be allowed near the apparatus.

Clean-Up

After the experiment has been completed, power to the cell should be turned off. The electrolytes can then be pumped out, neutralized, and disposed of down the sink (neutralization is necessary to comply with environmental regulations). Used anode materials are non-leachable and can be disposed of directly into the garbage (i.e., graphite, steel, etc.). The cell should be disassembled and thoroughly cleaned after each use: Water is usually sufficient, but acetone or methanol may have to be used to remove iron oxides.

Future Applications

The purpose of this experiment is to expose the student to a developing technology that may one day be of great use for hazardous waste destruction. Electrochemical oxidation is far milder and easier to control than incineration, for example, but it suffers from problems of electrode corrosion. Other problems hampering the wider application of the technology are the fact that the organic waste oxidation takes place only on or near the anode, where hydroxyl (OH.) radicals are generated. Hence a large anode area and/or a high flow rate past the anode are needed. Also, many wastes contain insoluble organics and sludges. Ways to circumvent these problems are needed. In this experiment, the approach is to examine existing engineering materials in the electrochemical oxidation environment and to show that they are either inadequate or too expensive for widespread use. This should encourage the student to suggest alternatives and to start thinking about the problem. Possible topics for discussion are plastic-based conductors and channelized anodes.

REFERENCES

1. Molton., P. M.; Fassbender, A. G.; Nelson, S. A.; and Cleveland, J. K.: "Hazardous Organic Waste Destruction by Electrochemical Oxidation," Proc. 13th Ann. Envir. Quality R&D Symp., USATHAMA, Nov. 15-17, 1988, Williamsburg, VA.

2. Molton., P. M.; Fassbender, A. G.; Nelson, S. A.; and Cleveland, J. K.: "Concentrated Hazardous Organic Waste Destruction by Electrochemical Oxidation," Proc. Dept. of Energy Model Conf., Oct. 3-7, 1988, Oak Ridge, TN.

3. Fassbender, A. G.; Molton, P. M.; and Broadbent, G.: "Electrochemical Oxidation of Hexone and Other Organic Wastes," Proc. Superfund '87, HMCRI 8th National Conference, Washington, D.C., Nov. 16-18, 1987.

4. Tilak, B. V.; Sarangapani, S.; and Weinberg, N. L.: Electrode Materials. Chapter IV., Technique of Electroorganic Synthesis, Part III; ed. Weinberg, N. L.; and Tilak, B. V. Vol. V of "Techniques In Chemistry" Series, ed. Weissberger, A., Publ. John Wiley & Sons, N.Y., 1982. ISBN 0-471-06359-2(r.3).

ACKNOWLEDGMENTS

The author wishes to acknowledge that this work was supported by the U.S. Department of Energy under Contract DE-AC06-76RLO 1830.

SOURCES OF SUPPLIES

All chemicals required for this experiment are available from most chemical suppliers (e.g., nitric acid, sodium hydroxide, solvents). The rarer electrode materials (platinum on titanium, graphite, nickel, etc.), and the Riapore 1035 ion-permeable membrane can be obtained, for example, from The Electro-Synthesis Co., Inc., P.O. Box 16, E. Amherst, N.Y. 14051. (No endorsement of this particular company is implied; other suppliers may prove equally suitable.) The electrochemical cell can be purchased from this or other supplier of electrochemical equipment, or made in the workshop. Prices are widely variable.

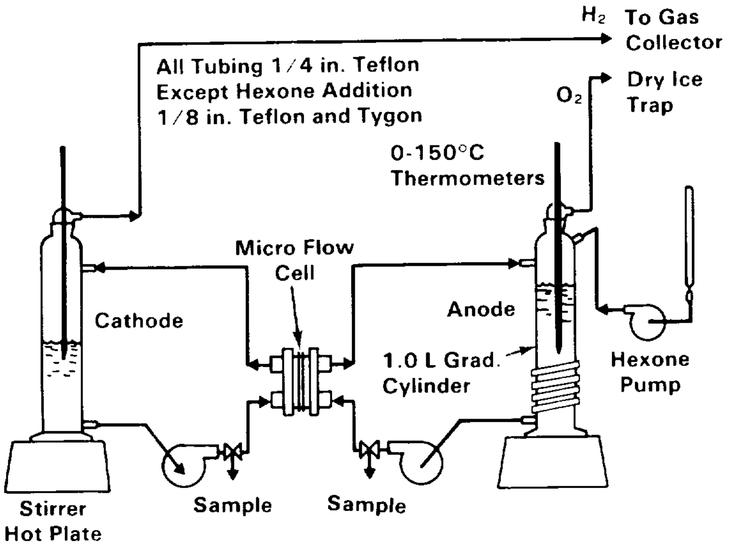


Figure 1: Diagram of Laboratory Apparatus

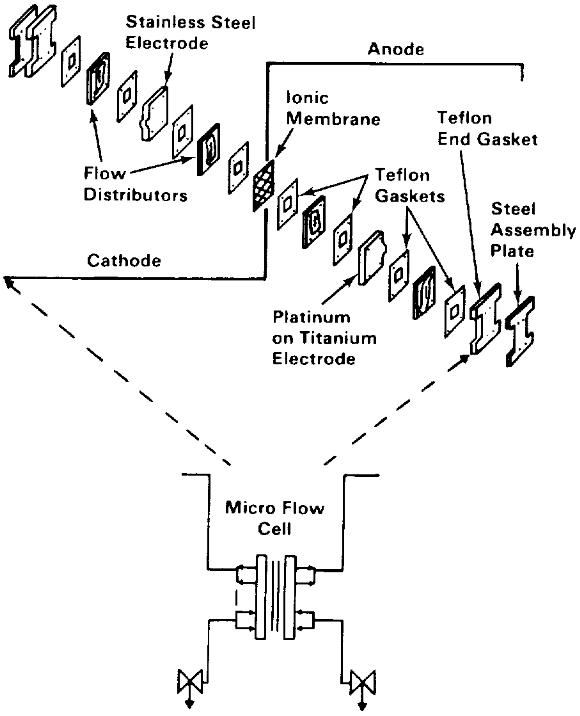


Figure 2: Exploded View of Electrochemical Cell

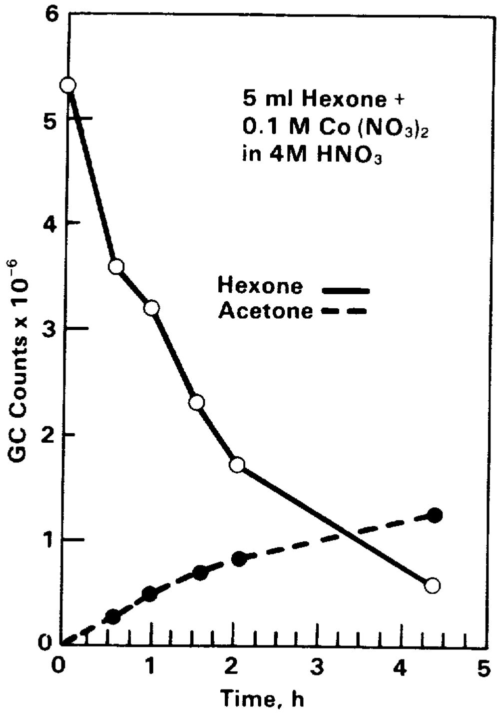


Figure 3: Example of Data Sheet for Hexone Oxidation

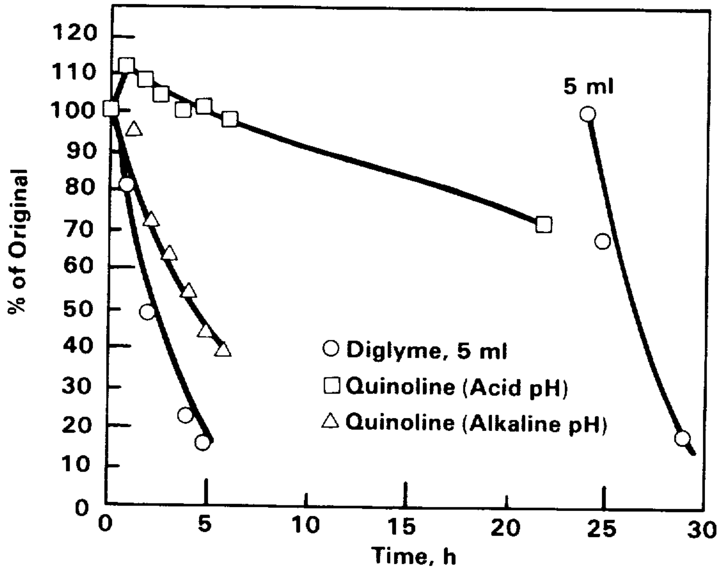
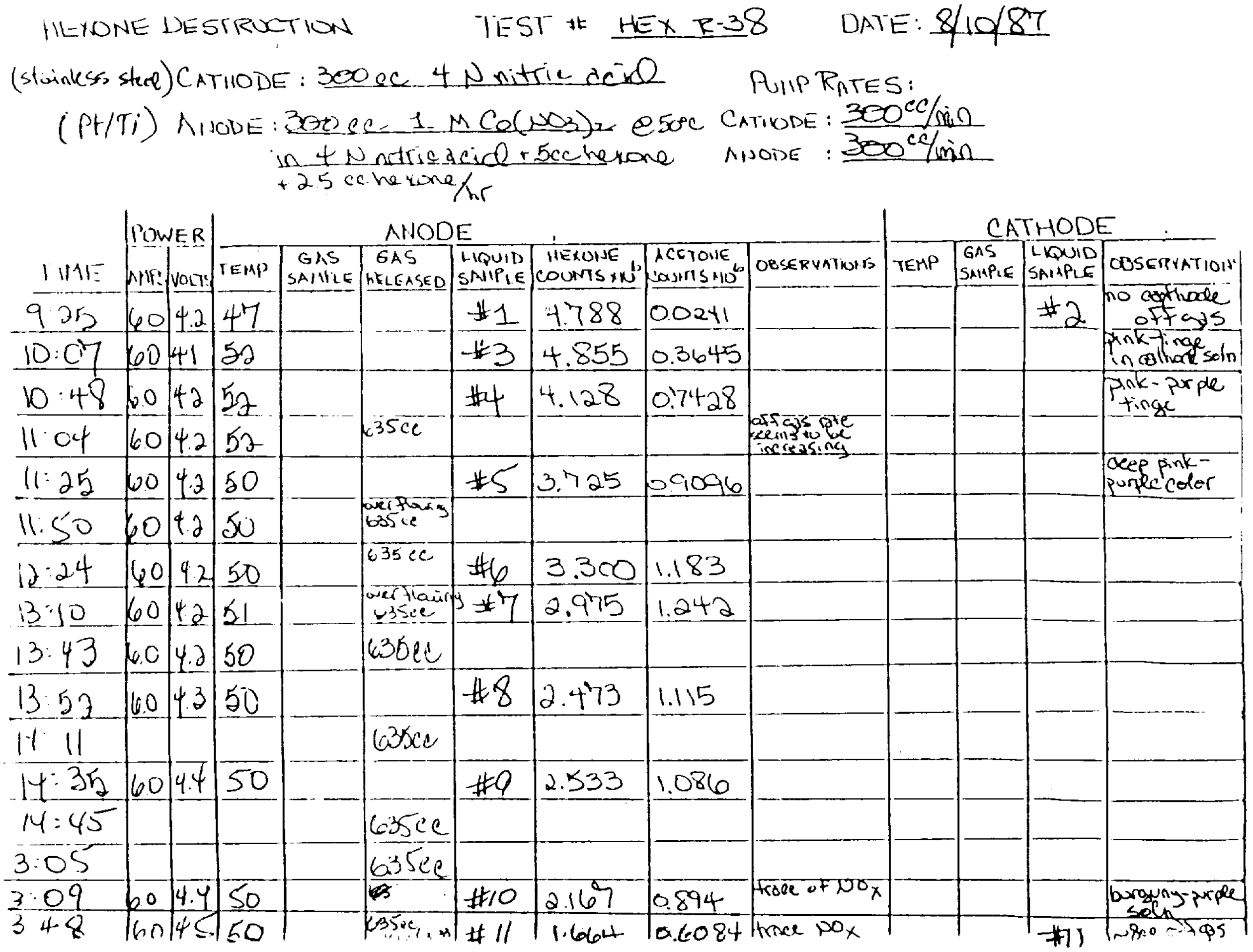


Figure 4: Example of Gas Chromatographic Data for Liquid Sample Analysis



HEXONE DESTRUCTION TEST # HEX R-38 DATE: 8/10/87

(stainless steel) CATHODE : 300 cc 4 N nitric acid

PUMP RATES:

(Pt/Ti) ANODE : 300 cc 1 M $Co(NO_3)_2$ @ 50°C in 4 N nitric acid + 5 cc hexone + 25 cc hexone/hr

CATHODE : 300 cc/min

ANODE : 300 cc/min

	POWER		ANODE							CATHODE			
TIME	AMP	VOLTS	TEMP	GAS SAMPLE	GAS RELEASED	LIQUID SAMPLE	HEXONE COUNTS $\times 10^6$	ACETONE COUNTS $\times 10^6$	OBSERVATIONS	TEMP	GAS SAMPLE	LIQUID SAMPLE	OBSERVATIONS
9:25	60	4.2	47			#1	4.788	0.0241				#2	no cathode off gas
10:07	60	4.1	52			#3	4.855	0.3645					pink tinge in catholyte soln
10:48	60	4.2	52			#4	4.128	0.7428					pink-purple tinge
11:04	60	4.2	52		635 cc				off gas rate seems to be increasing				
11:25	60	4.2	50			#5	3.725	0.9096					deep pink-purple color
11:50	60	4.2	50		overflowing 635 cc								
12:24	60	4.2	50		635 cc	#6	3.300	1.183					
13:10	60	4.2	51		overflowing 635 cc	#7	2.975	1.242					
13:43	6.0	4.2	50		635 cc								
13:53	6.0	4.3	50			#8	2.473	1.115					
14:11					635 cc								
14:35	60	4.4	50			#9	2.533	1.086					
14:45					635 cc								
3:05					635 cc								
3:09	60	4.4	50			#10	2.167	0.894	trace of NO_x				burgundy-purple soln
3:48	60	4.5	50		635 cc [illegible]	#11	1.664	0.6084	trace NO_x			#11	~800 cc gas

Figure 5: Example of Graphical Data Presentation for Hexone Oxidation

ORIGINAL PAGE IS
OF POOR QUALITY

HEXONE DESTRUCTION DATA ANALYSIS:

Gas Chromatograph Standard

% hexone	GC counts	slope	intercept
1	3566000	2.821E-07	-0.0059238
0.1	375500		

Date —) Elap. Min.	June 4, 87 Time	Interval	Hexone GC Counts	gms Hexone Remaining	gms Hexone Destroyed	Increment gms Hexone Destroyed	Hexone Destruction Rate gms/hr	Amps	Volts
-0	11:16		3290000	5.00				6	4.9
30	11:46	30.0	2546000	3.87	1.13	1.13	2.2614	6	4.9
60	12:16	30.0	1862000	2.83	2.17	1.04	2.0790	6	4.8
90	12:46	30.0	1515000	2.30	2.70	0.53	1.0547	6	4.9
180	14:16	90.0	390800	0.59	4.41	1.71	1.1390	6	4.9
210	14:46	30.0	112800	0.17	4.83	0.42	0.8450	6	5
240	15:16	30.0	23490	0.04	4.96	0.14	0.2715	6	5

Elap. Min.	June 5, 87 Time	Interval	Hexone GC Counts	gms Hexone Remaining	gms Hexone Destroyed	Increment gms Hexone Destroyed	Hexone Destruction Rate gms/hr	Amps	Volts
0	10:15		5228000	5.00				6	4.2
32	10:47	32.0	3870000	3.70	1.30	1.30	2.4352	6	4.2
90	11:45	58.0	1731000	1.66	3.34	2.05	2.1163	6	4.3
154	12:49	64.0	905800	0.87	4.13	0.79	0.7399	6	4.4
203	13:38	49.0	293000	0.28	4.72	0.59	0.7176	6	4.5
269	14:44	66.0	33960	0.03	4.97	0.25	0.2252	6	4.5

Figure 6: Example Data Presentation for Diglyme and Quinoline Oxidation