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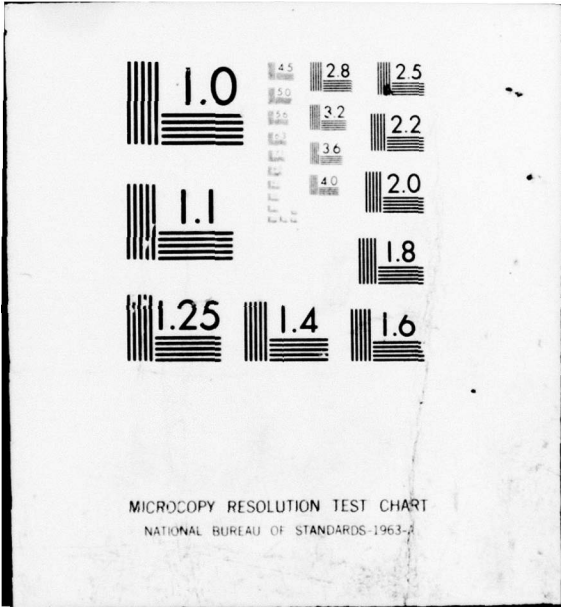
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POLAROGRAPHY OF RDX HYDROLYSIS PRODUCTS IN EFFLUENT OF ION EXCHANGE COLUMN TREATMENT OF RDX WATER.

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RDX in water solution can be measured directly by Rapid Scan Single Sweep Polarography. The lower limit of detection is about 0.5 ppm.			

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## INTRODUCTION

Dr. John Hoffsommer of NSWC, White Oak, Maryland has studied the hydrolysis of RDX in basic solution and has noted its decomposition along with the nature of the products of this hydrolysis. The same kind of hydrolysis of RDX has been noted on an ion exchange column (Amberlite 410- Strongly basic form) and it is this process that has been investigated as a possible method for treating waste streams from loading and/or demilitarization operations. It would be highly desirable to have a monitoring device on the effluent side of this column in order to know when the column has failed, or when the column needs to be regenerated. This study involves the use of Rapid Scan Single Sweep Polarography as a means of analyzing the effluent from the ion exchange column for monitoring purposes. This was suggested in that previous work done in this laboratory has shown that RDX does in fact show distinct reduction waves when this technique is employed.<sup>1</sup>

<sup>1</sup>Prestia, John V. USNA-EPRD-39 Report "Polarography of Ordnance Compounds," (Jun 1976)

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## EXPERIMENTAL

All measurements were made using a PAR Model 170 Electrochemical System employing the Rapid Scan Single Sweep Polarographic technique. Measurements were made vs. the Standard Calomel Electrode (SCE) and all voltages reported on this basis. Before reduction, the solutions were flushed with nitrogen gas for 15 minutes to expel dissolved oxygen which is known to interfere in the potential range of interest (-0.1 to -1.5 volts vs. SCE). The actual measurement was made using a hanging mercury drop electrode (a new drop for each sweep) in a still solution with a platinum wire as the current carrying electrode.

RDX solutions and dimethylnitramine were supplied by Dr. John Hoffsonmer of NSWC.

As long as care was taken to remove oxygen and maintain a clean capillary in the hanging mercury drop electrode assembly, reproducibility of curves for the same or similar samples was very good.

## RESULTS

### Supporting Electrolyte

Previous work indicated that the reduction waves of RDX were not altered when a change was made from KCl solutions to acetate buffers.<sup>1</sup> Since the pH of effluent of the ion exchange column was found to be about 10, it was decided to try a phosphate buffer with a nominal pH of 8-9 as the supporting electrolyte. Both 0.1 M KCl and 0.1 M phosphate buffer were used, but saturated solutions of RDX give identical reduction waves in the two media. In fact, when the RDX solution is run alone without additional electrolyte of any kind, the same polarogram results. Utilization of this fact is not practical, however, since at low concentrations of RDX (simple dilution with water to about one (1) ppm) the amount of electronic noise that develops in the recorder makes the polarogram useless. All work reported then is that done in 0.1 M phosphate buffer with a nominal pH of 8-9.

### Difficulties

The experimental technique, although straightforward, requires utmost care in order to obtain meaningful results. A considerable amount of time was spent in finding the optimum conditions necessary to obtain good polarograms as a matter of routine. Obviously, it is necessary to maintain glassware, electrodes, gas probes, etc. scrupulously clean as the instrument and the technique are very sensitive to trace amounts of impurities and foreign matter. The most important consideration, however, and the one factor that requires the most care is the condition of the capillary from which the mercury drop hangs. Anomalous results were explained in terms of the hanging mercury drop electrode in practically 100% of the cases where deviations from expected were noted.

### Monitoring of RDX

The essence of this study is the ability to monitor RDX in a given stream, the effluent of the ion exchange column degradation in this case. A sample of the RDX feed to the column (NSWC Cycle #1, 8 June 76) was diluted 1 to 6 with phosphate buffer and the polarogram recorded. See Figure 1. Since the concentration of RDX as given by Hoffsommer for this sample was 37.5 ppm, the actual concentration in the measured solution was 6.3 ppm. Figure 2 shows the

<sup>1</sup>Ibid.

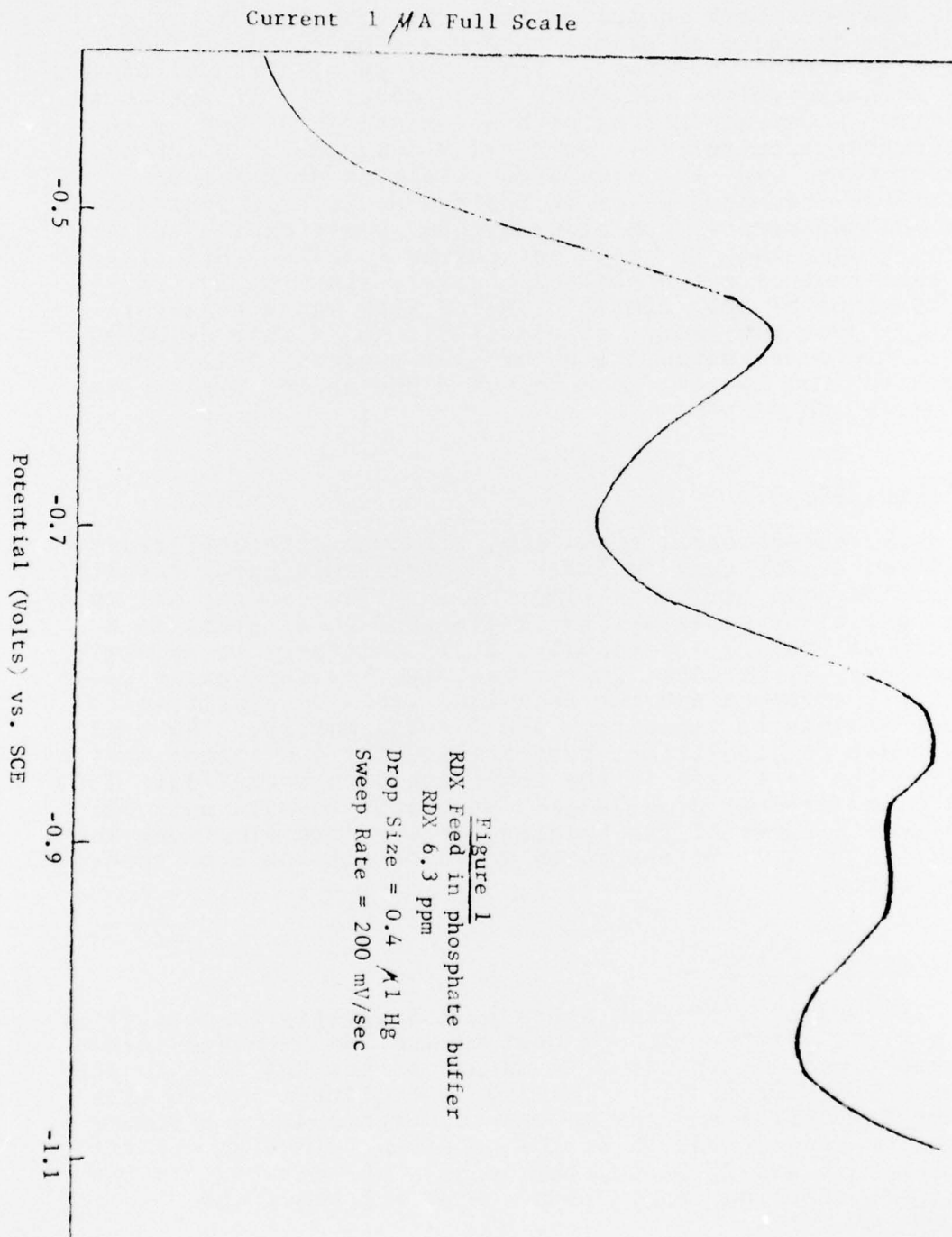


Figure 1  
RDX Feed in phosphate buffer  
RDX 6.3 ppm  
Drop Size = 0.4  $\mu$ l Hg  
Sweep Rate = 200 mV/sec



Current 1  $\mu$ A Full Scale

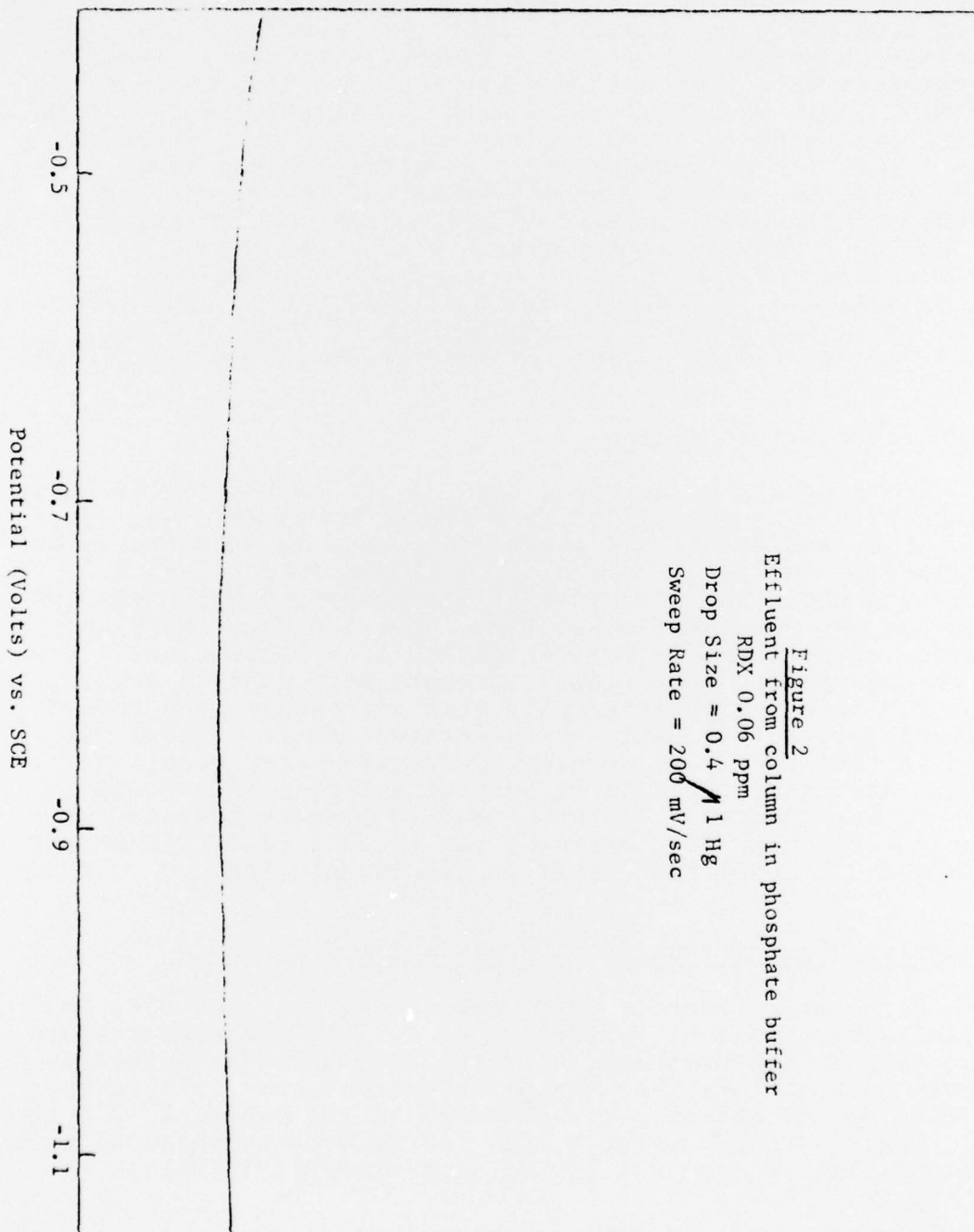


Figure 2  
Effluent from column in phosphate buffer  
RDX 0.06 ppm  
Drop Size = 0.4  $\mu$ l Hg  
Sweep Rate = 200 mV/sec

corresponding polarogram for the effluent from the same column, taken at the same time. The RDX concentration in this solution was 0.38 ppm and therefore upon dilution of 1 to 6 with the buffer, the resultant concentration was about 0.06 ppm. It is obvious that the instrument can distinguish between these two solutions with ease. These experiments were repeated with samples from NSWC Cycle #6 and NSWC Cycle #8 of July 1976 with identical results. Some attempt was made to set a lower limit to the concentration of RDX that can be detected by this method. Drop size, sweep rate, and sensitivity adjustment of instrument are undoubtedly involved in this determination, but by using the effluent samples as a starting point (see Figure 2) small samples of the RDX feed were injected as an RDX, spike. Based on a limited number of qualitative experiments, it is estimated that RDX concentrations of about 0.5 ppm would be detected if present in the effluent from the column.

#### Products of Decomposition

The products of decomposition of RDX on the ion exchange column have been identified by Hoffsommer<sup>2</sup> as  $\text{NO}_2$ ,  $\text{N}_2$ ,  $\text{NH}_3$ ,  $\text{N}_2\text{O}$ ,  $\text{CH}_2\text{O}$ , and  $\text{HCOO}^-$ . Of these, two would be expected to be retained by the anion column,  $\text{N}_2$  is known to be inert to reduction under the conditions of the polarographic technique used and the remaining three ( $\text{NH}_3$ ,  $\text{N}_2\text{O}$ , and  $\text{CH}_2\text{O}$ ) must be considered as possible active species at the electrode under the applied potential. Attempts were made to put  $\text{NH}_3$  and  $\text{CH}_2\text{O}$  into the polarographic cell and examine the resultant polarograms, but only a limited amount of work was done in this area. No apparent reduction waves resulted but in any case, the data is suspect and this work would have to be repeated. One point should be made however, that the flushing with nitrogen may in fact alter the amount of  $\text{NH}_3$  and or  $\text{CH}_2\text{O}$  that would remain in solution.

#### Reduction Characteristics of Other Nitro Compounds

Since many ordnance compounds are nitro compounds, RDX is in particular a nitramine, a few qualitative measurements were made on nitromethane, nitrobenzene, and dimethylnitramine. Both nitromethane and nitrobenzene show peaks in the current vs. potential plots obtained in the range of -0.4 to -0.5 volts vs. SCE. Figure 3 is the polarogram obtained when the phosphate buffer was spiked with dimethylnitramine.

<sup>2</sup>Hoffsommer, J.C., private communication.

Current 10  $\mu$ A Full Scale

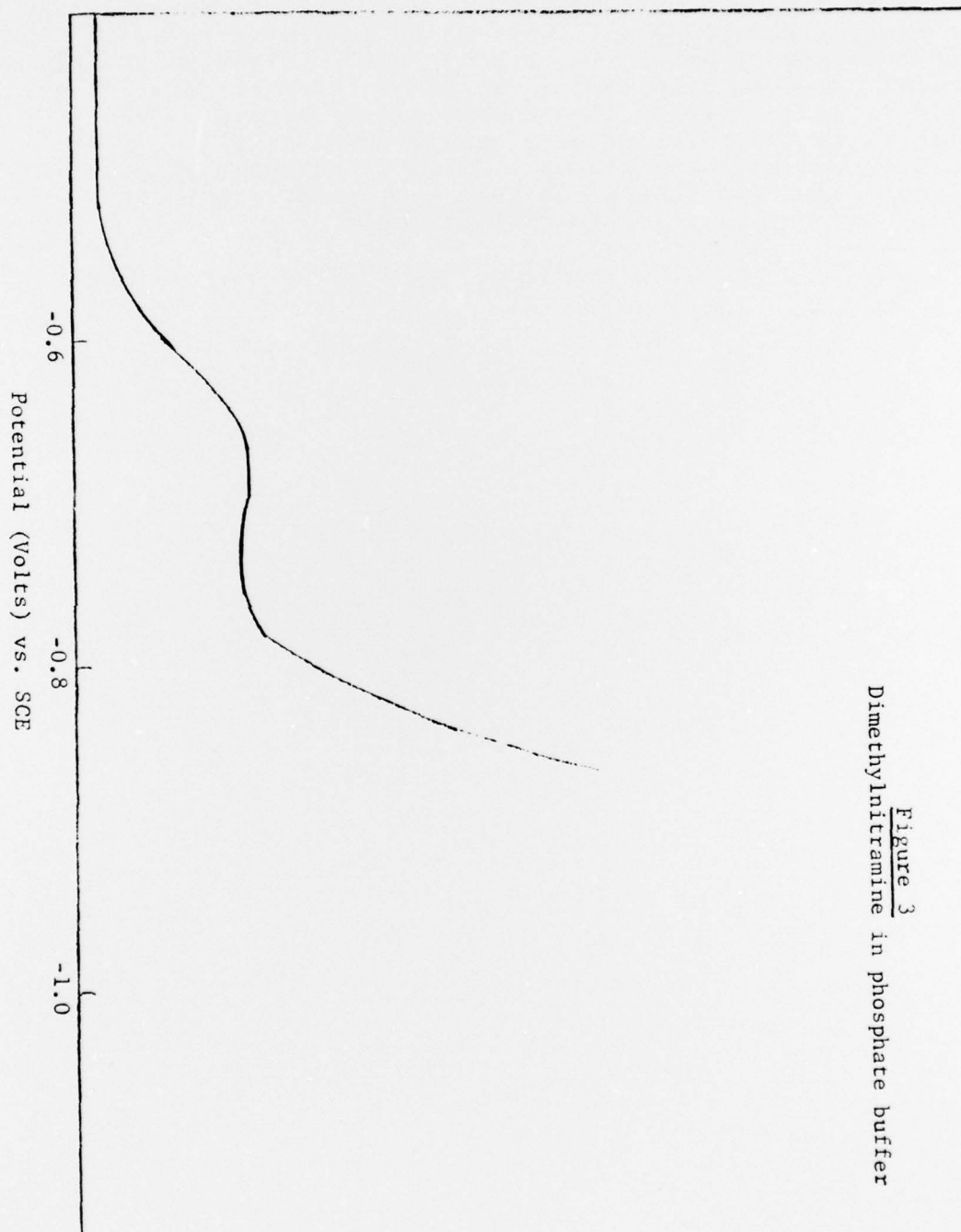


Figure 3  
Dimethylnitramine in phosphate buffer

## RECOMMENDATIONS

It is apparent that Rapid Scan Single Sweep Polarography at a hanging Mercury Drop Electrode is sensitive to small concentrations of RDX in water solutions. Extensive use of a buffer has been made in this work, but there are hints that little or no additional electrolyte may be needed. The system is to the point of development that installation of a polarograph on the effluent side of a treatment process is the next step. An instrument such as that described by Becktel and Whitnack is the obvious choice.<sup>3</sup>

<sup>3</sup>Becktel, W.J. and G.C. Whitnack, NWC TP 5860 Part 2 (Sept. 1976).

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