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SELECTIVE REMOVAL OF ORGANICS FOR WATER RECLAMATION

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SUMMARY

Electrolysis has been investigated as a means of purifying waste water. The feasibility of the direct electrochemical oxidation of urea has been demonstrated. Urea levels were reduced from 1200 ppm to 1 ppm forming the basis for a new approach to urine purification where the only consumable is electrical energy. Preliminary estimates of the energy requirements are 270 W/hr per liter of urine. Urea oxidation rates of around 350 mg urea/hr/m² were observed. It is anticipated that a 1 m² geometric area of electrode could treat urine for a crew of several persons. The low levels of organic contaminants resulting from this treatment indicate that the approach may have an impact as a post treatment process. Experiments are planned to investigate this later possibility.

INTRODUCTION

On long duration manned space missions, water will have to be recycled from waste waters such as humidity condensate, urine and wash water. Recycled water must be free from chemical contamination. The present report is concerned with a study of electrochemical approaches to the removal of organic contaminants from water for use in closed-loop life support systems.

Past studies on electrolysis for water reclamation have focused exclusively on the indirect electrolysis of urine [1,2]. In this approach, the anodic reaction leads to the formation of activated chlorine species such as hypochlorite in the electrolyte. Hypochlorite is a strong oxidizing agent and is very effective in eliminating the organic constituents of urine. Processes based on this approach, however, exhibit decreased efficiency with time due largely to the accumulation of insoluble chlorates and perchlorates generated at the high currents used. Electrode deterioration is another problem with this approach. To reduce problems associated with the "activated chlorine" mechanism, the direct oxidation of urea has been investigated as a means of dialysate regeneration for "artificial kidneys" [3,4]. The present report concerns the use of the direct electrochemical oxidation of organics for urine treatment and as a post treatment process for potable water recovery.

METHODOLOGY

1. Electrolysis Cell

Figure 1 shows the electrochemical cell that was used for all the experiments described below. It consisted of a glass compartment (volume approximately 40 ml) surrounded by a glass water jacket. The removable cover of the cell was made of teflon. An air-tight seal between the removable cover and the glass cell was formed using a rubber o-ring. The cover contains fittings for a gas inlet, reference electrode and a thermometer. Two wires approximately 0.5 mm in diameter were fitted through the cover to form the connection to the working and counter electrodes. Stirring was effected using a magnetic follower. It was possible to fabricate several identical cells of this design enabling at least two electrolysis experiments to be run concurrently.

2. Electrode Preparation

Electrolysis was performed on platinized platinum gauze electrodes. Both the anode and cathode were cylindrical in shape. One had a diameter of approximately 2.5 cm and a

height of 3 cm while the other electrode had the same height but a slightly smaller diameter so that it could fit inside the other. The electrodes were platinized according to the method described by Marrese [5]. The Pt black layer has the advantage of giving a large surface area. The smooth platinum gauze cylinders (geometric area approx. 60 cm²) were first cleaned in hot aqua regia for 10 minutes. After thorough washing, the electrodes were transferred to a 100 ml glass beaker containing platinic acid/lead acetate solution (1.5% PtCl₆²⁻ and 0.02% Pb²⁺) in 1 M HCl. The beaker was suspended in an ultrasonic bath (Bransonic) as shown in Figure 2. The gauze to be platinized was placed in the center of the beaker and a platinized platinum gauze was placed around the outside of the beaker to act as the counter electrode. A nylon mesh was used to separate the anode and cathode. Connections were made to a Princeton Applied Research 173 potentiostat/galvanostat. At the same time as the onset of the current, the ultrasonic bath was switched on. A current of 950 mA was applied for 20 minutes. Platinum black electrodes made using ultrasonic agitation are much more durable than nonultrasonically platinized electrodes. The increase in area during the platinization process is illustrated in Figure 3.

3. Membrane Preparation

A cylindrical shaped Nafion 117 cation-exchange membrane was used as a spacer between both electrodes. The membrane arrangement added to the convenience of the experimental system in that it allowed close positioning of the electrodes to minimize the resistance between the electrodes but also prevented electrical shorting. The membranes were cleaned by boiling in dilute H₂O₂ followed by several boiling steps in millipore water. The membranes were then boiled in 1.0 M NaOH to give the sodium ion form of the membrane. This was followed again by several boiling steps in millipore water.

4. Voltammetric Experiments

Voltammetric studies of urea oxidation were performed in the cells described above using platinum wire electrodes. The wire electrodes were sealed in a glass tube and were mounted in the cell through the opening in the teflon cover that normally was occupied by the thermometer.

Cyclic voltammetry was performed in 1 M H₂SO₄ to determine the real area of all the platinum electrodes used in the experiments described below by integrating the charge under the hydrogen adsorption peaks.

RESULTS

Figure 4 shows a cyclic voltammogram of urea using platinum electrodes. This result indicates the potential range in which urea can be oxidized. There is a potential "window" starting at 0.8 V vs. NHE until 1.2 V vs. NHE in which urea can be oxidized. The upper potential limit for urea oxidation on platinum is set by the occurrence of oxygen evolution.

Figure 5 shows a similar result performed in the presence of a buffer solution and in the presence of Cl^- . The saline-buffer solution was chosen to approximate the conditions of urine electrolysis. The result was much the same as in Figure 4. There is a potential region in which urea can be oxidized starting at about 0.8 V vs. NHE. The upper limit in this case would be set by the occurrence of oxygen evolution. These voltammetric studies provide crucial information concerning the potential at which urea can be oxidized directly.

Table 1 shows a series of experiments that were conducted on the electrolysis of urea-containing solution using constant potential electrolysis. The concentration of urea was 0.1 M (equivalent of 1200 ppm TOC) and the electrolyte was 1.0 M NaClO_4 . Using the data shown in Figure 4, the potential chosen used for the first electrolysis experiments was 1.44 V vs. NHE. Experiment A of Table 1 was conducted over a period of several days. Initially, the electrolysis current decayed to about 10 mA within an hour from the start of the electrolysis and within 2 hours the current was below 5 mA. To enhance the electrolysis current, at 1 hour intervals the potential of the electrolysis cell was reversed for 30 minutes to regenerate the working electrode. Nevertheless, under these conditions, the rate of oxidation of urea was very low.

Experiment B of Table 1 was identical to experiment A except that an automatic switching mechanism performed the potential reversal at minute intervals. The switching mechanism was constructed from 2 Idec RTE P12 electronic timers and 2 Idec RR 2PU relays. At the end of every minute, the applied voltage (1.44 V vs. NHE) was automatically switched by the relay to the counter electrode such that the anode became the cathode. Thereby, each electrode alternated as the cathode and anode and the intermittent cathodic treatment provided a method to continuously regenerate each electrode. This caused a considerable increase in the urea oxidation rate. The TOC value was approximately 1 ppm at the end of 24 hours, however, the magnitude of the current dropped considerably after just a few hours from starting the electrolysis indicating that the urea removal rate may have been more rapid than is indicated from this single TOC measurement.

Experiment C of Table 1 shows the effect of using 1.34 V instead of 1.44 V as the applied voltage. Using the intermittent potential reversal technique, rapid oxidation of urea was observed. An oxidation profile of this experiment is shown in Figure 6. The

significance of this experiment is that it demonstrates that the rapid oxidation of urea occurs at potentials below that required for chloride oxidation.

Experiment D of Table 1 is an identical experiment to experiment C except that a shorter interval between potential reversal was used (i.e. 20 seconds instead of 1 minute). This resulted in an approximately 3 fold increase in the rate of urea oxidation over experiment C.

The electrical power requirements of the electrolysis can be determined from the voltage drop between the anode and cathode and the electrolysis current. The voltage drop was 1.8 V but in an optimum system with a solid polymer electrolyte this would be expected to be slightly lower at 1.5 V. The mean current during experiment D in Table 1 was 300 mA. It took 24 hours for the completion of the electrolysis and the volume of solution was 40 ml.

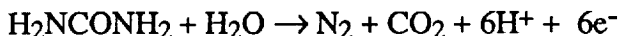
$$\text{Electrical Power} = 0.3 \times 1.5 = 0.45 \text{ W}$$

$$\text{Electrical Energy} = 0.45 \times \frac{1000}{40} \times 24 = 270 \text{ W-hr for 1 liter of urine.}$$

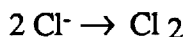
DISCUSSION

The research described above has a direct bearing on the recovery of potable water from urine and other forms of wastewater.

Primarily, this stage of the research has demonstrated the feasibility of utilizing electrolysis for urea removal from contaminated water. Using constant potential electrolysis, the oxidation of urea takes place directly according to the following overall reaction.



The corresponding cathodic reaction is hydrogen evolution. Since the anodic reaction takes place at or below 1.34 vs. NHE, the following reaction is avoided:



Consequently, the process does not involve activated chlorine oxidizing agents such as hypochlorites that can be problematical in urine electrolysis.

It is anticipated that the rates of urea removal can be further optimized. Taking experiment C of Table 1 as an example, the catalytic surface area used in this experiment was low and could easily be increased three-fold. It is likely that a similar increase could be realized by using a shorted potential reversal interval. Thus, the rate of urea removal could be increased from 0.26 g/hr/m² to at least 2.0 g/hr/m². This is well in excess of the endogenous urea production rate (0.33 g/hr). It is likely that a 1 m² electrode could treat urine for a crew of several persons. Further rate increases could be achieved by the design of a flow system.

In the second stage of the research project, the activation energy of urea oxidation will be determined by performing log*i*/V curves at different temperatures. This will be followed by performing constant potential electrolysis of urine using the intermittent potential reversal approach.

Polishing of potable water is a particular concern where it is desirable to achieve low levels of organic contaminants (<500 ppb) and the results described above have a direct bearing on the post treatment of recovered water. The electrolysis method reduced urea from 1200 ppm to a level close to 1 ppm within 24 hours, although the time taken to effect this electrolysis is largely dependent upon the amount of active surface area of the electrode. The low levels of TOC resulting from this treatment give grounds for considerable optimism that this approach can be used for the post treatment of potable water. This is especially true given that urea is relatively resistant to many post treatment processes.

REFERENCES

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TABLE 1 UREA ELECTROLYSIS

	Electrode Potential vs. (NHE)	Time Interval Between Potential Reversal	Electrode Surface (Real area)	Electrode Surface (Geometric area)	Urea removal rate based on real area	Urea removal rate based on geometric area	Final TOC Value
A	1.44	12 hrs	22988 cm ²	60.5 cm ²	.063 mg/hr/m ²	0.024 g/hr/m ²	617 ppm ^{1.}
B	1.44	1 min	5000 cm ²	57 cm ²	4 mg/hr/m ²	0.351 g/hr/m ²	1.05 ppm ^{2.}
C	1.34	1 min	8541 cm ²	60.5 cm ²	1.87 mg/hr/m ²	0.264 g/hr/m ²	220 ppm ^{2.} 2.0 ppm ^{3.}
D	1.34	20 sec	3801 cm ²	57 cm ²	5.26 mg/hr/m ²	0.350 g/hr/m ²	1.18 ppm ^{2.}

1. 165 hours of electrolysis
2. 24 hours of electrolysis
3. 53 hours of electrolysis

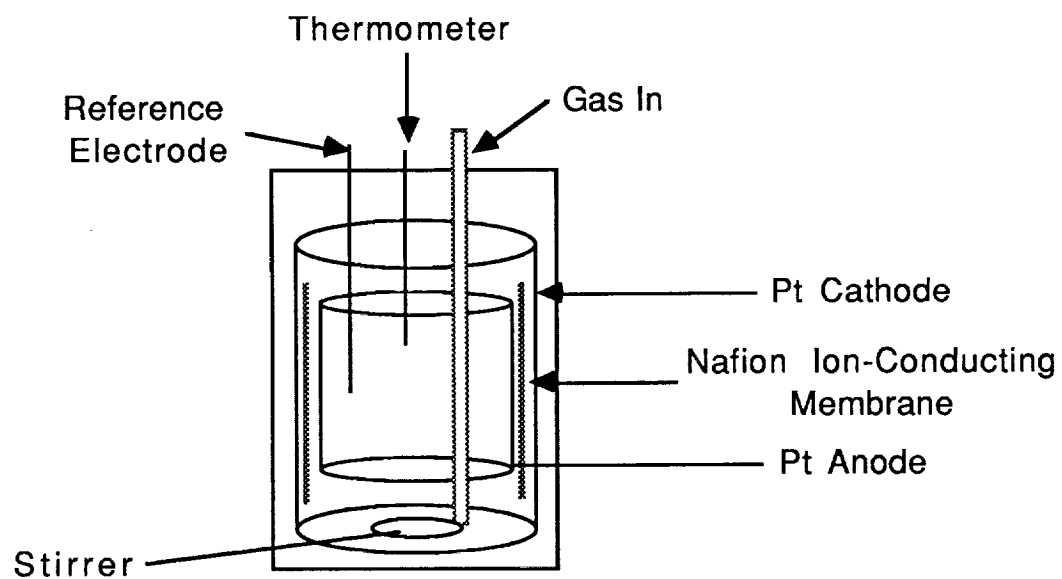


Figure 1: Electrolysis test cell incorporating an ion-conducting membrane

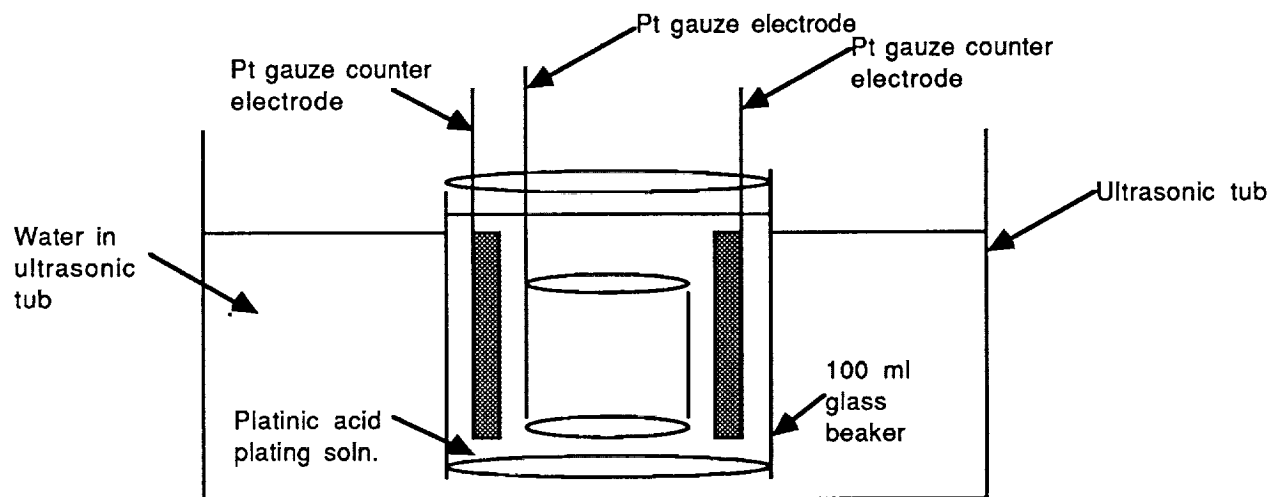


Figure 2: Schematic Diagram of Ultrasonic Plating Apparatus

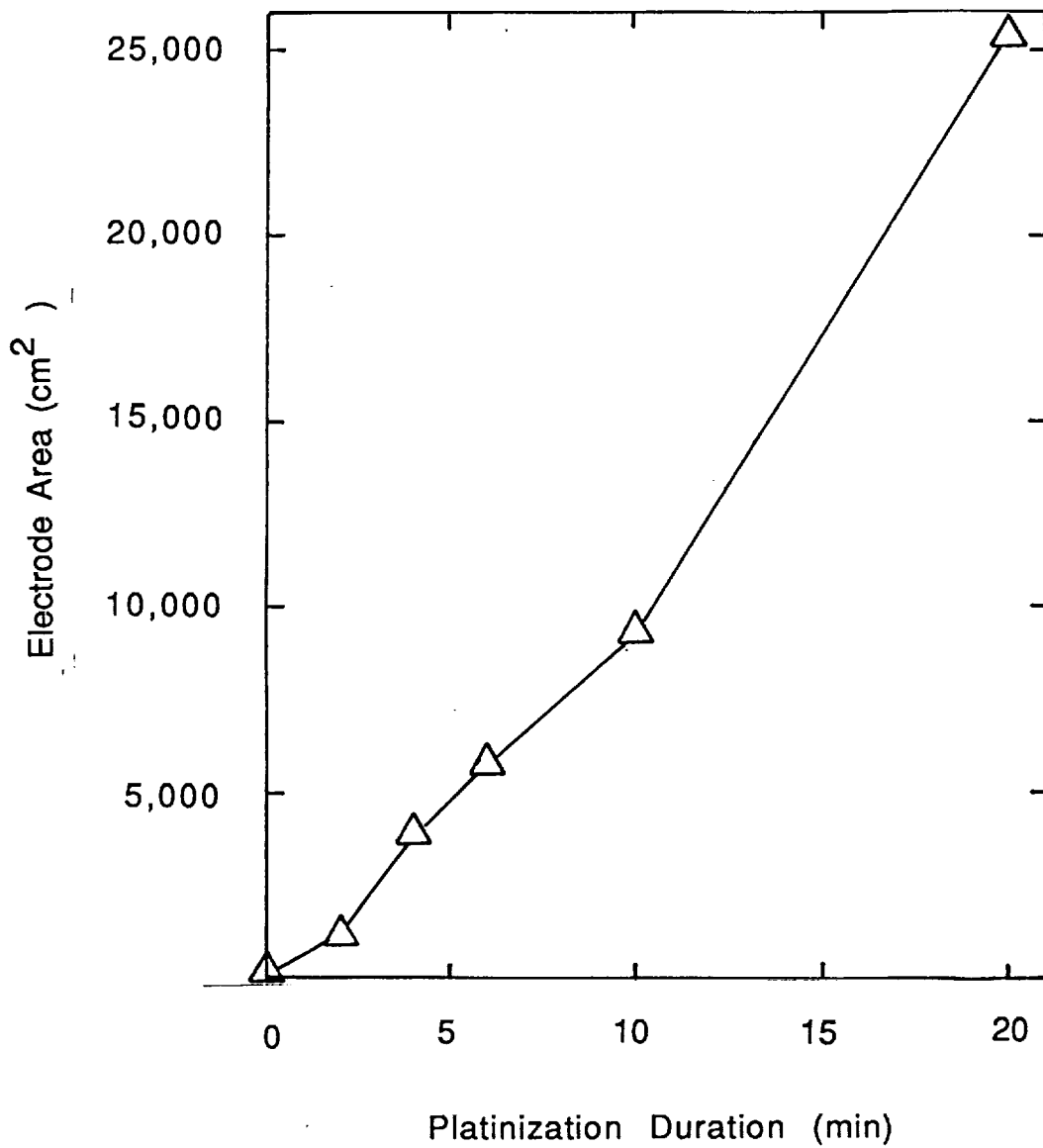


Figure 3: Increase in Electrode Area Versus Platinization Duration

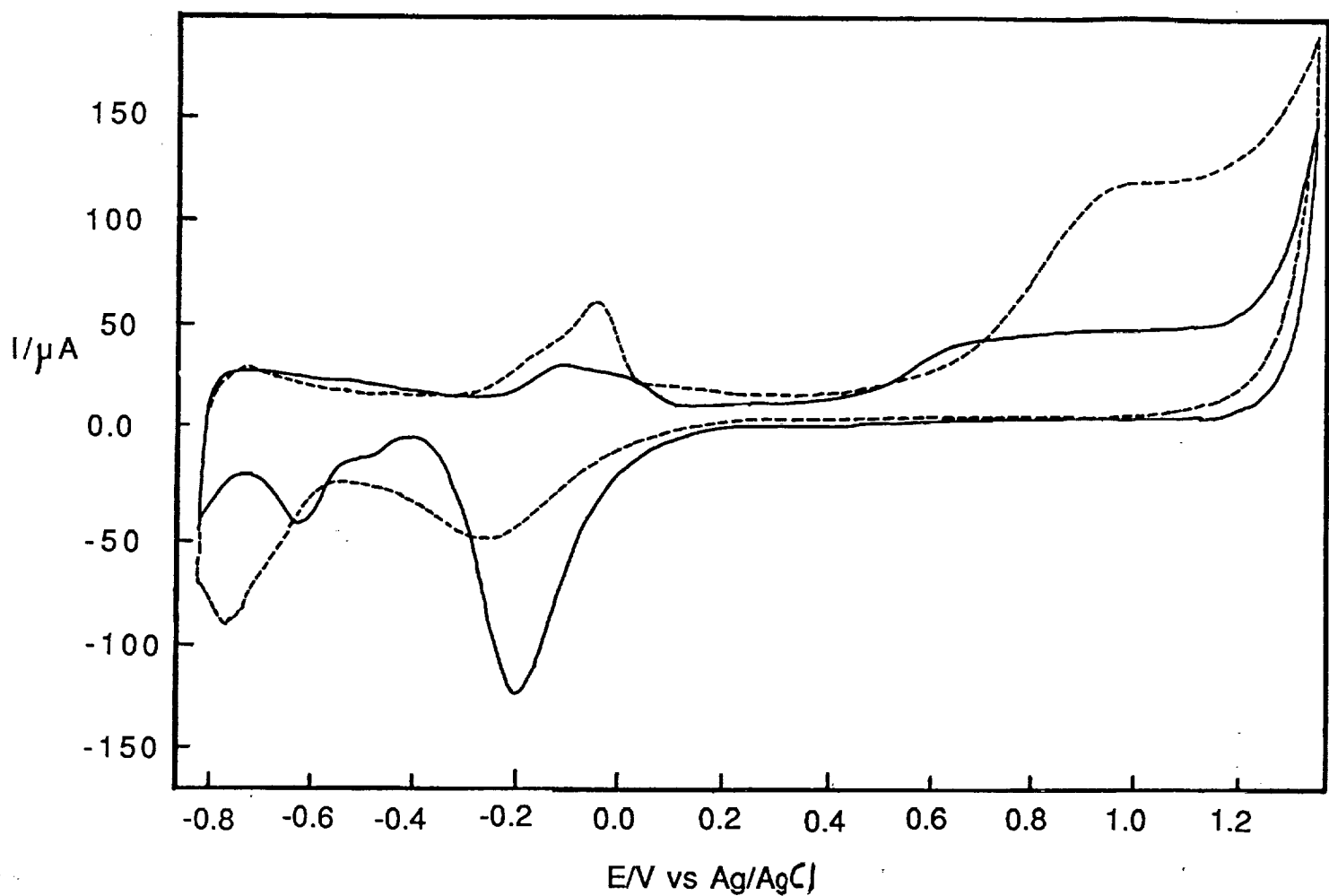


Figure 4: Cyclic Voltammogram of Platinum

The electrolyte was deoxygenated and contained 1.0 M NaClO_4 . The electrode area was 35.1 cm. The experiment was performed in the absence (—) and in the presence of urea at a final concentration of 0.1 M (- - -).

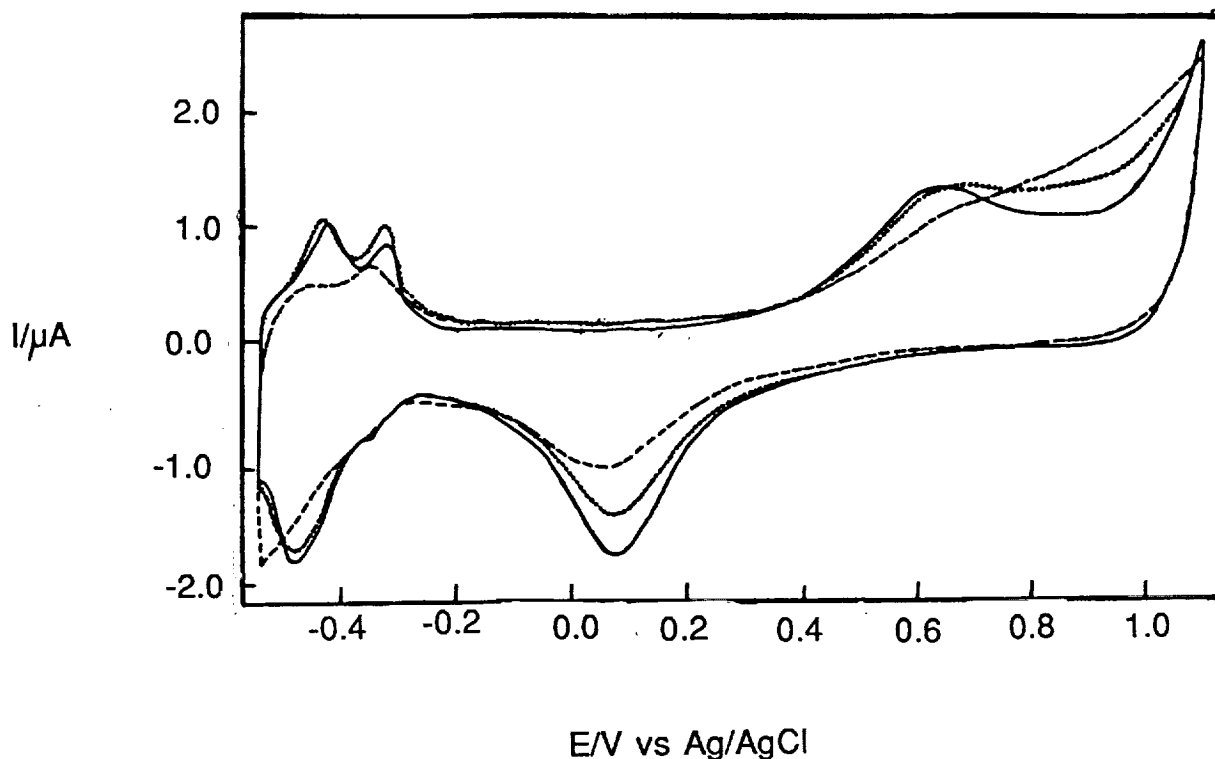


Figure 5: Cyclic Voltammogram of Urea on Platinum

The electrolyte was deoxygenated and contained phosphate buffer at a final concentration of 0.4 M and NaCl at a final concentration of 0.23 M pH = 7.0. The sweep rate was 100 mV per second and the electrode area was 0.23 cm². The voltammograms were performed in the absence of urea (_____) and in the presence of urea at final concentrations of 3.4 mM (.....) and 20.1 mM (----).

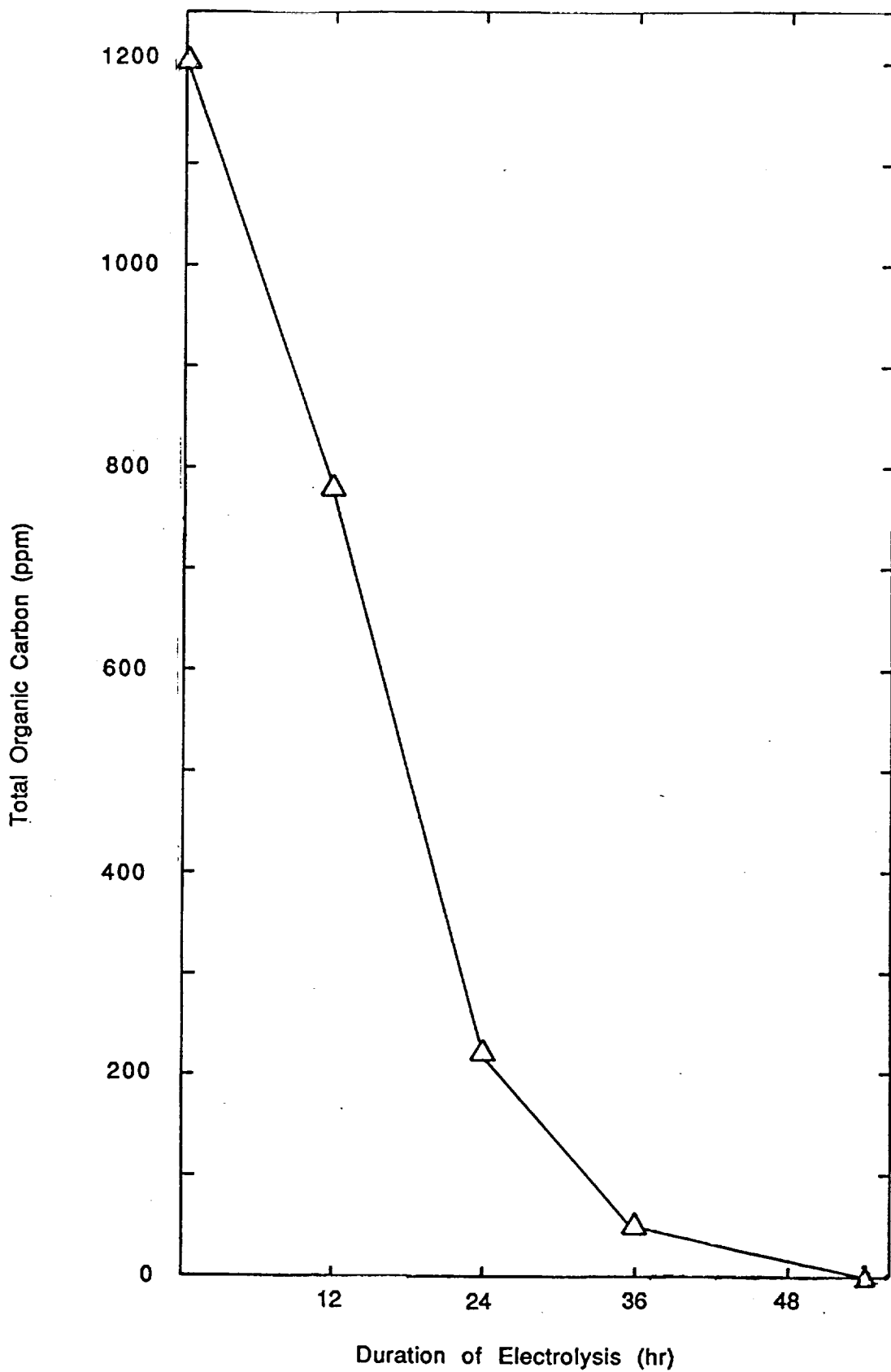


Figure 6: Total Organic Carbon Versus Electrolysis Time

The electrolyte volume was 40 ml and contained urea to a final concentration of 1200 ppm and NaClO_4 to a final concentration of 1.0 M.