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EVALUATION OF SOME THIONINE REDOX SYSTEMS AS POTENTIAL  
REGENERATIVE PHOTO GALVANIC BATTERIES

Dwight A. Fine, et al

Naval Weapons Center  
China Lake, California

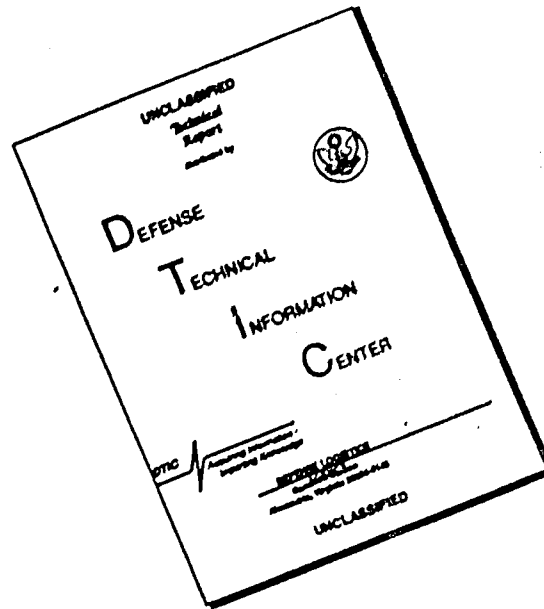
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# Evaluation of Some Thionine Redox Systems as Potential Regenerative Photogalvanic Batteries

by

Dwight A. Fine  
and  
Aaron N. Fletcher  
*Research Department*

FEBRUARY 1976

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## FOREWORD

Compared with the attention given solid state energy conversion devices during the past 20 years, the amount of study given photogalvanic batteries is insignificant. The preliminary investigations reported here use the little-studied cobalt-thionine system to explore problems associated with the development of a practical photogalvanic cell.

This report covers the period 1 July 1974 through September 1975. The study was funded under Task Assignment ZR01107. It was reviewed for technical accuracy by Milton Ritchie and Herbert Richter.

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(U) This report summarizes preliminary investigations on photoelectrical systems involving thionine dye and inorganic reducing agents; these systems offer potential for use as photogalvanic cells in solar energy conversion. The report stresses the thionine-cobalt(II)ethylenediaminetetraacetate (EDTA) system, which has yielded voltages and currents comparable to and in some cases exceeding those which have been reported for the thionine- $\text{Fe}^{3+}$  system. Measurements on the thionine- $\text{CoEDTA}^{2-}$  system have been carried out using two types of transparent electrode, tin dioxide and gold/palladium. Effects of concentration and aging on voltages are reported here, as well as results of closed-circuit measurements under load.

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## INTRODUCTION

The conversion of solar to electrical energy has attracted much attention in the past 20 years, and the recent energy crisis has intensified interest in the problem.<sup>1</sup> The development of a galvanic cell which can be activated by illumination is very desirable but presents many difficulties, the foremost being the finding of a suitable photo-electrochemical system and the designing of a cell having a respectable efficiency.

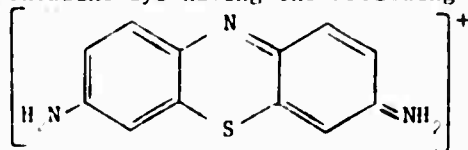
A particularly attractive system involves the use of photosensitive dyes such as thionine or methylene blue. Illumination with visible light raises the dye molecules to an excited state which can be reduced by reducing agents which do not react with the ground state. In the dark, the reduced dye is reoxidized to the ground state of the oxidized form. If this reverse reaction could be made to take place at an electrode rather than in the bulk of the solution, useful current could be drawn. Two means of achieving this would be (1) removal of reaction products and (2) use of a system in which the reverse reaction in solution is slow.

This report summarizes our investigations to date on systems involving thionine dye and inorganic reducing agents. Most of the effort has been devoted to the thionine-cobalt(II)ethylenediaminetetraacetate (EDTA) system.

## SURVEY OF POSSIBLE ELECTROCHEMICAL SYSTEMS

## THIONINE

Thionine is a thiazine dye having the following structure in water:



<sup>1</sup>For a review article with extensive references, see Archer, M.D. "Electrochemical Aspects of Solar Energy Conversion," J APPL ELECTRO-CHEM, Vol. 5 (1975), pp. 17-38.



The visible spectrum of the dye shows a strong absorption band with a maximum at 597 nanometers ( $\epsilon \sim 5 \times 10^4$ ). Illumination raises the molecule to a singlet state which then converts to a triplet state. The triplet can undergo reduction, first to semithionine and then to leucothionine. Both of the reduced forms are virtually colorless. The ground and triplet states, and the reduced forms as well, exist in varying degrees of protonation, depending upon pH.<sup>1-3</sup> The dye undergoes extensive dimerization in aqueous solution at concentrations  $> 10^{-4}$  M; the dimer is not electrochemically active.<sup>4</sup> Addition of organic solvents decreases dimerization, but also decreases the solubility of the dye.

The reduction potential of thionine is strongly dependent on pH. At a pH of ca. 3, where thionine solutions are most stable, the reduction potential is 0.3 to 0.5 volt. Illumination raises the potential to ca. 1.0 volt. Thus a reducing agent with a reduction potential between 0.3 and 1.0 volt is required in order to obtain a photoelectrochemical effect with thionine.

#### INORGANIC REDOX COUPLES

The problem of reducing or preventing the bulk back reaction would be alleviated if the oxidized form of the reductant were insoluble or

Rabinowitch, E. "The Photogalvanic Effect. I. The Photochemical Properties of the Thionine-Iron System," J CHEM PHYS, Vol. 8 (1940), pp. 551-59.

Faure, J., R. Bonneau, and J. Jousset-Dubien. "Etude en Spectroscopie par Éclair des Colorants Thiaziniques en Solution Aqueuse," PHOTOCHEM PHOTOBIOLOG, Vol. 6 (1967), pp. 331-39.

Bonneau, R., J. Faure, and J. Jousset-Dubien. "Study of the Kinetics and Acid-Base Properties of Semireduced Species in the Photo-reduction of Thiazine Dyes in Aqueous Solution," BER BUNSEN PHYS CHEM, Vol. 72 (1968), pp. 263-66.

Bonneau, R., P. F. de Violet, and J. Jousset-Dubien. "Mechanism of Photoreduction of Thiazine Dyes by EDTA Studied by Flash Photolysis. II. pH Dependence of Electron Abstraction Rate Constant of the Dyes in Their Triplet State," PHOTOCHEM PHOTOBIOLOG, Vol. 19 (1974), pp. 129-32.

Bonneau, R., P. F. de Violet, and J. Jousset-Dubien. "Consequences of a Newly Found  $pK_T$  of Thionine on the Mechanism in Basic Solutions," PHOTOCHEM PHOTOBIOLOG, Vol. 21 (1975), pp. 173-77.

Rabinowitch, E., and L. F. Epstein. "Polymerization of Dyestuffs in Solution. Thionine and Methylene Blue," J AMER CHEM SOC, Vol. 63 (1941), pp. 69-78.

somehow removable. Examination of published electrochemical data<sup>10</sup> revealed two possibilities: (1)  $\text{SbO} \cdot \text{SbO}^+$ ,  $E^\circ = 0.58$  volt, and (2)  $\text{VO} \cdot \text{VO}^+$  (at pH  $\sim 2$ ),  $E^\circ = 1.0$  volt. Exploratory experiments were done with each system.

In the case of the antimony couple, the low solubility of available  $\text{Sb(III)}$  salts rendered the use of the system impractical. Attempts to reduce thionine with vanadium oxysulfate were unsuccessful. Further experiments and published data<sup>11</sup> showed that vanadium pentoxide, which forms over a very narrow pH region, is strongly disproportionated to  $\text{VO}^+$  and  $\text{HVO}^-$ . These features of the solubility of the oxide makes the vanadium system impractical for use with thionine, as the thionine concentrations must be less than  $10^{-4}$  M.

The  $\text{Fe}^+/\text{Fe}^{2+}$  couple,  $E^\circ = 0.77$  volt, is well suited for photoelectrochemical reaction with thionine. Photogalvanic behavior of the system  $\text{Fe}^+/\text{thionine}$  has been studied extensively.<sup>12,13,14</sup> The chief disadvantage of the system is the rapidity of the back reaction between  $\text{Fe}^+$  and leucothionine. Several cell designs employing the system have been developed; the maximum engineering efficiency reported to date is 0.026 for incident sunlight.

The  $\text{Co}^+/\text{Co}^{2+}$  couple, in the absence of a complexing agent, has too high a reduction potential (1.81 volts) for use in aqueous solution, but complexation of the cobalt lowers the potential.<sup>15</sup> Complexation with EDTA yields a potential of 0.60 volt, which is quite suitable for photo-reduction of thionine. A possible advantage over the  $\text{Fe}^+/\text{thionine}$

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 Pourbaix, M. *Atlas of Electrochemical Equilibria in Aqueous Solutions*. Oxford, Pergamon Press, 1966.

Potter, A. E., and L. H. Thaller. "Efficiency of Some Iron-Thionine Photogalvanic Cells," SOLAR ENERGY, Vol. 3 (1959), pp. 1-7.

Hann, R. A., D. R. Rosseinsky, and P. Wassell. "Photogalvanic Output from Cells Containing Organic Dye," NATURE PHYS SCI, Vol. 244 (1973), pp. 126-27.

Boston University and Exxon Research and Engineering Co. "Photochemical Conversion of Solar Energy," by Norman N. Lichtin. Boston, Mass., Boston University, February 1975 (Annual Report for 1974). 63 pp. (Report No. NSF/RANN/SE/AER 72-03597/A03/74/4, publication UNCLASSIFIED.)

Rock, P. A. "The Contributions of Ligand Field Stabilization Energies to the Observed Variations with Ligand of Cobalt(II)-Cobalt(III) and Iron(II)-Iron(III) Oxidation Potentials," INORG CHEM, Vol. 7 (1968), pp. 837-40.

system lies in the kinetic inertness of cobalt(III) compared to cobalt(II); this would produce a slower back reaction than the iron system. A second advantage of the cobalt system is the feasibility of working at a higher pH than is possible with iron; the cobalt(II)EDTA and cobalt(III)EDTA complexes are stable at pH's where precipitation of ferric or ferrous hydroxides would occur. One study of photogalvanic properties of the CoEDTA<sup>3-</sup>-thionine system has been reported. In this study, carried out anaerobically at pH 6.5, the uncharged leucothionine species which predominates at this pH was extracted into ether, thereby achieving partial separation of reaction products. Potential differences as high as 0.3 volt between separated products and irradiated solution were observed.

We selected the CoEDTA<sup>3-</sup>-thionine system for detailed study because of the advantages mentioned above, and because of the lack of published information on the system.

#### STUDIES OF PHOTOELECTROCHEMICAL PROPERTIES OF CoEDTA<sup>3-</sup>-THIONINE SYSTEM

##### CHEMICALS AND EQUIPMENT

The thionine used in this study was Eastman Organic Chemicals 86%, recrystallized from ethanol. The cobaltous ammonium sulfate was Baker's Analyzed C.P. reagent  $\text{CoSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$ . The EDTA was obtained from Eastman Organic Chemicals in the form of (ethylenedinitrilo)tetraacetic acid, disodium salt ( $\text{Na}_2\text{H}_2\text{EDTA}$ ).

Stock solutions of thionine were prepared by dissolving the recrystallized salt in 0.001 M hydrochloric acid. Most stock solutions were ca.  $10^{-4}$  M in thionine. Stock solutions of CoEDTA<sup>3-</sup> were prepared by dissolving equimolar quantities of  $\text{CoSO}_4 \cdot (\text{NH}_4)_2 \text{SO}_4 \cdot 6\text{H}_2\text{O}$  and  $\text{Na}_2\text{H}_2\text{EDTA}$  in distilled water. Most stock solutions were 0.010 M in cobalt.

Hydrogen ion concentration was measured with a Radiometer 4d pH meter, standardized daily with Beckman buffer solutions.

Voltage measurements were made with a Keithley Instruments 615 digital electrometer.

Absorption spectra were measured on a Cary 14 spectrophotometer, Ser. No. 244.

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Srinivasan, V., and E. Rabinowitch. "Photochemical Reduction of Thionine by Cobalt(II)EDTA Complex in Water-Ether Emulsion," J CHEM PHYS, Vol. 52 (1970), pp. 1165-68.

The light source for the illumination experiments was a 500-watt tungsten-iodine lamp inside an KI Research Inc. Model 4085 spot heater. This heater concentrates the radiant heat onto a 0.64-centimeter-diameter spot. A 7-centimeter flowing-water filter was built into the spot heater. The lamp housing was air-cooled. Filters opaque to wavelengths  $> 700$  nanometers were inserted in a filter holder located between two condenser lenses. An additional filter blocked out light below 400 nanometers. An AC ammeter was used to measure the current to the lamp. Current control was established by the use of two variacs. A 16-junction bismuth-silver Eppley thermopile (Ser. No. 6802) in conjunction with narrow-band interference filters was used to determine the lamp energy distribution for a given electrical current.

#### BLEACHING STUDIES

The bleaching behavior of CoEDTA  $\pi$ -thionine solutions was studied in order to obtain information on concentration effects and on the rate of the reverse reaction. Stock solutions of thionine and CoEDTA  $\pi$  were pipetted into 10-milliliter volumetric flasks; the flasks were diluted to the mark and exposed to light from a 22-watt desk lamp. Solutions  $5 \times 10^{-7}$  M in thionine were bleached completely. More concentrated solutions were incompletely bleached, or not bleached appreciably. Solutions  $10^{-7}$  M in thionine required cobalt concentrations  $\geq 5 \times 10^{-6}$  M for complete bleaching. Solutions of pH 4 or 1 were not bleached.

The back reaction (recoloration) which occurred upon removal of the light source proved slow enough to be followed spectrophotometrically. This was done by filling an absorption cell with illuminated solution and immediately placing the cell in the sample compartment of the Cary. In some cases the visible spectrum was scanned repeatedly; in other cases the wavelength was set at 597 nanometers (the position of the absorption maximum in the visible band of thionine) and the chart was run at a low speed. This gave a direct display of absorbance versus time. Absorbance at a given wavelength showed an asymptotic increase to the original (unbleached) value. If  $A_t$  = absorbance at time  $t$  and  $A_\infty$  = absorbance of the unbleached solution, plots of  $\log [(A_\infty - A_t)/A_\infty]$  versus time were linear, indicating pseudo first-order conditions with respect to reduced thionine.

The rate of darkening showed a decrease with increasing thionine concentration. Initial runs at varying cobalt concentrations showed an increase in rate with increasing cobalt concentration, but runs at constant ionic strength (0.03, using sodium perchlorate - higher neutral salt concentrations caused precipitation of thionine) showed no variation in rate over a 25-fold range of cobalt concentration. Results of these studies are summarized in Table 1. The pseudo first-order rate constants,  $k_{obs}$ , were obtained from plots of  $\log [A_\infty - A_t]/A_\infty$  versus time. A better quantitative feeling for the darkening rate is provided by the values of  $t_{1/2}$ , the time in minutes required for the absorbance to reach one-half of its final value.

TABLE 1. Rate Data for Darkening of Bleached Solutions of Thionine + CoEDTA<sup>2-</sup>.

T, M x 10 <sup>3</sup>	Co, M x 10 <sup>3</sup>	pH	k <sub>obs</sub> , sec <sup>-1</sup> x 10 <sup>3</sup>	t <sub>1/2</sub> , min
0.56	1.0	~ 3	3.1	38
1.1	1.0	~ 3	1.4	83
2.3	1.0	~ 3	0.85	136
3.4	1.0	~ 3	0.66	175
1.0	0.20	3.2	0.58	201
1.0	1.0	3.0	1.1	104
1.0	5.0	2.6	2.1	56
1.0 <sup>1</sup>	0.20	~ 3	3.1	37
1.0	1.0	~ 3	3.0	38
1.0	5.0	~ 3	3.1	37

NOTE: T = total thionine conc., Co = total cobalt EDTA conc.

<sup>1</sup> At 25 ± 1°C.

<sup>2</sup> This series was run at a constant ionic strength of 0.03 (NaClO<sub>4</sub>).

A few experiments were made on solutions containing 50% ethanol v/v. Ethanol is known to inhibit formation of dimeric thionine.<sup>7</sup> However, it was found to produce two undesirable effects: (1) a decrease in the solubility of thionine and (2) an increase in the rate of the back reaction. These effects would seem to render the use of ethanol undesirable for the cobalt-thionine system.

The most important indication of the bleaching studies was that of a back reaction much slower than the back reaction of the thionine-iron system, where recoloration occurs in less than a minute after illumination.<sup>10</sup>

#### PRELIMINARY CELL MEASUREMENTS

Initial electrical measurements were made with a special cell. The electrodes were plastic plates with a thin coating of gold from Edmund Scientific. A wire lead was cemented to one edge of each plate. The plates were separated by one to five layers of 0.002-inch-thick teflon; a circular area 2 centimeters in diameter was cut from the center of

<sup>10</sup> Heidt, L. J. "The Photochemical Reduction of Thionine," J CHEM EDUC, Vol. 26 (1949), pp. 525-26.

each layer. For measurements, several drops of test solution were placed in the central area, the plates were clamped together, and the leads were connected to a voltmeter. The cell was clamped into position directly above the light source.

Two systems were tested with the cell- $\text{Fe}^{2+}$ -thionine and  $\text{CoEDTA}^{2-}$ -thionine. In both cases, it was found that the illuminated (lower) electrode became negative with respect to the other. Voltage differences between illuminated and dark solutions were small but appreciable. The largest difference obtained for an iron solution was 80 millivolts, for a solution  $1.5 \times 10^{-5} \text{ M}$  in thionine,  $10^{-2} \text{ M}$  in ferrous ammonium sulfate, and  $0.1 \text{ M}$  in sulfuric acid. The largest difference obtained for a cobalt solution was 50 millivolts, for a solution  $2.3 \times 10^{-5} \text{ M}$  in thionine and  $1.0 \times 10^{-4} \text{ M}$  in cobaltous EDTA complex.

#### MEASUREMENTS WITH TIN DIOXIDE ELECTRODE

##### Experimental Approach

It was decided to test different electrodes with the  $\text{CoEDTA}^{2-}$ -thionine system, and to vary solution composition so as to find the compositions yielding maximum voltage changes upon illumination. A primary consideration in electrode reactions is the rate of electron transfer for a given species with a given electrode. Such electron exchange reactions are of particular importance to photogalvanic cells where a variety of electroactive species are present at the electrodes. In order to simplify the observed effects, we chose to test, for most of our studies, a single electrode material in conjunction with a reference electrode, i.e., both dark and light reactions were observed at the same electrode. For those cases where no (or very little) current was drawn, we used a commercial calomel electrode with an asbestos wick as the reference electrode. Here, we relied on the  $10^{14}$ -ohm resistance of the electrometer to minimize any current being drawn from this type of cell.

The transparent electrodes tested were in the form of discs about 2.5 centimeters in diameter. Each electrode was cemented to the bottom of a 24/40 connecting tube from which the joint had been removed. A lead wire was cemented around the outside of each tube at the junction with the electrode, using electrically conducting silver paint. About 10 milliliters of the solution being tested was placed in the tube above the electrode, and the reference electrode was inserted into the solution from above. The tube was positioned so that the transparent electrode was just above the exit port of the light source. One tin dioxide and two gold/palladium electrodes were tested in this manner. The most extensive series of tests was made with a tin dioxide electrode, which was cut from commercial heat-reflecting Pyrex glass. This series will be described in the following sections.

### General Behavior

Illumination was performed using the full tungsten-iodine lamp output from 400 to 700 nanometers so as to subject the dye to any degradation effects from the wide range of energies that might be expected from sunlight. When the broad-band filters were used, the lamp irradiated the sample with 26 milliwatts. The peak of the thionine received 0.88 milliwatts when narrow-band filters were used.

The potential of the solution before illumination, hereafter called  $V_{\text{dark}}$ , often took 15 to 30 minutes to reach a steady value. Upon illumination of the solution through the bottom electrode, the voltage showed a rapid initial drop, followed by a slower decrease. The minimum value, hereafter called  $V_{\text{light}}$ , was usually attained in 5 to 10 minutes, and was much more reproducible for a given solution composition than  $V_{\text{dark}}$ . When the lamp was turned off, the voltage showed similar behavior in rising but rose much more slowly than it had fallen upon illumination. This behavior paralleled the fall and rise in absorbance studied in the bleaching experiments.

### Effect of Thionine Concentration

A series of solutions with identical cobalt concentrations and different thionine concentrations was prepared. Cobalt concentration was  $1.0 \times 10^{-3}$  M; thionine concentration ranged from  $2.7 \times 10^{-6}$  to  $2.2 \times 10^{-4}$  M. The pH of the solutions was not controlled, but was between 2 and 3 in all solutions. Voltage differences,  $\Delta V$ , between dark and illuminated solutions ranged from 40 to 67 millivolts. No significant differences in  $\Delta V$  were found for solutions  $> 10^{-5}$  M in thionine; less concentrated solutions showed smaller  $\Delta V$ 's. Solutions  $< 4 \times 10^{-6}$  M in thionine showed incomplete bleaching; solutions  $> 10^{-4}$  M showed fluorescence.

### Effect of Cobalt Concentration

A series of solutions having a thionine concentration of  $1.09 \times 10^{-4}$  M and cobalt concentrations ranging from  $5 \times 10^{-4}$  to  $9 \times 10^{-3}$  M was studied. Again, pH was between 2 and 3 in all solutions.  $\Delta V$ 's ranging from 46 to 83 millivolts were obtained. Results are shown in Figure 1. No significant increase in  $\Delta V$  is evident for cobalt concentrations  $> 3 \times 10^{-3}$  M, when the thionine concentration is  $1.09 \times 10^{-4}$  M. Bleaching was incomplete for the solutions  $< 2 \times 10^{-3}$  M in cobalt.

### Effect of pH

The potential of the thionine-leucothionine couple is known to decrease strongly with increasing pH.<sup>2</sup> Acidity is also known to have a

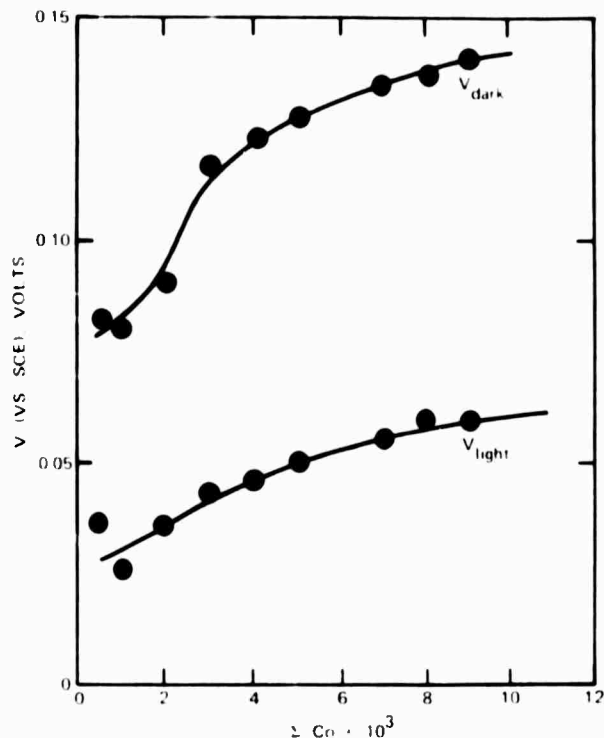


FIGURE 1. Effect of Cobalt Concentration on Potentials of Dark and Illuminated Solutions of Thionine + CoEDTA<sup>2-</sup>. Thionine concentration =  $1.09 \times 10^{-4}$  M in all solutions; pH = 2.6 to 3.1; electrode is tin dioxide.

strong effect on the potential of the illuminated iron-thionine system,<sup>15</sup> with the result that the strongest photogalvanic effects in this system have been observed in solutions which show very little bleaching.

A similar effect was found for the CoEDTA<sup>2-</sup>-thionine system. For example, a solution  $1.1 \times 10^{-4}$  M in thionine and  $5.0 \times 10^{-3}$  M in cobalt EDTA complex showed complete bleaching at a pH of 2 to 3, and gave a  $\Delta V$  of 78 millivolts. When the pH was raised to 6.5, the solution showed little bleaching and strong fluorescence, and gave a  $\Delta V$  of 200 millivolts. The CoEDTA<sup>2-</sup>-thionine system possesses a strong advantage over

<sup>15</sup> Rabinowitch, E. "The Photogalvanic Effect. II. The Photogalvanic Properties of the Thionine-Iron System," J CHEM PHYS, Vol. 8 (1940), pp. 560-66.



the iron system in that the cobalt(II)EDTA and cobalt(III)EDTA complexes are stable at pH  $\cdot$  3, whereas precipitation of ferric and ferrous hydroxides occurs in that pH region.

Results of a series of runs on solutions having constant thionine and cobalt concentrations and different hydrogen ion concentrations (adjusted with NaOH and HCl) are shown in Figure 2. These results indicate that pH is a critical variable, and that the optimum pH region for the photogalvanic effect is between 5 and 7.

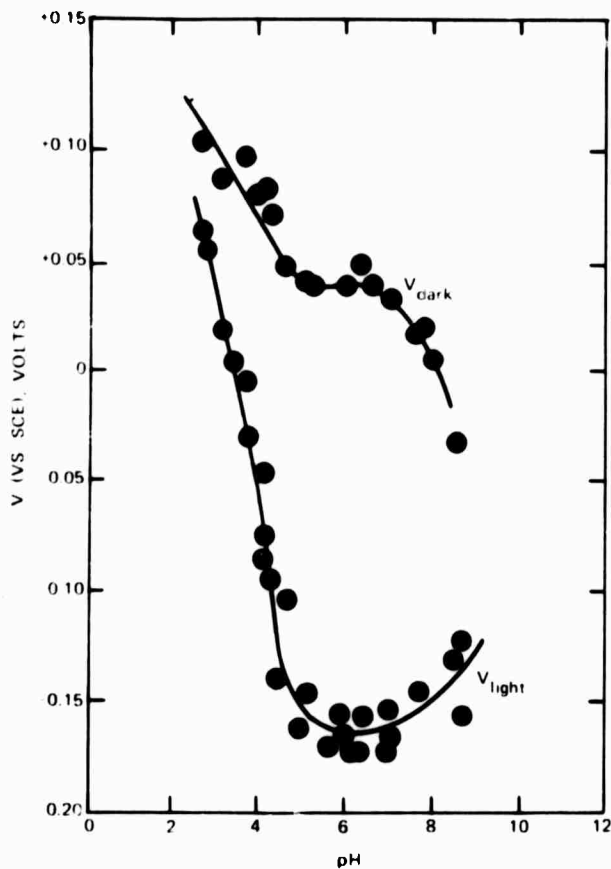


FIGURE 2. Effect of pH on Potentials of Dark and Illuminated Solutions of Thionine +  $\text{CoEDTA}^{2-}$ . Thionine concentration =  $1.06 \times 10^{-4}$  M and cobalt concentration =  $5.0 \times 10^{-3}$  M in all solutions; electrode is tin dioxide.

A series of runs at pH 6.5 on solutions with constant cobalt concentration ( $5.0 \times 10^{-4}$  M) and varying thionine concentrations showed no significant differences for thionine concentrations  $> 10^{-4}$  M; all gave V's of 200 to 225 millivolts. Solutions  $3 \times 10^{-4}$  M in thionine showed fluorescence.

The importance of pH in the CoEDTA<sup>-</sup>-thionine system is ascribable to the effect of acidity on both the dye and the reductant. The existence of different protonated forms of the ground state, triplet state, and reduced dyes has been mentioned. Published data on CoEDTA<sup>-</sup> and H<sub>2</sub>EDTA<sup>4-</sup> indicate an equilibrium between CoEDTA<sup>-</sup> and CoHEDTA<sup>-</sup> at pH 1 to 3, with the protonated species dominating at pH 1 to 2 and the two species present in approximately equal proportions at pH 3. At pH 4, at least 95% of any cobalt(II) present would be in the form of CoEDTA<sup>-</sup>.

#### Effect of Added Electrolyte

The effect of addition of sodium sulfate to solutions  $10^{-4}$  M in thionine and  $10^{-4}$  M in cobalt at pH 6 to 7 was tested. Concentrations of sodium sulfate 0.08 M caused precipitation of thionine. Lower concentrations had no apparent effect on  $\Delta V$ .

#### Effect of Aging

Aging was found to affect several aspects of the system. Stock solutions of both thionine and CoEDTA<sup>-</sup> showed changes upon standing. The deterioration of thionine solutions at pH  $> 3$  has been noted by others. The dye is gradually absorbed on the walls of glass vessels and slowly decomposed. The decomposition is slowed down by acid, but not entirely prevented. This behavior was observed in the present investigation; it was also found that the most dilute solutions showed the most rapid deterioration, as evidenced by decreasing absorbance and visible deposition of dye, and that the deterioration was accelerated by illumination.

Stock solutions of CoEDTA<sup>-</sup> showed a slow oxidation to CoEDTA<sup>0</sup>. The presence of cobalt(III) was readily detectable spectrophotometrically, as oxidation of more than 1% of the cobalt in a 0.010 M stock solution produces a noticeable absorbance at 380 nanometers, in a 2-centimeter cell. This air oxidation of cobaltous EDTA solutions proceeds much more slowly than the air oxidation of ferrous solutions; the 0.010 M stock cobalt solutions were stable for over a month.

The solutions used for photogalvanic measurements were found to be affected by aging; the principal effects were those described above for

<sup>1</sup> The Chemical Society, London. "Stability Constants of Metal-Ion Complexes," Special Publication No. 17. London: The Chemical Society, Burlington House, 1964, pp. 634-36.

thionine. Deterioration of the thionine produced a corresponding deterioration of the photogalvanic effect. Acidity and thionine concentration were the most important factors. All unbuffered thionine-cobalt EDTA solutions showed an increase in pH with time, as did aqueous solutions of thionine alone. For example, a solution  $1.0 \times 10^{-4}$  M in thionine showed an increase in pH from 4.72 up to 6.64 in 7 days. Comparable changes occurred in thionine-cobalt EDTA solutions. The optimum pH region for the photogalvanic effect, 5 to 7, is the region of most rapid deterioration of thionine. The deterioration is repressed at higher thionine concentrations. Some typical data are shown in Table 2.

TABLE 2. Effect of Aging on Photogalvanic Properties of Solutions of Thionine + CoEDTA<sup>2-</sup>.

Age, days	T, $\text{M} \times 10^4$	Co, $\text{M} \times 10^4$	pH orig. soln.	pH aged soln.	V orig. soln., mV	$\Delta V$ aged soln., <sup>a</sup> mV
7	1.1	5.0	6.13	7.96	178	76
6	5.5	2.0	6.01	7.58	261	184
7	10.9	5.0	6.91	7.74	250	224
12	1.1	2.0	5.79	7.51	254	98
12	10.9	1.0	6.47	7.39	226	189
12	10.9	5.0	6.29	7.72	225	169
12	10.9	9.0	6.11	7.68	194	176

NOTE: T = total thionine conc., Co = total cobalt conc.;  $\Delta V = V_{\text{dark}} - V_{\text{light}}$ .

<sup>2</sup> Stored at room temperature under oxygen in a Pyrex container.

It was found that the use of potassium dihydrogen phosphate buffers could stabilize the pH of thionine-CoEDTA<sup>2-</sup> solutions at values  $\geq 5.7$ . (Use of potassium hydrogen phthalate buffers of lower pH was impractical, as phthalate precipitates thionine.)<sup>17</sup> A solution  $10^{-4}$  M in thionine,  $5 \times 10^{-4}$  M in cobalt,  $3.4 \times 10^{-2}$  M in  $\text{H}_2\text{PO}_4^-$ , and  $2.7 \times 10^{-3}$  M in  $\text{HPO}_4^{2-}$  showed an increase in pH of 5.71 to 5.88, less than 0.2 unit, over 30 days. Simultaneous monitoring of pH and  $\Delta V$  on buffered and unbuffered solutions having identical thionine and cobalt concentrations revealed no appreciable change in either pH or  $\Delta V$  (ca. 200 mV) for the buffered solution over a period of 6 days, while in the unbuffered solution the

<sup>17</sup> Schatz, E. A. "The Photogalvanic Effect of Dye-Reducing Agent Solutions." Thesis, Polytechnic Institute of Brooklyn, 1961.

pH had increased from 5.73 to 6.47 and  $\Delta V$  had decreased from 199 to 98 millivolts. A gradual decrease in absorbance and  $\Delta V$  was observed for the buffered solution over a period of 3 weeks. Recently, Clark and Eckert reported no degradation of photogalvanic response of the iron-thionine system (over an unspecified length of time) under anaerobic conditions, using carefully purified thionine.<sup>14</sup> The combination of buffering and exclusion of air would probably give high stability to thionine-CoEDTA<sup>-</sup> solutions.

The studies described in this section indicate that the optimum concentration of thionine for the thionine-CoEDTA<sup>-</sup> system is ca.  $1 \times 10^{-4}$  M. Concentrations  $10^{-5}$  M produce lower  $\Delta V$ 's. Concentrations between  $10^{-4}$  and  $10^{-3}$  M produce comparable  $\Delta V$ 's for fresh solutions, but show faster deterioration with age. Increasing the thionine concentration above  $10^{-4}$  M leads to an increase in the proportion of electrochemically inactive dimers. Solutions  $1 \times 10^{-4}$  M in thionine are approximately 15% dimerized; solutions  $1 \times 10^{-3}$  M are about 50% dimerized. Also, solubility problems arise at concentrations  $5 \times 10^{-3}$  M. It was also found that, although the thionine stock solutions were fairly stable at pH  $\leq 5$ , fresh solutions yielded significantly larger  $\Delta V$ 's than aged solutions. The optimum cobalt concentration appears to be around  $5 \times 10^{-4}$  M.

#### MEASUREMENTS WITH GOLD/PALLADIUM ELECTRODES

Besides the tin dioxide electrode, two gold/palladium electrodes were tested. The electrodes were prepared by coating windows in a vacuum evaporator. The vacuum evaporator system was by Edwards Vacuum Components. The window was placed on a stage in the evaporator and the evaporator was pumped down to the  $10^{-5}$  torr range. The stage, with the window, was rotated while gold/palladium was evaporated from a hot tungsten filament. A coating of approximately 150 Å of 60% gold-40% palladium was obtained. Coating thickness was calculated from  $T = 40.3 d \sqrt{L}$ , where  $T$  = thickness in angstroms,  $d$  = lead wire diameter in mils = 8,  $L$  = lead wire length in cm = 7.5, and  $r$  = distance of filament to specimen in cm = 11.5.

The first electrode tested showed ca. 11% transmission throughout the visible region. Measurements on thionine-CoEDTA<sup>-</sup> solutions indicated a low transparency for this electrode. Solutions which showed  $\Delta V$ 's of 25 to 45 millivolts with the tin dioxide electrode showed  $\Delta V$ 's of only 2 to 5 millivolts with this gold/palladium electrode, which was not employed in subsequent photogalvanic measurements.

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<sup>14</sup> Clark, W. D. K., and J. A. Eckert. "Photogalvanic Cells," SOLAR ENERGY, Vol. 17 (1975), pp. 147-50.

The second gold/palladium electrode showed the following transmittance characteristics:

$\lambda$ , nm	% transmission
400-500	21
500-550	Rises from 21 to 27
550-600	Rises from 27 to 31
600-750	Rises from 31 to 35

This electrode yielded considerably higher  $\Delta V$ 's than the tin dioxide electrode when tested with identical solutions, even though the tin dioxide electrode had much higher transmission (60 to 70%) in the visible range. Solutions which showed  $\Delta V$ 's of 150 to 190 millivolts with the tin dioxide electrode showed  $\Delta V$ 's of 230 to 255 millivolts with the second gold/palladium electrode.  $V_{\text{dark}}$  versus the calomel reference electrode was 100 to 150 millivolts higher for the gold/palladium than for the tin dioxide electrode.

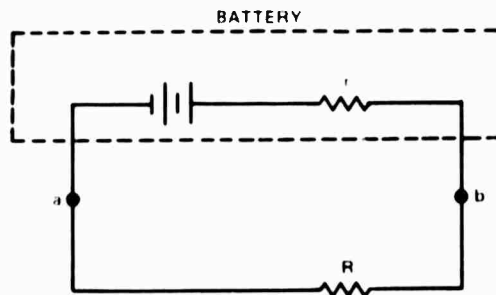
Gold/palladium thus appears to be a superior electrode material to tin dioxide, if the electrode is properly prepared. The second gold/palladium electrode was used in the closed-circuit measurements described in the following sections. The largest  $\Delta V$  obtained to date was obtained with this electrode: 352 millivolts, for a solution  $1.0 \times 10^{-4}$  M in thionine,  $5.0 \times 10^{-2}$  M in CoEDTA<sup>2-</sup>, pH 5.02.

#### CLOSED-CIRCUIT MEASUREMENTS

##### General Considerations

Previous measurements on the thionine-CoEDTA<sup>2-</sup> system had been open-circuit measurements. It is desirable to make closed-circuit measurements with varying resistances in the circuit, in order to obtain an indication of the internal resistance of the system, the current drawn by the system under load, and the efficiency of the system.

Let us consider the electrical circuit shown in the diagram below.



The internal resistance of the battery is  $r$ , the load resistance is  $R$ , the open-circuit voltage of the battery is  $\mathcal{E}$ , the voltage drop across points  $ab$  is  $V$ , and the current is  $i$ . Here

$$i = V/R = \mathcal{E}/(R + r) \quad (1)$$

The voltage of the battery under load is

$$V = \mathcal{E} - ir = iR \quad (2)$$

Rearrangement of Eq. 1 and 2 yields

$$r = R(\mathcal{E} - V)/V \quad (3)$$

The useful output power,  $P$ , is determined by

$$P = iV = i \cdot R = V^2/R \quad (4)$$

while the power lost to self-heating by the battery,  $p$ , is given by

$$p = i^2 r \quad (5)$$

The total power generated by the battery,  $\mathcal{P}$ , is determined by

$$\mathcal{P} = P + p = \mathcal{E} i \quad (6)$$

Considering the internal resistance of the battery to be represented by a resistance in series with the electromotive force element,  $\mathcal{E}$ , the maximum usable (output) power under load can be represented by<sup>19</sup>

$$P_m = 1/2 \cdot i_m^2 R = \mathcal{E}^2/4r \quad (7)$$

where  $i_m$  is the current at maximum output power. Under the conditions of maximum power,

$$2V_m = \mathcal{E} \quad (8)$$

$$r = R \quad (9)$$

and

$$2i_m = i_{SC} \quad (10)$$

where  $i_{SC}$  is the current when the cell is short-circuited (where  $\mathcal{E} = i_{SC}r$ ) and  $V_m$  is the voltage at maximum power.

The above relationships are due to the principle that power transferred from one part of a circuit to another is a maximum when the

impedances are equal.<sup>19</sup> Table 3 shows the variation that can be expected in the above parameters for differing values of the load resistance  $R$ . It should be noted that at the maximum output of the battery, no useful power can be drawn. The maximum useful power occurs when the battery is producing half of its maximum possible output power, and then only one-fourth of its maximum output power can be used in an external circuit.

TABLE 3. Example of Variation of Load Resistance Assuming Constant internal Resistance,  $r$ .

$R$ , ohms	$V$ , volts	$I$ , amps	$p$ , watts	$P$ , watts	$\eta$ , watts
0	0	$/r$	$/r$	0	$/r$
0.5r	$/3$	$/1.5r$	$/2.25r$	$/4.5r$	$/1.5r$
$r$	$/2$	$/2r$	$/4r$	$/4r$	$/2r$
1.5r	$3/5$	$/2.5r$	$/6.25r$	$/4.17r$	$/2.5r$
2r	$2/3$	$/3r$	$/9r$	$/4.5r$	$/3r$
		0	0	0	0

The cell power efficiency can be considered to be made up of the light incidence efficiency  $\eta(1)$ , the light absorption efficiency  $\eta(2)$ , the driving force efficiency  $\eta(3)$ , the current per photon efficiency  $\eta(4)$ , and the efficiency of transfer to the external circuit  $\eta(5)$ . Care must be used in the interpretation of the results of different workers, particularly with respect to  $\eta(1)$  and  $\eta(2)$ . In the reference cited in Footnote 11, for instance,  $\eta(1)$  and  $\eta(2)$  are not included, and the efficiency calculations are based only upon the light that is absorbed by the solution. The driving force efficiency  $\eta(3)$  for thionine is  $\Delta V/2.1$  if the absorption peak of thionine is taken as the wavelength at which light is absorbed.

#### Experimental Approach

The gold/palladium electrode described in the preceding section was employed for the closed-circuit measurements reported here. The reference electrode was a mercury-mercurous sulfate-saturated potassium sulfate electrode; the mercury had a surface area of  $7 \text{ cm}^2$ . This electrode had a flushable saturated potassium sulfate salt bridge. The electrode construction is shown as Figure XIV-5 of the reference cited in Footnote 20. A resistance bridge having resistors of 5.0, 10.0, 50.7,

<sup>19</sup> Sears, F. W. *Principles of Physics II - Electricity and Magnetism*. Cambridge, Mass., Addison-Wesley Press, Inc., 1964. Chapter 5, pp. 112-45.

<sup>20</sup> Lingane, J. J. *Electroanalytical Chemistry*. New York, Interscience Pub. Inc., 1952.

and 101.1 kilo-ohms was constructed. The test solution was illuminated, and when the minimum  $V_{light}$  was reached, the different resistors were inserted and the resulting voltage noted. Results for a series of measurements are shown in Table 4, along with values for short-circuit current (obtained by extrapolation to zero resistance) and calculated values for maximum power output.

TABLE 4. Data From Closed-Circuit Measurements Using Unfiltered Light and Gold/Palladium Electrode.

Soln. <sup>a</sup>	Output voltages, volts x 10 <sup>3</sup> :					i <sub>SC</sub> amps x 10 <sup>3</sup>	P, maximum output, watts x 10 <sup>3</sup>
	Open circuit (V <sub>OC</sub> )	Load resistance, ohms x 10 <sup>-3</sup>					
		101.1	50.7	10.0	5.0		
A	351	276	150	56	31	6.2	2.2
B	347	278	169	49	26	5.2	1.8
C	238	174	123	31	17	3.4	0.81
D	276	177	111	25	13	2.6	0.72
E	326	287	190	46	26	5.2	1.7

<sup>a</sup> Solution composition:

A:  $Co = 5.0 \times 10^{-4}$ , pH = 5.31

B:  $Co = 5.0 \times 10^{-4}$ , pH = 5.65

C:  $Co = 1.0 \times 10^{-4}$ , pH = 4.87

D:  $Co = 1.0 \times 10^{-4}$ , pH = 5.84

E:  $Co = 1.0 \times 10^{-4}$ , pH = 5.04

Thionine was  $1.0 \times 10^{-4}$  M in all solutions.

In order to calculate efficiency of power conversion, the power incident on the transparent electrode and the power absorbed by the solution must be known, as well as the power output. Also, monochromaticity of incident light is essential for quantum efficiency calculations. A calibration was made of power output of the tungsten-iodine lamp versus amperage of the controlling variac. A filter which transmitted light of 600-nanometers wavelength, the wavelength of maximum absorbance of thionine, was used during the calibration and during subsequent power output measurements. The calibration enabled calculation of the power incident on the transparent electrode. Transmission data for the electrode material permitted estimation of the power incident on the cobalt-thionine solution. At the concentrations and solution volumes employed, essentially all of this power should be absorbed by the solution. This was confirmed by single-beam transmission measurements of solutions before and after illumination. Comparison of absorbed flux versus maximum power output yields the monochromatic power efficiency.



Data and calculated efficiencies for a typical solution are shown in Table 5. Comparison with Table 4 shows that insertion of the 600-nanometer filter cuts down considerably on open-circuit voltage and on current drawn under load. The efficiency of power conversion is low, primarily because the system has a high internal resistance. The highest efficiency reported to date for a thionine system is 1.5% for total power output, or 0.75% for output at maximum useful power,<sup>1</sup> using a much more sophisticated arrangement of electrodes, solution, and illumination.

TABLE 5. Data From Closed-Circuit Measurements Using Monochromatic Light and a Gold/Palladium Electrode.

$V$  and  $i$  are voltage difference and current difference, respectively, between light and dark conditions at the electrode.

$R$ , ohms $\times 10^{-3}$	$V$ , <sup>2</sup> volts $\times 10^{-3}$	$i$ , amps $\times 10^{-7}$
10.0	10	1.0
50.7	42	0.86
101.1	76	0.76
	273 ( $V_{OC}$ )	0

<sup>2</sup> Solution composition: Thionine =  $1.0 \times 10^{-4}$  M, Co(EDTA)<sup>2-</sup> =  $5.0 \times 10^{-4}$  M, pH = 5.72 (buffered).

Calculated efficiencies from closed-circuit measurements using monochromatic light and a gold/palladium electrode are:

Power incident on electrode = 0.886 milliwatt  
 Power transmitted to solution = 0.274 milliwatt  
 Maximum power output =  $V_{OC} \times i_{SC} = 2.7 \times 10^{-7}$  watt  
 Output at maximum useful power =  $0.7 \times 10^{-7}$  watt  
 Maximum output power efficiency based on 600-nanometers light into solution = 0.026%  
 Driving force efficiency =  $(0.273/2.08) \times 100 = 13.2\%$

### CONCLUSIONS

The measurements described in this report indicate that the thionine-CoEDTA<sup>2-</sup> system offers possibilities for use in a photogalvanic cell. Voltages and currents comparable to and in some cases exceeding those reported for the thionine-Fe<sup>3+</sup> system have been obtained. The system possesses several advantages over the iron system: (1) the reverse reaction proceeds much more slowly, (2) work at higher pH is feasible, leading to larger voltages, and (3) solutions of cobaltous

EDTA complex are less sensitive to air oxidation than ferrous solutions. The use of a single electrode material for both "dark" and "light" reactions, however, yields a lower power efficiency than the two electrode materials used by Clark for the iron-thionine system.