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ELECTROCHEMICAL INCINERATION OF WASTES

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SUMMARY :

The problems posed by wastes are particularly demanding in space vehicles where it is desirable to utilise treatments that will convert wastes into chemicals that can be evantually recycled. The novel technology of waste removal by electrochemical methods is therefore of interest. The important consideration for waste oxidation is to select a right kind of electrode (anode) material .The material should be stable under anodic conditions and a poor electrocatalyst for oxygen and chlorine evolution.

The work has been carried out on seven different electrocatalyst. The current- voltage curve on each electrode for oxidation of fecal waste suggests that the waste can be oxidised in the potential range of 1.2 -1.6V /NHE.The electrode studied were Pt, PbO_2 , Gold ,graphite ,Pyrovskite ,tungten carbide and Ti_4O_7 coated with RuO_2.On the basis of long term electrolysis experiments on these electrode and on the basis TOC reduced, two best electrode viz.,perovskite and RuO2 coated on Ti_4O_7 (ebonex) have been identified.

The effect of redox ions on the electrolyte was studied and found to increase the rate of oxidation approximately 1.4 times.Though most of the experiments were done in mixtures of urine and waste, the experiments with redox couples involved 2.5 M sulfuric acid in order to avoid the precipitation of redox ions by urea.

Two methods for long term electrolysis of waste has been investigated. The oxidation of waste on Pt and lead dioxide electrodes were performed using the galvanostatic methods while other electrodes were tried using potentiostatic method.The advantage of the galvanostatic method is the faster rate of oxidation

however,the potential increases with time.Due to the increase of potential,the oxidation of waste begins to compete with oxygen and chlorine evolution resulting in production of more chlorine.The potentiostatic method does keep the potential constant but at longer times,the current decreases.Therefore,the chlorine evolution in this method is ten times less than that in galvanostatic method.

The research planned for the next year will be directed towards identifying quantitatively, a regenerative electrochemical process for recovery of carbon dioxide, water, hydrogen and nitrogen urine/feces mixtures without any chemical expendables. The research accomplished has shown that urine/feces mixtures can be oxidised to carbondioxide and water, but current densities are low and must be improved yto levels of atleast or better than 50mA/sq.cm. Current densities of 3-5mA/sq.cm. are now being attained with the perovskite and $Ti_4 O_7$ coated with RuO_2 . These are the best electrode materials found. Recent experiment with the redox agent eg.,Cerium sulphate, improves the current density; however, sulphuric acid is required to to keep the redox agent in solution in order for it to be effective for enhancing oxidation. It is desirable to reduce the use of acid and or find substitutes. Other methods that will be pursued include ultrasonics; increased temparature (100 to 200 C) and pressure(5-15 atms) ; flow through electrodes that provide increased electrode surface area to the urine/feces mixture; others; and combinations of these.

ELECTROCHEMICAL INCINERATION OF WASTES

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The pollution of air, earth and sea due to disposal of domestic and human waste in its raw states is a matter of increasing public and government concern. Earlier, it was regarded as permissible to reject wastes into the apparently infinite sink of the sea but during the past 20 years, it has become clear that this is environmentally unacceptable [1.2]. The combustion of waste to reduce biomass to ashes has been practiced but it is not acceptable due to production of harmful gases such as NO, CO, H_2S, etc. On the other hand, transportation of municipal waste away from cities involve high costs and uses fossil fuel such as gasoline which does not seem to be cost effective. The development of large sewage farms and drainage systems for cities and for new housing developments are also cumbersome and expensive to build and operate [3.4].

The problems posed by wastes are particularly demanding in space vehicles where it is desirable to utilize treatments that will convert wastes into chemicals that can be eventually recycled. Chemical treatments have proved relatively unsatisfactory and tend to be increasingly so with increase of the mission time. However, use of heat to destroy waste and convert them

to CO_2 by the use of air oxygen has the disadvantage and difficulties of dissipating heat in a space environment and the inevitable presence of oxides of nitrogen and carbon monoxide in the effluent gases [5.6]. Here in particular, electrochemical techniques offer several advantages including the low temperatures which may be used and the absence of any NO and CO in the evolved gases: CO_2, hydrogen and nitrogen [1].

For these reasons above, initiatives have been undertaken by us to develop a novel technology of waste removal by electrochemical methods.

Furthermore, in a recent analysis [8] Holtzapple and Little developed a closed Environment Life Support System [CELSS] which incorporates plants or algae to supplement the diet of astronauts. This analysis compared combustion and electrochemical incineration in space. A study was made on a four man crew, assumed to be eating stored food and potatoes which are grown in life support systems.

The status of the humans, equipment and storage tank is reported. The weight of a life support system (exclusive of potato production is calculated).

The system weight when wet, is in a range from 21,000 to 4,500 kgm depending on how much the diet is in potato. As the amount of potato is increased, the system weight increases.

The system weight when electrolysis of wastes is employed drops to to about 1200 kg and stays approximately the same although the waste electrolyzer weight increases with more potato in the diet, this is counter balanced by a reduction of the weight of the electrolyzer since most of the weight of the human oxygen metabolic needs are supplied by the plants. Correspondingly, the

thermal combustion equipment is about double the weight of the electrochemical device with no potatoes in the diet and increases to around four times greater when a larger amount of potatoes was included in the diet. Holtzapple and Little concluded that the use of waste electrolyzer reduced the life support system weight of a four person crew by 1000 to 3000 kg depending on the diet.

ELECTROCHEMISTRY OF ORGANIC OXIDATION TO CO_2

Studies of the electrochemical oxidation of hydrocarbons at platinum electrodes [9] and anodic oxidation of cellulose, lower carbohydrates [10] and coal [11-13] lead to a better understanding and inspired us to undertake the task of electrochemical incineration of waste, especially for space application.

The aqueous solutions have an electrode window in which substances can be oxidized without competition from oxygen evolution up to about 1.6 V on the normal hydrogen scale in acid solution at 25°C. Correspondingly, the oxidation potentials of some organic compounds found in human waste and chemical derived from biomass are shown in Table 1. It therefore is possible to carry out a complete oxidation of all the components in fecal waste, including urea present in urine, to CO_2 in aqueous solution. On the other hand, if the oxidation of wastes is incomplete in mixture of urine, there is a possibility of introducing them in molten carbonates, using anodic oxidation. The temperature coefficients of waste oxidation reaction are important in view of the work of Horri [14], who found that when lowering the temperature to zero degree C, during the reduction of CO_2 on Cu , a 90% yield of methane was obtained. At present, little is known about the temperature coefficient of

organic oxidation reactions, but in Kolbe-like oxidation reaction of material

formed from the dissolution of coal [13], it was found that (dE/dT) is -4 x

10^{-3} V/°C and (di/dT) ~ 0.1 mA/°C. From considerations of the oxidation of

coal product, it seemed that an expected range for the oxidation of wastes

would be around 1.0 - 1.5 V/NHE, thus, not enough to decompose water sig-

nificantly on platinum. The important consideration for waste oxidation is to

select a right kind of anode material. The material should be

(1) Remain unoxidized under highly anodic conditions

(2) A poor electrocatalyst for oxygen and chlorine evolution.

Lead dioxide is often used for organic oxidations since it is

highly conducting and has a high overvoltage for oxygen evolution [15,16].

The choice of a proper electrode for oxidation of waste therefore required

further studies in order to find an efficient electrode material. The stable

and efficient material such as perovskites has been made by Bockris and

Otagawa [17]. This has been shown that these perovskites are stable to oxygen

attack (but in alkaline solution). In addition, Ebonex (Ti_4O_7) and metal

oxide coated ebonex has been used as stable anodic and cathodic material in

acid environment [18,19].

Bockris et al. [10] showed that carbohydrates are completely oxidized to

CO_2 during electrolysis on platinum electrode. Initially, the electrolysis

was performed on simple carbohydrates, such as sucrose cellubiose (B-D-glucose

dimer) and glucose, in 40% H_3PO_4 or 5N NaOH at temperature of 80-100°C). A

platinized platinum gauze (52 cm^2) was used as the anode. The reactivity

decreased for molecules of increasing molecular weights, nevertheless, it was

found that cellulose could be broken down to CO_2 with a current efficiency of around 100% and only 2 faradays were involved in the evolution of 1 mol of CO_2 perhaps because of preliminary hydrolysis reactions. The oxidation reactions of casein were carried out in 1N NaOH [20] on platinum electrode. The electrochemical oxidation of carbonaceous material to produce hydrogen using waste as an anode polarizer has been reported where it has been shown that addition of waste in an anode compartment needs much less electrode potential than that required for oxygen evolution [21]. The electrochemical degradation of human waste on eighteen different metal electrodes has been investigated by Tischer et al. [7] but only platinum proved satisfactory. The electrolysis of waste mixtures can be achieved indirectly by the anodic generation of oxidizing agents which themselves bring about the oxidation of carbonaceous material in the solution. This approach has been utilized for urine purification in regenerative life support systems that were based on the generation of activated chlorine (Cl_2, HOCl and OCl^-) as the oxidants from Cl^- in urine [22-24]. These studies showed that close to 100% of the organic material could be removed by electrolysis using planar electrodes. Additional features include the production of OCl^-, a strong disinfectant and bleaching agent. The generation of activated chlorine has also been used as an effective means of treating mixtures of urine and fecal waste from humans [25, 26]. The waste mixture could be decolorized and clarified due to generation of activated chlorine on platinum electrode using current density of 50 mA/cm^2, furthermore, the odor was quickly lost. The quantitative estimates of the products, however, was not available although CO_2, O_2, and Cl_2 was detected.

An "indirect" electrochemical method of waste treatment has been developed recently by Partick and Dhooge [27]. In this approach, electrodes were used to regenerate redox couples which were circulated to a waste holding tank. The conversion of waste material such as cattle manure wood chips and sewage sludge into a pollution free effluent which contained no CO or NO was achieved. Two redox coupled called catalyst and cocatalyst were used in the system.

The method of electrochemical incineration could also be useful for recovery of shower water for manned space flight. The urea is an important contaminant of hygiene water and is present in millimolar range concentration. Human urine consists of inorganic ions such as Na^+, Cl^-, $H_2PO^-_4$, Ca^{2+}, Mg^{2+} and organic metabolics such as urea could be purified to recover water for daily needs. The inorganic ions from urine can easily be removed from urine and waste water by variety of purification techniques such as ion exchangers. However, urea cannot readily be separated by chromatography or ion exchange method, and unlike organic contaminants of waste water, it cannot be adsorbed into activated carbon. Therefore, innovative electrochemical ways of treating urine and human wastes are important technologies for long duration space exploration.

The use of new electrode material, redox couples, effect of ultrasound, wider ranges of temperature and the use of various flow systems to increase the contact time and eventually the increase in current density at electrochemical potential of interest is warranted. Therefore, the aim of the present work is to evaluate the proper conditions to utilize the less energy for electrolytical disposal of human waste in space environment. The use of

organic solvents or molten carbonate to increase the range of potentials without interference with oxygen belong to later stage of the investigation.

THE MAIN WORK FROM 1989 - FEB. 1990

The two main approaches were used in electrochemical incineration of waste.

A.   Separate Treatment of Solid Waste

In this approach the urine was excluded from the solid waste and dissolved in concentrated H_2SO_4. The current-voltage curve under steady state condition for each component of the fecal waste (cellulose, casein, oleic and etc.) was recorded after dissolving in H_2SO_4 in order to determine the oxidation potential of each component. It was found that each component of the fecal waste could be oxidized in the potential range of 1.3 V - 1.6 V/NHE on platinum and lead dioxide electrodes. This gave us an incentive for a long term electrolysis. The electrolysis experiments were performed at the current densities of the order of 5 to 10 mA cm2. The effect of redox couple Ce^{4+}/Ce^{3+} increased the current density and ultrasonic field helped to break down the complex molecules of solid. The reaction at the anode is production of CO_2 at more than 90% current efficiency, and the reaction of the cathode is entirely the production of H2 [13].

B.   United Treatment of Solid and Urine

Experiments on steady state current-voltage curve was recorded for mixture of fecal waste and urine. This gave us further information that all components of fecal waste plus urea (in urine) could be oxidized in the same

range of potential, i.e., around 1.3-1.4 V/NHE on pt and PbO_2 electrode. Experiments were carried out with success on the electrolysis of solid and urine together [28, 29]. At a current density of 8 mA/cm^2 the color and odor was changed. The consumption of carbon is 95% complete in 96 hours. The anodic gases were CO_2 and Cl_2. However, the chlorine was less than 0.1%.

The electrolysis was performed on a waste mixture in urine consisting of 33% fiber, 32% microorganisms, 10% protein, 20% fat, 5% inorganic material, to represent the constitution of human waste [30, 31] in a three compartment cell (Fig. 1). These experiments were performed on platinum and lead dioxide electrodes.

Results

During the electrolysis, the total organic carbon (TOC) in the electrolyte was reduced by 95%, between the start and the end of the electrolysis experiment, considerable changes in the nature of the waste solution was visible. Material started as a dark black solution where particulate material could easily be distinguished. During the electrolysis, the solution became transparent to light. The detailed result of electrolysis on platinum and pbO_2 electrode has been published [28, 29] and included in an earlier report.

The experimental results on some oxide electrode, e.g., Ti_4O_7 (Ebonex), NiO_2, PbO_2 coated Ti_4O_7, IrO_2 coated Ti_4O_7 and RuO_2 coated Ti_4O_7 on the basis. Steady-state current-voltage curves on individual component of fecal mixture and urea were obtained and were included in an earlier report. It was concluded that cellulose and urea on these electrode oxidizes at around 1.25 V - 1.40 V/NHE.

PHENOMENOLOGICAL CONCLUSION OF THE WORK 1989 - FEB. 1990

1. The limiting currents in amps cm^{-2} increased with increase of the size of the molecule.

2. The energies of activation are about (6 ± 2 kcal $mole^{-1}$) for all substances examined.

3. The I-V curve limiting current plateau is around 1.4 V for cellulose, casein and yeast.

4. Lead dioxide is a better electrocatalyst than pt by a factor of 2 and it is also cheaper.

5. The addition of Ce^{4+} increases the real current density for oxidation by c. 1.4 times.

6. The total organic carbon decreased by about 95% after 96 hours.

7. CO, NO, NO_2, NH_3 and methane could not be detected in gaseous effluent.

8. The chlorine evolution is less than 0.1%.

9. The sequence of catalytic activity for the oxidation of cellulose is $Ti_4O_7 > RuO_2 > NiO > PbO_2 > IrO_2$.

OBJECTIVE OF PRESENT WORK (Feb. 1990 - August 31, 1990

The electrolysis of fecal waste could be done by two methods (1) galvanostatic, and (2) potentiostatic. In the galvanostatic method a constant current is applied between electrode, however, there is no control over the potential. This method has disadvantages in the sense that the potential

increases to the value where oxidation of waste competes with oxygen evolution as well as with chlorine evolution. It was found that chlorine evolution in galvanostatic experiment was much more than in the potentiostatic methods. The advantage of the galvanostatic method is a supply of constant current, the evolution of chlorine makes OCl^- which decolorizes the waste and removes the odor within one hour. The removal of carbon is also faster in this case and evolution of CO_2 is greater.

However, in the case of potentiostatically controlled experiments the potential is constant but current shows a decreasing trend and the result is the slower rate of electrolysis. The advantage of this method is that oxidation reactions does not compete with O_2 and Cl_2 evolution provided potentials are within the range of the fecal waste oxidation region. The long term electrolysis experiments indicates that the amount of chlorine evolution is at least 10 times less than that of galvanostatic method.

It is important to choose a right kind of anode material where the potential of waste oxidation and oxygen evolution are separated in order to avoid the competition. The anode material should be inexpensive, stable to oxygen attacks and poor catalyst for Cl_2 evolution. The most important aspect for good electrocatalyst is to oxidize the fecal waste at lower potentials.

Therefore, the objective of the present work is to search for a proper anode material which can operate at lower potential with and a higher current density in a mixture of urine and fecal waste. The effect of temperature and concentration of fecal waste and the ratio of urine and fecal waste has also been evaluated. The activation energy for oxidation and effect of redox couple on current density has been studied. The economics has been calculat-

ed on the best electrode on the basis of long term electrolysis experiments and results.

METHODOLOGY

Electrochemical Cells and Apparatus :

The electrochemical experiments were conducted in all glass cells. Two kinds of cells were fabricated in a glass shop of the chemistry departmenat Texas A&M university.The cell shown in Fig. 2 was used for all of the work done with addition of redox ions. The volume of the anodic and cathodic compartment was 200 cc. Both the working and counter electrodes were fitted through the top of the cell with ground glass joints. The electrolyte was stirred by a magnetic follower. The outlet gas was carried through a water trap which absorbed most of the chlorine. The remaining gases were further went through a blank trap from which Robot took the samples and feed to gas chromatograph for gas analysis. The blank trap was connected to a water displacement jar of 1000 ml where all gases excluding chlorine were measured. The cell rested on a hot plate and the temperature was monitored using a thermometer fitted into the anodic compartment using ground glass joint. This cell provided the separation of anodic and cathodic compartment. After each experiment, the glass cells were cleaned by treatment in an oven at 500°C in air to eliminate organic waste products, washed with H_2SO_4 and finally with distilled water.

A Pine Instrument RDE4 potentiostat was used for potentiostatic experiments for long term electrolysis experiments. The current versus potential and current versus time curves were recorded on a Hewett-Packard X-Y recorder

(Model 7044B).

Waste Materials and Solution :

Two types waste material were used for the experiments. Most of the experiments were carried out with a synthetic mixture of material which represented the main constituents of feces. The synthetic mixture was made up in a supply of 4.6 kgm that was sufficient for all the waste experiments and was kept frozen between the experiment. Though the nature of fecal waste [31] can vary considerably, generally one third of its contents is made up of microorganisms from the intestinal flora and approximately one-third is made from undigested fiber. The remainder is made up from lipids, and inorganic materials; the waste mixture shown in Table 2 reflects these proportions. The microorganisms Torpuliner and E. coli were obtained in powdered form (Sigmal Chemical Co.) and the remaining contents were obtained from standard chemical supplies. The mixture had a paste-like consistency and gave off a strong odor. The conversion factor wet waste: dry waste was determined by leaving known samples of waste in the oven at 150°C and the weight was monitored for a number of days until a constant value was obtained; 1 gm wet weight of waste was shown to be equivalent to 0.39 gm dry weight. All amounts of waste are given in terms of dry weight.

The experiment with real feces were carried out in a urine as electro-lyte. The current-voltage curve indicates that the oxidation of real and synthetic mixture in urine takes place at the same potentials.

For experiments involving electrolysis in urine, the material was weighed and treated in a pestle and mortar to which a small amount of urine

was added. The material was further homogenized by stirring. Following this treatment, the waste material was transferred to the anode compartment containing urine as electrolyte. No treatment to urine was necessary. The experiments were run at 80°C.

The urine was collected from laboratory personnel and mixed with the solid waste material using the procedures described above.

For experiments with redox ion 20 ml sulfuric acid was added to the urine to make acid concentration of 2.5 M. This was needed for these experiments due to the fact that Ce^{4+} ion marked as complex with urea present in the urine and precipitate at pH = 6. By addition of 2.5 M H_2SO_4 the pH of the electrolyte was brought down which allowed cerium to remain in the ionic form.

Electrode (Anode Materials) :

The platinum electrode of 4x4 cm was used as counter electrode. The reference electrode was calomal electrode. However, the potential referred in text and figures are referred on normal hydrogen scale.

Different electrode materials were chosen as anode material.

1. Gold

2. Graphite

3. Tungsten Carbide

4. Ti_4O_7 Coated RuO_2

5. Perovskite $(La_{0.79}Sr_{0.20}Mn,O_3)$

6. Platinum

Source of Purchase and Fabrication :

The gold plate of 2.5x2.5 cm^2 was purchased from Alfa Chemical Company and used without any treatment. The graphite sheet of 25x50 cm was purchased from Johnson Mathey & Co. The small pieces of 12 cm^2 was cut from this sheet and soldered to a pt wire to fabricate electrode. The Pt wire was sealed into a glass tube. The tungsten carbide was purchased from A. Baker Hughes Co. Houston and small electrodes were cut for use. The abonex coated RuO$_2$ electrode of 12 cm^2 was gifted by Ebonex Technologies Ltd., 5915 Hollis St., Emeryville, CA. The base material is Ebonex of 2 mm thick plate on which thin film of few micron size RuO$_2$ is coated by electrochemical method.

Pyrovskite was purchased as powder from HVA Associates, 45 Johnson Street, Rolla, MO 64501 which had La0.79 Sr$_{0.20}$ MnO$_3$ composition. The powder was pressed into pellets of 1.5 cm diameter using a hydraulic machine. The pellets were pressed under a 3 ton pressure. The pellet prepared under such condition was heated to 1000°C for 48 hrs. The electrical connections were made using conducting silver epoxy purchased from ACME, New Haven, Connecticut. The electrodes prepared were mechanically stable.

Chemical Analysis and Product Sampling :

A Varian (Model 3400) gas chromatograph with a Carbo Sieve II column with thermal conductivity detector was used for the gas analysis. Helium or Argon was used as the GC carrier gas at a flow rate of 30 ml/min. Chromatograms were recorded using a HP 3390 A integrator which provided digital readouts of the retention times and integrated areas of the different peaks. The rate of CO$_2$, hydrogen and nitrogen evolution was monitored by gas chroma-

tography and calibration curves for CO_2, H_2 and N_2 were performed on a regular basis. The CO_2, H_2 and N_2 calibration graph gave a slope of 9.00×10^{-5} ul 9×10^{-6} ul and 6.3×10^{-5} ul per integrated count; this is equivalent to 4.0×10^{-9}, 4.02×10^{-10} and 2.8×10^{-9} moles of CO_2, H_2 and M_2 per integrated count. The other gases such as CO, CH_4, NO and NO_2 were absent and were not seen in gas chromatograms.

Robotic Gas Sampling System :

A Perkin Elmer Master Lab Robot 9000 was used for gas sampling which takes the gas samples every 30 minutes through a septum placed in the gas flow immediately downstream from the reaction cell but after the water trap. This assembly as shown in Fig. 3 allowed automatic sampling of gases reducing the labor and error which otherwise would be performed manually. The Master Lab Robot had a 50 ul syringe in its arm and programmed in such a way to enable it to take a gas sample every 30 minutes and feed it to the Varian gas chromatograph (Model 3400) which analyze and separate the gases according to its retention time.

The Master Lab System comprises:

(1) Robot and Robot Drive Electronics: The robot is an articulated arm with removable and interchangeable grippers which can grasp objects of different shapes. It is fully programmable and the programs are portable from one Perkin-Elmer robot to another. The robot has an arm and a rotating base.

(2) System Controller: This is an IBM PC which can be equipped with up to ten RS232 communications ports for interfacing with the various modules of the master lab sytem.

(3) PERL (Perkin-Elmer Robot Language): A software language devised for use in the Master Lab automated sample system. It facilitates communication in a robotics system.

Chlorine Analysis :

In the electrolysis experiments of fecal wastes and urine, chlorine evolution was examined by collecting the off-gases in the water trap described above. Chlorine is easily dissolved in water and was transferred to the trace analysis unit at Texas A&M University and chlorine was analyzed by neutron activation analysis. However, some samples were analyzed by gas chromatographs also.

Neutron Activation Analysis :

Neutron activation analysis consists of three stages

(1) Irradiating a sample with neutrons to produce radionucleides.

(2) Determining the activities of radionucleide products.

(3) Relating the activities to the quantities of the elements originally present in the sample.

The radioactive nuclei decay at a rate -(-dN/dt) proportional to the number nuclei N where $t^{\frac{1}{2}}$ is the half-life of the nucleide. Radioactive

$$- \frac{dN}{dt} = \frac{0.693}{t^{1/2}} N$$

isotopes are produced artificially by exposing nuclei to neutrons from a neutron source, usually a nuclear reactor.

Cl which occurs naturally as the Cl ^{37} is converted by irradiation to racioactive Cl^{38}

The $^{38}17Cl$ decays with a half life of ~ 30 min, and emits gamma rays with energies of 1642 M ev and 2167 ev.

Neutron activation analysis is a very sensitive technique. As little as $1x10^{-7}$ gm of an element can be analyzed readily by neutron activation. Factors that contribute to high sensitivity are high cross section and high isotopic abundance of the potent isotope; low atomic weight, high neutron flux and high detection efficiency. Cross section is the most important of these characteristics and varies by a factor of 10^6 for various isotopes.

The calculation of the quantity of an element in a sample from all the factors contributing to the measured radioactivity is feasible in principle, but very difficult in fact. Therefore, a standard consisting of a known quantity of the element being determined is almost always used in activation analysis.

Chlorine Analysis by Neutron Activation Analysis :

About 2 ml of water sample in which Cl_2 is collected is sealed into a 3.5 cc polyethylene vial. The standard solutions of known chlorine content are handled in the same ways.

Standard samples and quality controls are sequentially analyzed by irradiation in the Texas A&M University 1 MW TriGa research reactor at neutron flux of about 2×10^{13} neutrons cm^{-2} S^{-1} for ten minutes. Following irradiation, the material is drawn from the vial using a syringe and a portion ($\sim$ 1.0g) weighed into another polyethylene vial. After a delay of about five minutes, the sample is placed in a high resolution lithium germanium [Ge(Li)] gamma ray detector. Characteristic gamma from the reaction product 38 Cl of 1642 and 1267 kev are detected and used for quantification. Samples are compared to a standard material to compute chlorine content.

Total Organic Carbon :

Total organic carbon analysis of the electrolyte before and after the electrolysis experiments was determined by means of a model 700 TOC analyzer infrared instrument in conjunction with persulfate oxidation of CO_2 trapping technique (EPA Method 415). These measurements were made at Intermountain Laboratory, College Station, Texas.

The TOC is determined by the measurement of carbon dioxide released by chemical oxidation of the organic carbon in the sample. After the sample has been acidified and purged of TIC, potassium persulfate ($K_2S_2O_8$), a strong oxidizer, is added. This oxidant quickly reacts with organic carbon in the sample at 100°C to form carbon dioxide. When the oxidation reaction is complete, the carbon dioxide is purged from solution concentrated by trapping them desorbed and carried into a non-dispersive infrared analyzer (NDIR) which has been calibrated to directly display the mass of carbon dioxide detected.

The resulting carbon mass in the form of carbon dioxide is equivalent to the mass of organic carbon originally in the sample.

EXPERIMENTAL RESULTS

Electrochemical Reaction of Waste :

The electrochemical investigation of the general reactions of waste components was performed on a platinum anode using each of the main constituent materials present in the artificial waste mixture, i.e., oleic acid, cellulose and casein and microbial biomass consisting of Torpulina. These experiments, however, were carried out in sulfuric acid electrolyte.

(1) Oleic Acid:

The sweep voltammogram of oleic acid at three different temperatures is shown in Fig. 4. The curve shows the potential region in which oxidation of oleic acid occurs at reasonable rate. It is noteworthy that there are two limiting currents manifested on this curve which possibly is due to oleic acid oxidation and may be due to smaller fragments of oleic acid which formed due to dissolution in concentrated sulfuric acid. The curve indicates that complete oxidation of oleic acid could occur at potential of 1.4 V/NHE (1.2 V/SCE). The concentration of oleic acid in these experiments were 14 g/liter. The reaction for the complete oxidation of oleic acid is

$$C_{17} H_{38} COOH + 34H_2O \rightarrow 18\ CO_2 + 102H^+ + 102e^-$$
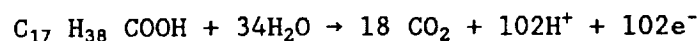
The oxidation of per molecule of oleic acid therefore produces 12 molecules of CO_2 and around 50 molecules of hydrogen.

(2) <u>Cellulose:</u>

The current potential curve of cellulose as a function of electrolyte temperature is shown in Fig. 5. The limiting current occurs in the vicinity of 1.4 volts/NHE.

The cellulose is normally hydrolyzed to glucose therefore electrochemical reaction of glucose in

$$C_6H_{12}O_6 + 6H_2O \rightarrow 6CO_2 + 24H+ + 24e^-$$
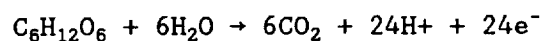
The result showed that for each CO_2 molecule, 2.8 electrons are required [2]. Thus, in addition to hydrolysis, some oxidation had occurred to remove carbon atoms from glucose [2]. Therefore

$$C_5\ H_8\ O_7 + 3H_2O \rightarrow 5CO_2 + 14H^+ + 14e^-$$
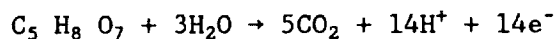
In this scheme, 2.8 electrons would be required for each CO_2 evolved which is consistent with the experimental results. The efficiency of 100% at 80°C is, however, exceeded at higher temperature. At higher temperatures the current efficiency of around 300% was obtained probably due to thermal degradation of cellulose to oxalic and because of acid hydrolysis which undergoes oxidation according to the following reaction:

$$H_2C_2O4 \rightarrow 2CO_2 + 2H^+ + 2e^-$$
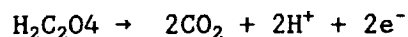
However, the potential of oxidation was 1.4V/NHE.

(3) <u>Torpulina</u>:

The current potential curve of torpulina at different temperatures is shown in Fig. 6. The heat of activation is 7 k cal per mole.

The oxidation potential for torpulina was around 1.4 V/NHE with current density of 6 mA/cm^2 at 150°C.

(4)   Casein:

The current potential curve for casein is shown in Fig. 7 which indicates the oxidation potential is around 1.1 V/NHE. However, the activation energy was 7 kcal/mole, the current density was around 1 mA/cm^2.

The studies on electrochemical reactions of individual component of fecal waste suggested that all components of the fecal waste has a potential window between 1.1 V to 1.4 V/NHE. Therefore, the combined electrolysis of all these components will enable us to electrolyze the fecal waste at around 1.4 V/NHE. It is noteworthy that these experiments were conducted on Pt electrode and in 12 M H$_2$SO$_4$.

The different electrode may have different oxidation potential (i.e different overpotential) of the mixture and this quantity also depends on the nature of electrolyte.

Therefore, the study was directed towards the determination of oxidation potential in a mixture of fecal waste with urine as electrolyte.

ELECTROCHEMICAL REACTIONS OF FECAL WASTE

I.   Gold Electrode :

Fig. 8 shows the current-voltage curve of artificial fecal waste in 5 M H$_2$SO$_4$. The concentration of waste was 4.68 gm/liter. The limiting current density increases with increasing the temperature and is 1.65 mA/cm^2 at 90°C.

The temperature variation of the limiting current in sulfuric acid is seen in the log scale in Fig. 9. The heat of activation is c. 6 kcal/mole.

Fig. 10 shows limiting current densities as a function of potential at different waste concentrations. The limiting current densities are in the range of 4 to 5.8 mA/cm^2.

Fig. 11 shows the limiting current densities as a function of waste concentration. The maximum solubility appears to be in the region of 14.04 gm/liter in urine at 90°C.

The current voltage curve of artificial fecal waste at 25, 60, 75 and 80°C is shown in Fig. 12. Instead of a plateau in the case of H$_2$SO$_4$, the curve gives a peak at about 1.3 V/NHE. It appears that the peak is obtained only when urine is taken as electrolyte. The appearance of this peak may be due to the oxidation of urea or uric acid along with the fecal waste. The current density at maximum peak potential is 4.2 mA/cm^2. Note that limiting current density was much less in H$_2$SO$_4$. The presence of urea in urine possibly increases the current density due to its easy oxidation.

The temperature variation of the limiting current, in urine as electrolyte is seen in log scale in Fig. 13. The activation energy is 7.0 kcal/mole.

Fig. 14 shows the current-voltage curve of real feces in urine as electrolyte. The increase in temperature increased the current density. The oxidation peak is at 1.4 V/NHE and the current density is around 2.75 mA/cm^2. The comparison of artificial fecal waste with real feces indicates that the oxidation potential differs only by 0.1 V/NHE which is not very high. The variation of limiting current with temperature for real feces in urine is shown in Fig. 15. The activation energy is around 6 kcal/mole.

Electrolysis on Gold :

The long term electrolysis of fecal waste in urine was conducted but failed because gold was dissolving in the electrolyte due to evolution of small amount of chlorine. The gold was forming aurous chloride which deteriorated the electrode.

The TOC samples were not analyzed for the long term electrolysis experiments, nor the CO_2 was determined.

II. Graphite Electrode:

Fig. 16 shows the current-voltage curve of artificial fecal waste in urine as an electrolyte at three different temperatures. The limiting current density plateau is between 1.1 V to 1.3 V/NHE and the current density shows increasing trend with increase in temperature. The highest current density at 90°C is around 2.0 mA/cm^2.

The temperature variation of the limiting current is seen on the log scale in Fig. 17.

Electrolysis on Graphite:

The long term electrolysis of artificial fecal waste and urine mixture was conducted using potentiostatic method. The potential of 1.35 V/NHE was applied between the graphite anode and reference electrode and current was monitored between working and counter electrode. The area of graphite electrode was 12 cm^2 while counter electrode was a platinum mess of 100 cm^2. The average current obtained during such electrolysis was 65 mA at 80°C. The gases analyzed with gas chromatography technique shows CO_2, H_2 and N_2. No oxygen was detected.

<u>Carbon Dioxide</u>:   The amount of CO_2 obtained is plotted vs. time of electrolysis and is shown in Fig. 18. The total CO2 in 24 hrs. was around 24×10^{-3} moles which is equivalent to 587 ml of CO_2.

<u>Hydrogen</u>:   The total amount of hydrogen in 24 hrs. of electrolysis was 38.5×10^{-3} moles which is equivalent to 851 ml of hydrogen. The plot of H_2 produced vs. time of electrolysis is shown in Fig. 19 a.

<u>Nitrogen</u>:   The total amount of N_2 produced for 24 hrs of electrolysis is 41×10^{-3} moles (896 ml). The plot of N_2 produced vs. time of electrolysis is also shown in Fig. 19 b.

Total Organic Carbon (on Graphite):

During the electrolysis, TOC in the electrolyte was reduced by 75% in 45 hrs. However, the TOC still could be decreased to 98% by increasing the time of electrolysis. Between the start and end of the electrolysis, considerable visible change in the nature of the waste solution occurred. The material started as a dark black solution where particulate material could easily be distinguished but as the electrolysis proceeded, the solution became transparent to light. The reduced TOC vs. time is shown in Fig. 20.

Calculation :

The calculations were made for the electrolysis at graphite electrode for the period of 24 hrs for material balance.

The total oxidation of fecal waste in 24 hrs was 2.2 gms/liter. There-fore the total amount of CO_2 should be 27.5×10^{-3} moles (616 ml). The total amount of CO_2 detected during electrolysis in 24 hrs, however was around 587 ml. The error of 5% is expected because of the fact that CO2 is collected using water displacement method and some of the CO_2 evolved is expected to dissolve in the water which it is displacing during collection.

The amount of hydrogen determined by gas chromatography is 38.5×10^{-3} moles (851 ml) and nitrogen is 41×10^{-3} mole (896 ml).

The total amount of gas collected during 24 hrs was 2200 ml which is 100 ml less than that observed by gas chromatography. The error in the amount of gases collected and that measured by gas chromatography was only 4.4%.

III. Tungsten Carbide Electrode:

Fig. 21 shows the current-potential curve of artificial fecal waste (4.68 gm) in urine as electrolyte. The limiting current density plateau is between 0.8 to 1.0 V/NHE and current density being 5.5 mA/cm^2 at 90°C.

The temperature variation of the limiting current is seen in log scale in Fig. 22. The activation energy is about 6.48 kcal/mole.

Electrolysis on WC :

The electrolysis was conducted on a 16 cm^2 electrode of WC at 80°C and at the potential of 1.0 V. The average current density obtained during electrolysis was 170 mA. The analyzed gases were CO_2, H_2 and N_2 without any oxygen.

Carbon Dioxide:

Fig. 26 shows the current-voltage curve of fecal waste in urine as electrolyte. It is noteworthy that the limiting current plateau was not observed in this case. However, the potential was shifted to lower side as temperature increased. It appears that the O_2 evolution and oxidation potential of fecal waste is not separated very well and it was difficult to know at what potential oxidation of fecal waste occurs without competing with O_2 evolution. Therefore a separate experiment of current-voltage curve of fecal waste in 5 M H_2SO_4 was conducted.

The current-voltage curve for oxidation of fecal waste in 5 M H_2SO_4 is shown in Fig. 27. The limiting current plateau was observed at about 1.0-1.2 V/NHE and current densities is in the rane of 1.7 mA/cm^2 to 3.8 mA/cm^2.

The log i vs. 1/T plot is shown in Fig. 28 which gave activation energy of 6.45 kcal/mole.

Electrolysis on Ti_4O_7/RuO_2:

The long term electrolysis experiment was conducted on a 12 cm^2 Ti_4O_7/RuO_2 electrode at potential of 1.2 V. The average current density obtained during electrolysis was 192 mA. The gas analysis showed CO_2, H_2 and N_2. The O_2, NO or NO_2 was not detected.

Carbon Dioxide :

Fig. 29 a shows the amount of CO_2 produced during electrolysis. The total amount of CO_2 produced in 24 hrs is 9.5x10-3 moles (312 ml).

Hydrogen :

The amount of hydrogen produced during electrolysis is also shown in Fig. 29 b. The total amount of H_2 is 12.2×10^{-3} moles in 24 hrs.

Nitrogen:

The amount of nitrogen produced on Ti_4O_7/RuO_2 electrode is 2×10^{-3} moles and the plot is shown in Fig. 29 c.

Total Organic Carbon (Ti_4O_7/RuO_2) :

The amount of TOC reduced during 24 hrs period was 3.1 gm. However, the TOC reduced to 4.2 gm in 40 hrs time. Fig. 30 shows the reduction of TOC with time. There 76.3% of TOC was reduced from the electrolyte in 40 hrs. The oxidation of fecal waste becomes slower when the concentration of waste drops down. However, the decreasing trend in TOC was observed with time.

V. Perovskite Electrode ($La_{0.79}Sr_{0.2}Mn,O_3$):

Fig. 31 shows the current-voltage curve of fecal waste in urine on perovskite electrode at three different temperatures. The limiting current plateau is between 1.1 to 1.3 V/NHE and highest current density of 6 mA/cm^2 was observed at 90°C. The temperature variation of the limiting current, in urine on $Ti4O_7/RuO_2$ electrode on log scale is shown in Fig. 32. The heat of activation is c. 8.10 kcal/mole in urine.

Electrolysis on Perovskite :

The electrolysis of fecal waste in urine is conducted on a 14 cm^2 round electrode. The applied potential is 1.44 V/NHE and average current density

during electrolysis is 65 mA. The evolved gases were CO_2, H_2 and N_2 and chlorine.

Carbon Dioxide:

Fig. 33 shows the amount of CO_2 evolved during electrolysis. The total amount of CO_2 in 24 hrs is 30×10^{-3} moles which is equivalent to 672 ml.

Hydrogen :

The amount of hydrogen produced using perovskite as anode is also shown in Fig. 34 a. The total amount of hydrogen produced in 24 hrs is 37.5×10^{-3} moles or 840 ml.

Nitrogen :

The plot of N_2 produced vs. time is shown in Fig. 34 b. The total N_2 produced in 24 hrs is 23×10^{-3} moles or 515 ml.

Chlorine :

Fig. 35 shows the plot of chlorine produced vs. time. The total amount of chlorine produced in 24 hrs was 0.45 ml which is equivalent to 2.0×10^{-5} mole. The amount of chlorine, however, is 0.02% of the total gases evolved during electrolysis.

TOTAL ORGANIC CARBON (Perovskite):

Fig. 36 shows the plot of reduced TOC vs. time of electrolysis. The reduced TOC in 24 hrs of perovskite-electrode is 3.2 gm/liter which is 65% of

initial TOC before electrolysis. The extrapolation to 40 hrs results in 81% of TOC reduced. Between the start and end of the electrolysis, considerable visible changes in the nature of the waste solution occurred. The material started as dark black solution become decolorized in 5-6 hours and becomes transparent in about 20 hrs. However, some particle still remains which appears to be cellulose.

Redox Couple Studies:

In the experiments on the electrolysis of dissolved products from coal, it was found by Murphy and Bockris [13] that addition of cerric compound was effective in increasing the current density. Similar work has been performed by Su Moon Peak and colleagues [32].

In our earlier work on addition of cerium [29] in the electrolyte we observed a five times increase in the current, however, long term electrolysis experiment indicated that the CO_2 produced increased by only 1.4 fold in presence of cerium ion. Thus, the apparently excellent increase in current is due largely to oxidation of the cerous ion and the concomitant take up of the oxidation of the fecal waste in the solution by the cerric is less than the increase in limiting current. The experiment conducted with cerium ion was done in the mixture of fecal waste and 12 M H_2SO_4. Therefore, this study was extended to the urine as electrolyte. These experiments were conducted on platinum electrode.

Problems of Using Redox Couple:

There are problems of using redox couple when urine is taken as electrolyte. The redox couples Ce^{4+}/Ce^{3+}, Fe^{3+}/Fe^{2+} and Mn/Mn were studied and it was found that all the metal ions makes metal-complex with urea and precipitates resulting in the absence of any free metal ions in solution. The catalytic activity of redox couple is efficient only if redox couples remain in ionic form in the solution to be studied. This seems to be a pH effect.

EFFECT OF REDOX COUPLE:

Platinum Electrode:

The current voltage curve of fecal waste in mixture of urine and 2.5 m sulfuric acid is shown in Fig. 37. The curve A in Fig. 37 is taken only in mixture of urine and 2.5 m H_2SO_4. The peak at potential of 1.3 V/NHE is due to the oxidation of urea present in urine. The curve B represents the oxidation of urea along with oxidation of fecal waste. The effect of addition of Cl^{4+} in concentration of 1×10^{-2} M is seen in Curve C. The increase in concentration of Ce^{4+} to 2×10^{-2} M and 5×10^{-2} M is shown in Figs. D and E.

It is apparent that four fold increase in the current density was observed by addition of Ce^{4+} ions.

The current-voltage curve of fecal waste on platinum electrode in mixture of urine and 5 M sulfuric acid is seen in Fig. 38.

The increase in current-density in 5 M sulfuric acid is 5 fold. The current density reached to 10 mA/cm^2 compared to 2 mA/cm^2 in the presence of Ce^{4+} ions.

Electrolysis on Pt:

The electrolysis of fecal waste in a mixture of urine and 2.5 M sulfuric acid was conducted at potential of 1.4 V/NHE. The average current density in absence of cerium ion was 40 mA. However, the average current density was increased to 60 mA in the presence of 2×10^{-2} M Ce^{4+} ion in the form of Ce $(SO_4)_4$

Carbon Dioxide (Pt):

Fig. 39 shows the effect of cerium ion on evolution of CO_2 in presence and absence of Ce^{4+} ion. The total amount of CO_2 evolved in 24 hrs time is 17.5×10^{-3} moles in absence of Ce^{4+}, however, the amount of CO_2 is presence of 2×10^{-2} M of Ce^{4+} is 40×10^{-2} M which is twice the volume observed without Ce^{4+} ion.

Comparing the apparent increase in limiting current (Fig. 37) with the increase in CO_2 (Fig. 39), the 4 fold increase in current does not give an equivalent increase in CO_2: the CO_2 produced increased by only 2 fold in the presence of cerium.

Nitrogen :

Fig. 40 shows the amount of nitrogen produced in presence and absence of cerium ion. The increase is again two fold. The amount of N_2 in 24 hrs is 16×10^{-3} moles or 358.4 ml in absence of Ce^{4+} while the amount was increased to 680 ml in presence of 2×10^{-2} M $Ce4+$ ion.

Hydrogen:

The hydrogen produced during electrolysis in presence and absence of Ce^{4+} is shown in Fig. 41.

Total Organic Carbon:

The amount of TOC reduced without addition of Ce^{4+} ion is shown in Fig. 42 curve a. The TOC in 24 hrs was reduced only by 1 gm/liter. However, the addition of $2x10^{-2}$ M of Ce^{4+} ion increased the reduced TOC to 2 gms/liter.

<div align="center">PHENOMENOLOGICAL GENERALIZATION</div>

1. The five new electrode materials were studied for their properties to electrolyze the mixture of fecal waste and urine, c. gold, graphite, WC, Ti_4O_7/RuO_2 and perovskite.

2. The most efficient anode material is ebonex coated with RuO_2. However, the perovskite is comparable to Ti_4O_7/RuO_2 electrode in terms of total TOC reduction.

3. The CO_2, H_2, N_2 and chlorine was produced on all electrodes. The NO, NO_2, CO and CH_4 was not detected.

4. The chlorine evolution was less than 0.1% of the total gas evolved.

5. The potentiostatic method for electrolysis has an advantage over galvanostatic method due to less evolution of chlorine and better control of potential current.

6. The 60-80% of TOC can be reduced during 24 hrs of electrolysis. However, the TOC could be reduced by 98% in 100 hrs. It is to be noted that surface area of electrode is between 12-16 cm^2.

7. The addition of redox ion during electrolysis increases the CO_2 evolution twice compared to that of without Ce^{4+} ion.

DISCUSSION

The potential at which limiting current was obtained is different for oxidation of fecal waste in urine for each electrode studied. In the case of Ti_4O_7/RuO_2 and perovskite electrodes the potentials were 1.24 V/NHE and 1.42 V , respectively. However, on the WC, graphite and gold,the potential were 0.85 V , 1.44 V and 1.60 V,respectively. The heat of activation for these reactions were 6-7 kcal/mol which is characteristic for a diffusion controlled reaction. The Tafel lines are not well developed which is not exceptional for complex systems in the presence of a large amount of impurities.

The approximate estimation of exchange current density can be made by assuming that the reversible potential is in the region of 0.8 V.

$$\eta = 0.25 \log i/i_o.$$

where η is the overpotential, i is the average current in the limiting region is 5×10^{-3} A cm^2, cm i_o of $3x10-3$ A cm-2 was calculated at 90°C.

The porous electrode or flow through electrode in which the dissolved waste compounds have to be recirculated over a large electrode area, has several advantages over stationary electrodes. The advantage is primarily connected with substantial or total decrease of mass transport limitation. One consequence of using such electrodes is that interior mass transfer and ohmic resistance effect may lead to a non-uniform potential distribution, thereby affecting the selectivity which might otherwise be achieved. The porous or flow through electrode increase the time of contact and area for the

solution. The limiting current obtained on a porous electrode is expressed by following the following equation [33]:

$$I = nFC_oVR$$

n is the number of electrons transferred per molecule of the electroactive species, F is the Faraday constant, C_o is the initial concentration, V is the flow rate and R is limiting degree of conversion of the electroactive species.

$$R = 1 - exp\ (-jSa^{1-\alpha}V^{\alpha-IL})$$

where S is the specific internal surface, a is cross section area, L is the length of porous electrode and j and α are constants, α being a fraction of 1.

The enhanced current density in presence of Ce^{4+}/Ce^{3+} redox couple is due to the breakdown of a bigger organic molecule to a smaller one according to the following reaction

$$Ce^{4+} + ORGANIC \xrightarrow{\hspace{1.5cm}} Ce^{3+} + CO_2$$

$$Ce^{3+} + e \xrightarrow{\hspace{1.5cm}} Ce^{4+}$$
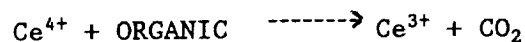
The role of mediator therefore basically is a chemical reaction between Ce^{4+} and organic. The Ce^{3+} generated due to chemical reaction get oxidized back to Ce^{4+} ion on the electrode. The redox mediators were used on the notion that they would have higher i_o than that of the organic materials and carry out homogeneous oxidation of the materials in solution. However, the increase in current density of only twice was rather disappointing.

The oxide electrodes such as $La_{0.79}Sr_{0.29}Mn,O_3$ (perovskite) and Ti_4O_7/RuO_2 electrode were more effective at waste oxidation than platinum, gold, WC and graphite presumably due to reduced competition from oxygen. The high porosity of these electrodes and overpotential for O_2 evolution of 1.7 V, made these electrodes work more efficiently compared to others.

The other advantages of these electrodes are high chemical stability in both acid and alkaline environments and can function alternately as an anode and cathode without degradation. The principle use for these materials is the formation of OCl- from Cl^- without formation of deposits and electrode poisoning effects. The evolution of Cl_2 gets reduced due to formation of OCl^- which is also helping to remove the odor and coloration of fecal waste.

FUTURE WORK

The ideal system for oxidation of fecal waste for commercial or space use should have limiting current density of 50 mA/cm^2. There are many ways of increasing the limiting current density.

It would be advantageous to use redox couples with redox potentials lower than that of Ce^{3+}/Ce^{4+}. Such Br_2/Br^- (1.08 V) or $Fe2+/Fe^{3+}$ (0.69 V). The combination of catalysts such as V^{5+} with Fe^{2+}/Fe^{3+} has been tried for long term electrolysis and results of TOC are awaited. Dhooge [7] has used CO_2 with Fe^{2+}/Fe^{3+} for oxidation of cattle waste and sewage sludge and shown improved performance in current density.

The use of porous electrodes or flow-through electrodes is an another area of increasing current density for waste oxidation as discussed earlier.

Bockris and coworkers [39] have shown that use of ultrasonic for purpose of increasing current density is an alternative. The action of ultrasound, up to 7 W cm^{-2} increased the current density of waste oxidation by 2.5 times. The increase in current density was linear with power output and hence, it is reasonable to expect a greater increase in current density at greater ultrasound intensities. Huck et al. [39] showed that at ultrasound at 2 W cm^{-2} increased the limiting current by one order of magnitude for electrochemical reactions of Fe^{2+}/Fe^{3+} and $[Fe(CN)_6]/[Fe(CN)_6]4^-$.

The further investigation is therefore required and will be pursued to determine if increased power output of ultrasound can substantially increase the current density for waste oxidation. The study will be restricted only on two electrodes studied so far viz. $La_{0.79}Sr_{0.29}Mn,O_3$ (perovskite) and Ti_4O_7/RuO_2. The high intensity ultrasonic processor has been purchased for this work.

CALCULATION AND ECONOMICS

The seven electrocatalysts so far studied have been compared for their efficiency for oxidation of fecal waste in urine as electrolyte. Table 3 gives the amount of area of anode electrode, TOC reduced, CO_2, N_2, H_2 and Cl_2 evolved during 24 hrs of electrolysis at 80°C.

The most efficient electrode in terms of reduced TOC is perovskite and RuO_2. An assessment of operational parameters of a waste electrolysis subsystems can be made based on the experiments described above and from information on solid waste production in closed life support system. The solid waste production including urine solids is 128 g dry weight man day^{-1} as

estimated by Wyderen [34]. Therefore, these values have been used for calculation of the operational parameters of a waste electrolysis subsystem.

In the experiments described above (Table 3) electrolysis using an electrode of Ti_4O_7/RuO_2 with a geometric area of 12 cm^2 resulted in a decrease in TOC of 3.1 gm over a period of 24 hrs. Calculations show that to oxidize 128 gm TOC over a 24 hour cycle an electrode of 0.049 m^2 is required assuming that current will increase proportional to the area.

Power requirements for an electrolysis subsystem operating on a 24 hour cycle are calculated below using the cell voltage of 1.4 V and assuming that current density at operating conditions is 4 mA/cm^2.

Total current = 0.004 x 495

= 1.98 A

Power = current x voltage

= 1.98 x 1.4

= 2.772 W

Note that in our earlier experiments for oxidation of fecal waste in 12.0 H_2SO_4 on platimum electrode, the calculation showed that 0.5 m^2 electrode is capable of oxidizing 128 gm TOC over a 24 hour cycle and the power required for such a system is 40.0 W.

Therefore the present study on electrocatalyst search has proven very useful and two best electrodes for electrolysis of fecal waste into CO_2, H_2 and N_2 has been found.

Under the conditions used in these calculations, approximately 14.2 liters of CO_2 will evolve from the anode in 24 hours provided there is no competition from oxygen evolution. The carbon dioxide can be utilized for the

regeneration of oxygen in closed life support system using Sabatier [35],
Bosch method or CO_2 reduction on solid oxide electrolyte cells [36]. The CO_2
is a valuable resource for food generation using plants or for cell protein on
long duration space missions [37, 38].

The amount of hydrogen to be produced at cathode according to above
calculation will be 20 liters. If the evolved hydrogen is recycled in a fuel
cell operating at 70% efficiency. Approximately 30% of the electrical energy
utilized in the electrolysis can be regenerated. However, the electrical
energy of 2.77 W could easily be obtained from photovoltaic solar cells kept
on panels of space craft. The evolution of N_2 could be used for growing
plants for long term missions.

OVERALL ACHIEVEMENT

1.   The seven electrocatalysts were studied so far and two best anode
     materials. Ti_4O_7 coated RuO_2 and perovskite has been identified for the
     future work on electrochemical incineration of waste.

2.   It has been proved that redox couples increases the rate of oxidation by
     1.4 times.

3.   Different intensities of ultrasound is capable of increasing the current
     density.

4.   The 128 gm of human waste can be oxidized to CO_2 in a 24 hour cycle time
     on Ti_4O_7/RuO_2 electrode of area 0.0495 m^2.

WORK DURING COMING YEAR

1. Effect of ultrasound intensity and increased power output on current density for oxidation of waste.The use of microwave will be an another approach.

2. Effect of adding cocatalyst or combination catalyst such as V^{5+} with Fe^{2+}/Fe^{3+}, CO^{2+} with Br_2/Br^-, Ru^{3+} with Br_2/Br^-, Rh^{3+} with Fe^{2+}/Fe^{3+}.

3. Use of porous or flow through electrode for oxidation of fecal waste.

4. The jet approach which derives from the concept of jet etching when jet of electrolyte are thrown at great velocity against the surface of an electrode. The investigation of theoritical and then practical approch.

5. Recycling of evolved hydrogen to fuel cell for generation of electrical energy to be utilized in the electrolysis process.

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	E_o	$E_{p}/2$	Ref
Urea	$-0.738_{(a)}$		
Glucose	-0.36		
Formate		-0.432	[38]
Mannitol	$+0.02_{(a)}$		
Succinate	$+0.11_{(a)}$		
Glutamine	$+0.11_{(a)}$		
Butaraldehyde	$+0.11_{(a)}$		
Casein		$(E_p)\ +1.0_{(b)}$	[22]
Adenine		$+1.25_{(c)}$	[38]
Uric Acid		$+0.86_{(d)}$	[38]
Saccharomyces cerevisae		$(E_p)\ +0.98_{(e)}$	[39]

Peak or half wave potentials are signified by E_p or $E_p/2$ repectively.

(a) Calculated from $\Delta G_o f$ values given in Ref 40.

(b) 0.1M NaOH on Platinum.

(c) Aqueous buffer (pH 5.7) on platinum.

(d) 2M H_2SO_4 on graphite.

(e) 0.1M phosphate buffer (pH 7.0) on graphite.

Table 2   **Contents of Artificial Fecal Waste**

Waste Component	Weight (kg)	% Of Total Dry Weight
Cellulose	0.60	33%
Torpulina	0.43	25%
E.coli	0.12	7%
Casein	0.17	10%
Oleic acid	0.37	20%
KCl	0.04	2%
NaCl	0.04	2%
CaCl$_2$	0.03	1%
Water	2.8	-

TABLE 3

Electrode	Area cm^2	Pot/ NHE	Average Current	Ingred- ient	Temp °C	Time (hour)	TOC Re- duced gms	CO2 mMol	Cl_2 ml
Gold	12.5								
Tungsten carbide	32cm²	0.85	170 mA	Urine & Waste	80	24	3.0	13 mMol	0.15
Graphite	20	1.44	50	Urine & Waste	80	24	2.2	25 mMol	0.18
Perovskite	12	1.44	65	Urine & Waste	80	24	3.2	32 mMol	0.45
Ti_4O_7/RuO_2	20	1.24	190	Urine & Waste	80	24	3.1	30 mMol	0.07
Pt	220	1.56	30	2.5 H_2SO_4 in urine & waste	80	24	1.0	1.5 mMol	
Pt/Ce^{4+}	220	1.56	40	2.5 M H_2SO_4	80	24	2.2		

A	Purge Gas Inlet
B	Purge Gas Inlet
	and Thermometer
F	Glass Frit
G	Sample Gas Outlet
CW	Cold Water Inlet
W	Water Outlet
RE	Saturated Calomel
	Reference Electrode
WE	Working Electrode
CE	Counter Electrode
M	Magnetic Stirring Bar
T	Solution Exit Trap

GC
GCMS
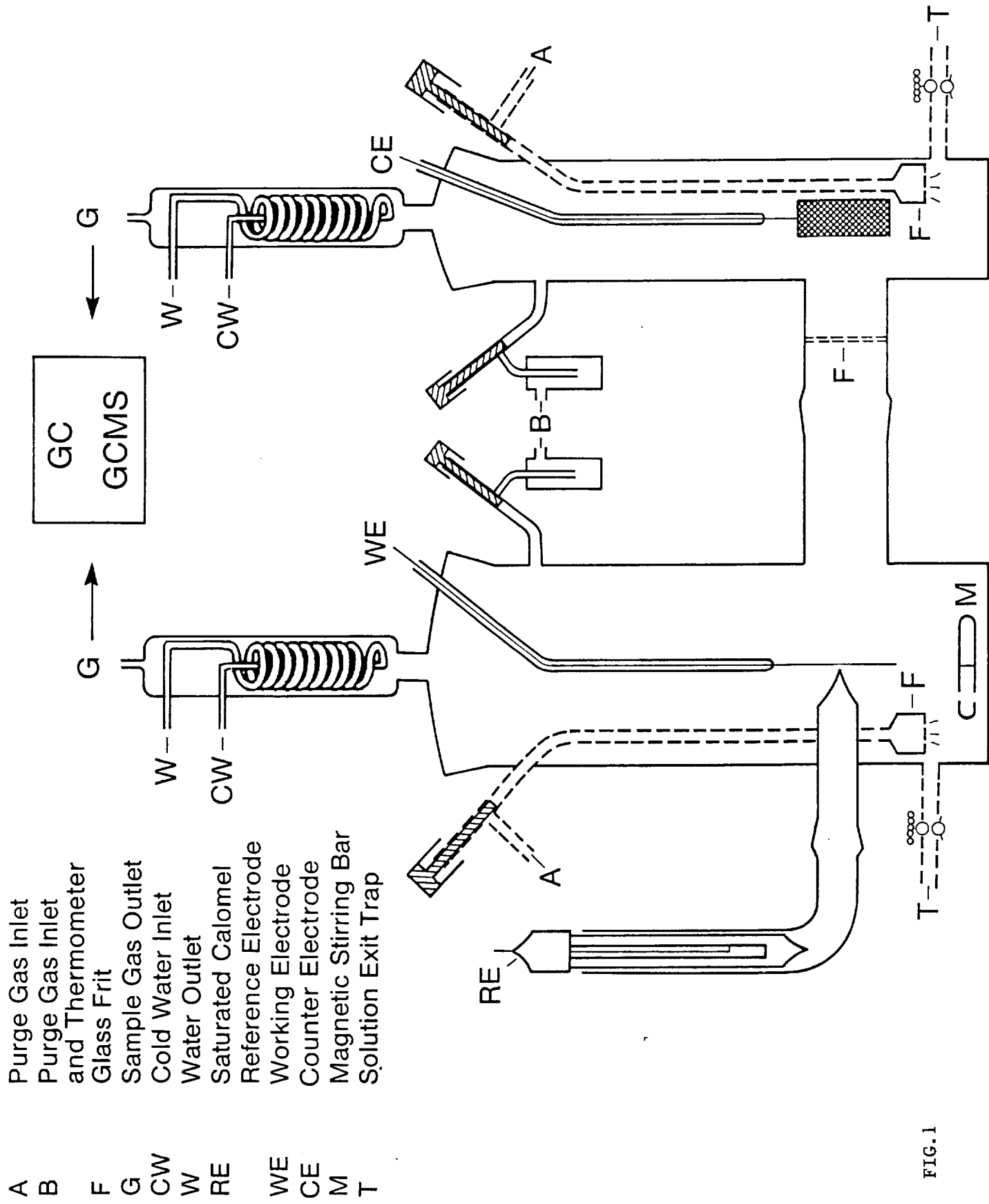
Schematic Diagram of Electrolysis 'H' Cell

FIG.1

WE   CE

A —   — G A —   — G
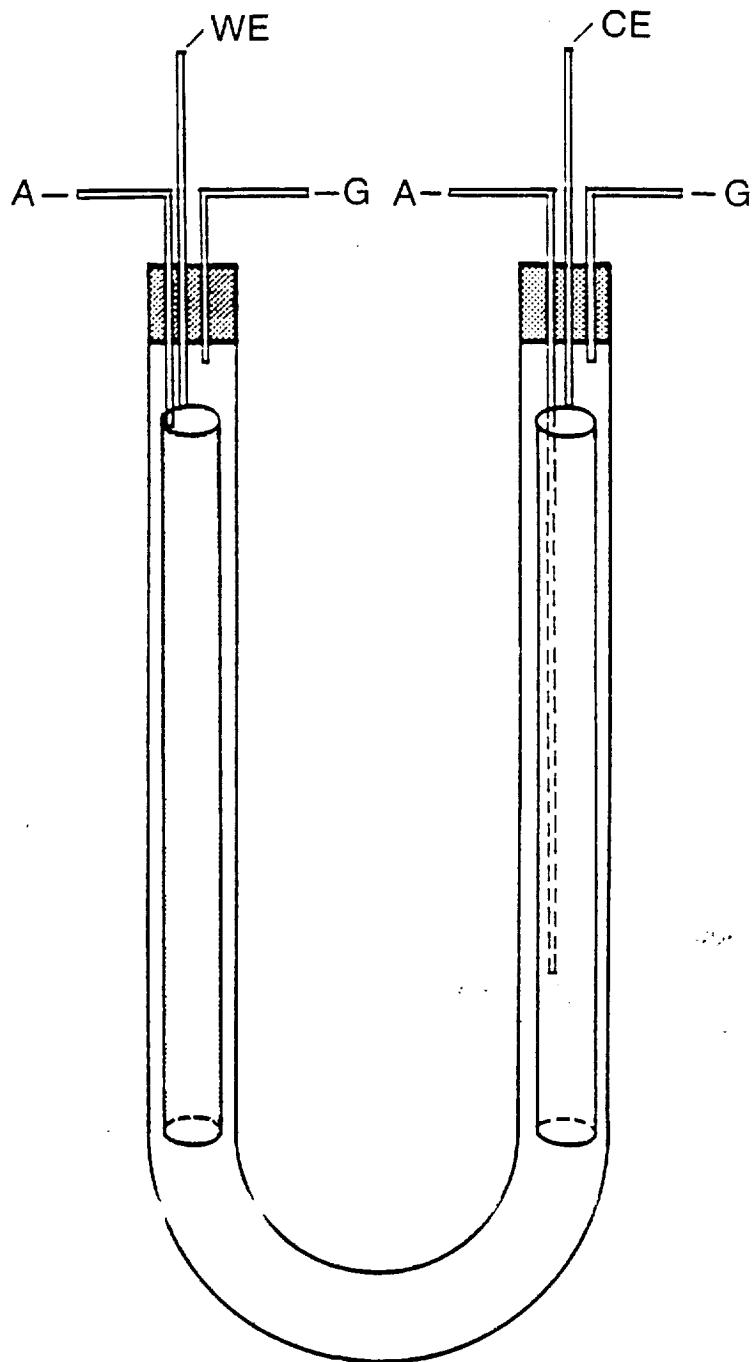
FIG.2   Schematic Diagram of Electrolysis 'U' Cell
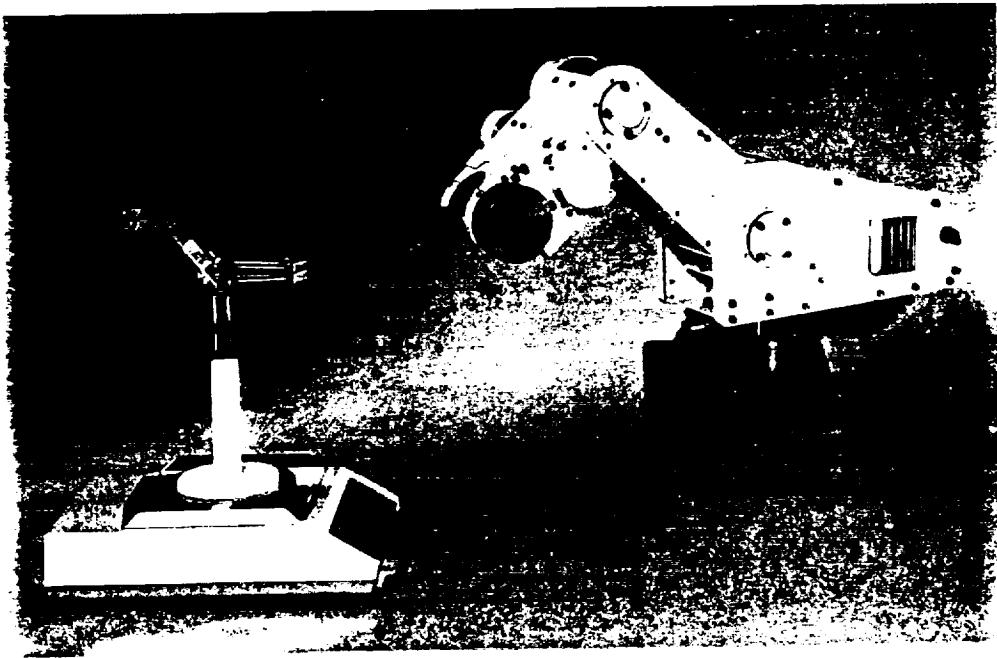
FIG.3 ROBOTIC SAMPLING
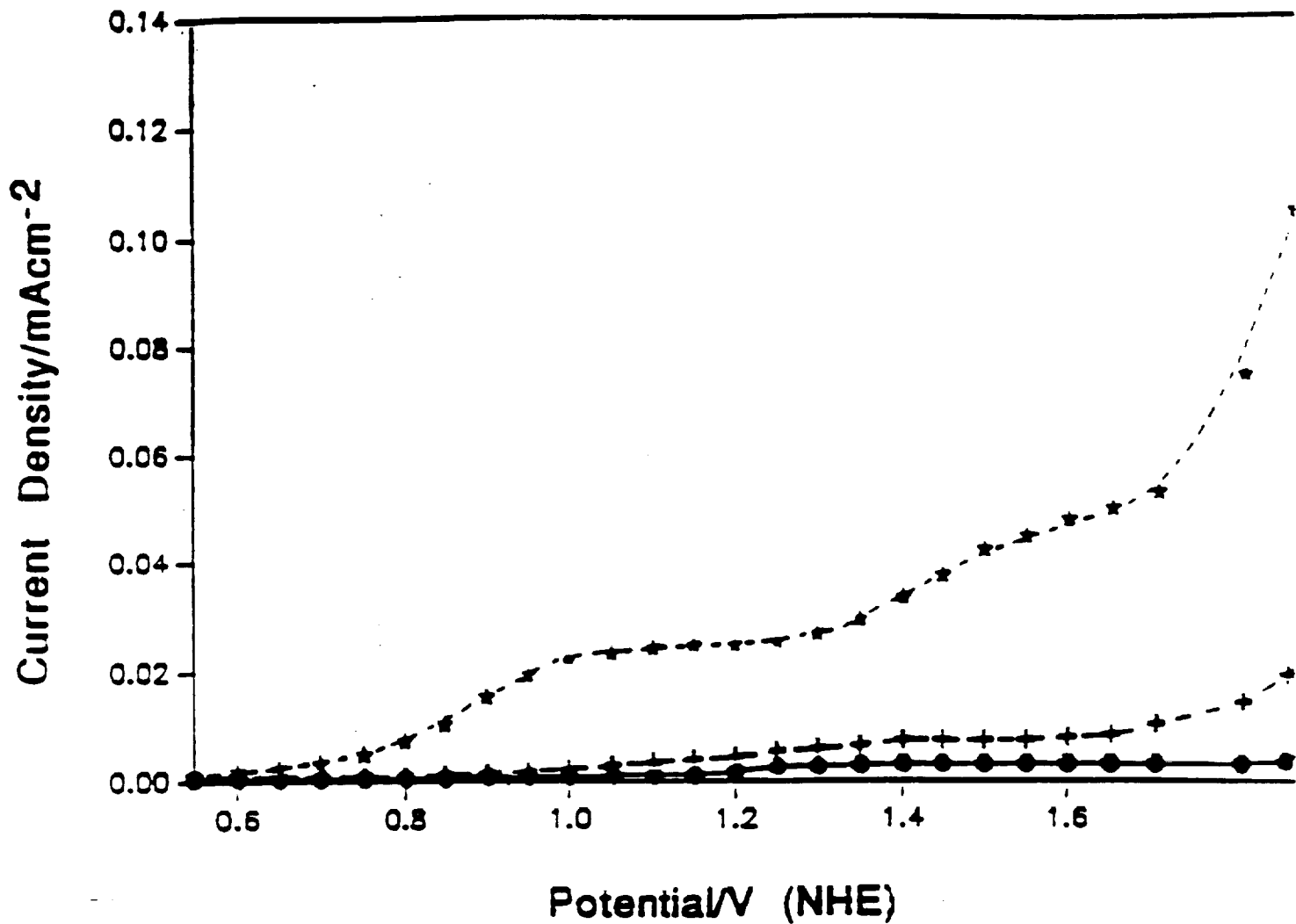
Figure 4: Current potential curves for oxidation of oleic acid in 12M H_2SO_4 at different temperatures. (○ 25°C, + 80°C, ♦ 120°C). Potential limits 0.4 - 2.0 v (NHE). Scan rate 1 mv/s. T - 150°C. Oleic acid concentration 14 g/liter.
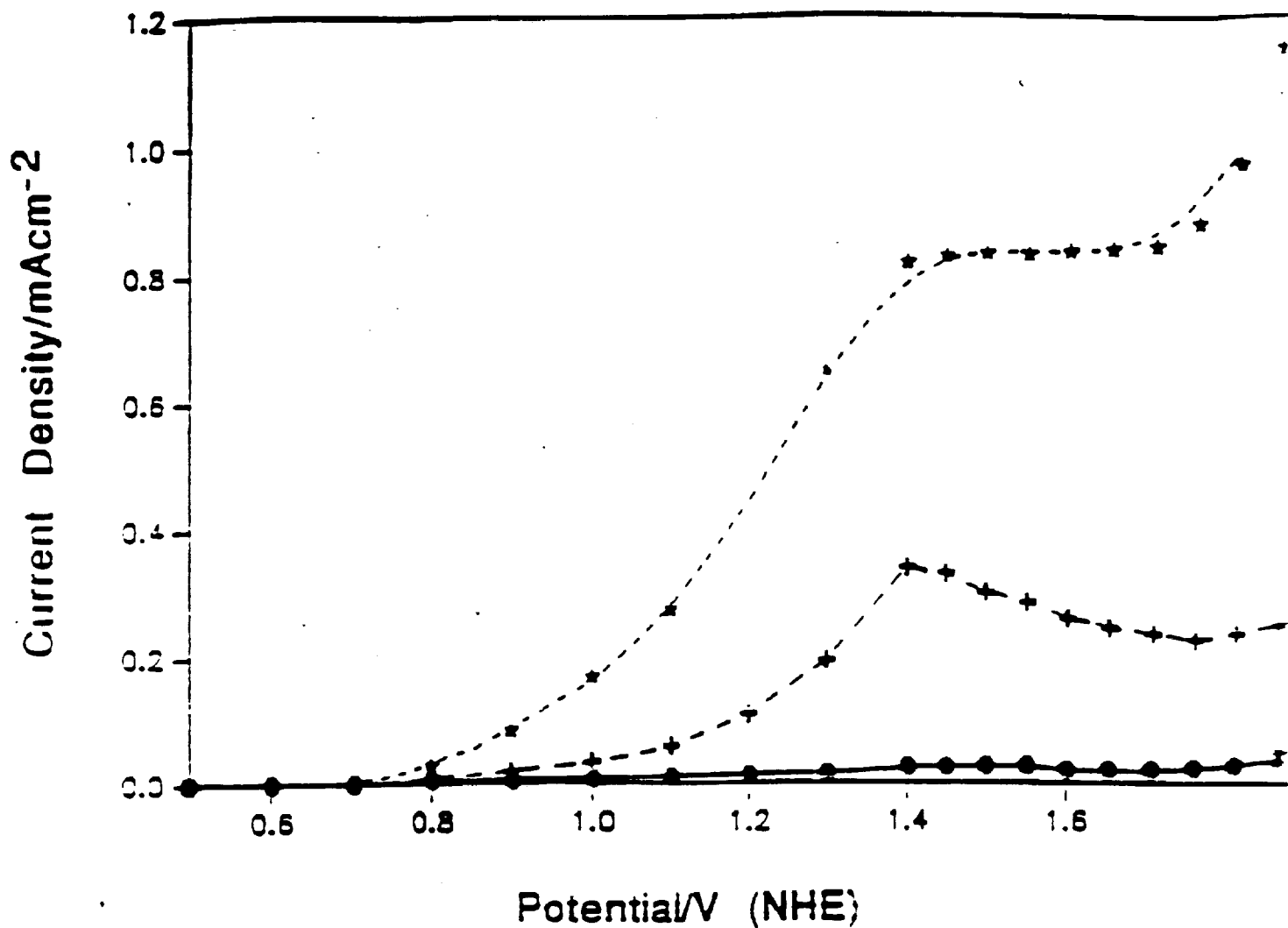
Figure 5 : Current potential curves for oxidation of cellulose in 12 M H_2SO_4 at different temperatures (● 25°C, ✚ 80°C, ★ 150°C). Potential limits 0.5 - 2.0 v (NHE). Scan rate 1 mv/s. T - 150°C. Cellulose concentration 14 g/liter.
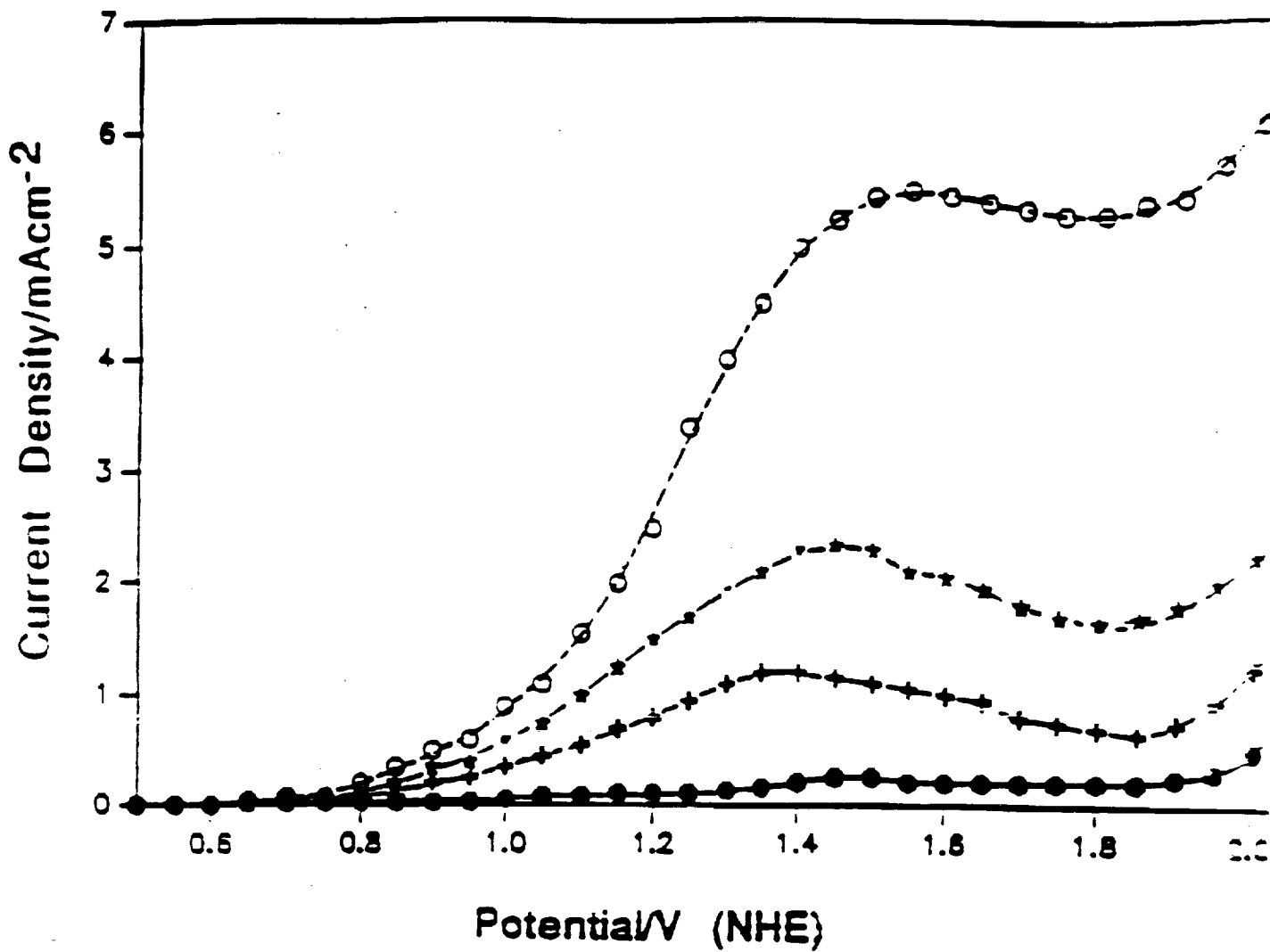
Figure 6 : Current-Potential curves for oxidation of yeast in 12 M H_2SO_4 at different temperatures. Potential limits 0.5 - 2.0 v (NHE). Yeast concentration 14 g/liter. (● 25°C; + 80°C; ★ 120°C; ○ 150°C).
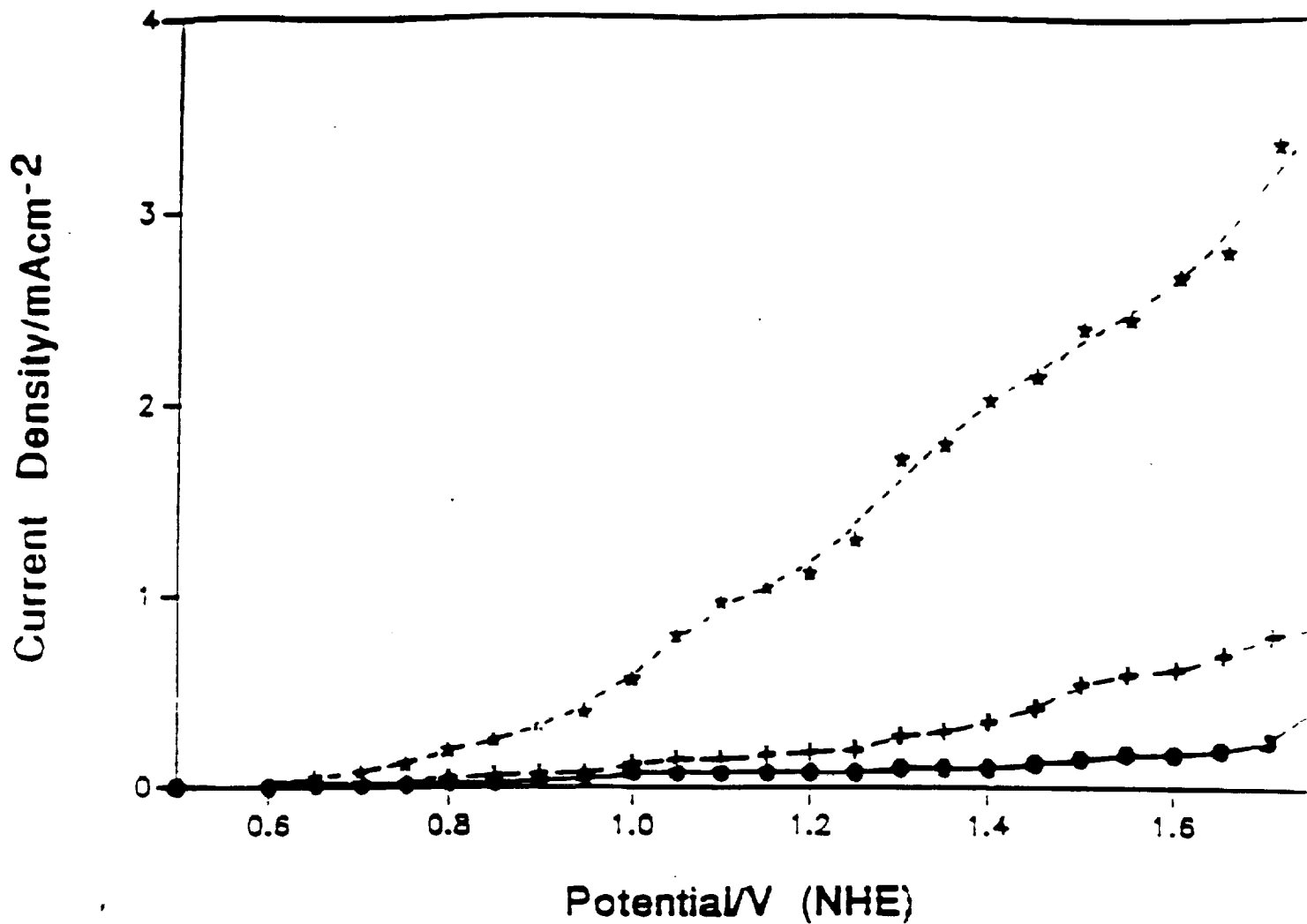
Figure 7 Current-potential curves for oxidation of casein in 12 M H₂SO₄ at different temperatures. (● 25°C; + 80°C; ★ 150°C). Potential limits 0.5 - 2 v (NHE). Scan rate 1 mv/s. Casein concentration 14 g/liter.
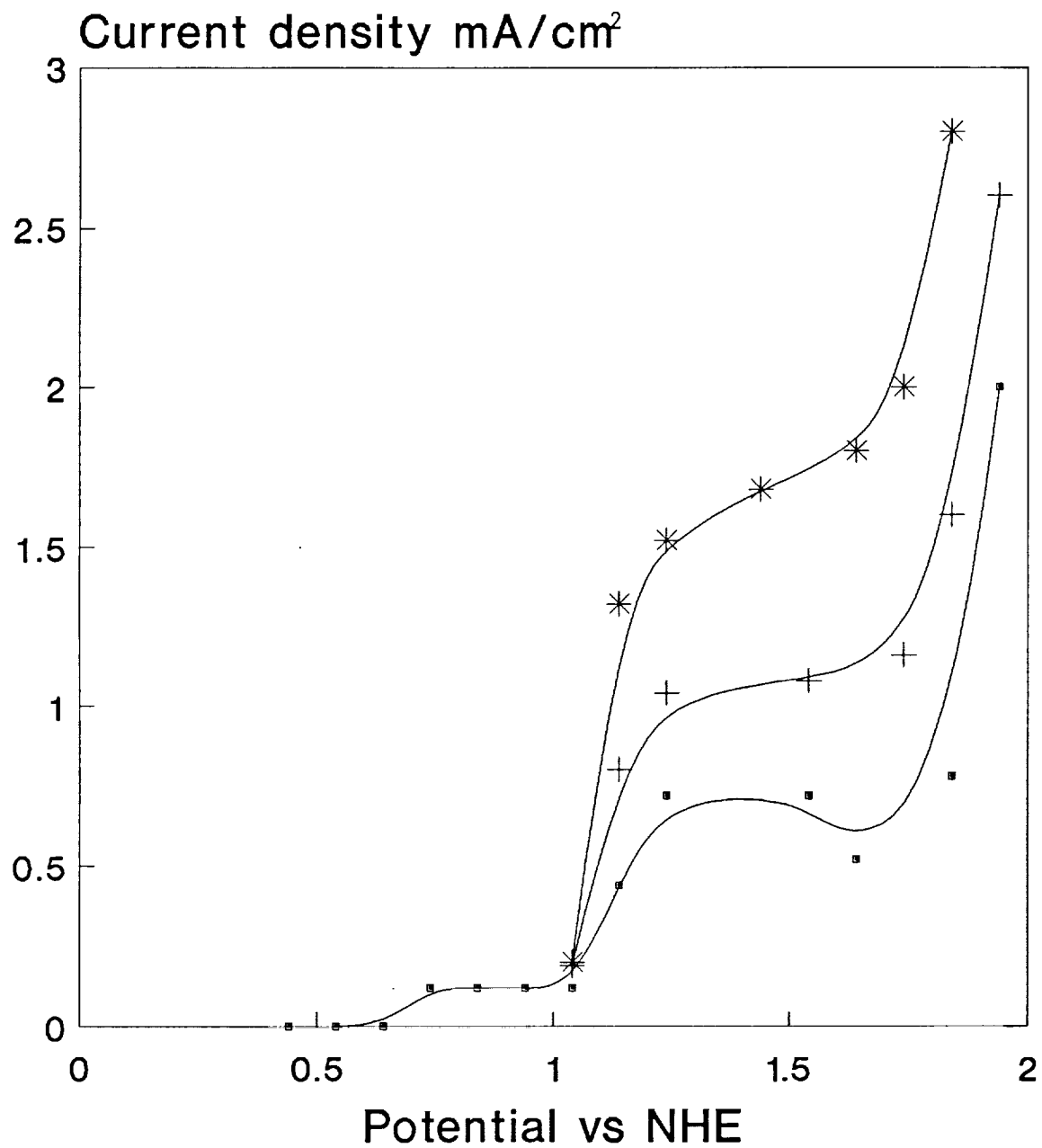
FIG.8 Current Voltage Curves for Oxidation of Fecal waste in 5M
       H_2SO_4 on Gold electrode.

       (■ 60°C), (+ 80°C) and (✷ 100°C)

Waste Conc. 4.68 gms/litre

Current density mA/cm²
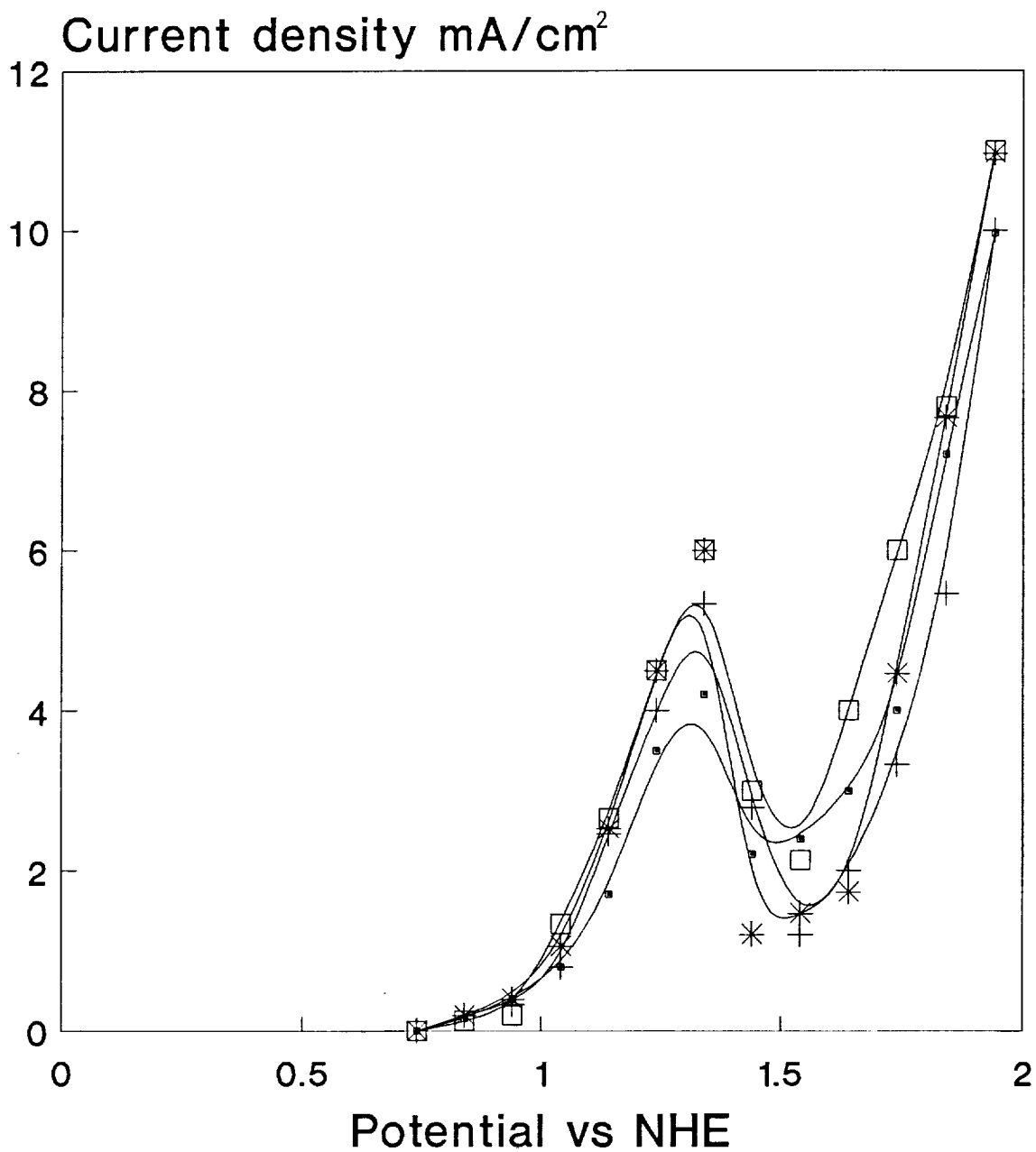
FIG.10 Current Voltage Curves for Oxidation of Fecal waste in Urine at 90°C. Gold electrode.

Waste Conc. (■ 4.68 g/litre; + 9.36 g/litre; ✕ 14.04 g/litre and □ 18.72 g/litre)

At different waste conc.

Figure 9
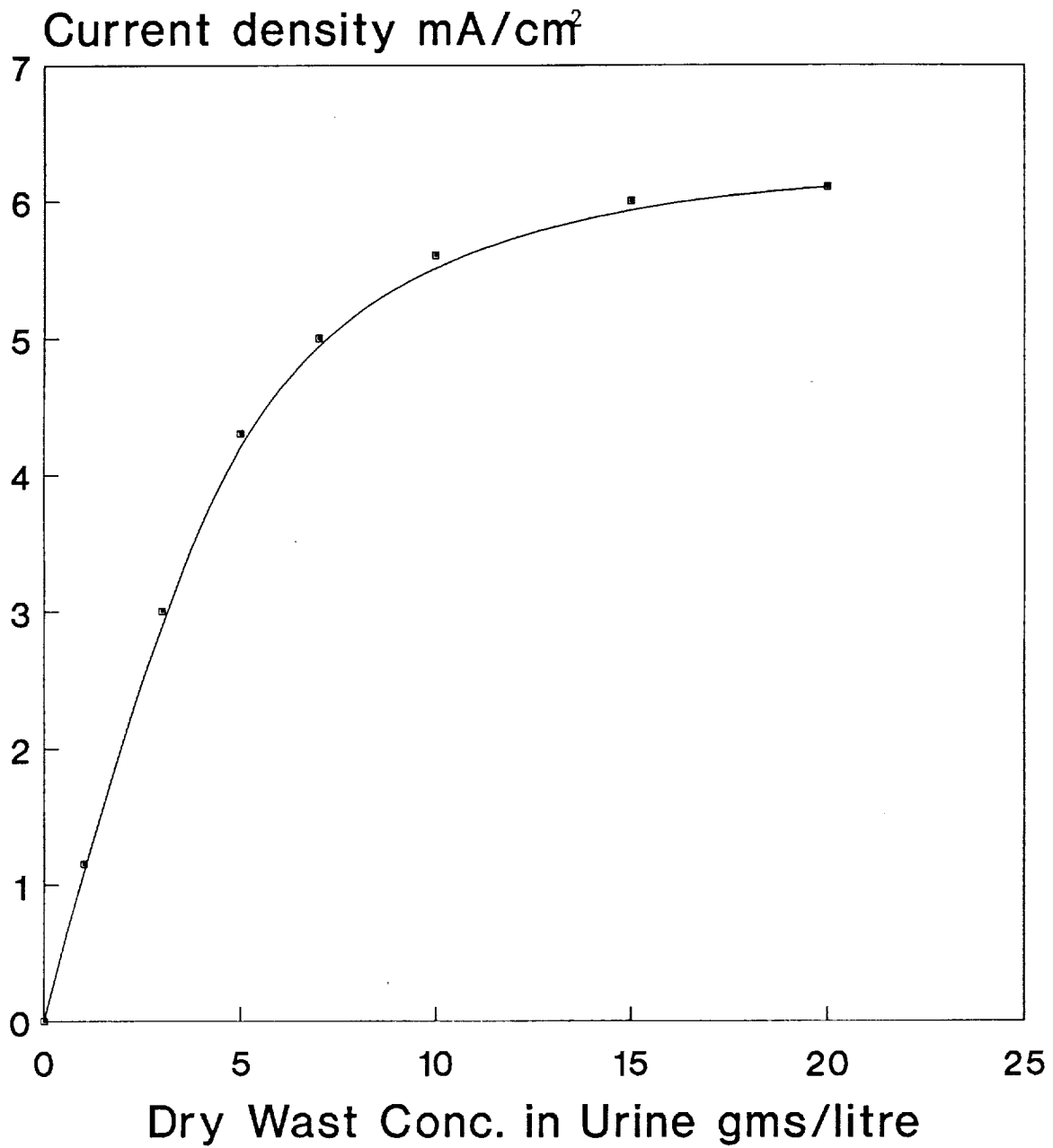
FIG.11   Effect of Fecal waste concentration on the limiting current
         density at 90°C in Urine at Gold electrode

Current density mA/cm^2

Potential vs NHE
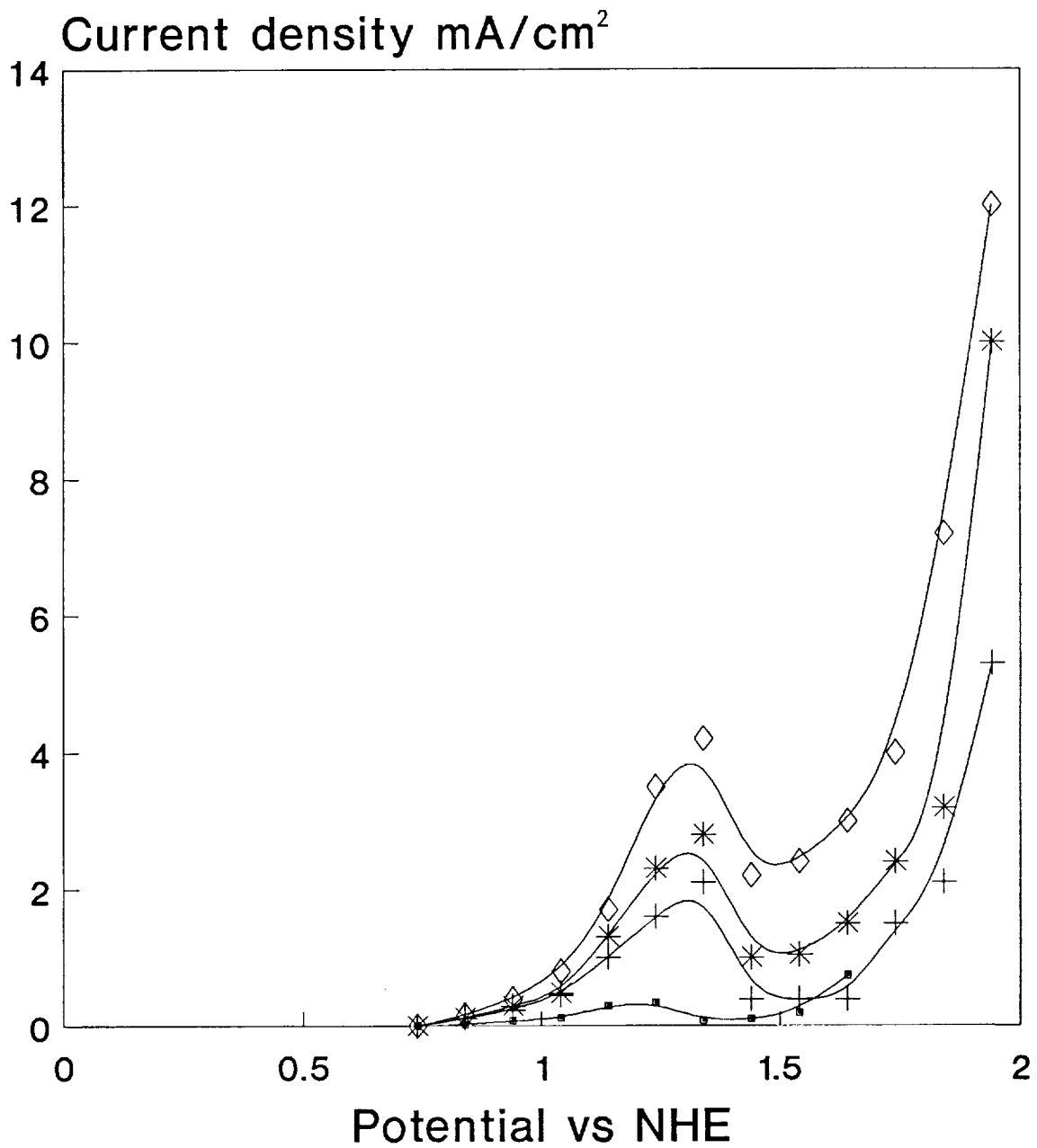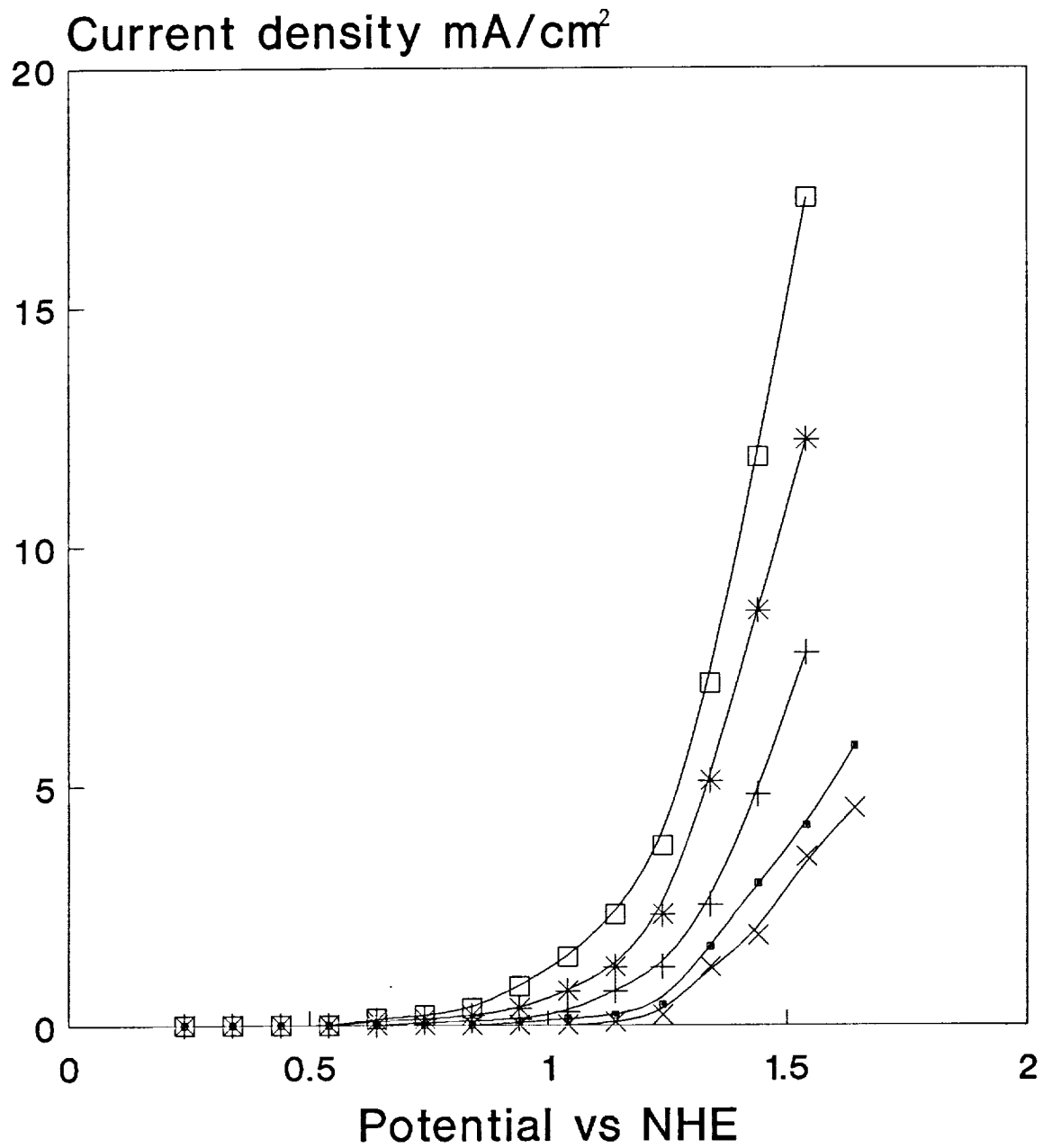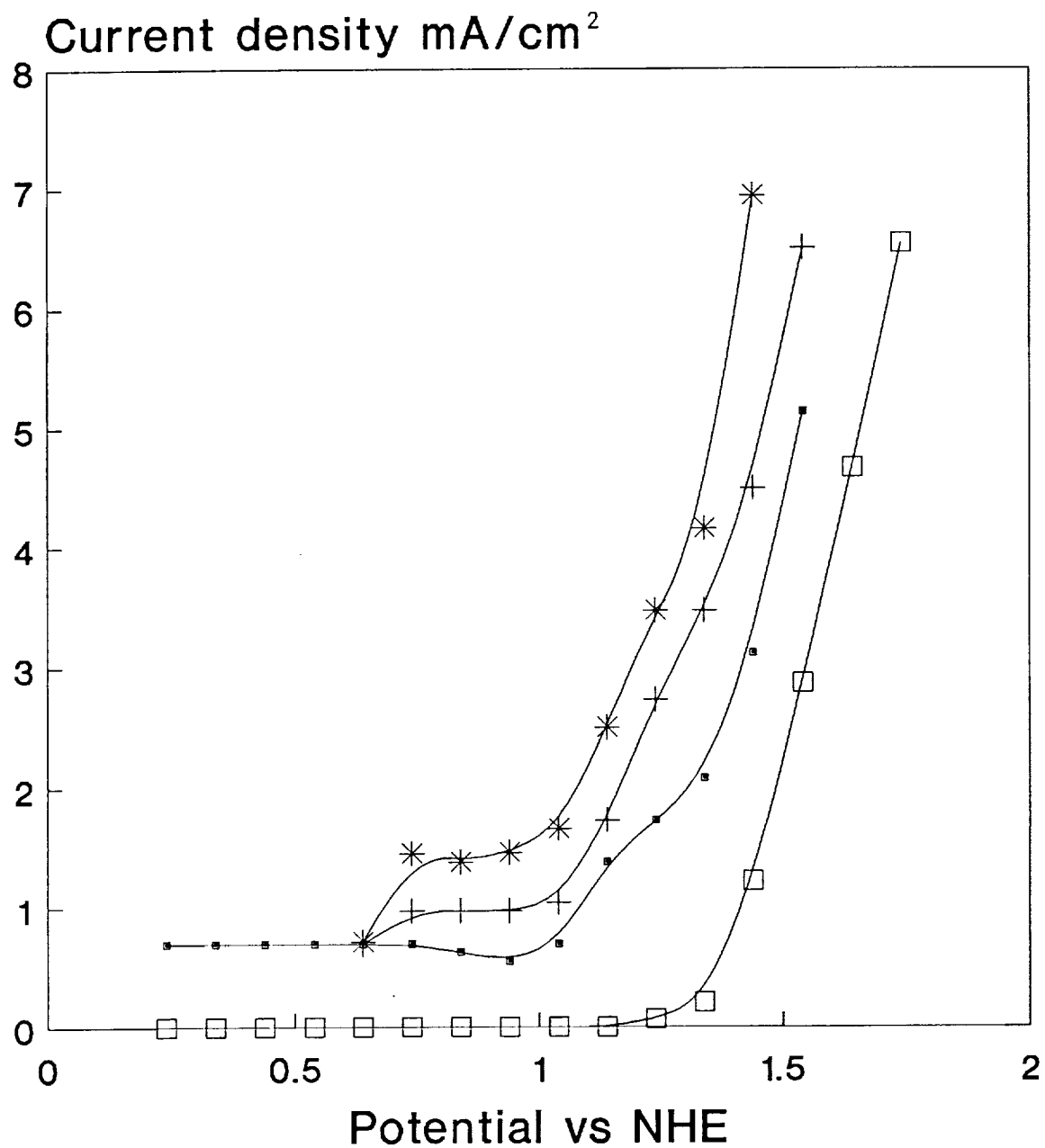
FIG.12   Current Voltage Curves for oxidation of Fecal waste in Urine
        at different temperature at Gold electrode. Waste Conc. 4.68 g/litre
        (■ 25°C; ➕ 60°C; ✳ 75°C and ◇ 90°C)
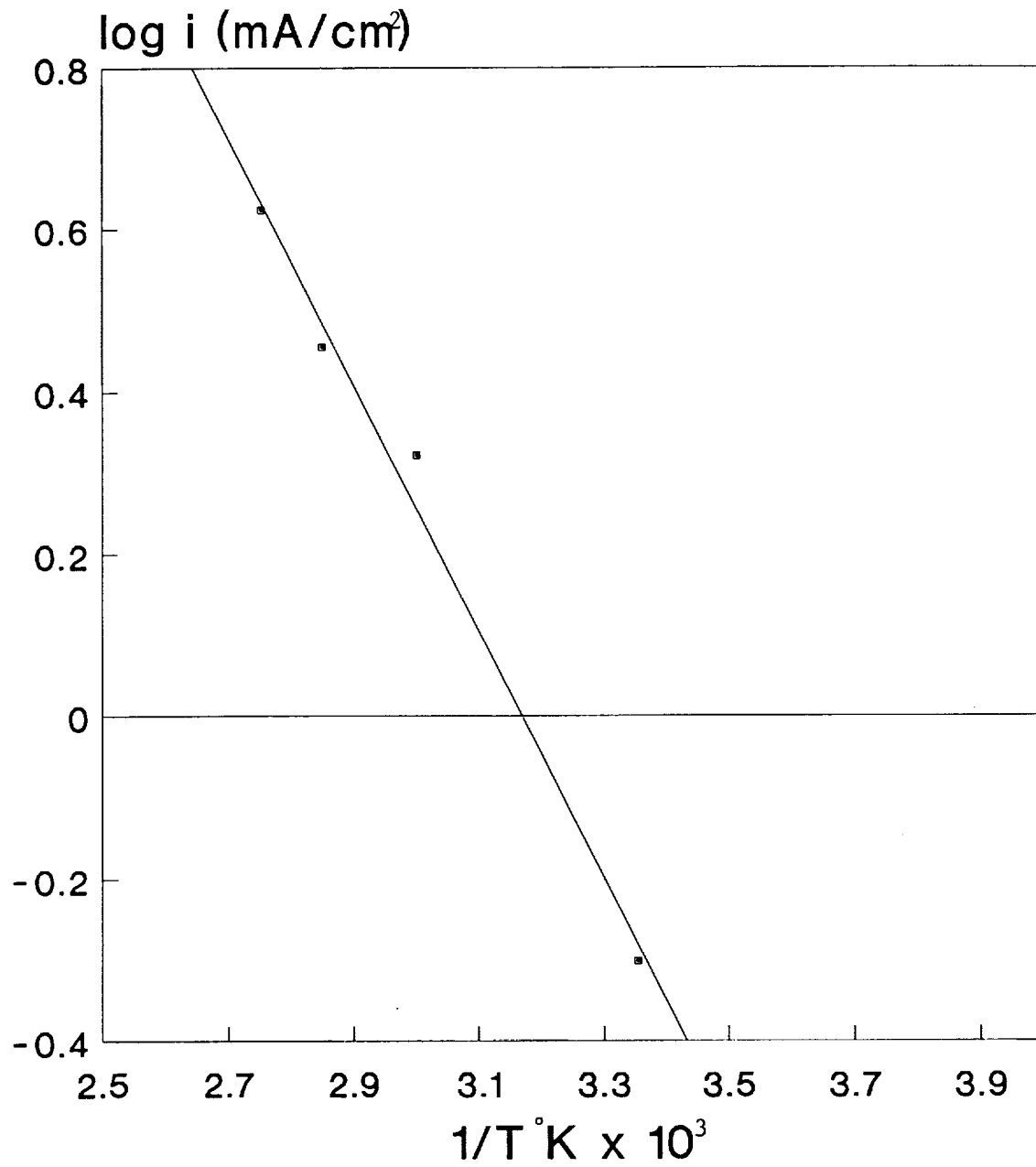
FIG.13 Variation of limiting Current density as function of
        Temperature on Gold electrode.
        Waste conc. 4.68 g/litre in Urine.

Activation Energy 7.0 Kcl/mole

Current density mA/cm²

Potential vs NHE
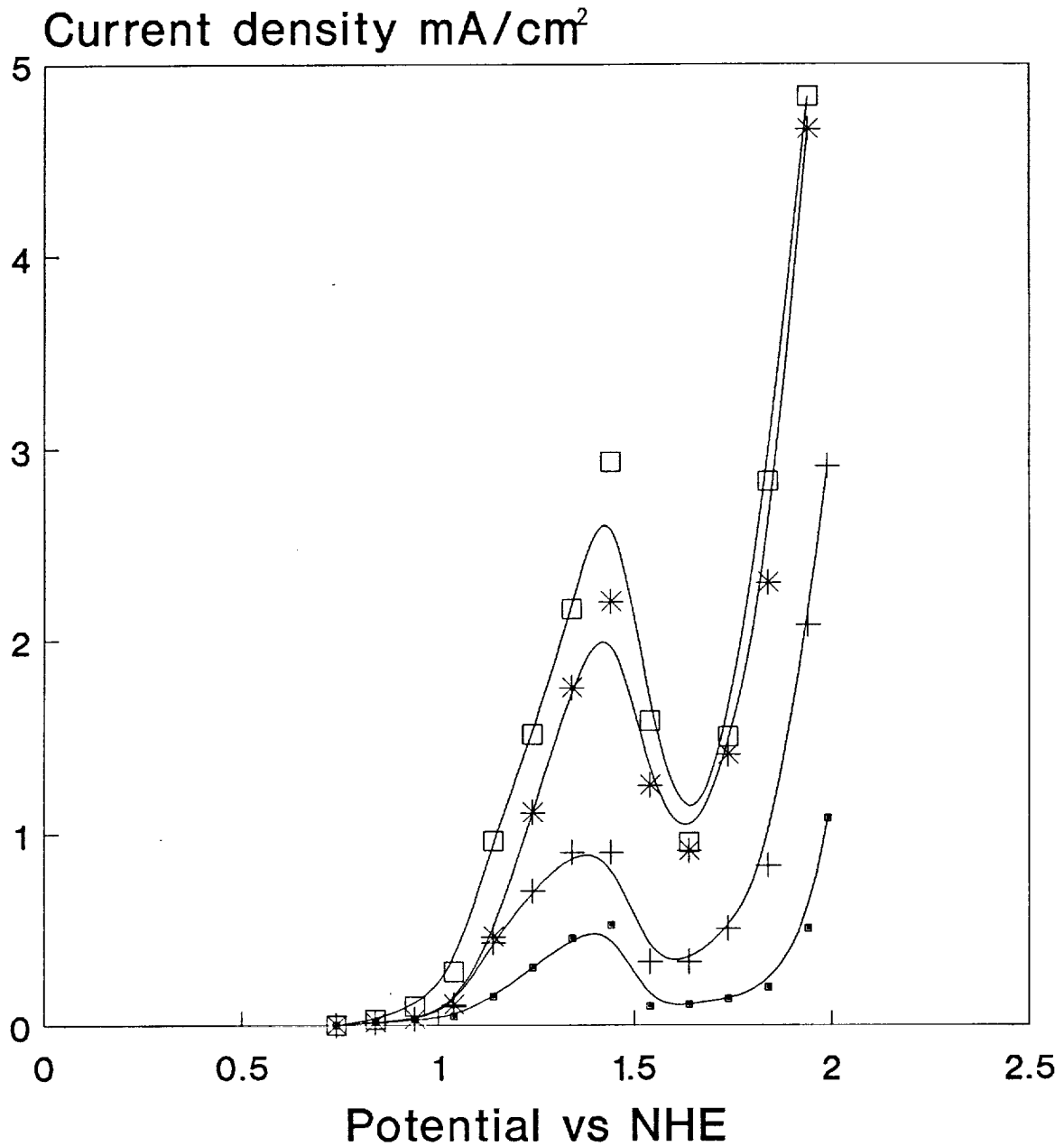
FIG.14 Current Voltage Curves for oxidation of Real human waste in
Urine at different temperature on Gold electrode.
Real human waste conc. 14.04 gms/litre in Urine.

(▪ 25°C; + 60°C; * 75°C and ☐ 90°C)

Real Feces
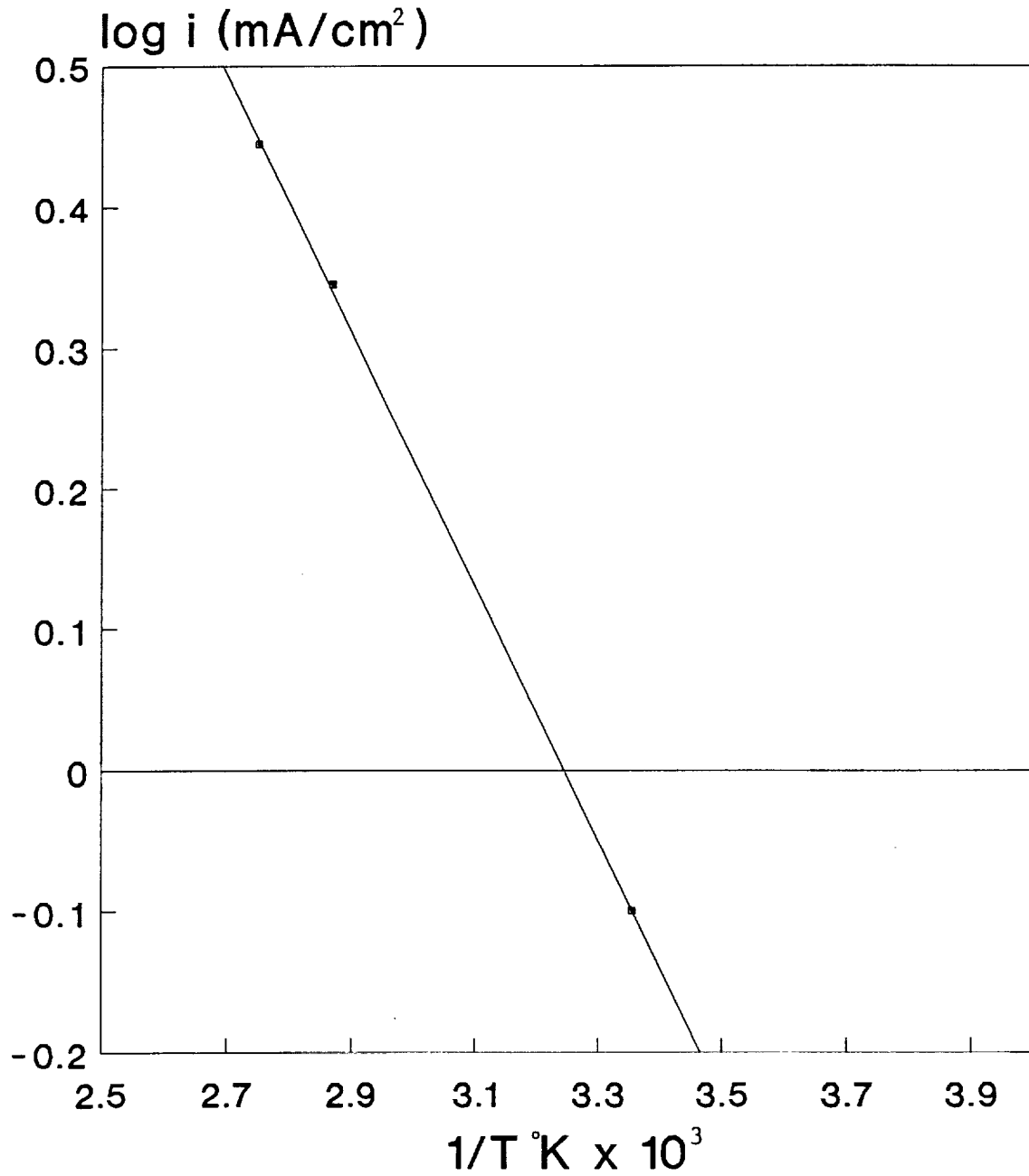
FIG.15 Variation of limiting Current density as a function of
        Temperature on Gold electrode.
        Real human waste conc. 14.04 gms/litre in Urine.

Real feces at Gold
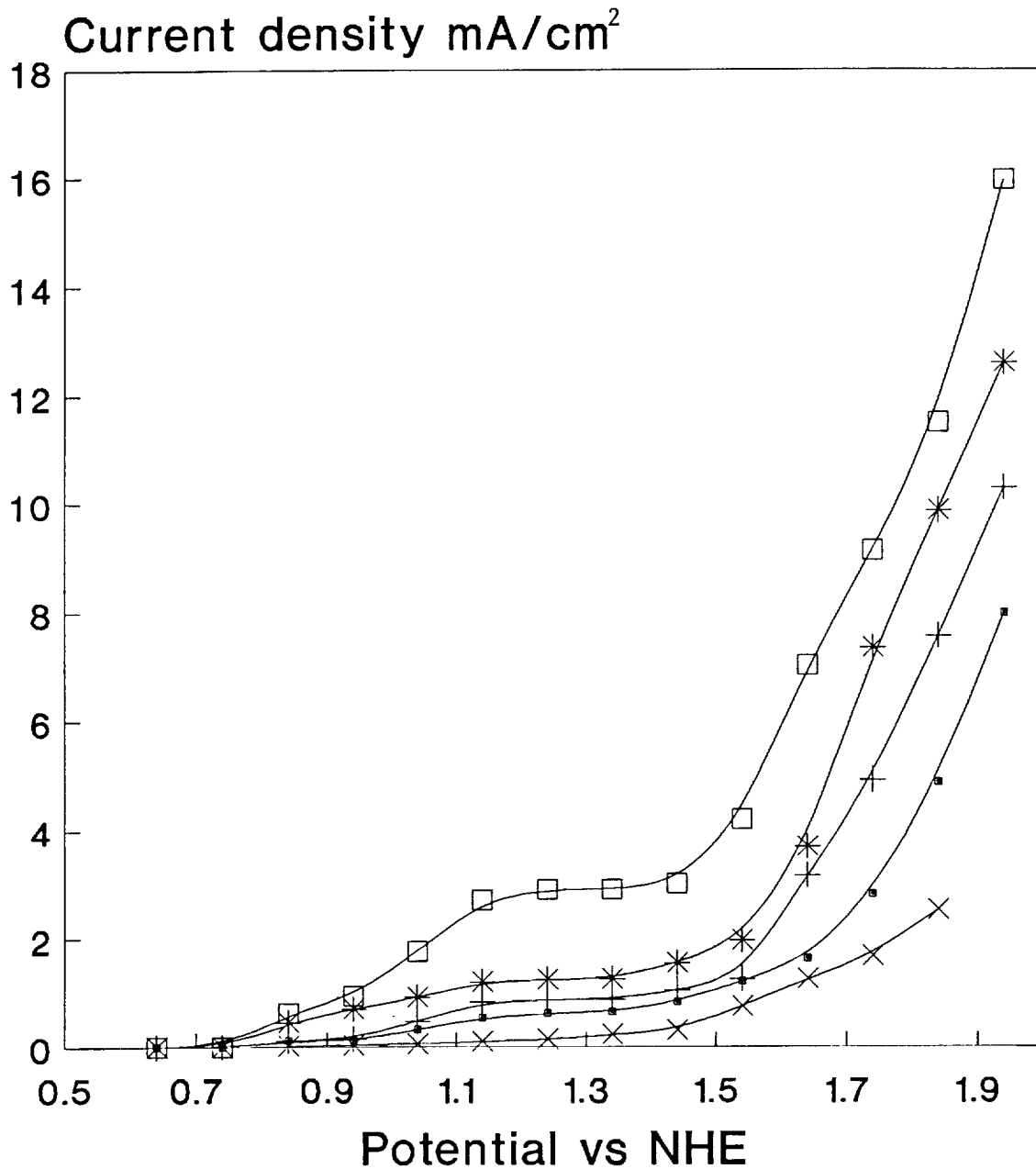
FIG.16 Current Voltage Curves for oxidation Fecal waste in Urine
at different temperature on Graphite electrode.
Waste conc. 14.04 gms/litre.

(x Blank 9.0 g/litre of NaCl solution in water)
(◘ 25°C; + 60°C; * 75°C and □ 90°C)
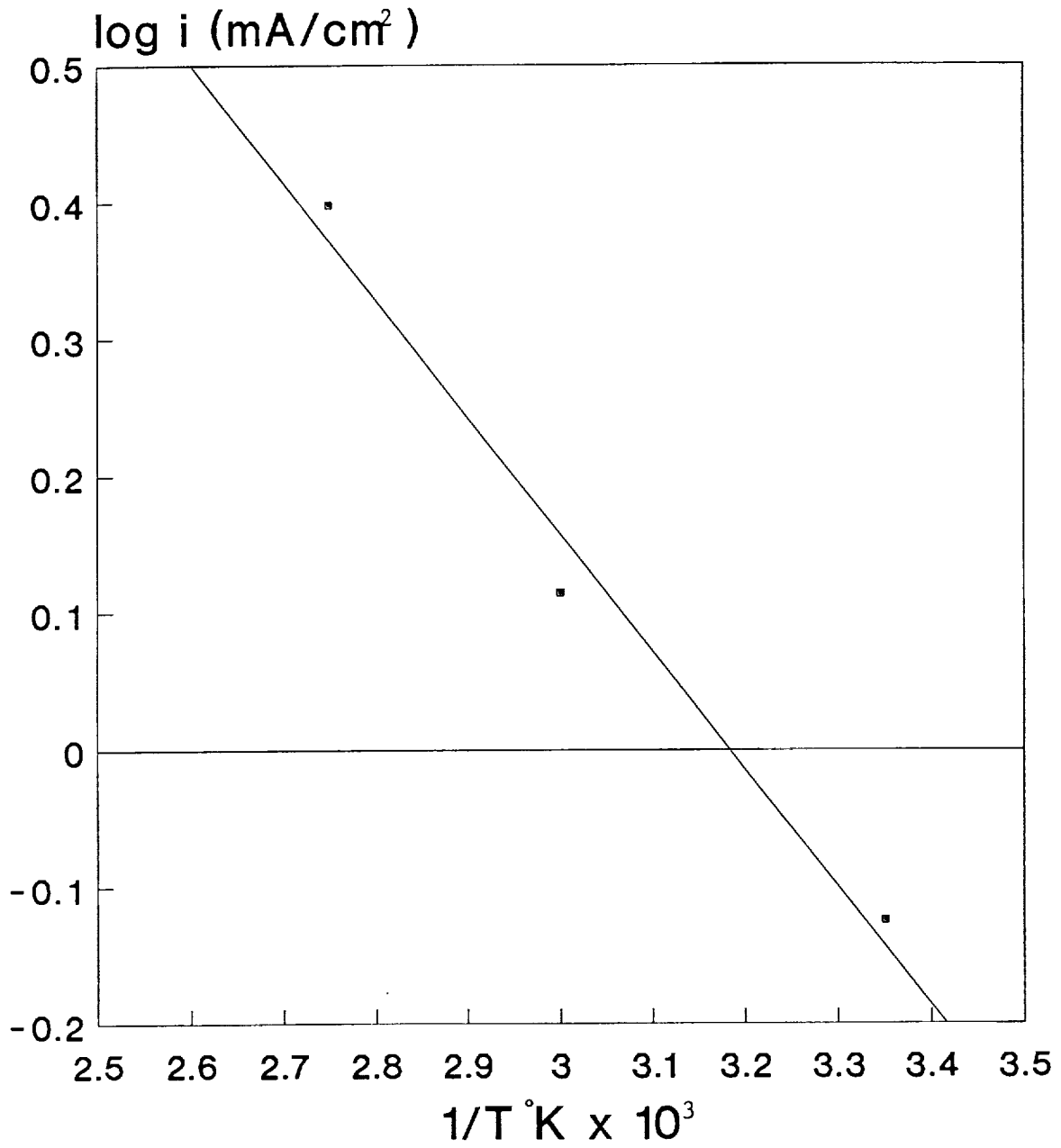
FIG.17   Variation of limiting Current density as a function of
         Temperature on Graphite electrode.
         Waste Conc. 14.04 gms/litre in Urine
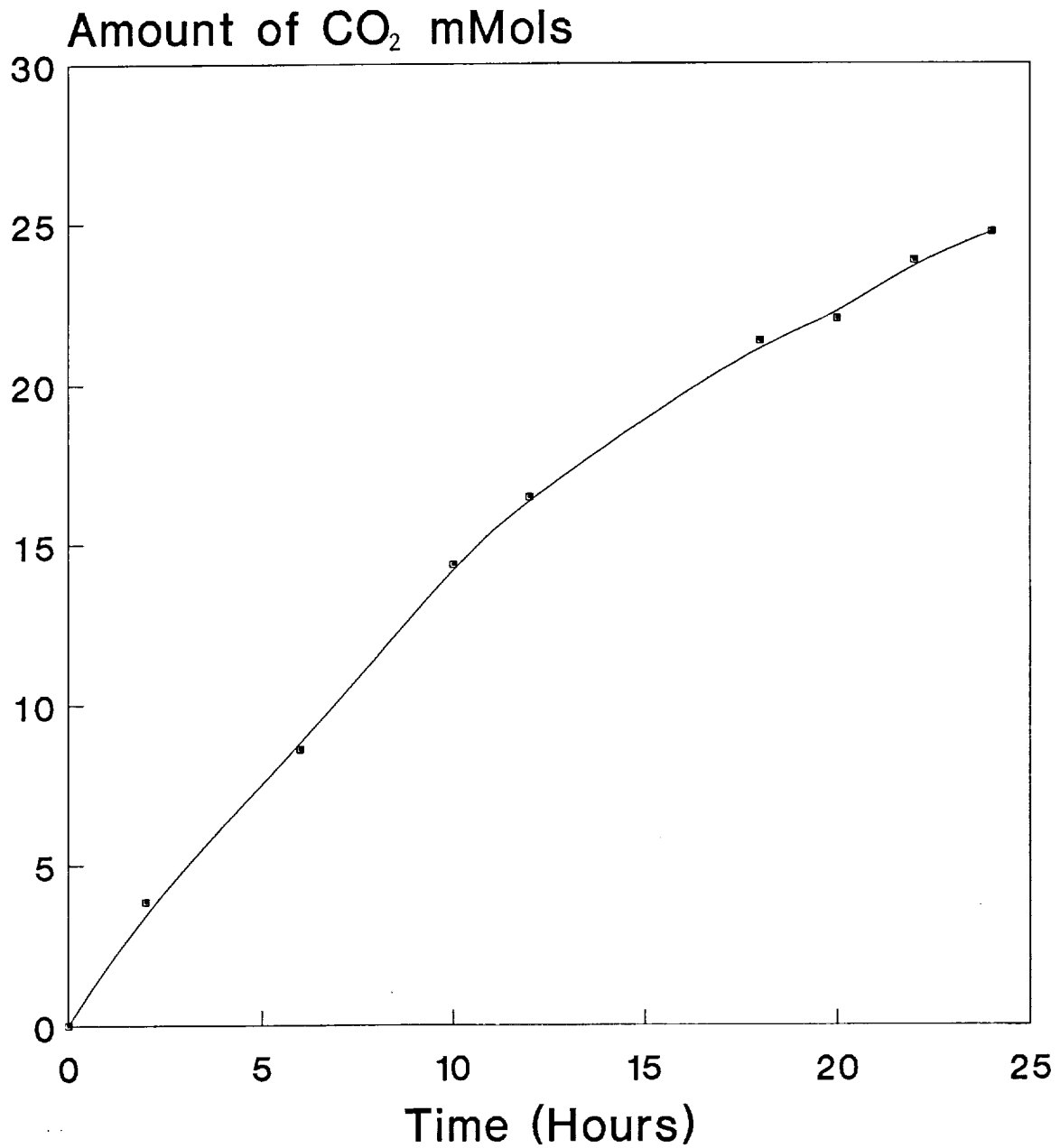
FIG.18 Electrochemical production of CO_2 during fecal waste
        electrolysis in Urine at 90°C. Waste Conc. 14.04 g/litre.
        At Graphite electrode.

Amount of Hydrogen mMols
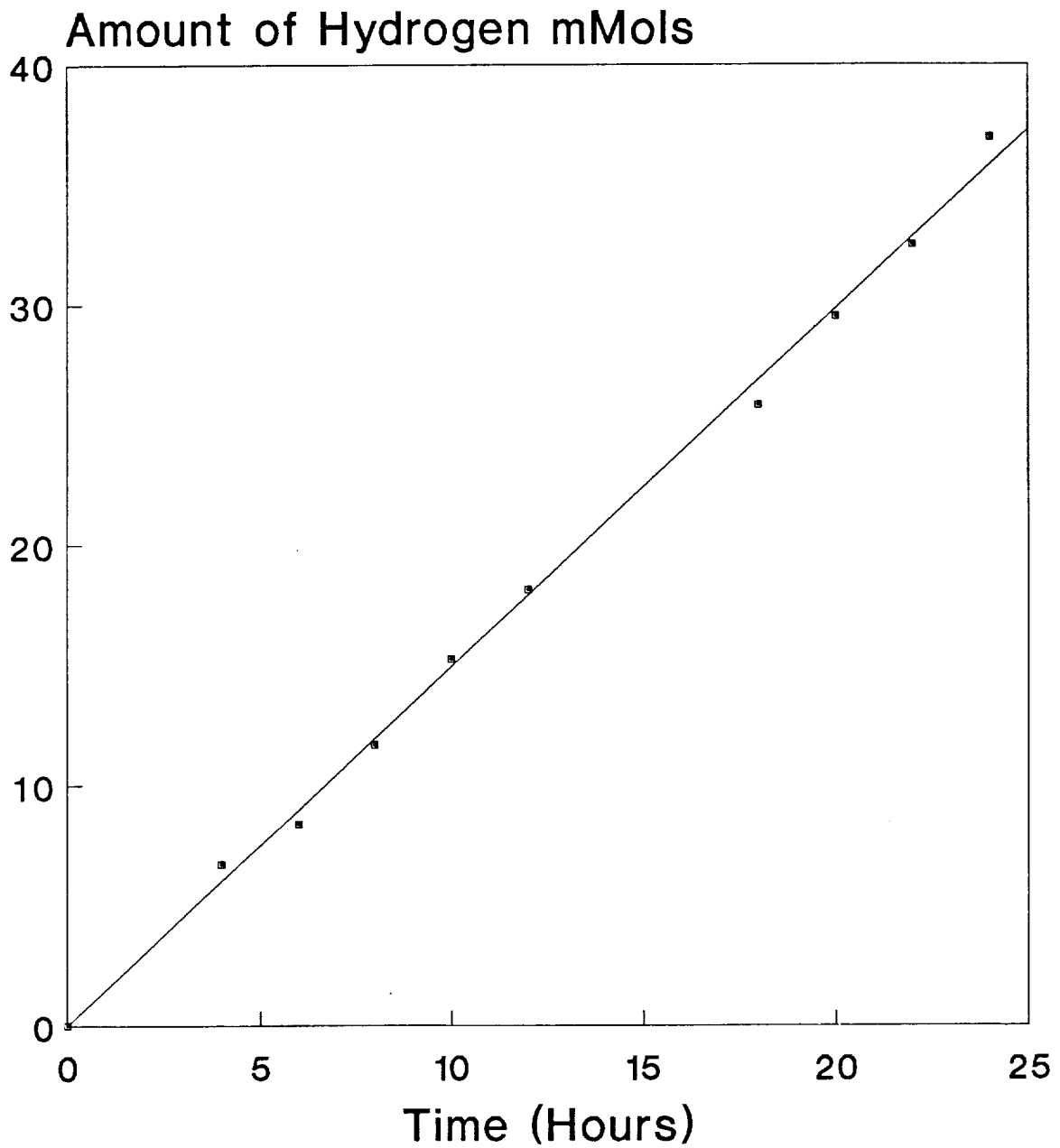
FIG.19(a)   Electrochemical production of Hydrogen during fecal waste
electrolysis on Graphite electrode.
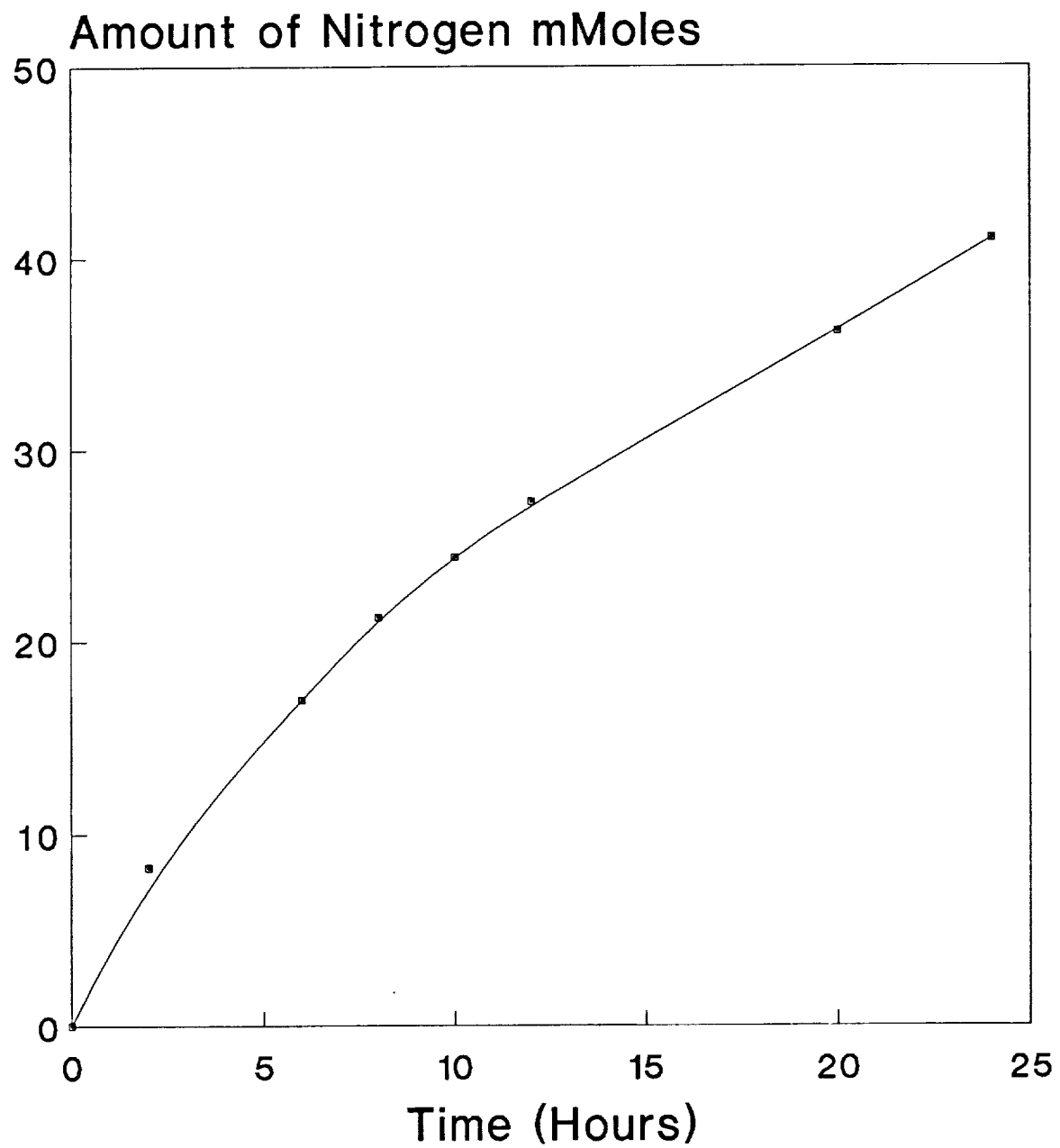
FIG.19(b)   Electrochemical production of Nitrogen during fecal
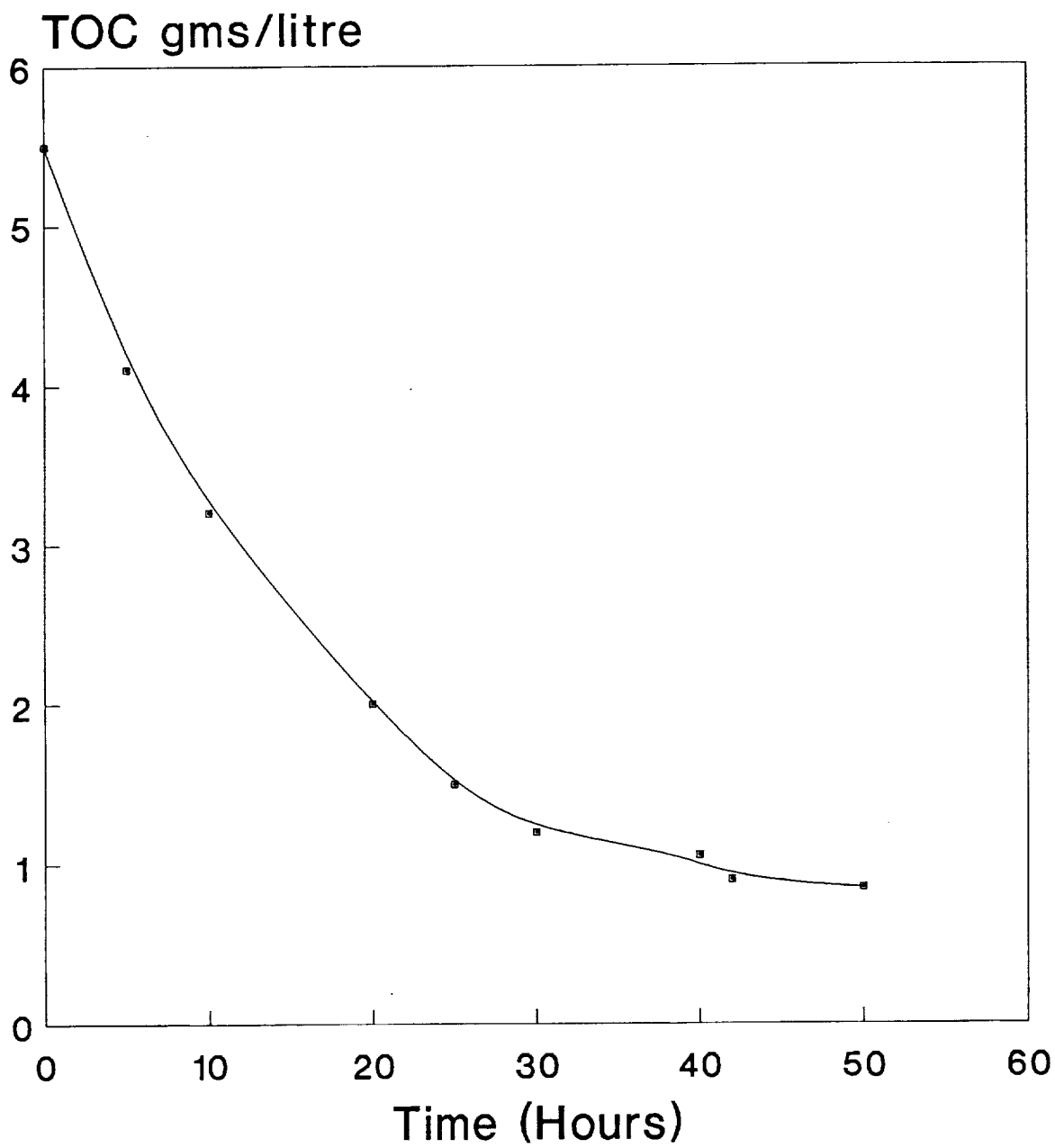   waste electrolysis on Graphite electrode.
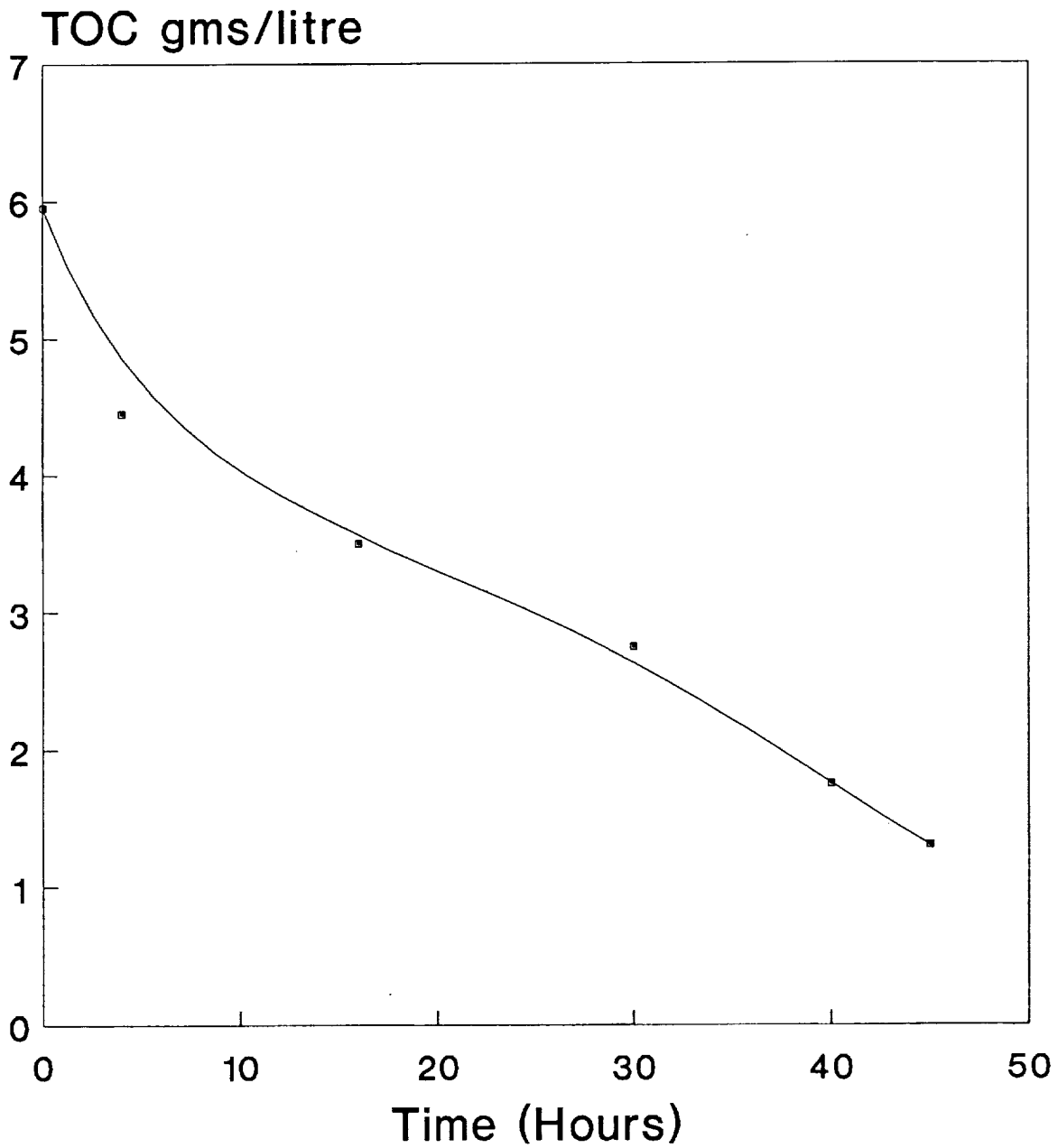
FIG.20 Total organic carbon variation with electrolysis time of fecal
waste in Urine at 90°C on Graphite electrode.
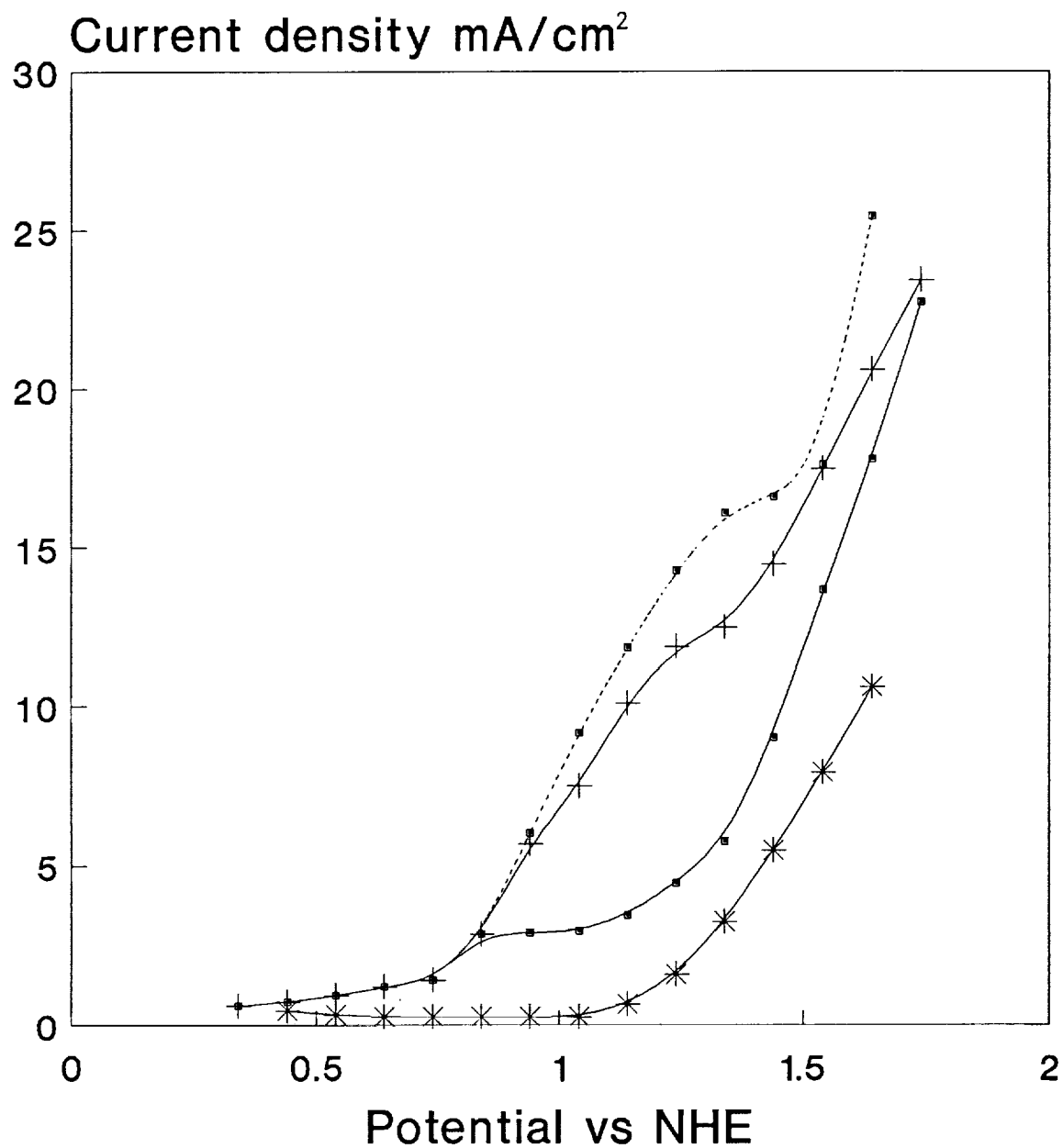
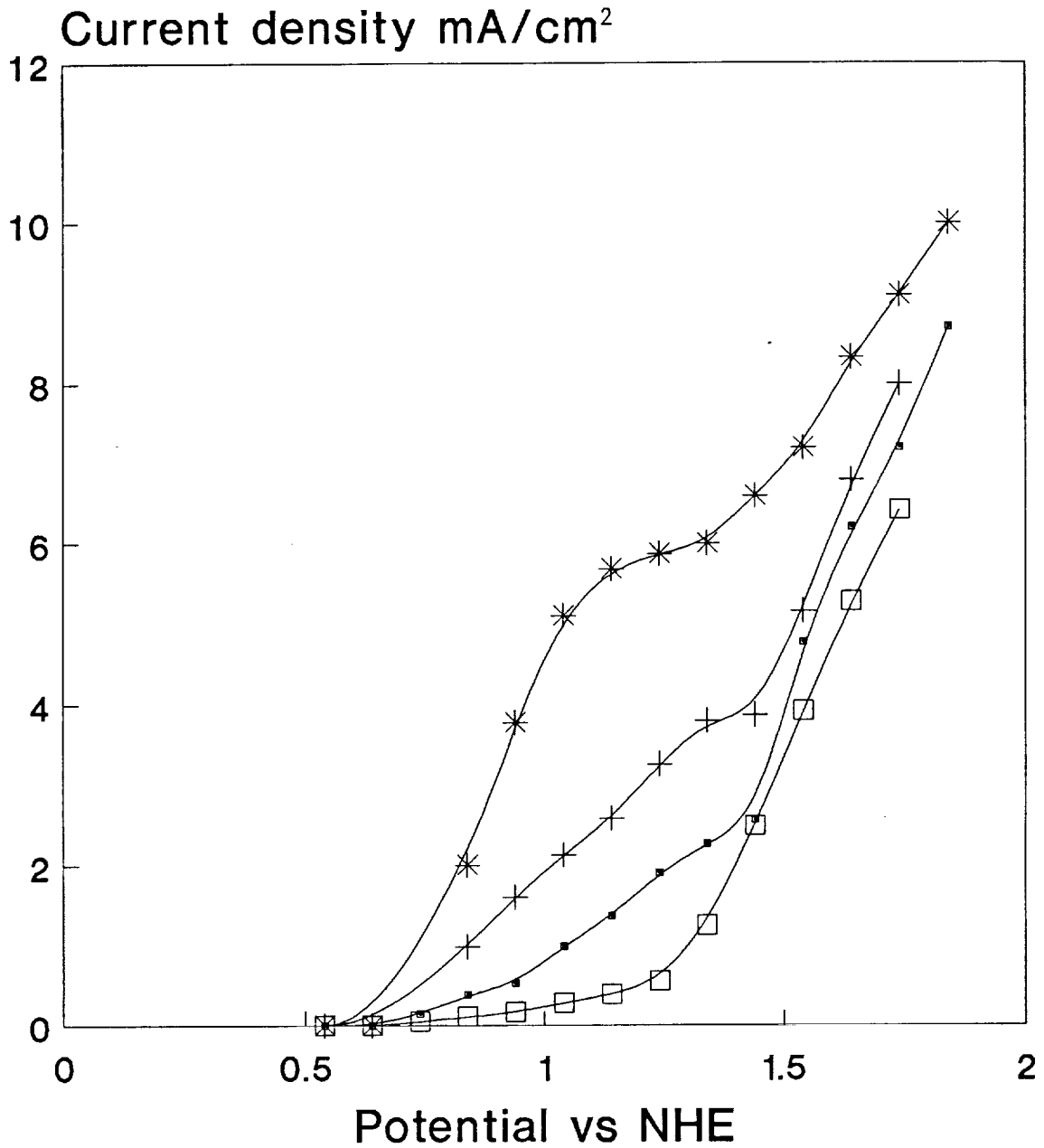FIG.21 Current Voltage Curves for oxidation of fecal waste in Urine at different temperature on Tungsten carbide electrode.

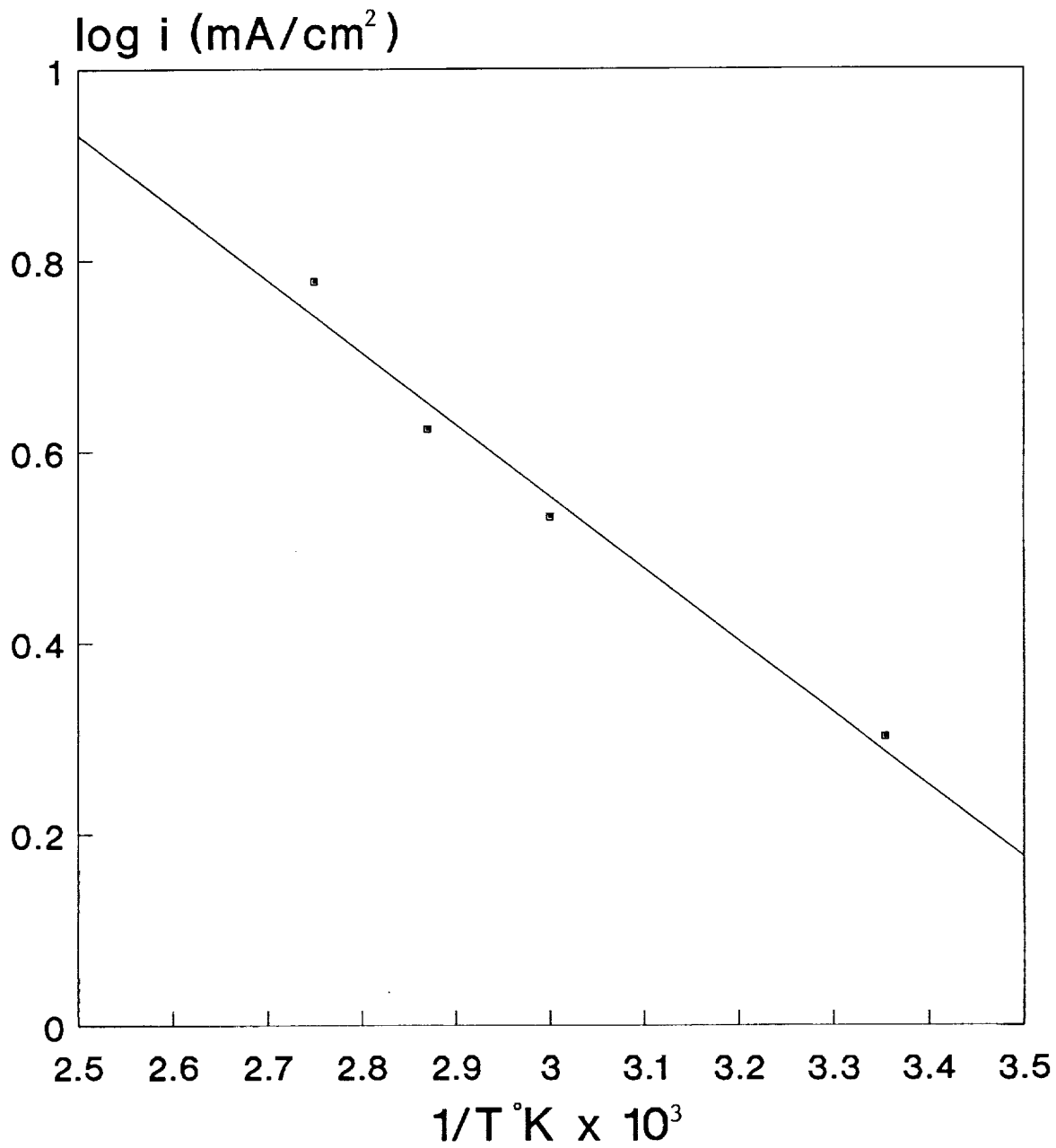(* Blank without waste; ▣ 25°C; + 75°C; and ■ 90°C)
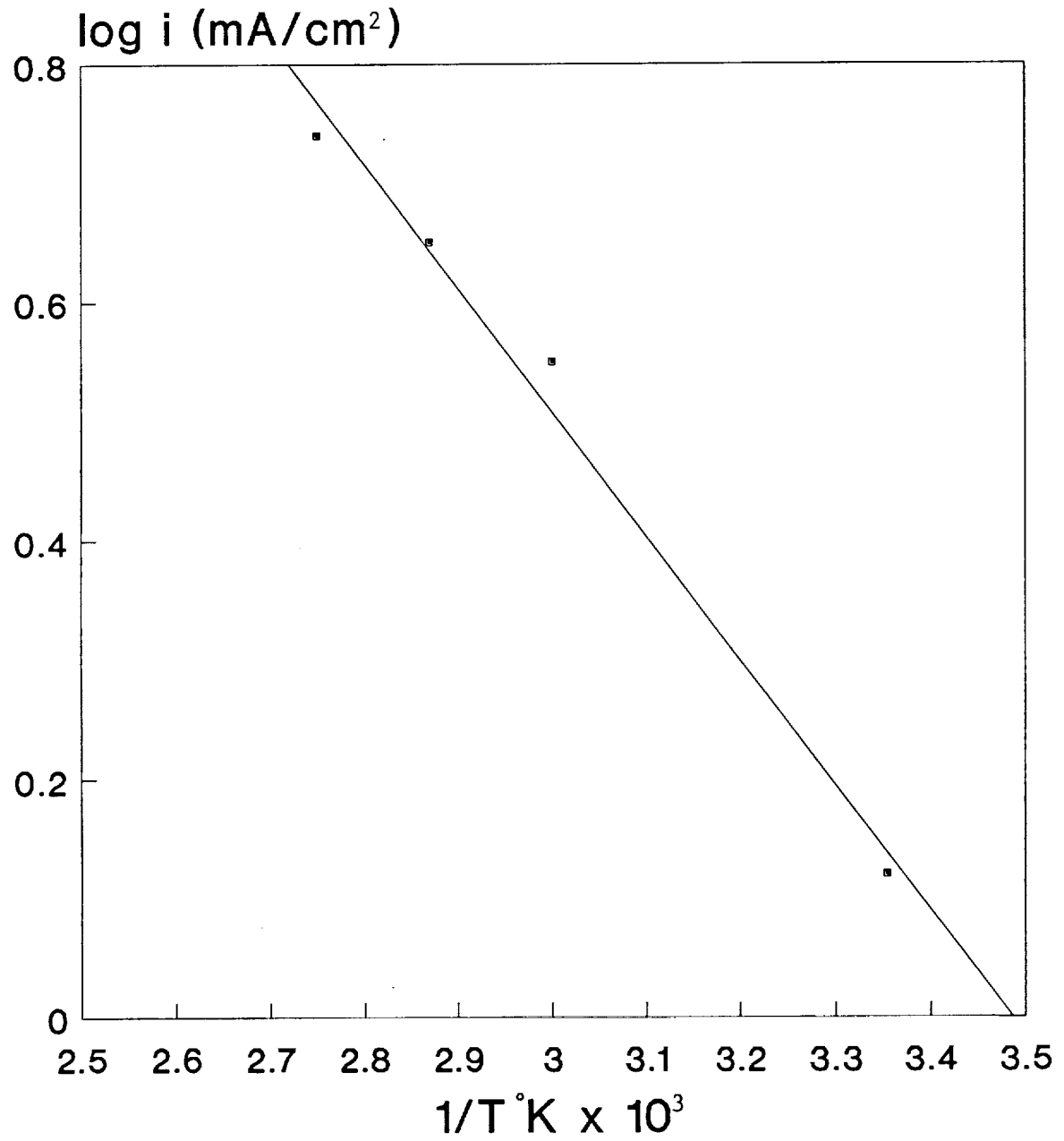
FIG.22 Variation of limiting Current density as a function of
        Temperature on Tungsten carbide electrode.
        Waste Conc. 14.04 gms/litre.
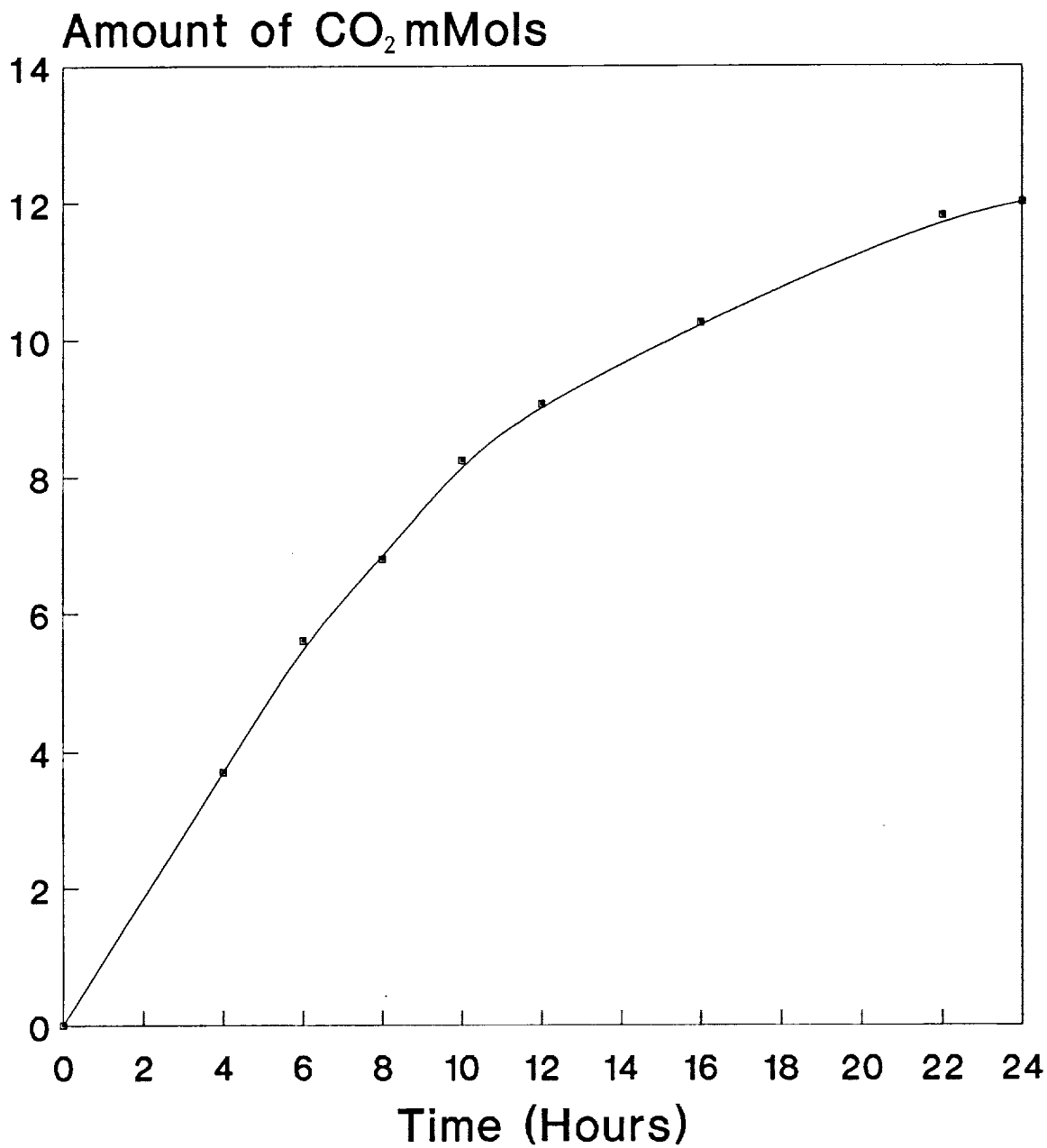
FIG.23 Electrochemical production of CO_2 during fecal waste
electrolysis in Urine at 90°C on Tungsten carbide electrode.
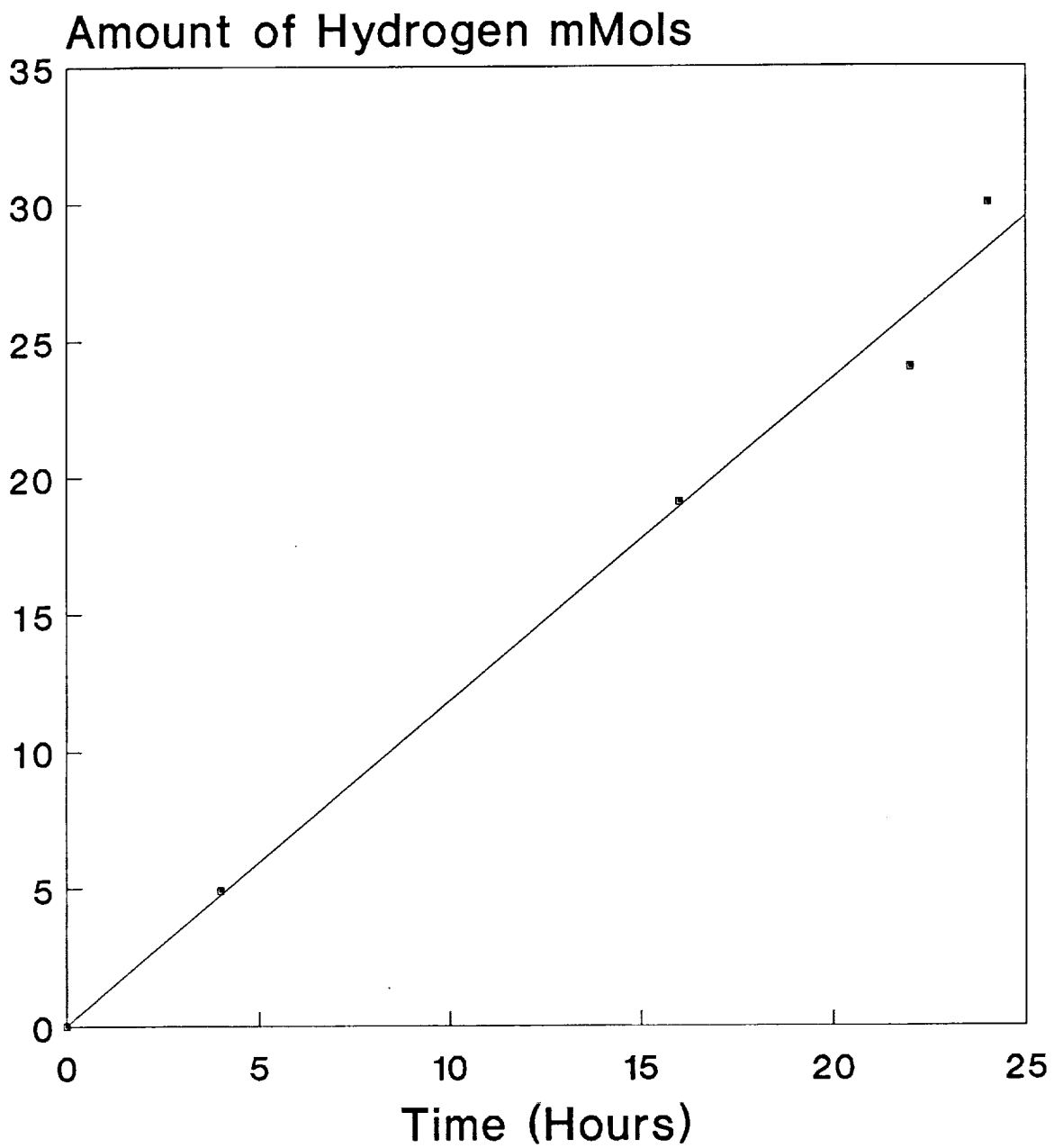
Amount of Hydrogen mMols

FIG.24(a) Electrochemical production of Hydrogen during fecal waste
electrolysis on Tungsten carbide electrode.

Amount of Nitrogen mMols
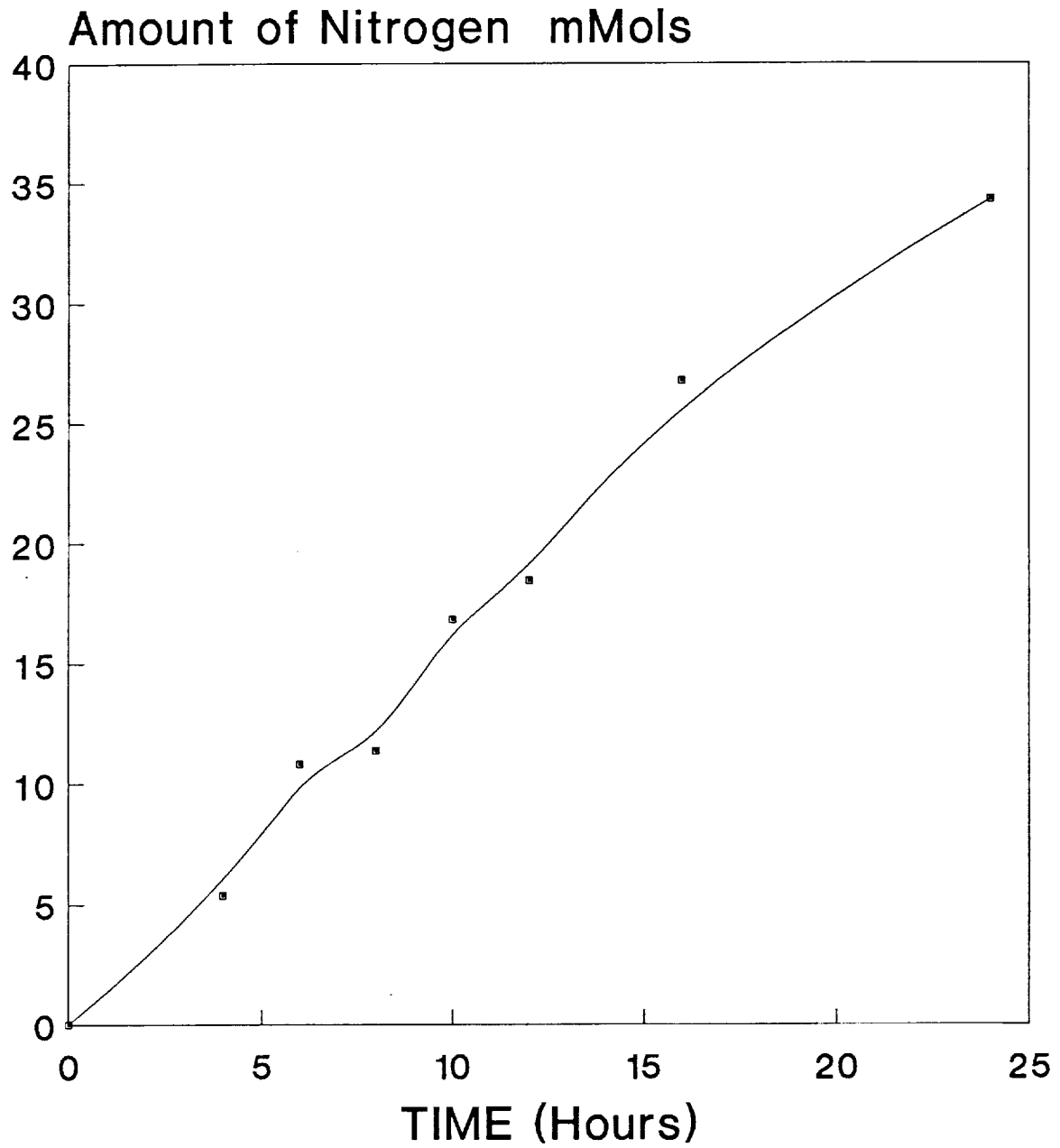
FIG.24(b)   Electrochemical production of Nitrogen during fecal waste
electrolysis on Tungsten carbide electrode.
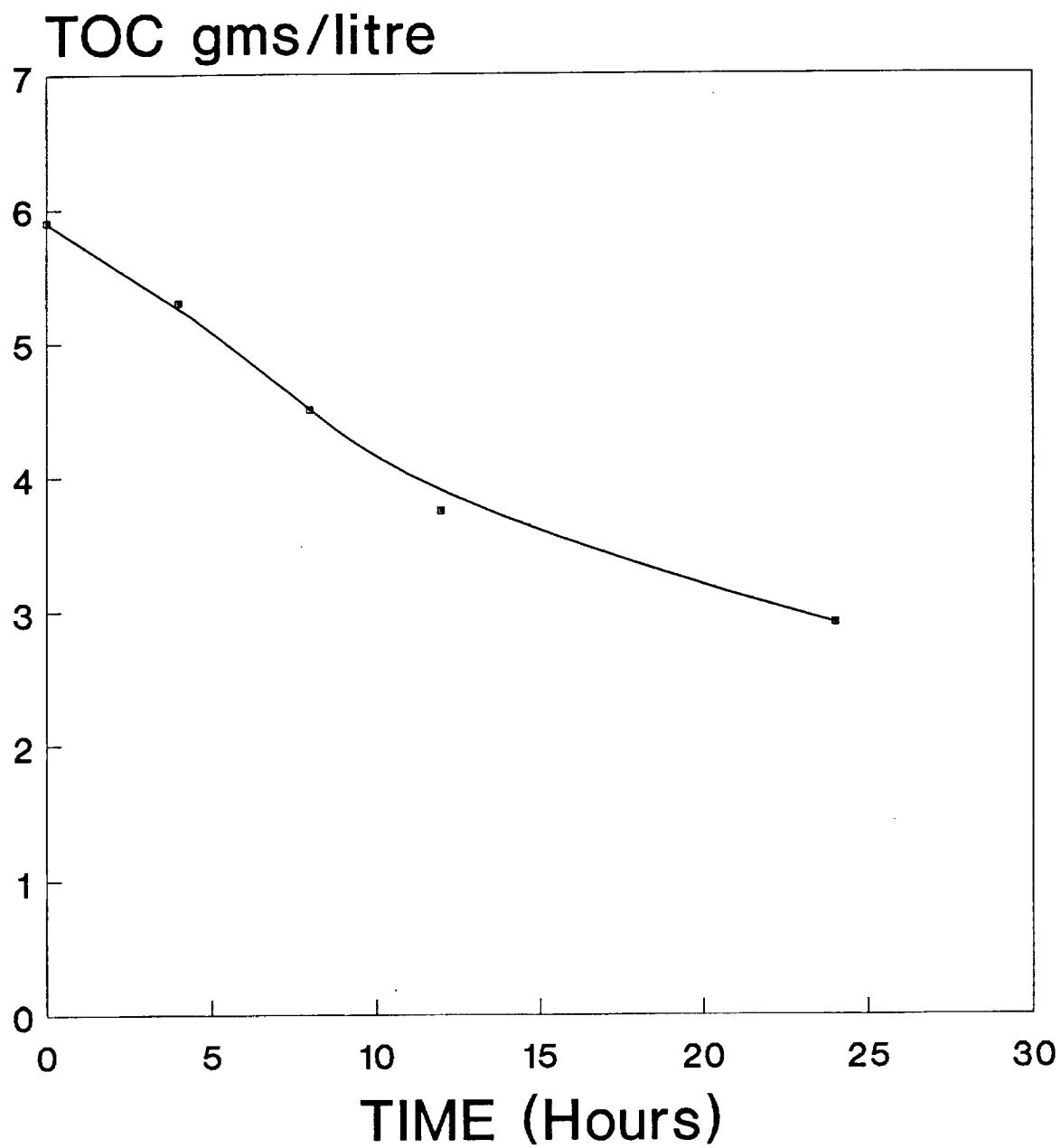
FIG.25 Total organic carbon variation with electrolysis time of fecal
waste in Urine at 90°C on Tungsten carbide electrode.

FIG.26 Current Voltage Curves for oxidation of fecal waste in Urine
at different temperature on Ruthenium oxide electrode.

(x Blank without waste & Urine; ◙ 25°C;   + 60°C;   * 75°C
and □ 90°C)

FIG.27   Current Voltage Curves for oxidation of fecal waste in
5M H_2SO_4 at different temperature on RuO_2 electrode.
Waste Conc. 23.4 gms/litre.

(□ Blank without waste; ▪ 60°C;   +80°C and * 100°C)
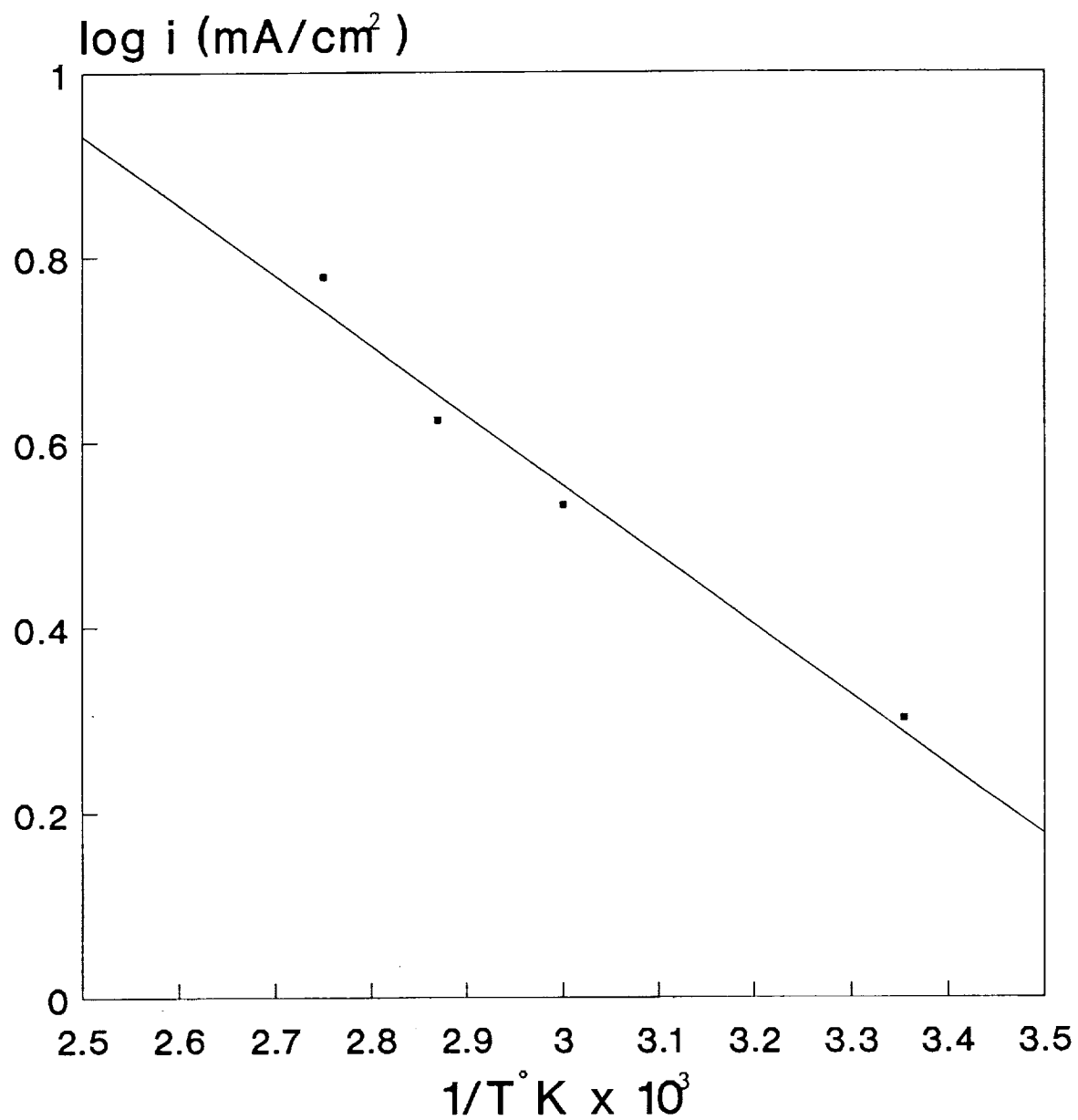
FIG.28 Variation of limiting Current density as a function of
Temperature on RuO₂ electrode. Waste in Urine.
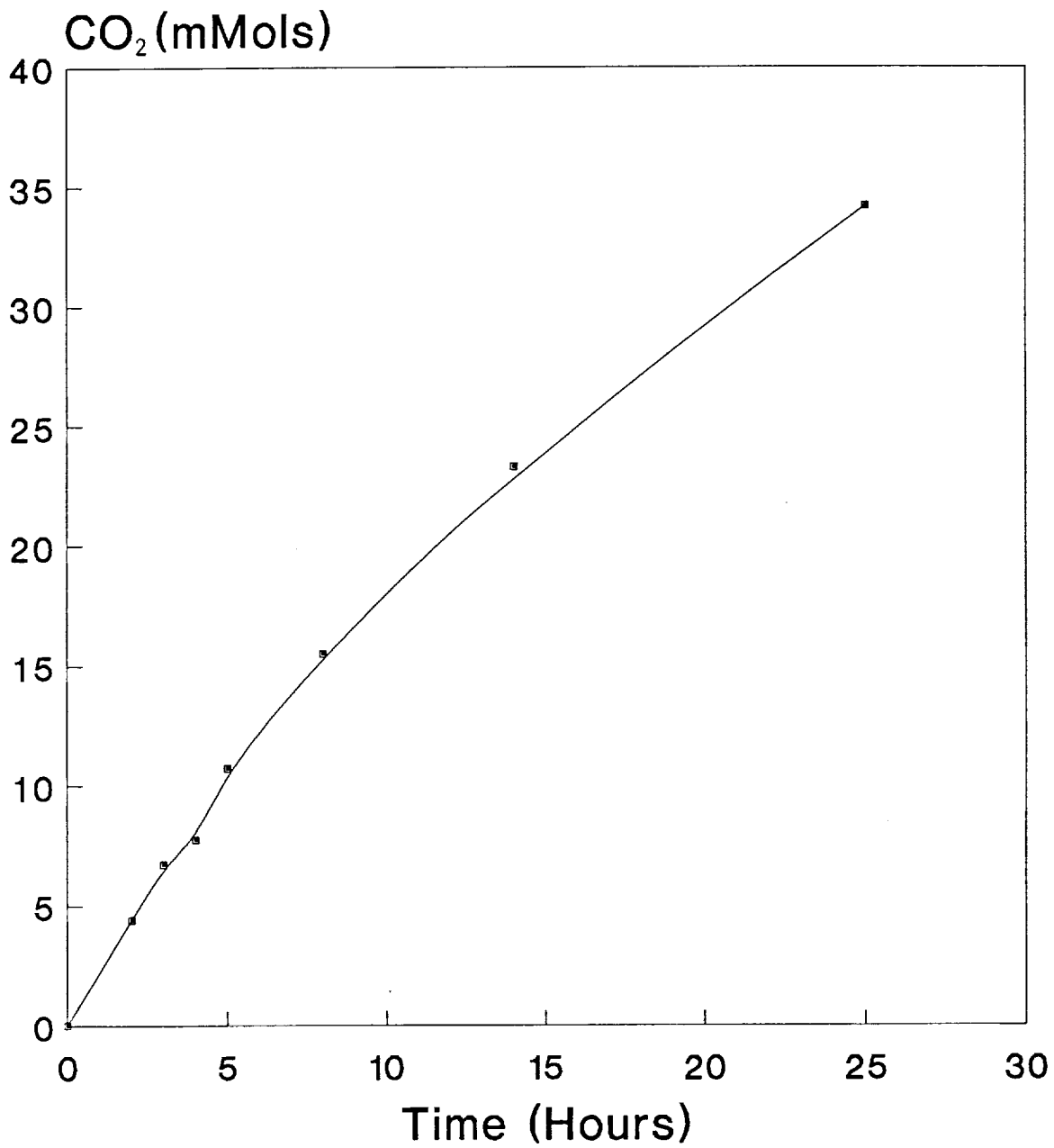
FIG.29(a)   Electrochemical production of CO_2 during fecal waste
            electrolysis in Urine on RuO_2 electrode.
            Temperature 90°C.
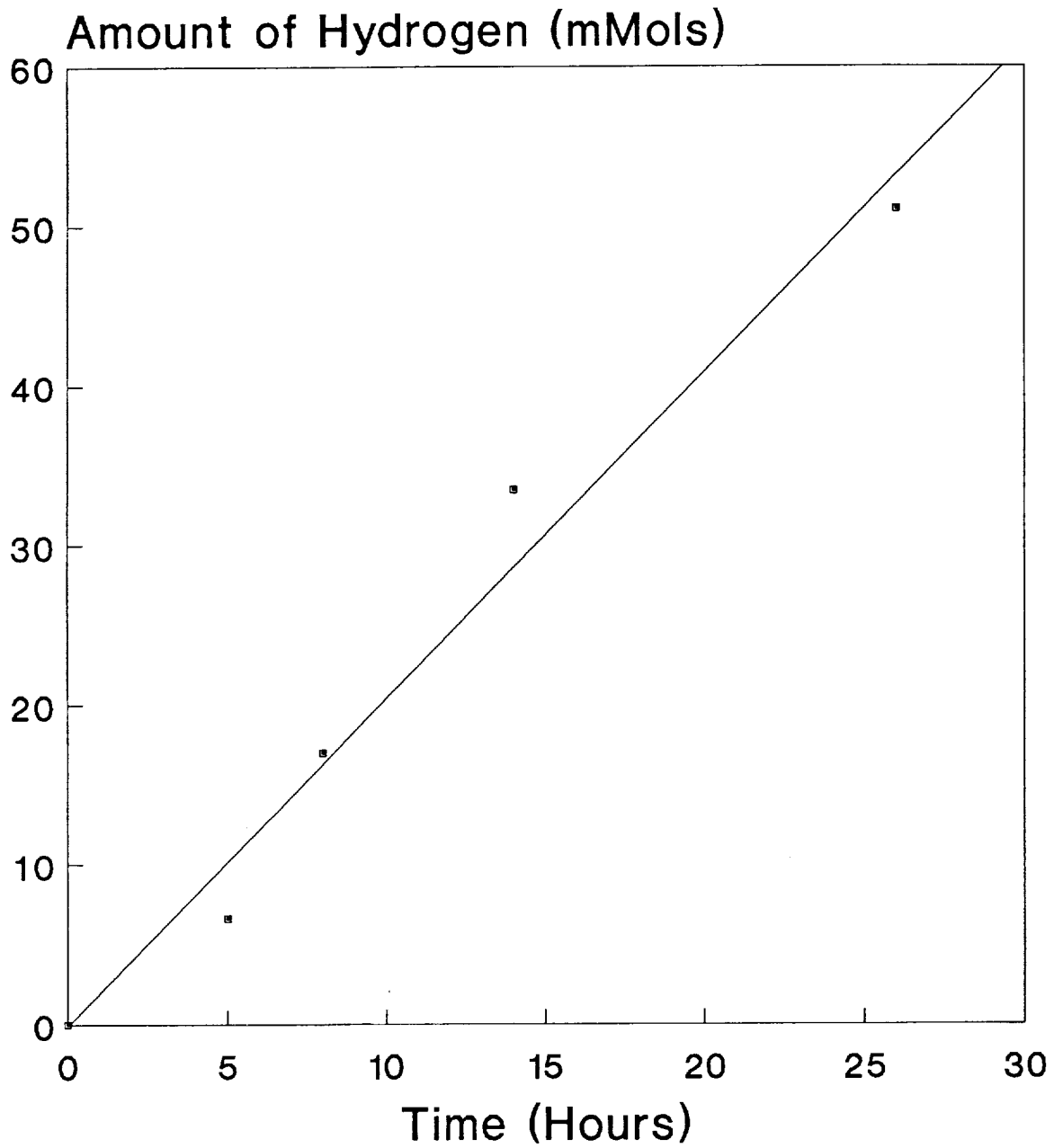
FIG.29(b)   Electrochemical production of Hydrogen during
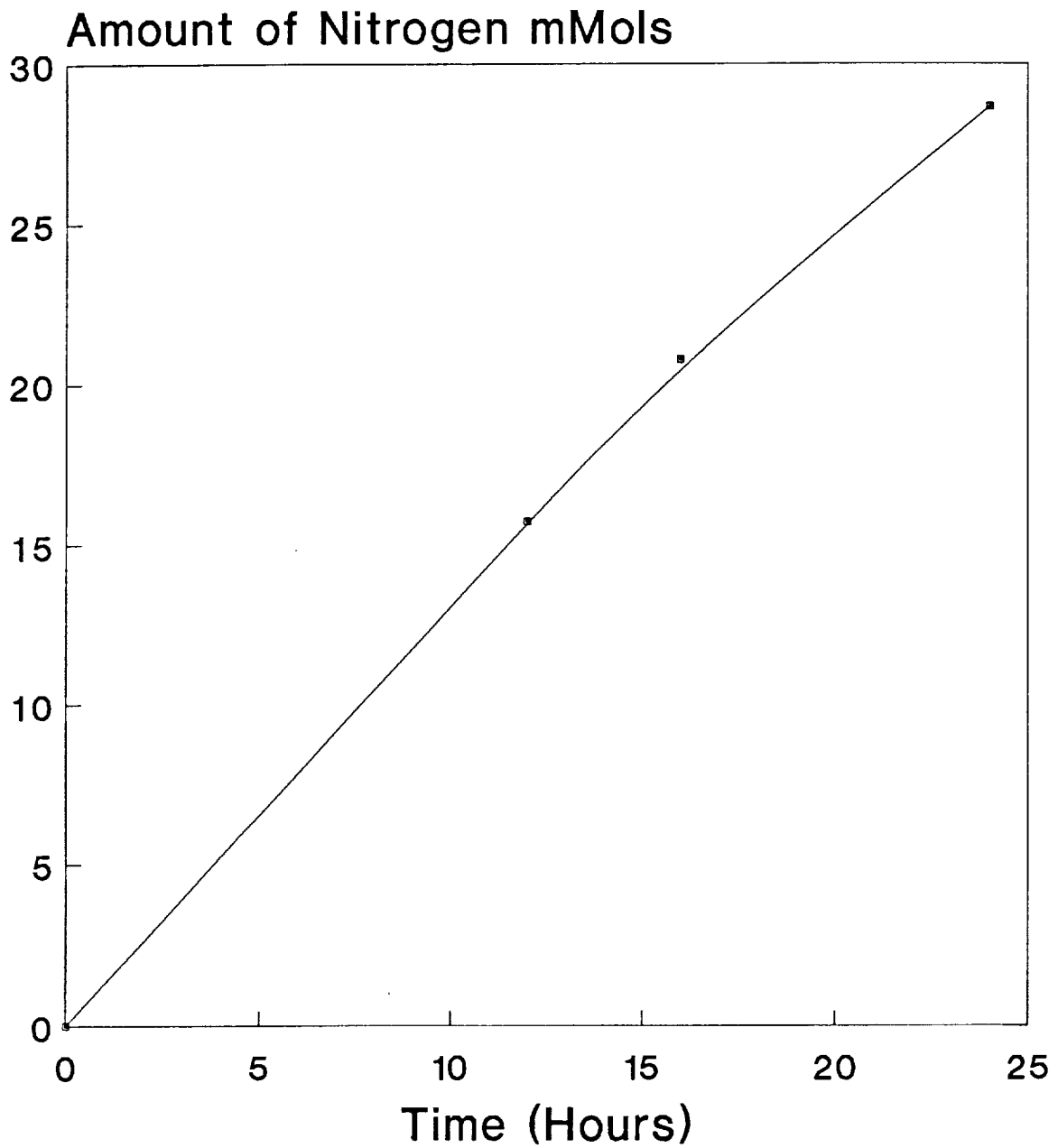   electrolysis of fecal waste in Urine on RuO_2.
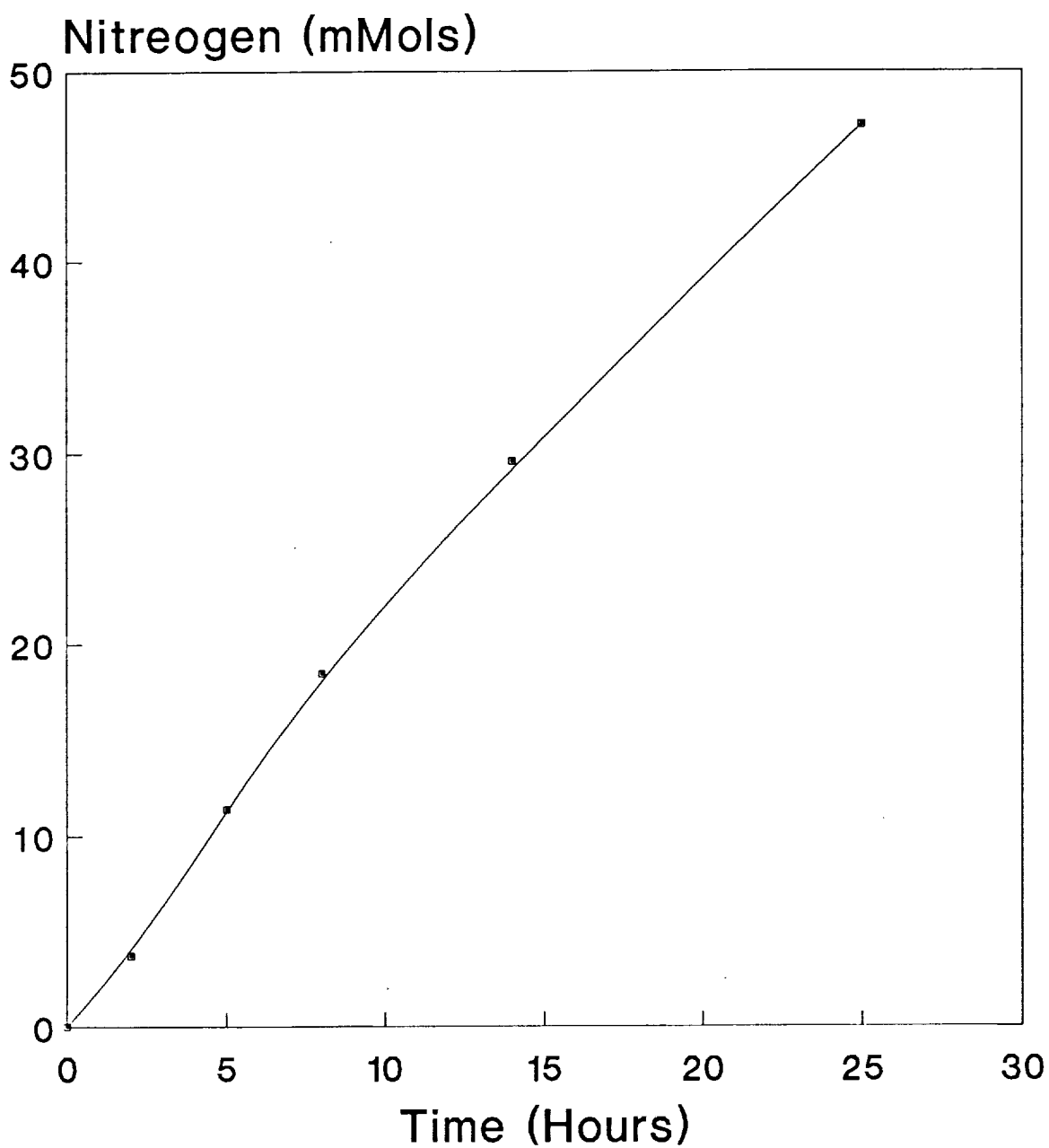
FIG.29(c)   Electrochemical production of Nitrogen during electrolysis
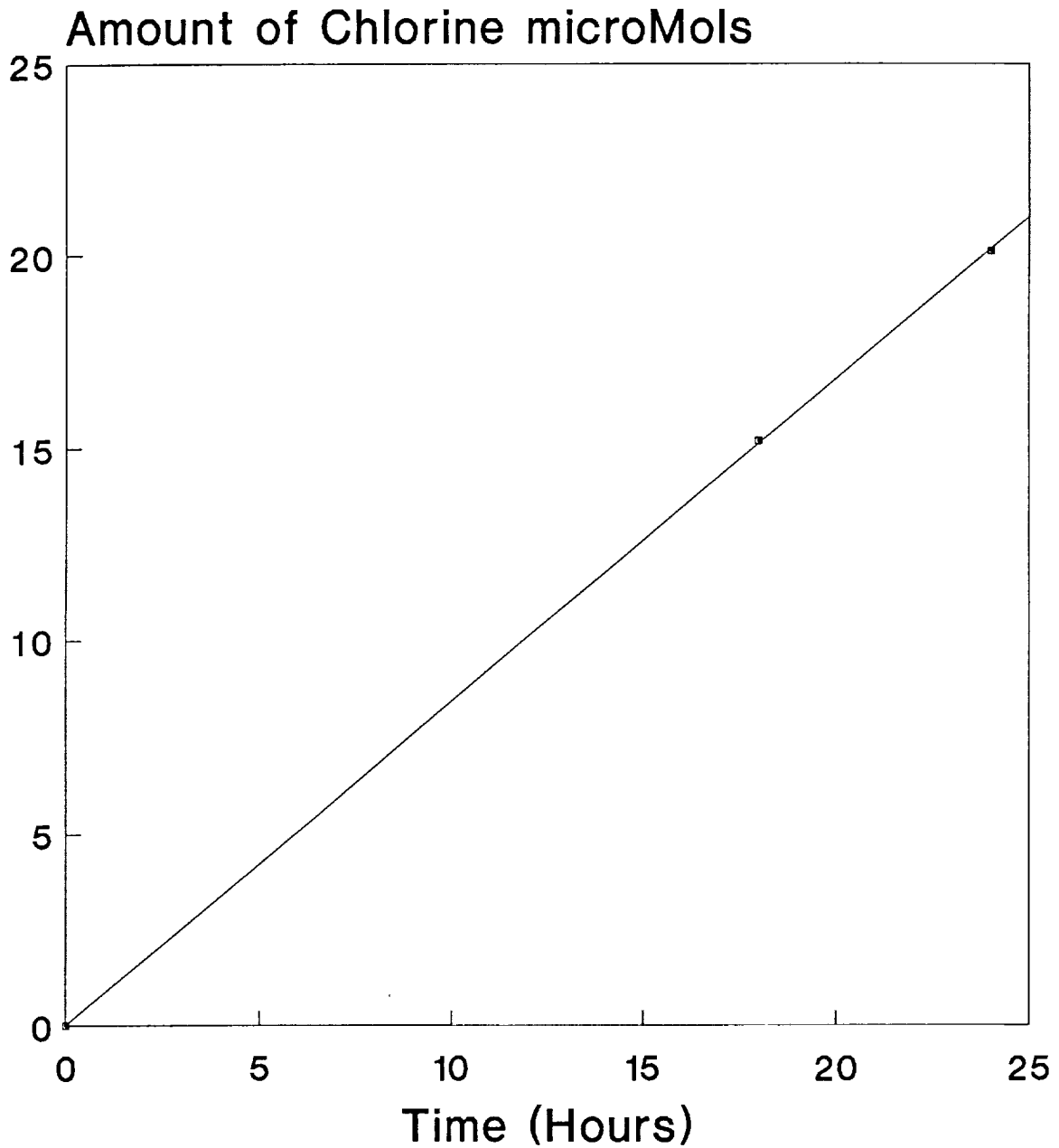of fecal waste in Urine on RuO_2 electrode.

FIG.30 Total organic carbon variation with electrolysis time of fecal
waste in Urine at 90°C on Ruthenium oxide electrode.

Current density mA/cm²

FIG.31 Current Voltage Curves for oxidation of fecal waste in Urine
at different temperature on Perovskite electrode.
Waste Conc. 14.04 gms/litre.

(□ Blank without waste & Urine; ▪ 25°C; ✛ 60°C and * 90°C)

FIG.32 Variation of limiting Current density as a function of
        Temperature on Perovskite electrode.
        Waste Conc. 14.04 gms/litre.
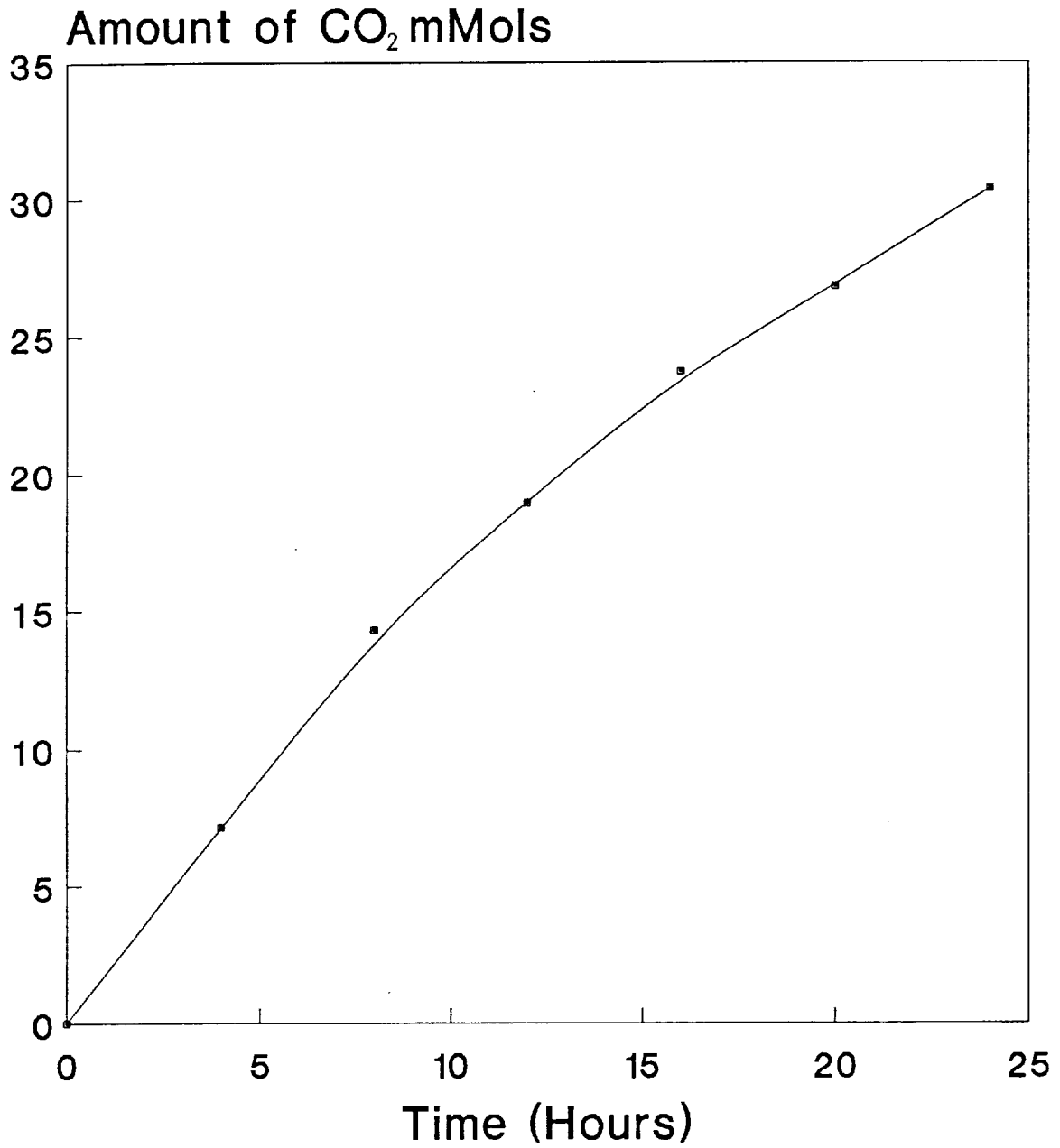
FIG.33   Electrochemical production of CO_2 during electrolysis of fecal waste in Urine on Perovskite electrode. Temperature 90°C.

Amount of Hydrogen mMols
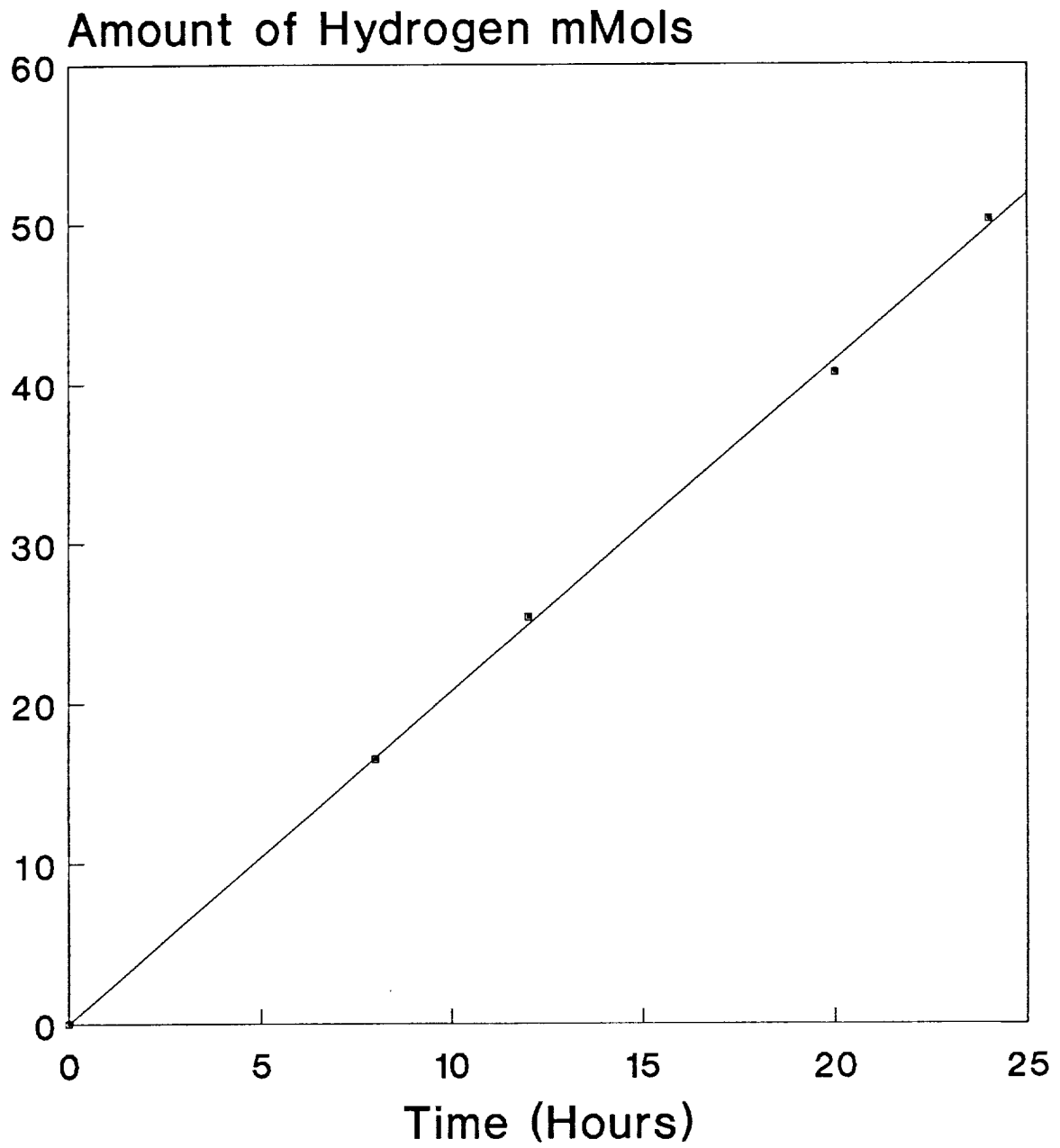
FIG.34(a) Electrochemical production of Hydrogen during electrolysis of
          fecal waste in Urine on Perovskite electrode.

FIG.34(b) Electrochemical production of Nitrogen during electrolysis
of fecal waste in Urine on Perovskite electrode.

Amount of Chlorine microMols

FIG.35   Electrochemical production of Chlorine during electrolysis of
         fecal waste in Urine at 90°C on Perovskite electrode.
         Waste Conc. 14.04 gms/litre.
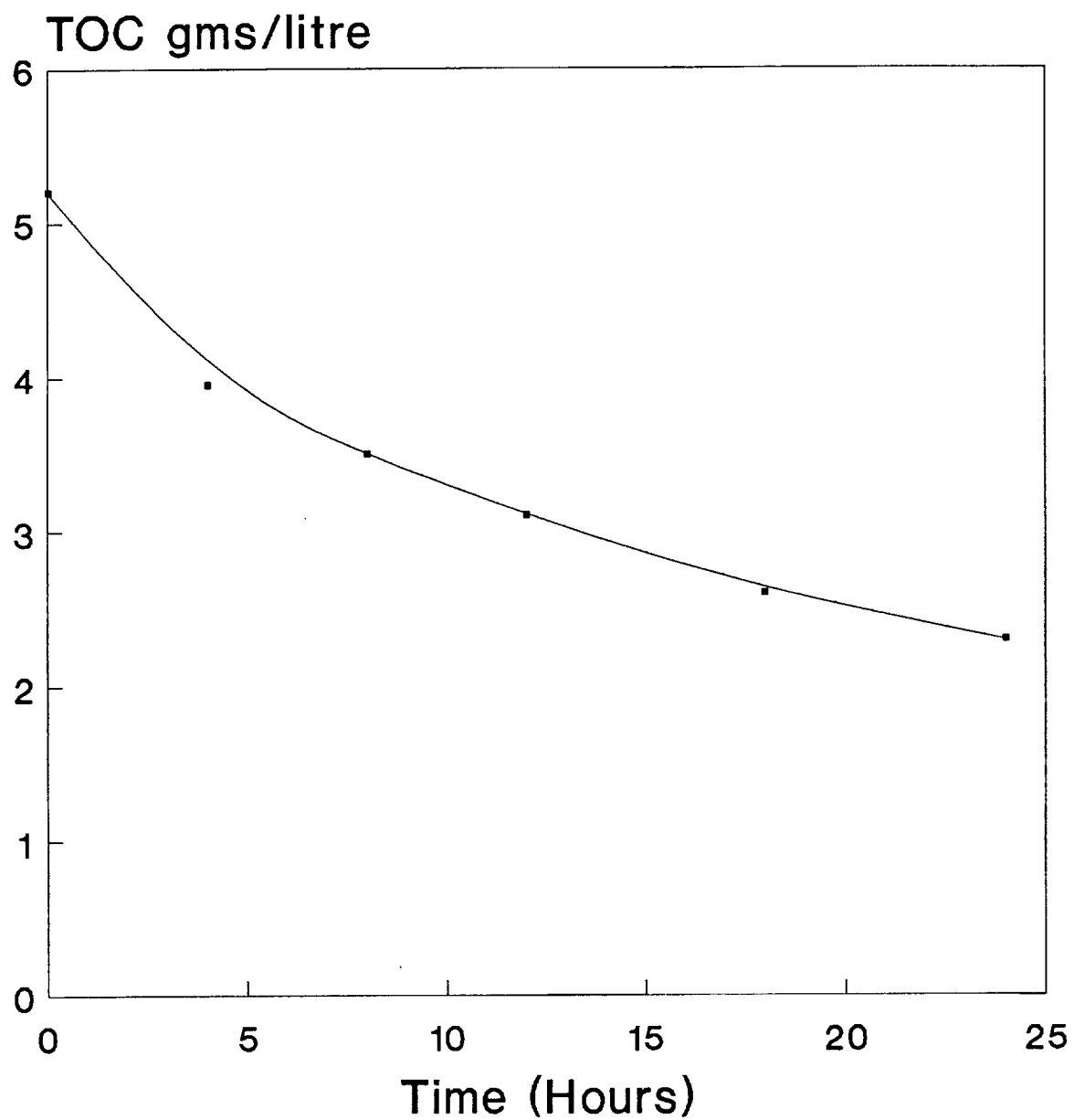
FIG.36 Total organic Carbon variation with electrolysis time of fecal
waste in Urnie at 90°C on Perovskite electrode.
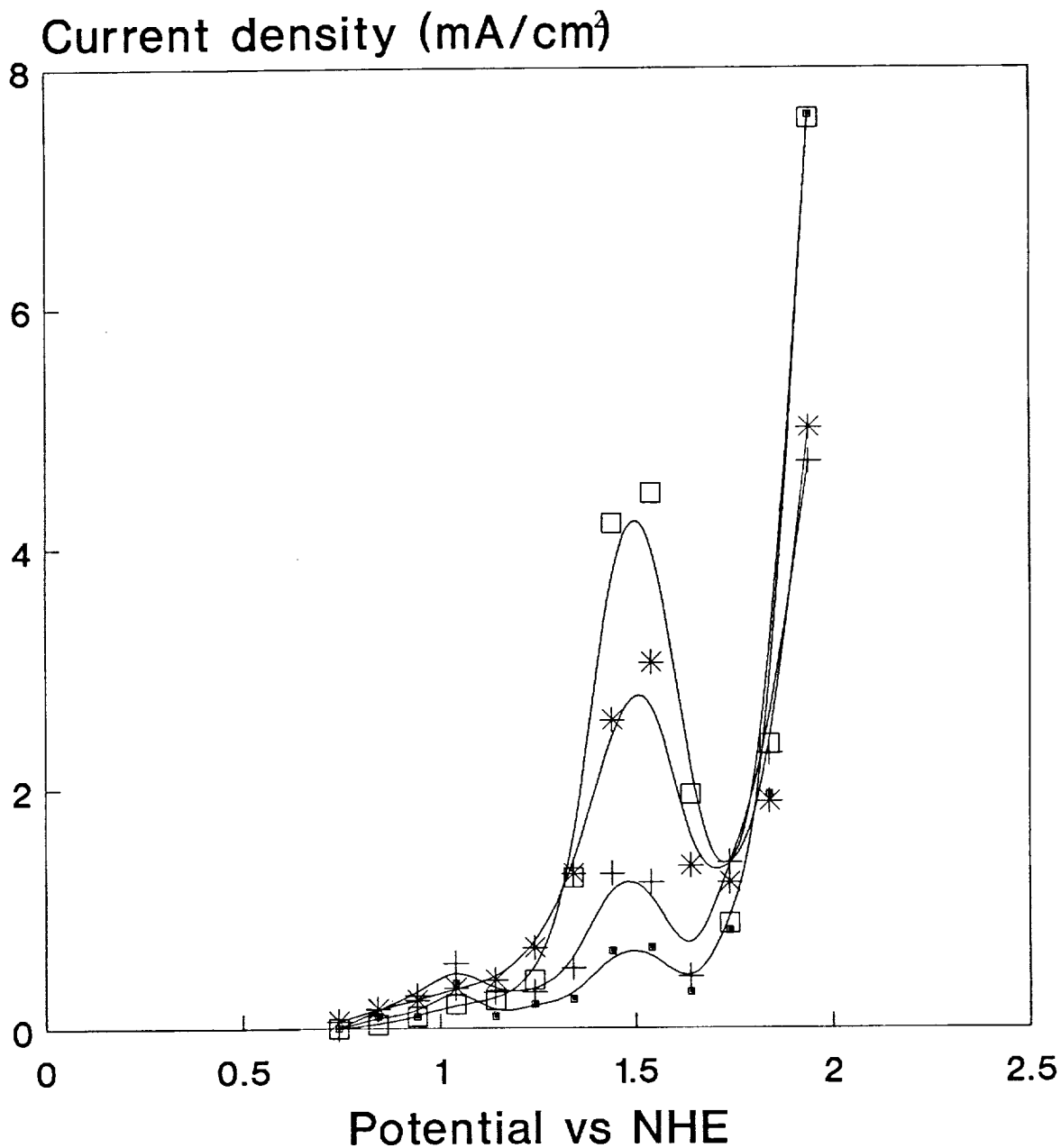
FIG.37 Current Voltage Curves for oxidation of fecal waste in 2.5M H_2SO_4 in Urine at different conc. of Ce^{4+} redox ion. Temperature 90°C. Pt electrode.

(■ 2.5M H_2SO_4 in Urine only; + Urine + Waste; * Urine + Waste + $1x10^{-2}$M Ce^{4+} and □ With $2x10^{-2}$M Ce^{4+})
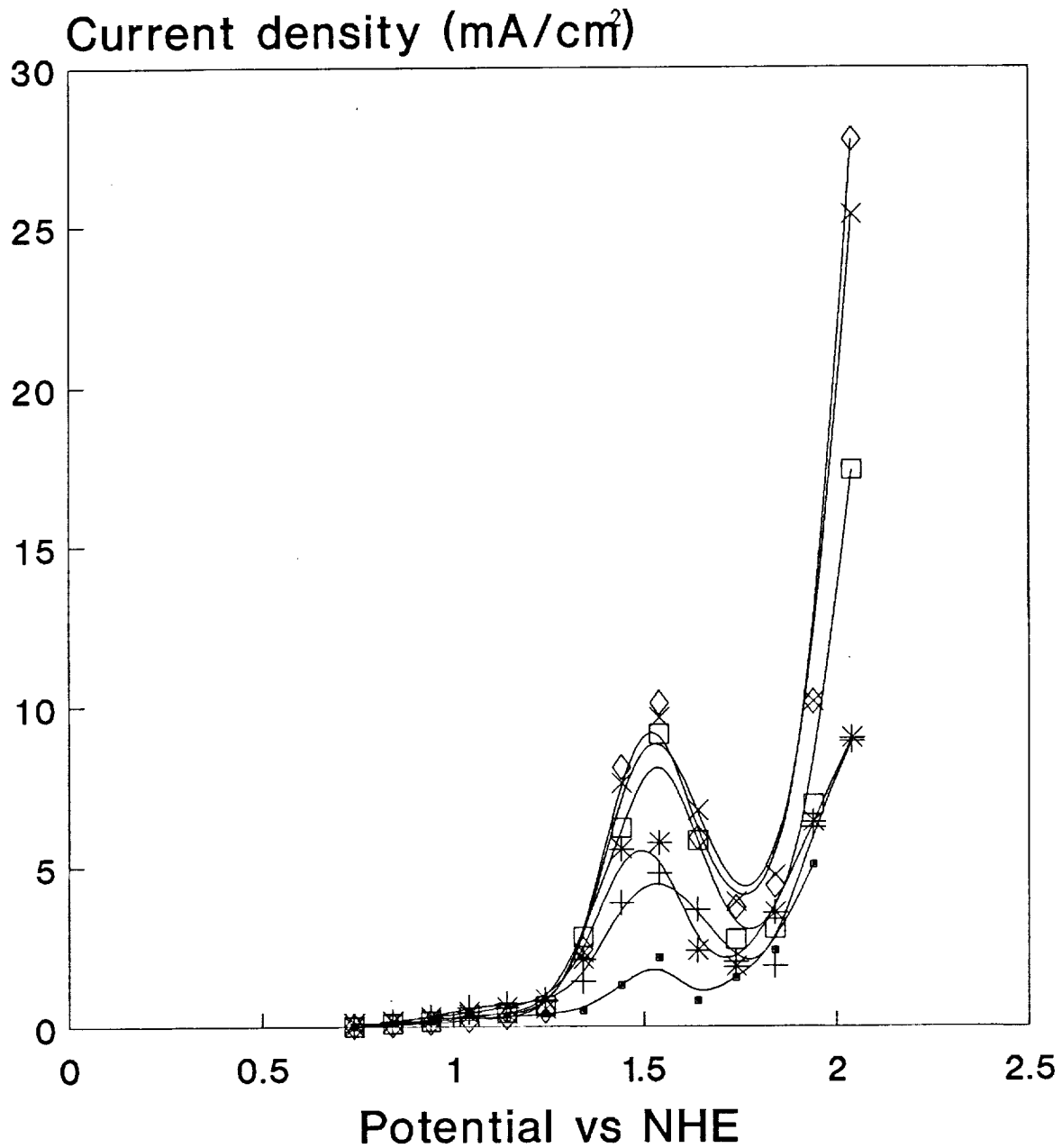
FIG.38 Current Voltage Curves for oxidation of fecal waste in 5M
H_2SO_4 in Urine at different conc. of Cerium redox ion on
Pt electrode. Temperature 90°C.

(▪ 5M H_2SO_4 in Urine only; ✦ Urine + Waste; * With $1x10^{-2}$M
Cerium; ▢ With $2x10^{-2}$M Cerium; X With $5x10^{-2}$M Cerium and
◇ With $7x10^{-2}$M Cerium)
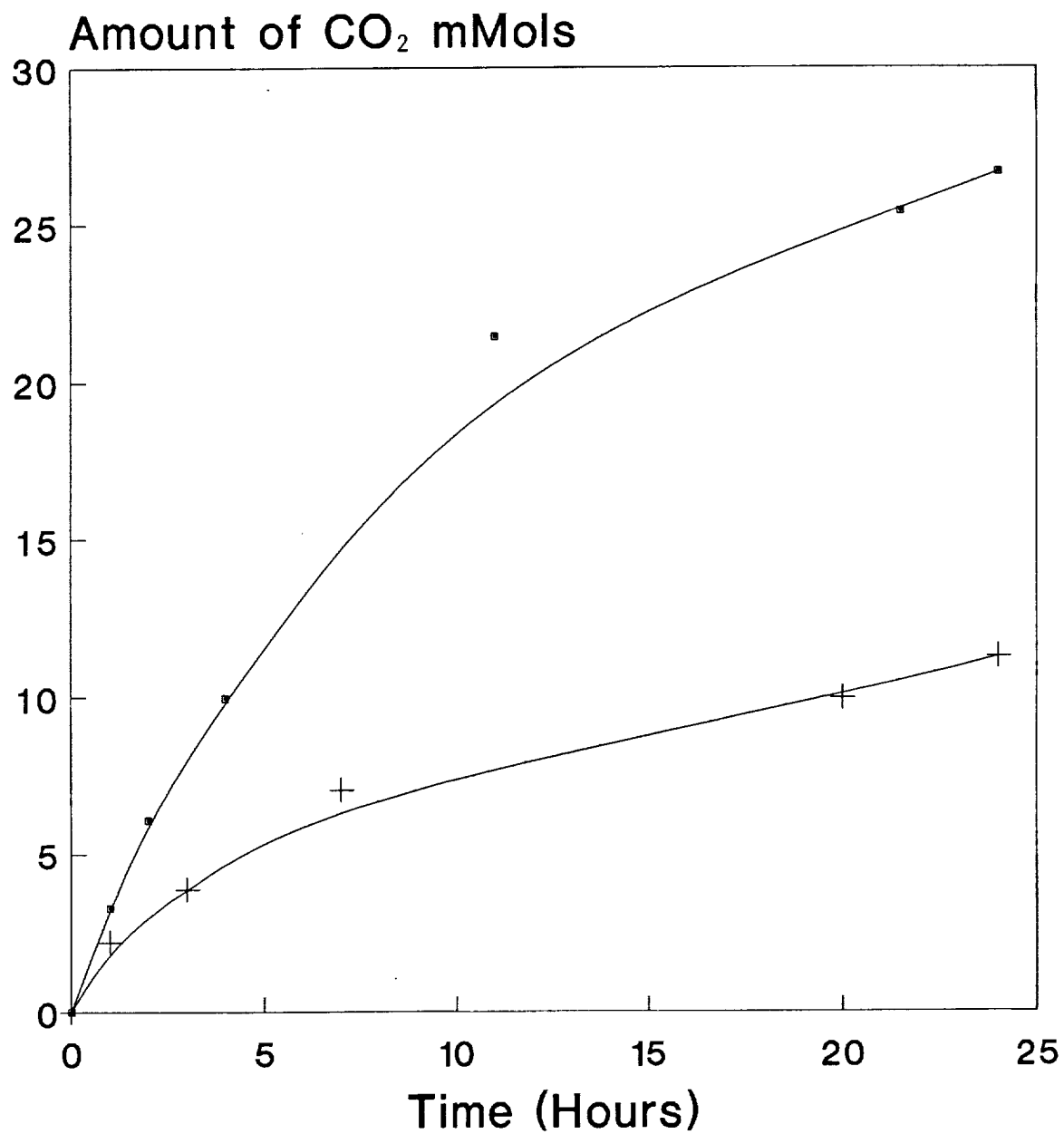
FIG.39 Electrochemical production of CO_2 during electrolysis of fecal
waste in 2.5M H_2SO_4 in Urine at 90°C on Pt electrode.

(+ Without Ce^{4+} and ■ With Ce^{4+})

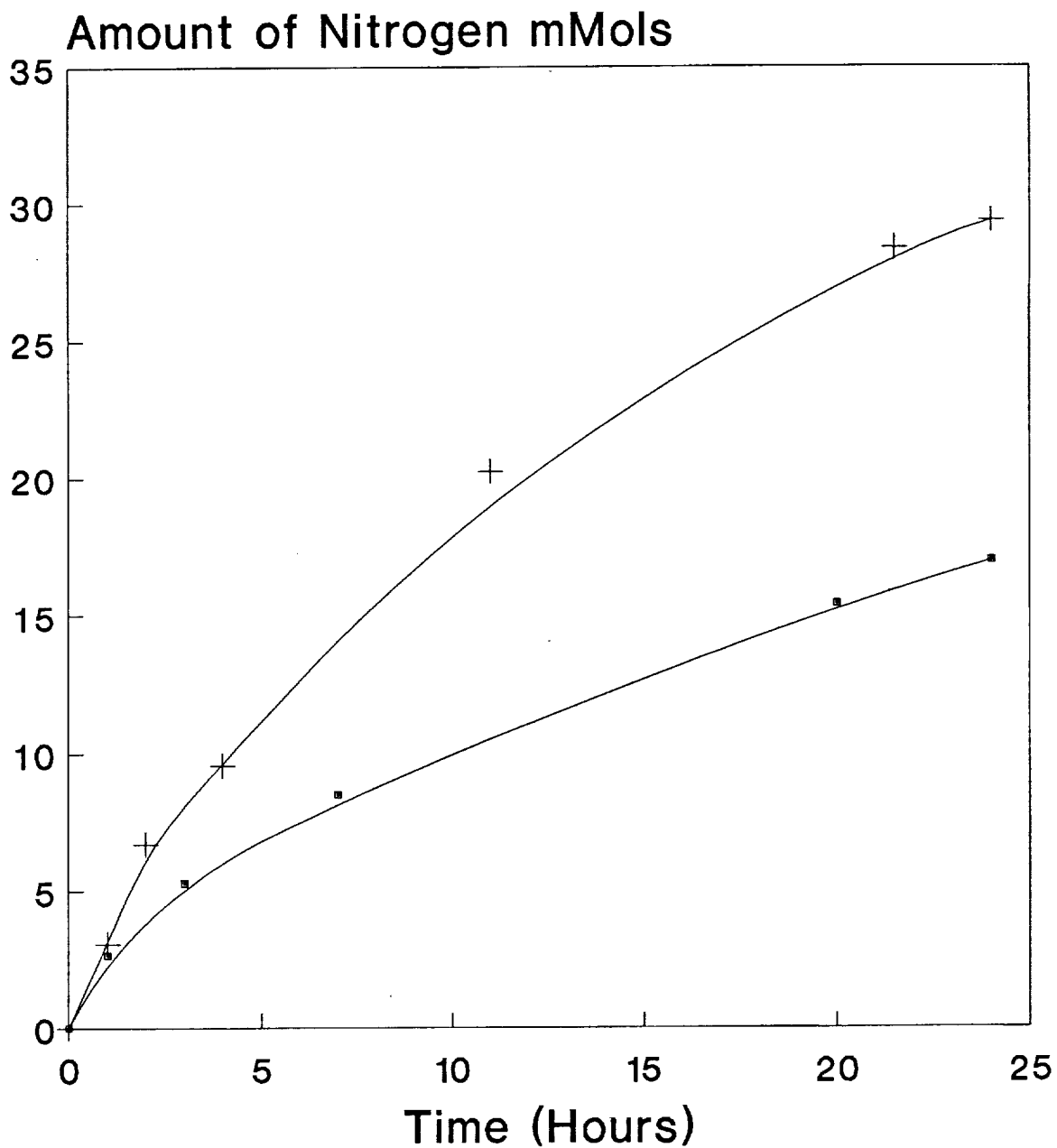FIG.40   Electrochemical production of Nitrogen during electrolysis of
         fecal waste in 2.5M H_2SO_4 in Urine at 90°C on Pt electrode.
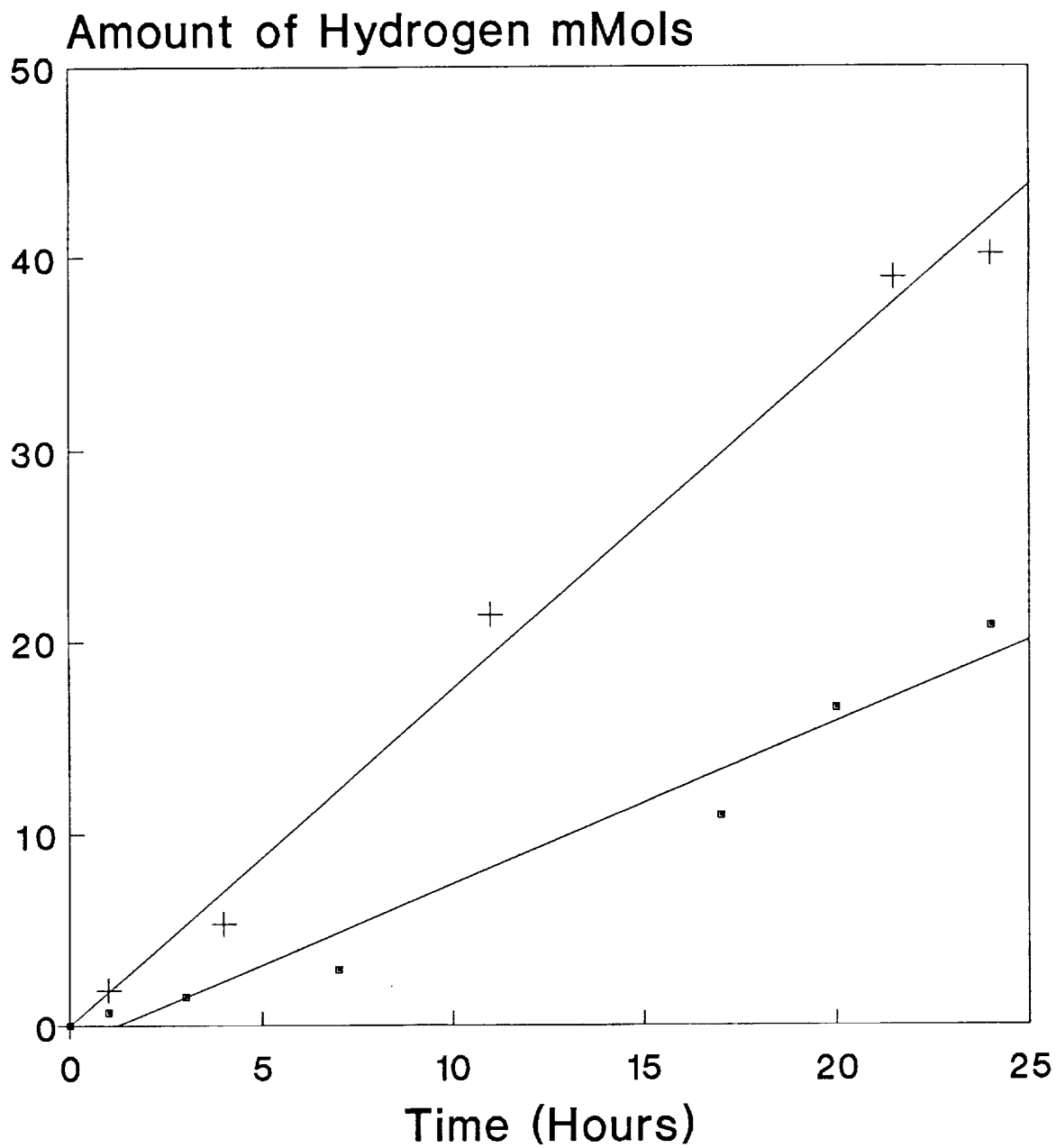   (▪ Without Ce^{4+} and + With Ce^{4+})

FIG.41 Electrochemical production of Hydrogen during electrolysis of
fecal waste in 2.5M H_2SO_4 in Urine on Pt electrode.

(■ Without Ce^{4+} and + With Ce^{4+})

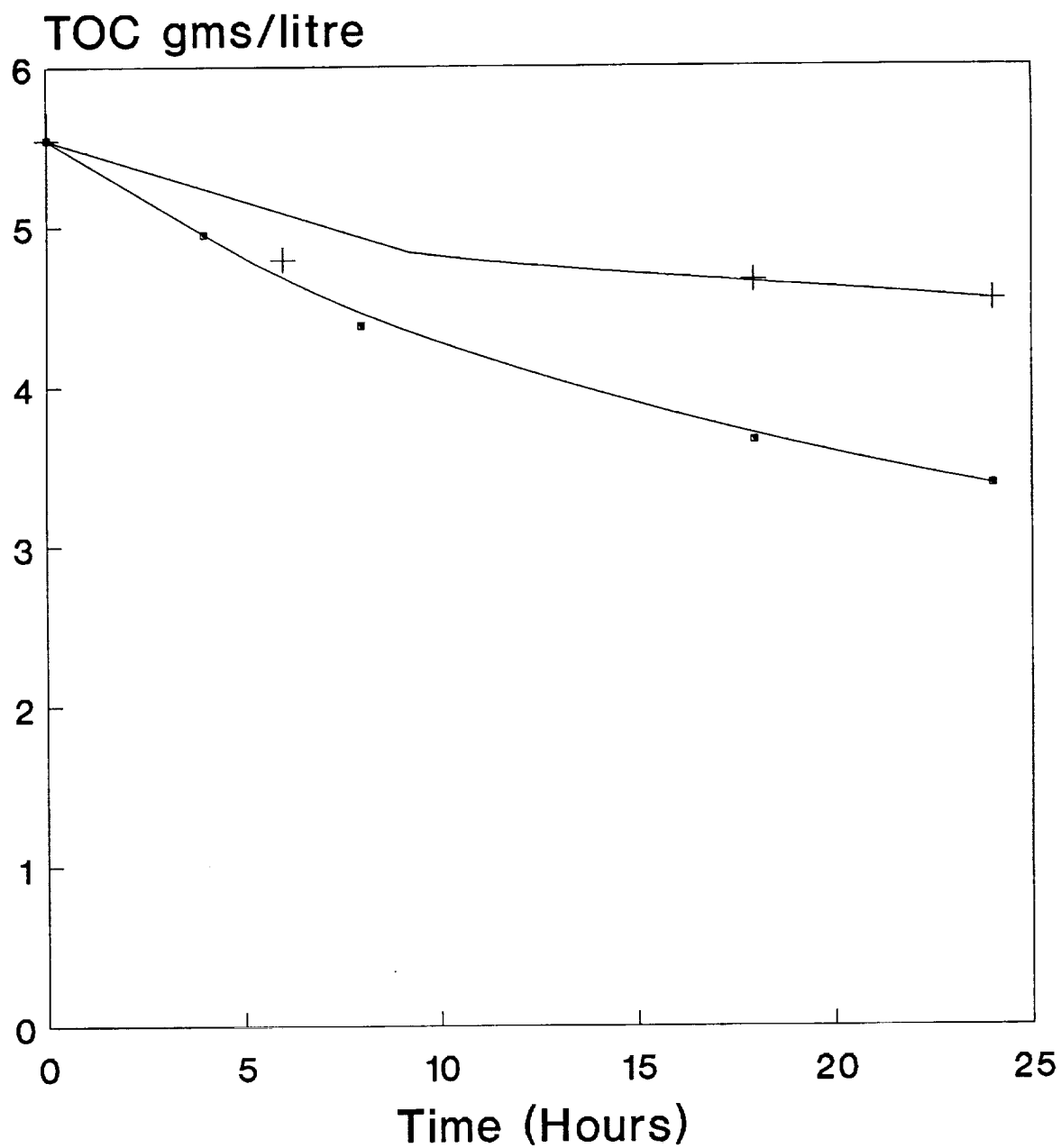FIG.42 Total organic carbon variation with electrolysis time of fecal
waste in 2.5M H_2SO_4 in Urine at 90°C on Pt electrode.

(+ Without Ce^{4+} and ◘ With Ce^{4+})