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PRELIMINARY STUDY OF SOME GRAPHITE ELECTRODE SURFACES RESPONSIV--ETC(U)
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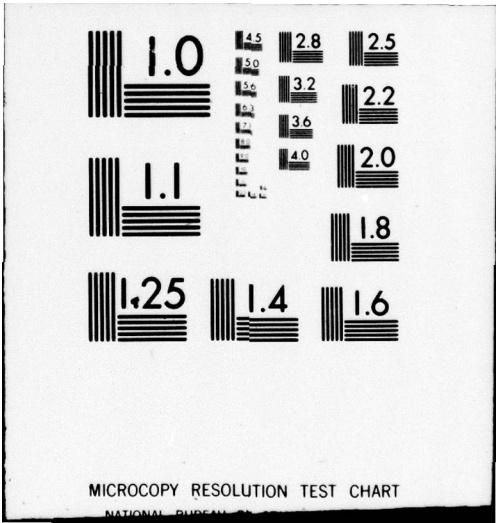
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PRELIMINARY STUDY OF SOME GRAPHITE ELECTRODE SURFACES
RESPONSIVE TO IRON AND HEAVY METALS BY
SINGLE-SWEEP VOLTAMMETRY.

by

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Gerald C. Whitnack
Research Department

(18) GIDEP

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INTRODUCTION

The objective of this preliminary study is to see if it is feasible to use some new chemically modified graphite surfaces as electrodes in the field analysis of iron and heavy metals such as copper, lead, cadmium, and zinc in aqueous solution by single-sweep peak voltammetry.¹

Mercury electrode surfaces such as the dropping mercury electrode (DME), mercury pool, and the hanging mercury drop, along with pyrolytic graphite and wax-impregnated graphite electrodes, have been used successfully in the laboratory for the voltammetric analysis of iron and heavy metals;¹⁻⁹ however, all these electrodes have a decided disadvantage in environmental analytical work because of the toxicity and handling of mercury and difficulties in handling and operating the electrodes in the field. Thus, the replacement of the DME with a solid electrode such as the chemically modified graphite type should greatly increase the use of voltammetry in the field analysis of heavy metals and other toxic materials.

Many types of graphite electrodes (pyrolytic, glassy carbon, wax-impregnated, etc.) have been fabricated and studied during the past 20 years.¹⁻⁸ Voltammetric and chronopotentiometric investigations indicate the electrodes are useful to the determination of both inorganic and organic substances; however, poor results are usually obtained with the pyrolytic graphite types in acid solutions, where the acid penetrates the electrode in a non-uniform manner with time. Impregnating the graphite electrode with wax under vacuum helps some in the acid solution performance but major problems still exist in the use of the wax-impregnated electrodes.

¹ R. N. Adams. *Electrochemistry at Solid Electrodes*. Marcel Dekker, Inc., New York, 1969.

² R. G. Clem. *Anal. Chem.*, Vol. 47 (1975), p. 1778.

³ R. G. Clem, G. Litton and L. D. Omelas. *Anal. Chem.*, Vol. 45 (1973), p. 1306.

⁴ P. J. Elving, I. Fried and W. R. Turner. *Polarography 1964*. Graham Hills, Editor, Vol. 1, MacMillan and Company, Ltd., London, 1966, p. 277.

⁵ J. J. Lingane. *J. Am. Chem. Soc.*, Vol. 68 (1946), p. 2448.

⁶ K. G. McLaren and G. E. Batley. *J. Electroanal. Chem.*, Vol. 79 (1977), p. 169.

⁷ R. S. Nicholson and I. Shain. *Anal. Chem.*, Vol. 36 (1964), p. 706.

⁸ Louis Meites. *Polarographic Techniques*. Interscience Publishers, New York, 2nd Edition, 1965.

⁹ S. L. Tackett and L. F. Wieserman. *Analytical Letters*, Vol. 5 (9) (1972), p. 643.

A new approach to the chemical modification and fabrication of graphite electrodes has been recently reported by Clem and co-workers.^{2,3} The present investigation focuses on the voltammetric application of some styrene-impregnated graphite electrodes prepared by Clem. The preparation of the electrode consists of impregnating the graphite with styrene monomer in a quartz tube under <1 atm of helium. The monomer is polymerized, cross-linked, and chemically grafted to the graphite by prolonged β - γ irradiation in a 5000 Ci, 60 cobalt source. The surface of the electrode is renewed rapidly by wiping the surface a few times with a No. 5 filter paper before placing the electrode into a new sample. In a nitrogen stirred solution the surface of the Clem-prepared graphite electrode appeared to be renewed sufficiently to give excellent reproducibility of single-sweep voltammograms with iron and heavy metals. Satisfactory results were obtained in neutral, weakly acidic solution (pH 3-6), or weakly alkaline solutions (pH 7-9) with these electrodes. This report presents data for iron and some heavy metals obtained from some preliminary experiments performed at NWC with the new graphite electrodes of Clem and NWC polarographic equipment. A short discussion of the results with some conclusions related to future work is given.

EXPERIMENTAL

APPARATUS AND MATERIALS

A single-sweep polarograph known as the A-1660 Davis Differential Cathode-Ray Polarotrace (DCRP), manufactured by Southern Analytical Instruments Company, England, and a DCRP constant-temperature bath and stand were used in this study. A Moseley 2D X-Y recorder was used to obtain the data. Figure 1 shows the polarograph with stand and recorder. A field digital polarograph, designed and built at NWC, was also used in some of the work. Figure 2 shows this instrument with DCRP stand and a field cell. Typical solid electrodes used in this study are shown in the foreground.

The measurements are made at $25^{\circ} \pm 0.1^{\circ}\text{C}$ on two milliliters of solution placed into a 5 milliliter capacity quartz cell. Oxygen free nitrogen is bubbled through the solution before and during the voltage scans. A continuous voltage sweep of 250 mV per second is applied to the DME or graphite electrode by the instrument. A 500 mV span in voltage is covered every two seconds, followed by a 5 second delay before the cycle repeats; thus, every 7 seconds, a current-voltage curve is recorded by the X-Y recorder and can be seen on the cathode-ray tube screen of the A-1660 polarograph.

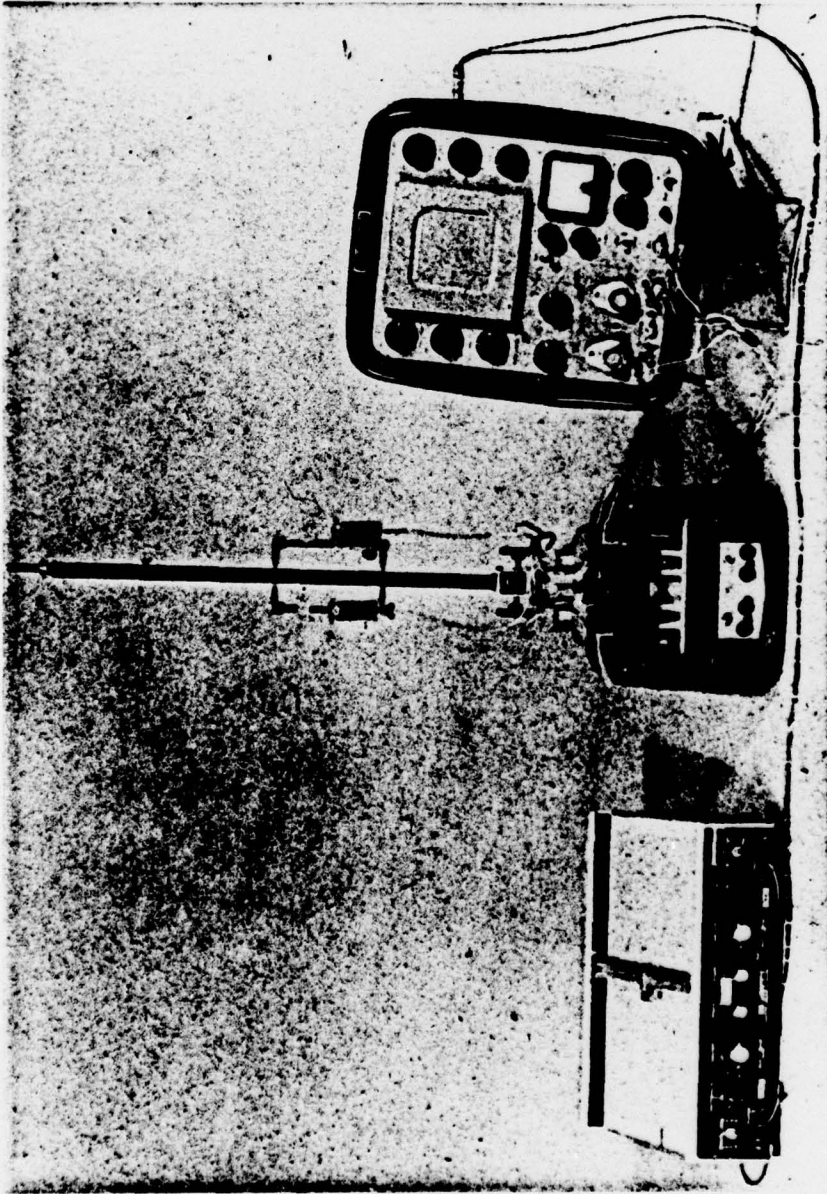


FIGURE 1. Davis Differential Cathode-Ray Polarotrace
With Stand and Recorder. (Neg. SL 097771)

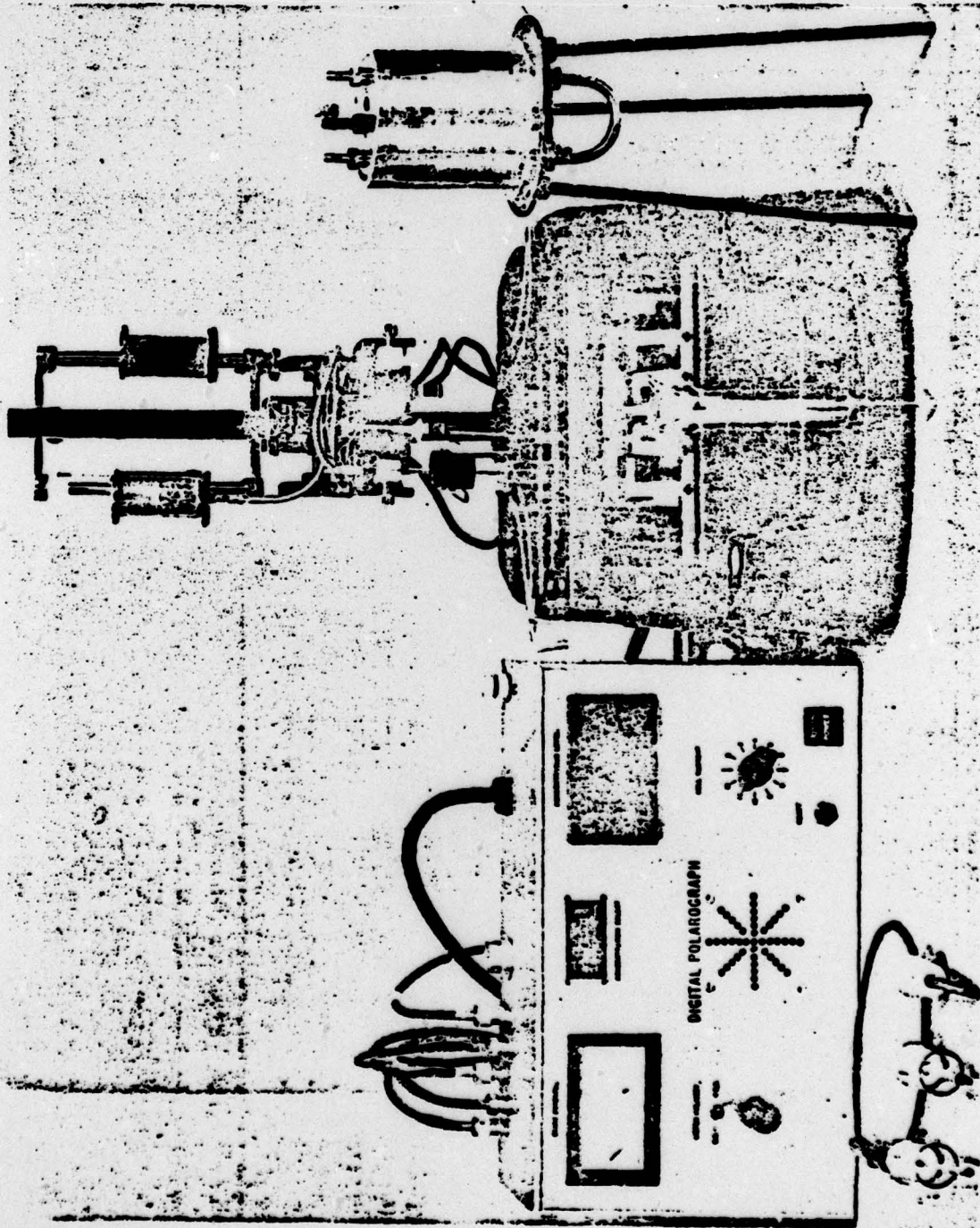


FIGURE 2. Digital Polarograph With Field Cell and Stand.

A mercury pool is used as a quiet electrode in this work, with either a DME or a graphite electrode serving as the working electrode. The graphite electrodes are mounted in the DCRP stand electrode holder in the same manner as the DME. The graphite electrode is lowered into and raised out of the solution easily by the DCRP electrode holder. Mild solution agitation, to keep the graphite electrode surface renewed before each single sweep of voltage, is provided by a slow rate of nitrogen bubbles continuously entering the cell solution from the side of the cell. The bubbles rise directly to the surface of the solution along the side of the electrode, and thus keep the solution stirred and the electrode surface clean, without causing serious noise problems during the recording of the current-voltage curve.

Standard solutions of the heavy metals were prepared in the 10^{-3} Molar concentration range from c.p. reagent grade chemicals. Aliquots of these solutions were added to various supporting electrolytes for polarographic and voltammetric study. Fe(II) and Fe(III) stock solutions were made up in 10^{-3} Molar HCl solution. Nitrogen was bubbled through the 10^{-3} Molar HCl prior to dissolution of Fe(II) salt. $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $\text{FeNH}_4(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$ salts, respectively, were used to prepare the iron standard solutions.

A supporting electrolyte that was 0.5 Molar with respect to both sodium carbonate and oxalic or citric acid, respectively, was prepared from c.p. Bakers Analyzed Chemical Reagents. This solution was chosen as the best for the simultaneous determination of Fe(II) and Fe(III) in natural water or wastewater solutions.

In addition to the graphite electrodes prepared by Clem, a glassy carbon electrode prepared and sold by Chemtrix, Inc., Beaverton, Oregon, was used in this investigation.

INVESTIGATIVE PROCEDURE (VOLTAMMETRY)

The procedure is essentially that developed by the writer and reported in the open literature.¹⁰

A 2-ml sample is placed into a 5-ml-capacity A-1660 polarographic cell to which has been added a small amount of mercury. The graphite electrode, whose tip surface has been wiped clean with No. 5 filter paper and rinsed well with distilled water, is lowered into the cell solution and positioned such that the tip of the electrode is just below the side arm of the cell (N_2 purge tube). A slow and steady rate

¹⁰ G. C. Whitnack. *Anal. Chem.*, Vol. 47 (4) (1975), p. 618.

of nitrogen gas is allowed to purge the cell solution of dissolved oxygen (about 3-5 minutes) before the polarograph is switched to the on position. The start potential of the polarograph is then set to sweep the desired voltage range. The sweep rate of the polarograph is fixed at 500 millivolts in 2 seconds. A 5-second delay in the circuit then allows the cell conditions to equilibrate before the next voltage sweep occurs. The cycle is 7 seconds and so a new polarogram can be seen on the cathode-ray screen of the polarograph every 7 seconds. With a DME the mercury drop is knocked off by the instrument at precisely the same time in the growth of the drop, and affords excellent reproduction of the polarogram from one drop to the next drop (each new drop provides a new surface). With the styrene-impregnated graphite solid electrodes, the 5-second quiescent period appears to allow enough time for the graphite surface to be washed free of reaction products, under nitrogen purge conditions described above, to the extent that good reproducible voltammograms are obtained on successive sweeps of the polarograph. When the nitrogen gas flow through the solution in the polarographic cell is stopped, a steady decrease in current with each successive sweep of voltage is observed. As long as a steady flow of nitrogen is allowed to bubble up through the cell solution around the graphite electrode, good reproducible curves can be obtained with these surfaces over long periods of continuous operation (hours). The electrode surface can also be renewed quickly by removing the electrode from the sample solution, wiping the tip briskly with No. 5 filter paper, and then washing the surface well with distilled water before reuse. Electrodes treated in this manner appeared to reproduce well in the same sample solution under the same polarographic conditions. The electrodes also appear to have good shelf life. If washed with distilled water, and then rubbed briskly with No. 5 filter paper followed by a water rinse, they can be stored in the laboratory in a closed container for several months without any apparent loss in surface response.

RESULTS AND DISCUSSION

Fe(II) and Fe(III) can be determined simultaneously in wastewater samples by conventional polarography at a DME. An average relative percent error of 2.2% for Fe(II) and 2.1% for Fe(III) over a range of 10 to 500 ppm has been previously reported.⁹ A supporting electrolyte, 0.5 Molar with respect to both sodium carbonate and oxalic acid, proved satisfactory. A typical DME polarogram in this electrolyte, Fe(II)-Fe(III) mixture [34 ppm Fe(II) and 43 ppm Fe(III)], is shown in Figure 3. The pH of the supporting electrolyte was 3.0 and the Fe(II) was measured at +0.10 volt and Fe(III) at -0.60 volt, respectively, after subtraction of the supporting electrolyte residual current.

Since citric acid solutions containing large amounts of iron were one of the wastewater types needed to be monitored in the field, by a polarographic analytical device, a supporting electrolyte 0.5 Molar

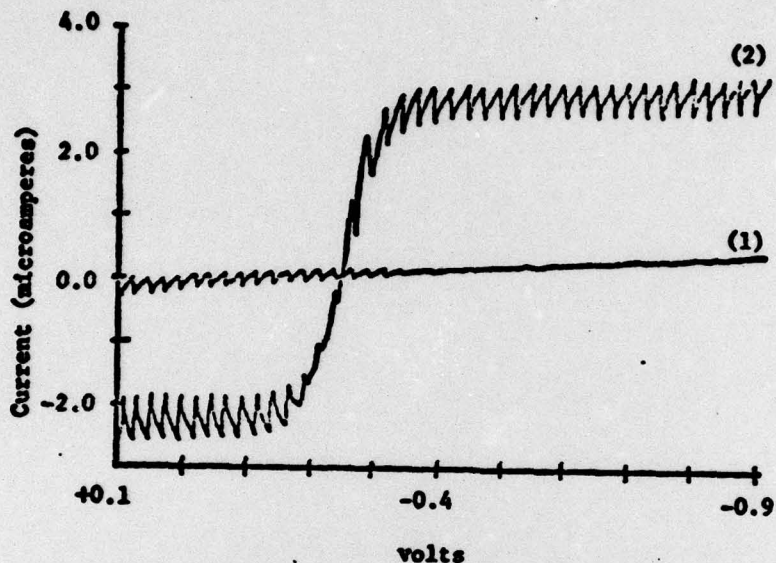


FIGURE 3. Polarogram of (1) Electrolyte, (2) Fe(II)-Fe(III) Mixture in Electrolyte.

with respect to both sodium carbonate and citric acid was tried and found satisfactory. Citric acid solution alone was unsatisfactory. A typical Fe(III) single-sweep polarogram (2 ppm) obtained at a DME in the sodium carbonate-citric acid solution is shown in Figure 4. The pH of this solution was 5.30. Lingane⁵ has previously shown that in 0.5 Molar sodium citrate solution of pH 6.1, the ferric-ferrous couple is strictly reversible and states that "a 0.5 Molar citrate solution of pH between 6 and 7 should be very useful for analyzing mixtures of ferric and ferrous iron by polarography."

In this study, the new graphite electrodes of Clem were substituted for the DME and the polarographic conditions described herein under "Investigative Procedure" were used. Well defined and reproducible polarograms were obtained for iron, copper, lead, cadmium, and zinc in the part-per-million concentration range with these chemically modified graphite electrodes. Some typical single-sweep voltammograms obtained for copper and for zinc in sea water with these electrodes are shown in Figure 5. The sea water sample was shown to contain no polarographically measureable copper and zinc before standard additions of copper and zinc were made to the sample. Good linearity is shown in Figure 6 for added concentrations of copper from 5 to 20 parts-per-million. Lead, cadmium, and zinc (Figure 7) all showed good linearity in sea water at the "Clem" electrodes in this part-per-million concentration range. Though it has been reported previously⁶ that zinc in high concentrations ($200 \mu\text{g l}^{-1}$) was not very electroactive at wax-impregnated graphite electrodes, no such effect with zinc was observed with the "Clem" electrodes in the 5 to 20 ppm range.

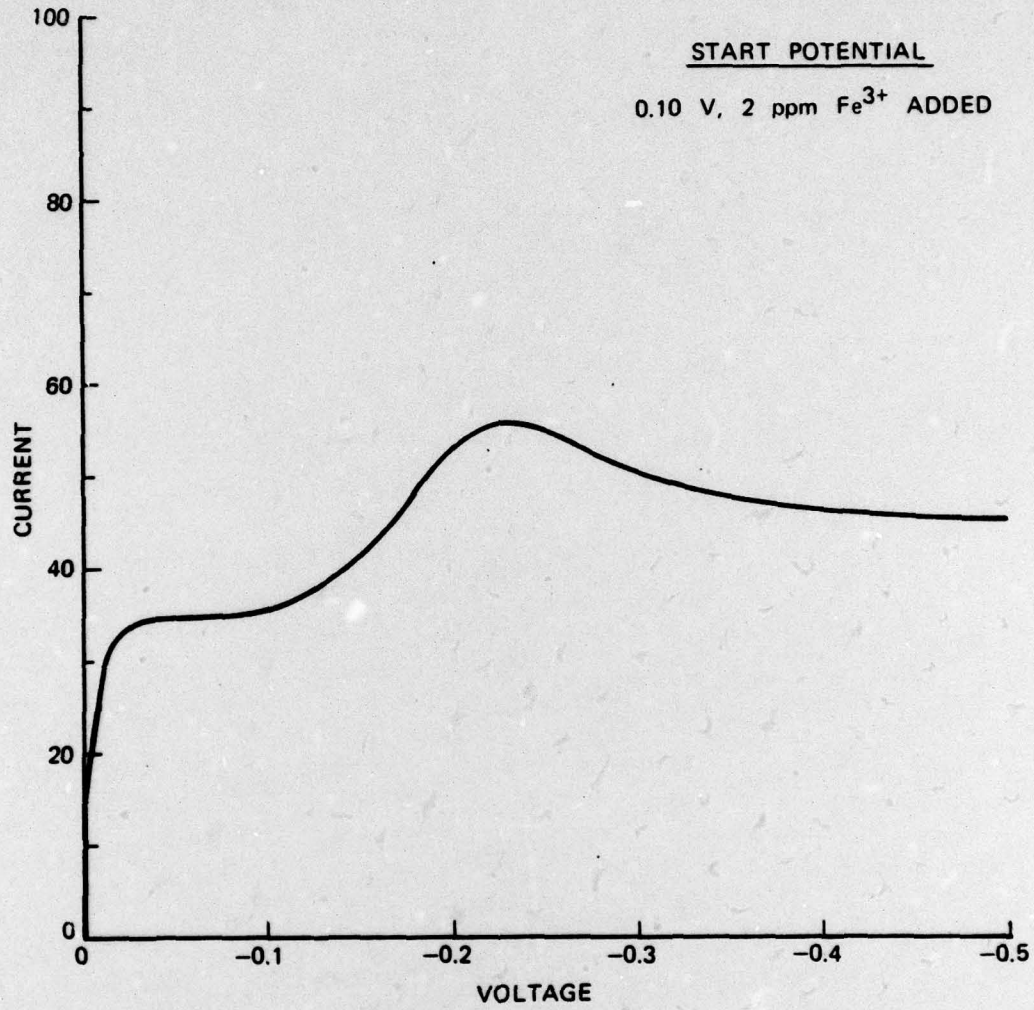


FIGURE 4. Fe³⁺ in Sodium Carbonate - Citric Acid Electrolyte.

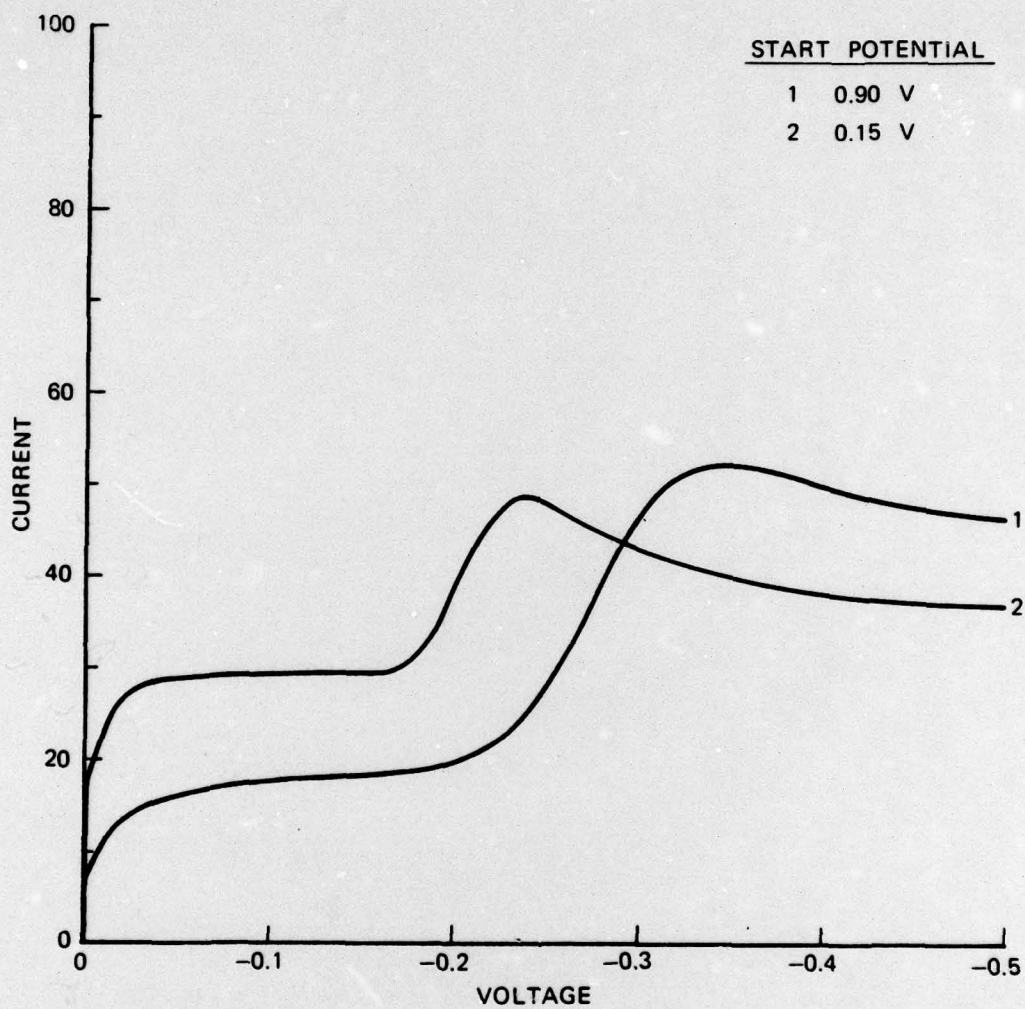


FIGURE 5. Voltammograms of Cu^{2+} and Zn^{2+} in Sea Water. Curve 1, 15 ppm Zn^{2+} added; curve 2, 5 ppm Cu^{2+} added.

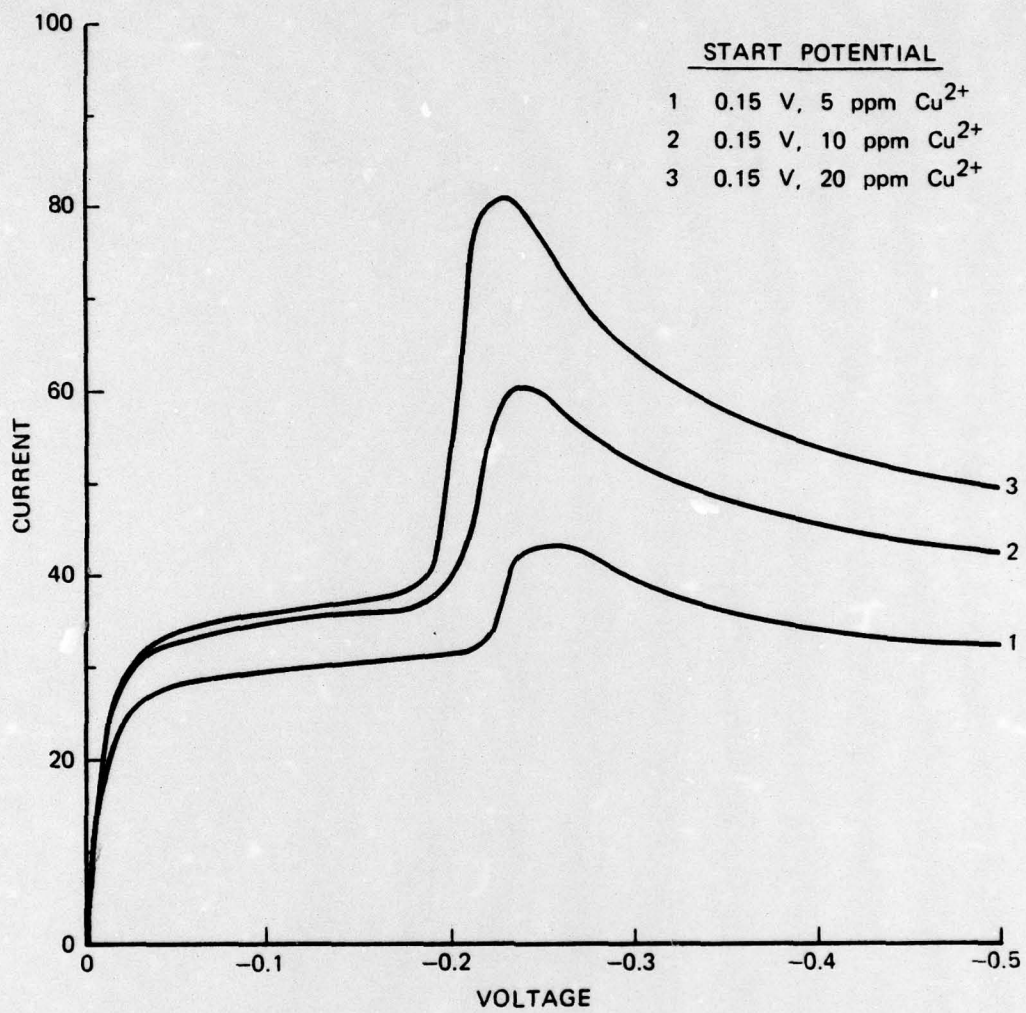


FIGURE 6. Cu^{2+} Added to Sea Water.

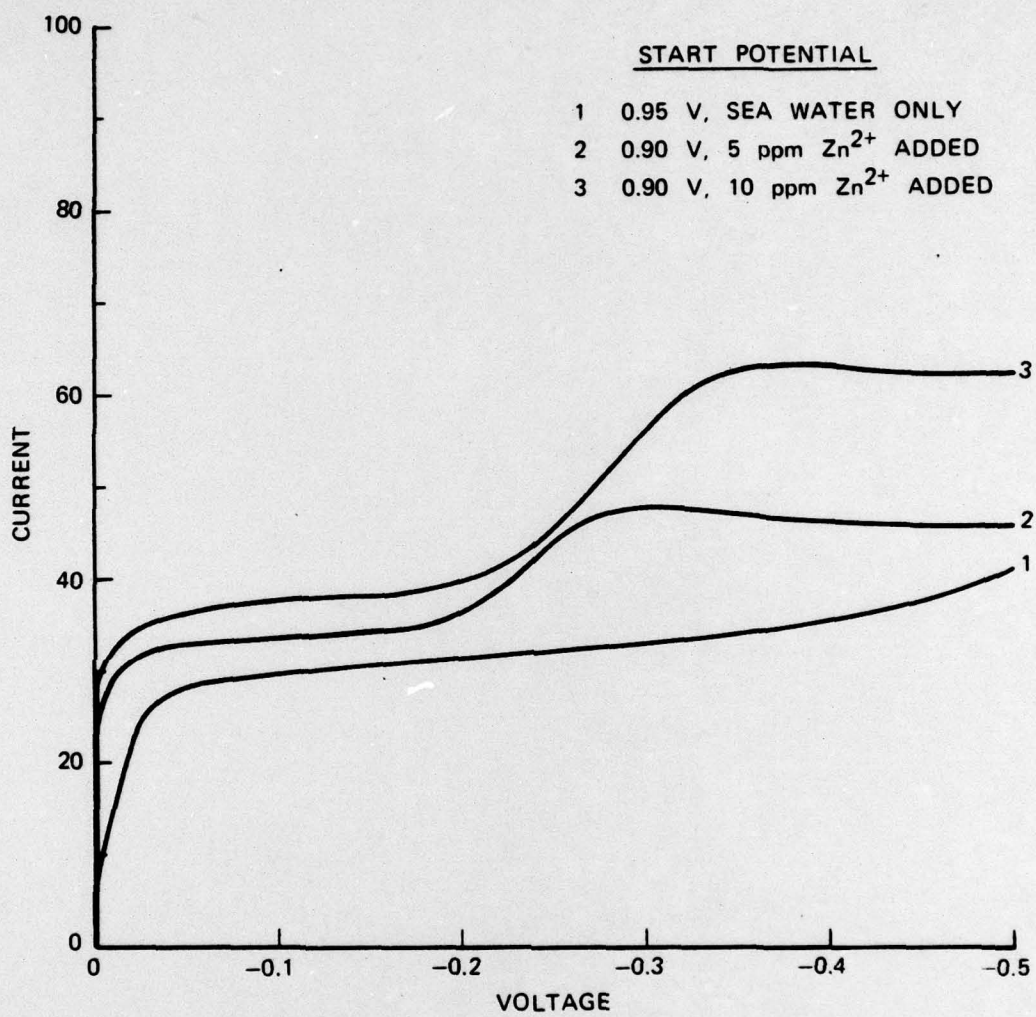


FIGURE 7. Zn²⁺ Added to Sea Water.

The "Chemtrix" glassy carbon electrode was also substituted for the DME and the same types of single-sweep curves were obtained with iron, copper, lead, cadmium, and zinc solutions, using both the digital polarograph and the A-1660 polarograph with the 5 ml capacity polarographic cell and the described single-sweep technique. Previous work on Fe(II) and Cu(II) was carried out by Zittel and Miller at a glassy carbon surface.¹¹ They reported analytically useable E_p and i_p values for these ions under voltammetric conditions.

CONCLUSIONS

From this study, it appears that either the "Clem" polymer-impregnated graphite electrode or the "Chemtrix" glassy carbon electrode might be used as a replacement for the DME for the field analysis of iron, copper, lead, cadmium, and zinc with either the A-1660 or NWC portable digital polarograph.

Using the NWC single-sweep instruments and technique described herein, sensitivity with the polymer-impregnated graphite electrodes and glassy carbon electrode examined appeared to be near 50 micrograms per liter (0.05 ppm) for iron and the heavy metals studied. A high hydrogen overvoltage (> -1.3 volt) was also found with all the electrodes studied.

Both glassy carbon and polymer-impregnated graphite electrodes can also be used in the anodic stripping voltammetric mode with copper, lead, cadmium, and zinc. Sensitivities to detection levels (3X noise) of 0.01-0.04 $\mu\text{g/l}$ have been reported by anodic stripping voltammetry in the differential pulse mode.⁶ However, for field use, these methods are not practical with present day instrumentation. They are strictly laboratory techniques.

It should be possible to develop a single-sweep polarographic method using either a styrene-impregnated graphite electrode or a glassy carbon electrode, with an instrument like the NWC digital polarograph, for the simultaneous field analysis of Fe(II) and Fe(III) in citric acid wastewaters and cleaning solutions. A supporting electrolyte 0.5 Molar with respect to both sodium carbonate and citric acid was found useful for such an analysis.

¹¹ H. E. Zittel and F. J. Miller. *Anal. Chem.*, Vol. 37 (1965), p. 200.