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Voltammetric Analysis of Ordnance Materials Part 1. Detection and Quantitation of Nitrate Esters and Various Nitro Compounds in Water by Voltammetry

by
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APRIL 1984

NAVAL WEAPONS CENTER
CHINA LAKE, CALIFORNIA 93555

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FOREWORD

The work described in this report was performed as part of a general program of electrochemical analysis of ordnance materials. The work was sponsored by the Naval Sea Systems Command, Task Area Number WF65559, Program Element 62765N, by the U.S. Army Toxic and Hazardous Materials Agency, Task R904.10.0163, and by the Naval Underwater Systems Center, WPN Source, AA17X492.3790.

This report summarizes efforts to find suitable voltammetric methods for analysis of nitrate esters and aromatic nitro compounds and is presented in two parts under the general title, "Voltammetric Analysis of Ordnance Materials." Part 1 is "Detection and Quantitation of Nitrate Esters and Various Nitro Compounds in Water by Voltammetry," and Part 2 will be "A Portable Digital Voltammeter for Use with a Silver Wire Working Electrode."

This report has been reviewed for technical accuracy by Aaron N. Fletcher and Arnold T. Nielsen.

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15 March 1984

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(U) Voltammetric Analysis of Ordnance Materials. Part 1. Detection and Quantitation of Nitrate Esters and Various Nitro Compounds in Water by Voltammetry, by Dwight A. Fine and Melvin H. Miles, Naval Weapons Center, April 1984. 24 pp. (NWC TP 6505, publication UNCLASSIFIED.)

(U) Effort has been directed toward developing a suitable solid working electrode for the voltammetric determination of various ordnance materials in water. Of the electrode materials tested, silver wire showed the most promise, and a suitable silver wire electrode has been developed. Linear sweep voltammetric, cyclic voltammetric and exhaustive electrolysis studies of the reduction of nitrate esters and aromatic nitro compounds on the electrode have been carried out. These studies indicate usefulness of the electrode in the analysis of waste water for PGDN, NG, DNT, TNT, and nitroguanidine. A portable voltammeter suitable for use in conjunction with the electrode has been developed.

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INTRODUCTION

Concern over the strong toxicological properties of certain ordnance materials has led to a search for accurate and convenient methods for detection of and for determining the amount of these materials in effluent waters from ordnance facilities. Of particular concern to the Navy is 1,2-propylene glycol dinitrate (PGDN), the principal constituent of Otto fuel. Other materials of interest to Navy and Army ordnance facilities include nitroglycerin (NG), dinitrotoluene (DNT), trinitrotoluene (TNT), 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX), 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), and nitroguanidine. The maximum allowable concentration of these materials in effluent waters has been set at 1 ppm by the Bureau of Medicine (BuMed).

Since nitrate esters such as PGDN and NG and aromatic nitro compounds such as DNT and TNT undergo electrochemical reduction at sufficiently negative potentials, electrochemical means of analysis have been sought. Electrochemical methods fall into two principal areas: polarography, in which the reaction of interest takes place at a dropping mercury electrode (DME), and voltammetry, in which the reaction takes place at a solid electrode.

Polarographic methods for determination of a number of ordnance materials have been devised.[1-4] The standard equipment used for these methods is too expensive, cumbersome and complicated for purposes of bench and field testing at ordnance facilities; therefore, initial efforts at the Naval Weapons Center (NWC) were directed toward design and fabrication of a simple polarographic analyzer. A digital field polarograph designed specifically for the determination of PGDN in effluent water from torpedo installations was built at NWC and tested

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[1] A. R. Holland and A. G. S. Benham. "Continuous Polarographic Determination of Small Amounts of Nitroglycerine in Plant Effluent," Analyst (London), Vol. 93 (1968), pp. 87-91.

[2] J. S. Hetman. "Polarography of Explosives," Z. Anal. Chem., Vol. 264 (1973), pp. 159-164.

[3] G. C. Whitnack. "Single-Sweep Polarographic Techniques Useful in Micropollution Studies of Ground and Surface Waters," Anal. Chem., Vol. 47 (1975), pp. 618-621.

[4] Naval Underwater Systems Center. The Polarographic Investigation of Organic Nitrate Esters I, The Electroanalytical Determination of Propylene Glycol Dinitrate, by Walter G. Cox, Newport, R. I., NUSC, December 1972. (NUSC TM SB322-4546-72, publication UNCLASSIFIED.)

successfully at the Naval Torpedo Station, Keyport, Washington, and at the Naval Magazine Area, Lualualei, Hawaii, installations.[5-7]

The use of a DME, however, poses problems in connection with the storage, handling, and toxicity of the mercury. Accordingly, effort has been directed toward finding a suitable solid working electrode, and toward design and fabrication of a simple, portable voltammeter for use in conjunction with the electrode. This report describes the experiments and results connected with the search for an electrode, and presents a brief description of the voltammeter. Part 2 will describe the circuitry, software, and operational characteristics of the voltammeter in detail.

APPARATUS AND MATERIALS

Most of the laboratory voltammetric measurements were made with a Princeton Applied Research (PAR) model 174 polarographic analyzer. Results were recorded with an X-Y recorder (Hewlett-Packard 7005A or 7047A). The cyclic voltammetry and exhaustive electrolysis studies were done with a PAR model 173 potentiostat/galvanostat equipped with a model 176 current follower plug-in and a PAR model 175 programmer.

All of the solutions were prepared from reagent grade chemicals and distilled water. Stock solutions of PGDN were prepared by weighing aliquots of a mixture of 10 g of PGDN dissolved in 200 g of acetone, followed by dilution to yield final concentrations of 100-1,000 parts per million (ppm). Stock solutions of NG were prepared from pharmaceutical tablets (Nitrostat, Parke-Davis) containing 0.6 mg of NG. Solutions of DNT, TNT, RDX, and nitroguanidine were prepared by weighing out pure solids and dissolving in water that was being stirred. Concentration

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[5] Naval Weapons Center. Applied Polarography for Analysis of Ordnance Materials. Part 1. Determination and Monitoring of 1,2-Propyleneglycoldinitrate in Effluent Water by Single-Sweep Polarography, by Gerald C. Whitnack and Walter J. Becktel, China Lake, Calif., NWC, June 1976. 20 pp. (NWC TP 5860, Part 1, publication UNCLASSIFIED.)

[6] ------. Applied Polarography for Analysis of Ordnance Materials. Part 2. An Inexpensive Solid-State Field Polarograph with Digital and Analog Output, by Walter J. Becktel and Gerald C. Whitnack, China Lake, Calif., NWC, September 1976. 18 pp. (NWC TP 5860, Part 2, publication UNCLASSIFIED.)

[7] ------. Applied Polarography for Analysis of Ordnance Materials. Part 3. Field Tests of NWC Digital Polarograph and Pollution Monitoring System, by Gerald C. Whitnack, China Lake, Calif., NWC, January 1979. 16 pp. (NWC TP 5860, Part 3, publication UNCLASSIFIED.)

and purity of stock solutions were checked by chromatographic analysis. Solutions in the 0-10 ppm range were prepared by pipetting the calculated amount of stock solution into the electrolyte solution. In most of the voltammetric and electrolysis studies, the supporting electrolyte was 0.50 M sodium chloride.

Electrochemical measurements were made in several types of cells. Most of the measurements were made in cylindrical glass cells fitted with a rubber cap which supported the electrodes and the inert gas purging tubes. Other measurements were made in commercial cells (IBM and ECO) fitted with plastic screw-on caps. In all cases, the auxiliary (counter) electrode was platinum wire, and the reference electrode was a commercial standard calomel electrode (SCE) or silver/silver chloride electrode. Unless otherwise noted, all of the potentials listed in subsequent sections are relative to SCE. All of the experiments were conducted at room temperature (23-25°C).

EXPERIMENTS WITH VARIOUS SOLID ELECTRODES

Initial experiments with solid electrodes were conducted using aqueous solutions of PGDN. The first electrodes tested were gold amalgam electrodes that had been prepared at NWC. One such electrode showed a wave with PGDN versus a mercury pool anode, but further attempts with the same electrode and with new gold/mercury electrodes were unsuccessful.

The carbon electrodes graphite/calomel and POCO graphite were the next electrodes tested. The graphite/calomel electrodes were prepared from National spectroscopic graphite, Sonneborn wax, and calomel (mercurous chloride).* A typical batch used 800 mg of graphite, 800 mg of calomel, and 1 g of wax. The graphite and calomel were mixed by shaking, then placed in a test tube with the wax. The tube was placed in boiling water; when the wax melted the mixture was stirred. The glass tubing (5 mm outer diameter) which served as the electrode body was then dipped into the molten mixture, withdrawn, and cooled. In some cases cupric oxide was mixed with the graphite/calomel before addition of the wax. Two methods for reduction of the mercury and copper in the electrodes were tried: electrochemical and chemical (dipping the electrode in hydrazine hydrate solution). Only one of these electrodes, prepared by reduction with hydrazine, gave a voltammetric wave for PGDN. Several electrodes gave good waves for a 2 ppm solution of TNT.

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* Mr. Ray Clem of the Lawrence Berkeley Laboratory at the University of California, Berkeley, California, and Dr. Walter Cox of Naval Underwater Systems Center (NUSC), Newport, R. I., made the graphite/calomel electrodes while on a visit to NWC. Mr. Clem also constructed the POCO graphite electrode.

POCO graphite is a low-porosity graphite manufactured by Union Oil Co. A POCO graphite electrode which gave a response to PGDN and NG was constructed. The electrode consisted of a cylindrical section of graphite (1/4-inch diameter by 1/2-inch long) embedded in lucite; the lucite screwed into a stainless steel cylinder which contacted the graphite. After assembly, the electrode was dipped in wax and then it was encased in heat-shrink tubing. Under contract with NWC, the Lawrence Berkeley Laboratory (LBL), University of California, Berkeley, California, developed a model for a cell-electrode system. The electrode was rotated continuously during the voltammetric scan. The cell contained silicon carbide grit which scoured the electrode surface during the rotation process.

In tests performed at NWC, the direct current mode of the PAR 174 analyzer was employed at a scan rate of 20 mV/s. For PGDN, the supporting electrolyte was 1 $\underline{M}$ NaOH, so as to shift the hydrogen evolution wave to as negative a potential as possible. A single wave was produced in the range from -0.23 to -1.4 V. The wave height at -1.2 V increased linearly with the PGDN concentration up to about 17 ppm, with negative deviation from linearity at higher concentrations. One ppm could be detected. For NG, the supporting electrolyte was 0.5 $\underline{M}$ NaCl, buffered to pH 9.7 with ammonium acetate. A wave was observed in the range of +0.1 to -1.0 V. The wave height at -0.8 V increased linearly with the concentration up to 12 ppm, the highest concentration investigated. As little as 1 ppm could be detected. Later, a cell/electrode assembly was completed under contract at LBL and delivered to NWC. Initial tests of this system were unsuccessful and revealed inconveniences in the design of the cell. The inconsistency of results with carbon electrodes, the difficulties associated with surface renewal, and the need for strongly alkaline solutions (in the case of PGDN) ruled out carbon as a convenient electrode material for the present purposes.

Various metals were tested as working electrodes for the reduction of PGDN. Reduction was observed on silver, gold, copper, and mercury, but reduction was not observed on platinum, iridium, nickel, tungsten or molybdenum. Interestingly, all of the metals on which reduction occurs are metals with filled d-orbitals. On the basis of further tests, silver was judged to be the best solid electrode material. The remainder of this report is devoted to results obtained with a silver working electrode.

The final design selected for the silver electrode is shown in Figure 1. The silver wire was 1.0 mm in diameter and was obtained from Alfa Products. The wire was spot-welded to a nickel lead and sealed in glass tubing with epoxy. The protruding length was about 1.5 cm, giving a geometric area of about 0.47 cm^2. The use of a sturdy grade of epoxy was found to be essential in order to avoid the development of cracks or crevices (especially in the area of the electrode seal). Wire electrodes performed much better than disc or spherical electrodes.

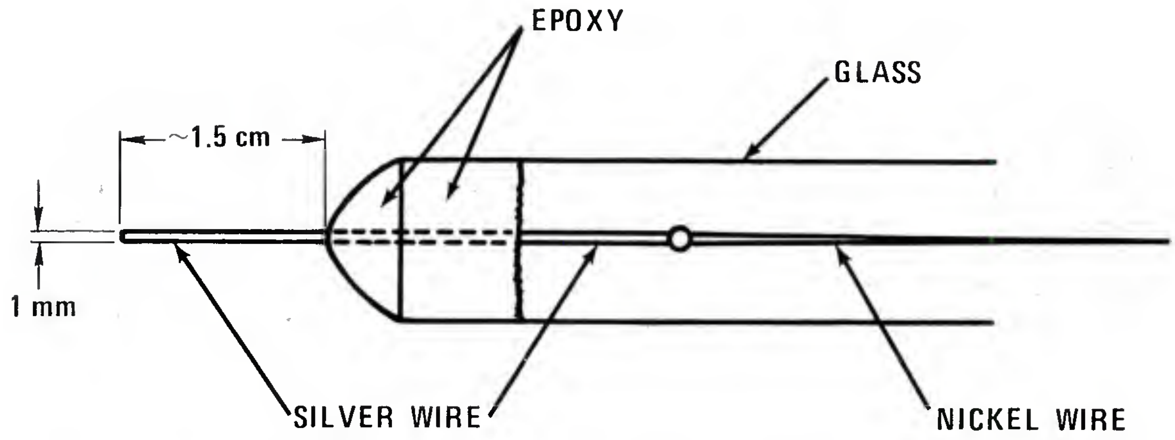

FIGURE 1. Design of Silver Wire Electrode

RESULTS OBTAINED WITH SILVER WIRE ELECTRODE

This section summarizes the results of voltammetric measurements on various ordnance materials, using the silver wire working electrode. The principal results, experimental details, and conclusions have been published in the open literature.[8,9]

The most important procedure in obtaining reproducible results was electrochemical conditioning of the electrode by several rapid potential scans (50 or 100 mV/s) down to the region of the hydrogen evolution wave, prior to each recorded scan. The electrodes were usually wiped with Orion paper prior to each day's runs, but omission of this cleaning produced no adverse effects.

Solutions were deaerated with nitrogen or helium gas prior to voltammetric measurements. We found it necessary to have a long deaeration period of about 20 minutes in order to obtain reproducible base lines. This deaeration period could be shortened by use of strong stirring during the bubbling. Inert gas was passed over the surface of the solution during the actual measurements.

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[8] M. H. Miles and D. A. Fine. "The Reduction of Propylene Glycol Dinitrate and Other Related Nitrate Esters on Ailver Electrodes," J. Electroanal. Chem., Vol. 127 (1981), pp. 143-155.

[9] D. A. Fine and M. H. Miles. "The Reduction of Propylene Glycol Dinitrate, Nigroglycerin, Dinitrotoluene and Trinitrotoluene on Silver Electrodes," Anal. Chim. Acta., Vol. 153 (1983), pp. 141-147.

LINEAR SWEEP VOLTAMMETRY

We found the optimum pH for the linear sweep voltammetry (LSV) measurements to be around 10. At higher pH, a flattening of the waves occurred, and at lower pH, interference from the hydrogen evolution wave became a problem. A buffering to pH 10 is easily achieved by the addition of equimolar quantities of sodium carbonate and sodium bicarbonate. All of the linear sweep voltammograms presented in this section were obtained on solutions 0.50 M in NaCl and 0.01 M in $NaHCO_3/Na_2CO_3$. The scan rate for the recorded scans was 5 mV/s. Each recorded scan was preceded by three rapid cleaning scans (50 mV/s), from -0.1 or -0.3 down to -1.1 or -1.3 V.

Typical voltammograms for dilute solutions of PGDN are shown in Figure 2. From these it is seen that 1 ppm of PGDN is readily detectable, and that the response is linear. Results for more concentrated

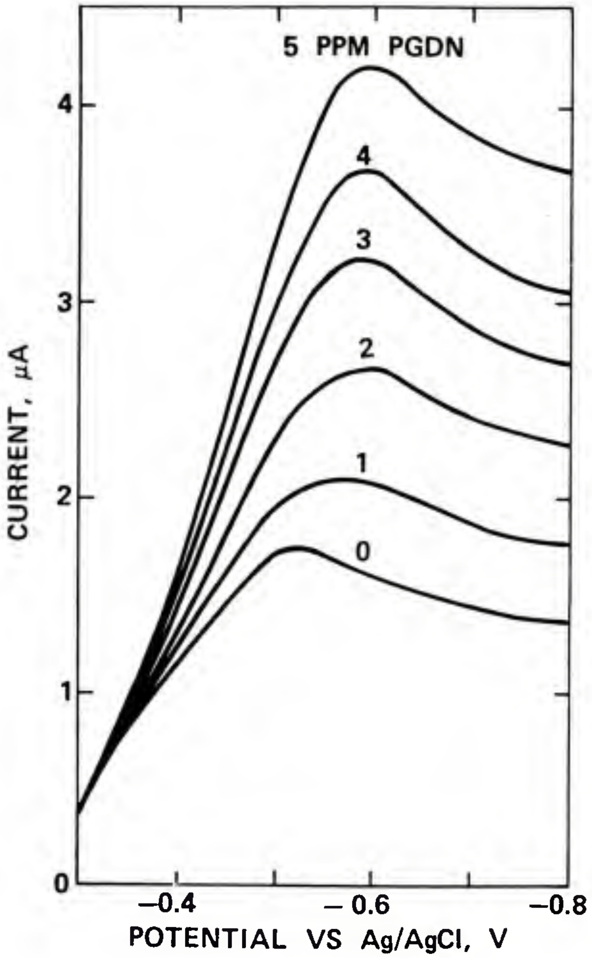

FIGURE 2. Linear Sweep Voltammograms of PGDN.

solutions are shown in Figure 3a. A plot of peak current versus concentrations is shown in Figure 3b; the plot shows good linearity, indicating that standard curve or standard addition methods could be used for the voltammetric determination of PGDN.

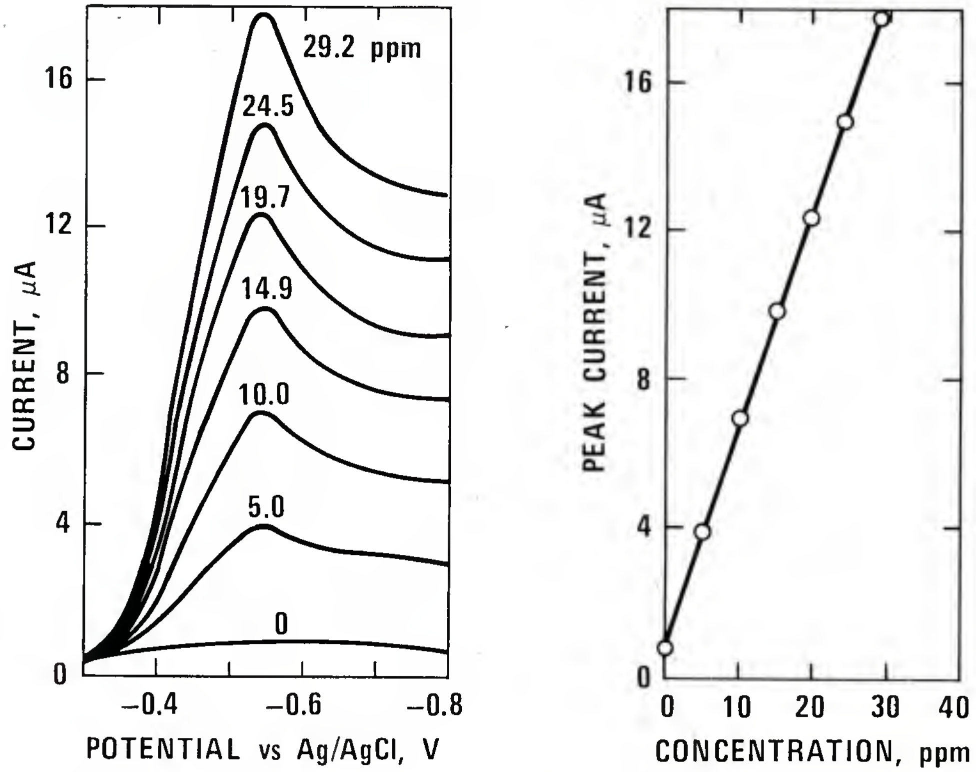

FIGURE 3. (a) Linear Sweep Voltammograms of More Concentrated Solutions of PGDN; (b) Plot of Peak Current versus Concentration.

Results for NG are similar to those obtained for PGDN. Some typical voltammograms of NG are shown in Figure 4.

In the case of DNT, voltammetric behavior was found to be dependent on isomeric composition. The most abundant DNT isomers are those with meta dinitro substitution (2,4-, 2,6-, and 3,5-DNT); all three show a single reduction wave with peak potential E_p between -0.52 and -0.56 V. Results for 2,6-DNT are shown in Figure 5. The two ortho isomers (2,3- and 3,4-DNT) and the para isomer (2,5-DNT) show two definite waves. The first wave occurs at approximately the same potential for all concentrations, but the position of the more negative wave shows a concentration dependence. In the case of 2,3-DNT, the first E_p occurs at -0.52 V; at concentrations <2.0 ppm, the second E_p occurs at -0.56 V, and at concentrations >4.5 ppm this second E_p has shifted to -0.76. Curves suggesting the possible occurrence of three reduction processes are obtained for intermediate concentrations.

Typical traces are shown in Figure 6. The 3,4-isomer shows the same behavior, with the first E_p at -0.45 V, the second at -0.59 V for concentrations <1.5 ppm and at -0.79 V for concentrations >2.5 ppm. Traces are shown in Figure 7. In the case of the para isomer (2,5-DNT), the first E_p is seen at -0.40 V; the shift of the second E_p occurs at higher concentrations than for the ortho isomers. Traces are shown in Figure 8. The differing reduction potentials can be correlated with calculations of the electron densities in the benzene ring.

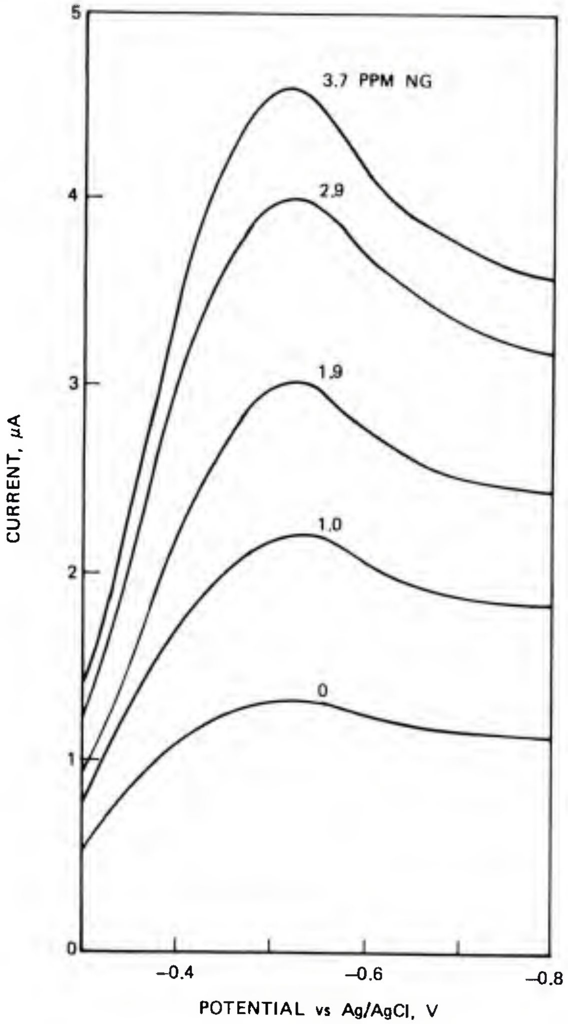

FIGURE 4. Linear Sweep Voltammograms of NG.

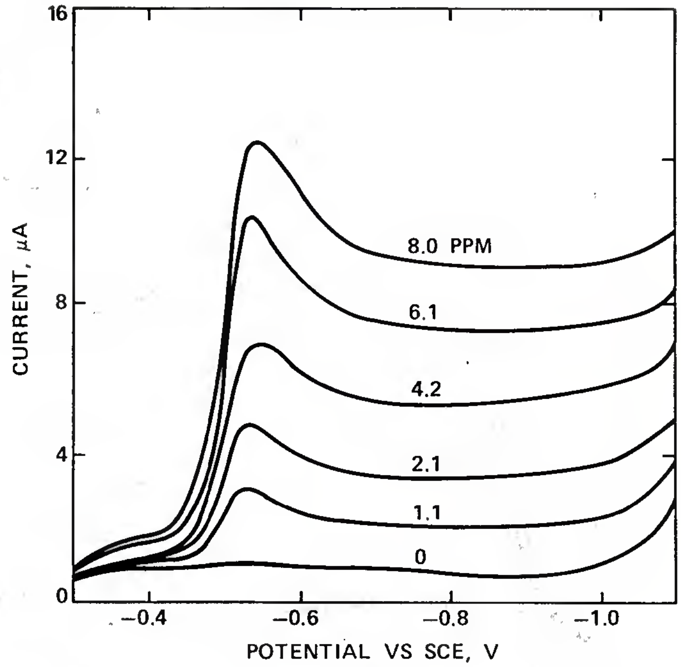

FIGURE 5. Linear Sweep Voltammograms of 2,6-DNT.

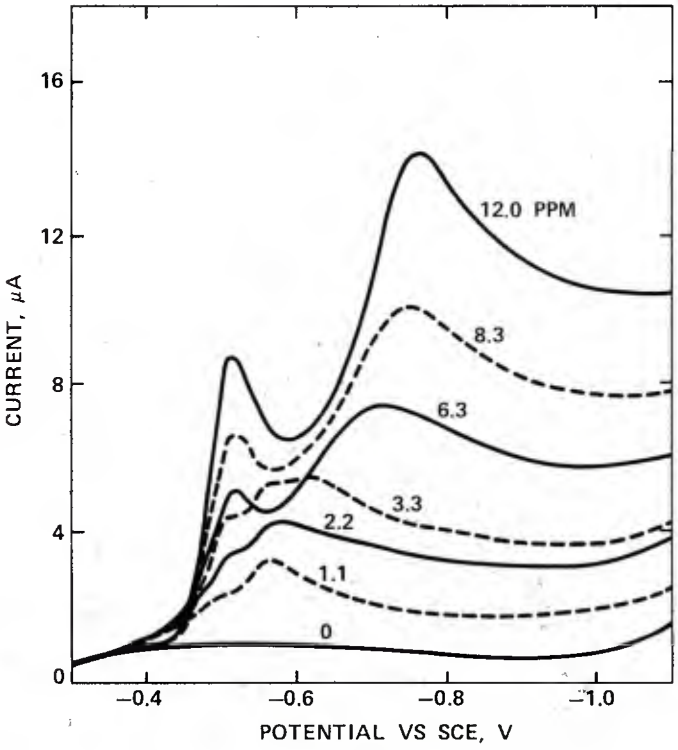

FIGURE 6. Linear Sweep Voltammograms of 2,3-DNT.

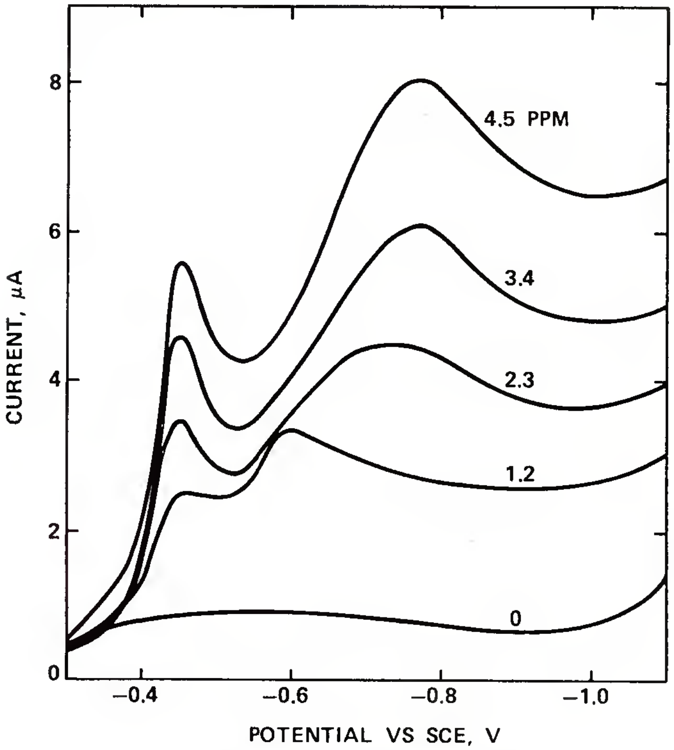

FIGURE 7. Linear Sweep Voltammograms of 3,4-DNT.

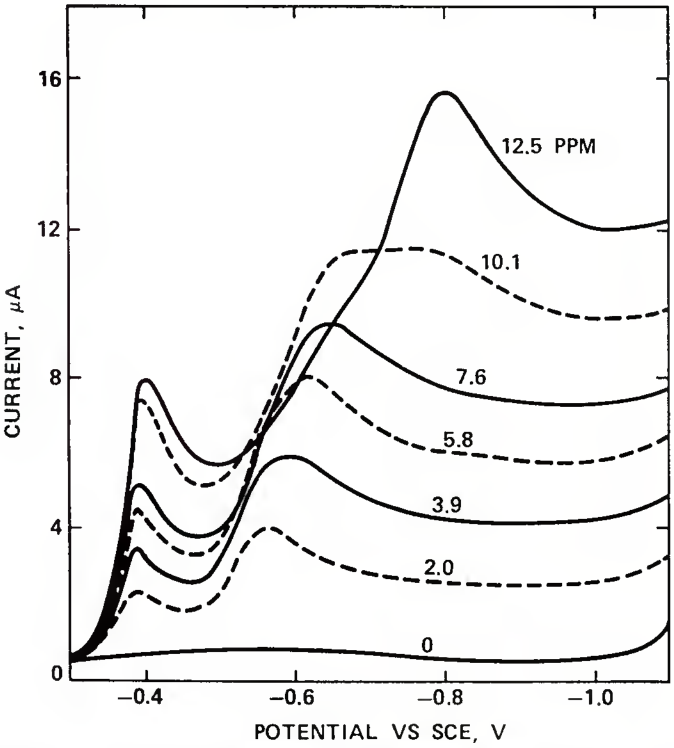

FIGURE 8. Linear Sweep Voltammograms of 2,5-DNT.

Results for TNT are shown in Figure 9. One reduction wave is seen at concentrations >3 ppm, with E_p at about -0.52 V. At higher concentrations, a broadening of this wave occurs with hints of another wave at more negative potentials.

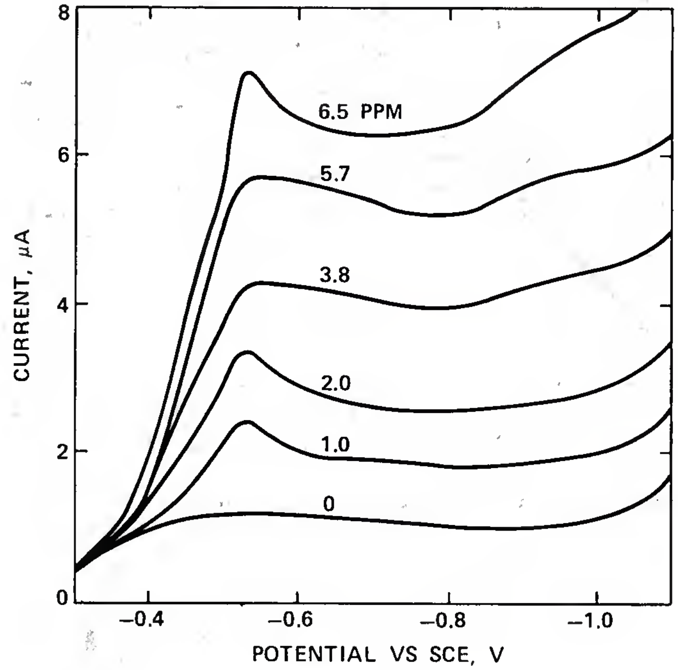

FIGURE 9. Linear Sweep Voltammograms of TNT.

RDX shows a peak and a broad wave in the region from -0.2 to -1.0 V, but the response is not as sensitive as for the nitrate esters and aromatic nitro compounds, and the linearity of response is not as good. Voltammograms of RDX are shown in Figure 10.

Nitroguanidine, $HN{=}C(NH_2){-}NH{-}NO_2$, shows a peak and a wave (Figure 11). Both the peak and the wave shift to more positive potentials with decreasing pH, indicating an acid-dependent reduction process.

The effect of variation of the supporting electrolyte anion was studied for PGDN, NG, 2,6-DNT, and TNT, using 0.2 M solutions of sodium salts. Results are summarized in Table 1. They have been discussed elsewhere.[9] The order of increasing negative reduction potentials is the same as the order of increasing anion adsorption (NO_3^- $F^- < Cl^- < Br^- < I^-$). No advantage over chloride was observed for the other anions investigated, except perhaps in the case of TNT, where three distinct peaks are observed with bromide.

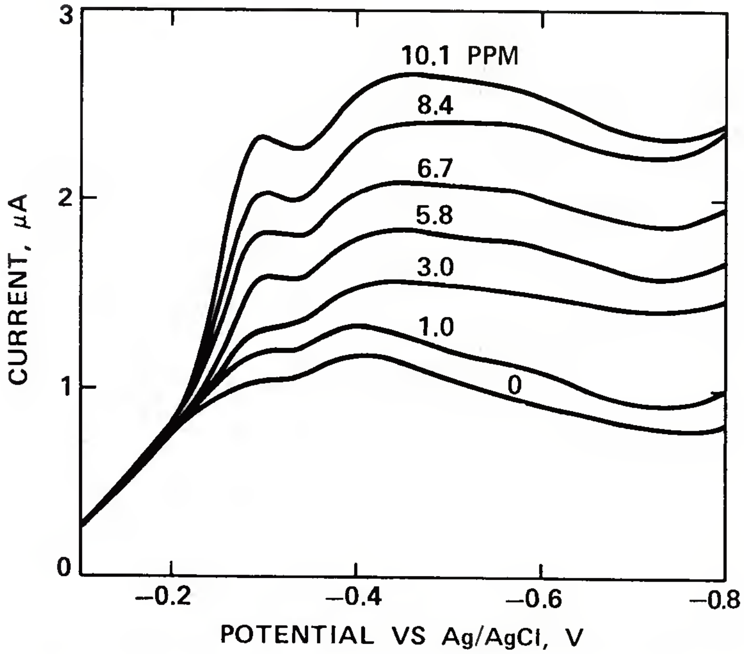

FIGURE 10. Linear Sweep Voltammograms of RDX.

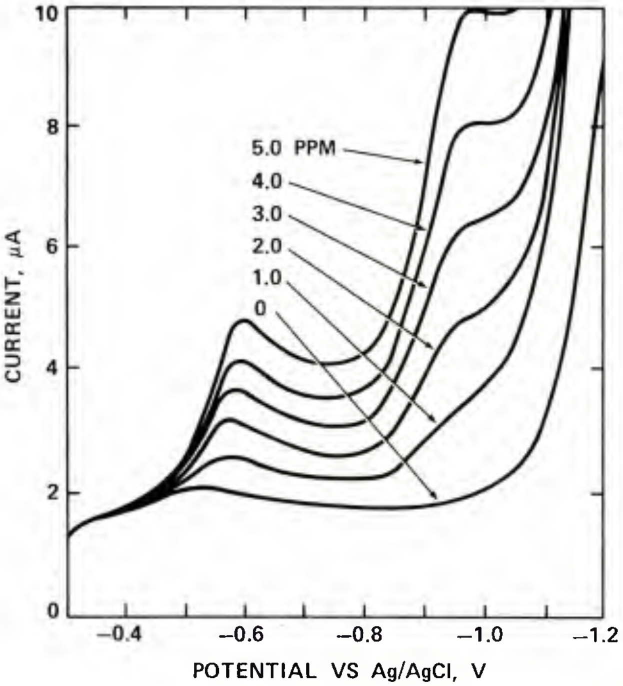

FIGURE 11. Linear Sweep Voltammograms of Nitroguanidine.

TABLE 1. Anion Effects on the Reduction of PGDN, NG, DNT, and TNT on Silver Wire Electrodes at Concentrations <5 ppm. Potential Sweep Rate = 5 mV s^{-1}, Electrode Area = 0.48 cm^2, pH = 10 Unless Otherwise Noted.

Electrolyte (0.20 M)	E_p (V vs. SCE)			
	PGDN	NG	DNT[a]	TNT
NaF	-0.5^b	-0.5^b	-0.6^b	-0.5^b, -0.7^b
NaCl	-0.52	-0.52	-0.52	-0.49, -0.7^b
NaBr	-0.70	-0.71	-0.64	-0.49, -0.66, -0.75
NaI[c]	-0.97	-0.95	-0.8^b	-0.8^b, -0.96^b
$NaNO_3$	-0.5^b	-0.5^b	-0.6^b	-0.5^b, -0.6^b -0.8^b

[a] 2,6 isomer.
[b] Peak poorly defined due to broadness of reduction wave.
[c] pH = 12.

The results of the LSV studies indicate usefulness of the silver wire electrode in the analysis of waste waters for PGDN, NG, DNT, TNT, and nitroguanidine. For each compound, 0.5 ppm is readily detectable. For PGDN and NG, plots of peak current i_p versus concentration are linear for concentrations less than 30 ppm. For DNT and TNT, not all of the observed waves yield linear plots of i_p versus concentration, but the current at certain fixed potentials does show linearity with concentration. Values of slopes obtained from linear plots are summarized in Table 2.

TABLE 2. Slopes of Plots of Current Versus Concentration, From Voltammograms Obtained with Silver Wire Working Electrode ($A = 0.47\ cm^2$).

Compound	Potential, V (SCE)	Slope, $\mu A\ ppm^{-1}$	Standard deviation, σ^a
PGDN	-0.57 to -0.59[b]	0.50	±0.06
NG	-0.53 to -0.55[b]	0.65	±0.10
DNT[c]	-0.90	1.0	±0.15
TNT	-0.80	0.79	±0.06
Nitro-guanidine	-0.57 to -0.60[b] -1.0	0.5 1.5	---

[a] Calculated where data from at least 7 different runs are available.

[b] Peak potential.

[c] Varying isomeric composition.

CYCLIC VOLTAMMETRY

Cyclic voltammetric studies were run on PGDN and the meta and para dinitro isomers of DNT. Solutions were 0.5 M in NaCl and 0.1 M in $Na_2CO_3/NaHCO_3$. For PGDN, the peak current was found to be proportional to the concentration of PGDN and to the square root of the scan rate. The peak potential was independent of concentration and dependent on scan rate. This behavior indicates that the reduction of PGDN on silver is diffusion-controlled and irreversible. For 2,4- and 2,6-DNT, peak potential was independent of scan rate; the 3,5-isomer showed a dependence of peak potential on scan rate. For 2,5-DNT, the first peak showed the same behavior as the reduction peak for PGDN, while the second peak was independent of the scan rate.

EXHAUSTIVE ELECTROLYSIS

A large silver electrode ($A = 50\ cm^2$) was used for studies of exhaustive electrolysis. Results are shown in Table 3. Striking color changes occurred during the reduction of the ortho and para dinitro isomers of DNT. For 2,5-DNT, the solution turned bright reddish orange during the first wave and faded to colorless during the second wave. The ortho isomers (2,3 and 3,4) showed a color change to deep violet during the first wave. The meta isomer (2,4) showed no color changes and only one wave. Further details are given elsewhere.[8,9]

TABLE 3. Results of Exhaustive Electrolysis Studies with Silver Electrode.

Compound	Number of reduction waves	Number of electrons per wave
PGDN	1	4
NG	1	6
2,5-DNT	2	3, 5
2,3-DNT	2	3, 5
3,4-DNT	2	3, 5
2,4-DNT	1	8

Potentiostatic reduction experiments on PGDN solutions showed linear Tafel regions between 0.5 and 20.0 μA (1-50 μA cm^{-2}). The Tafel slope, 0.11 V, corresponds to an experimental transfer coefficient (α) of 0.53.

A mechanism for the reduction of nitrate esters which is consistent with all of the experimental observations is given by

$$RONO_2 + e^- \rightarrow RO^- + NO_{2(ads)} \qquad \text{(slow)}$$

$$NO_{2(ads)} + e^- \rightarrow NO_2^- \qquad \text{(fast)}$$

$$RO^- + H_2O \rightarrow ROH + OH^- \qquad \text{(fast)}$$

APPLICATION TO ANALYSIS OF EFFLUENT WATER FOR PGDN

The pollution problem of greatest concern to Naval weapons stations is the contamination of effluent water with Otto fuel. Otto fuel contains 76% PGDN, 22.5% di-n-butyl sebacate (a desensitizer) and 1.5% 2-nitrodiphenylamine (a stabilizer). Waste water at these facilities goes through a two-stage purification process. Water from the sump is first sent to an oily water separator; after removal of oily constituents, manual discharge valves take the water to a series of carbon columns designed to remove the remaining PGDN. A means of monitoring the final purification stage is needed in order to be sure that the water emerging from the last column contains less than 1 ppm PGDN.

The silver wire electrode was tested for ability to detect and quantitate PGDN in diluted solutions of Otto fuel, and in samples of sump and effluent water. Each sample was salted and deaerated, and the DC voltammograms between −0.3 and −0.8 V were obtained. Figure 12 shows the voltammogram of three different 10^5:1 dilutions of Otto fuel, and the voltammograms obtained after standard additions of 14 ppm pure PGDN. Comparison indicates a concentration of 8 ppm PGDN in the diluted solution, in agreement with the known 76% concentration in the original Otto fuel.

Figure 13 shows the voltammogram of a sample of sump water from the Naval Weapons Station (NWS), Yorktown, Va., after processing by the oily water separator, but before passage through the carbon columns. The standard addition indicates a concentration of 11 ppm PGDN in the water,

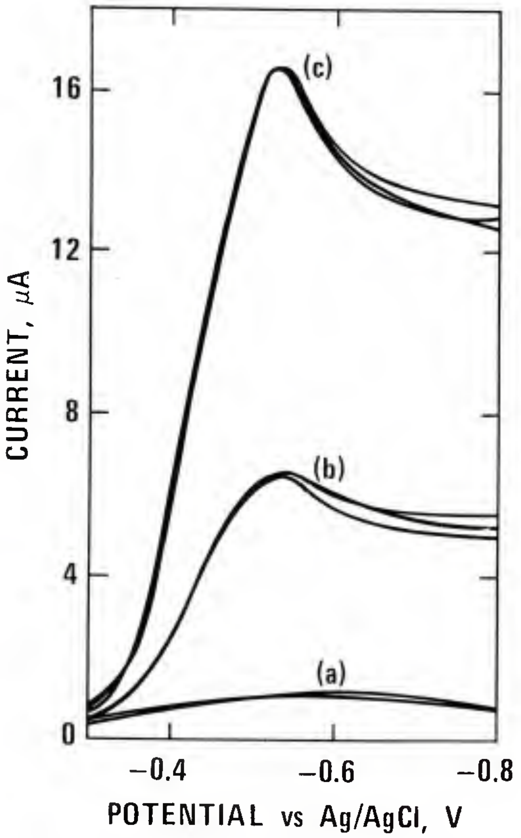

FIGURE 12. Linear Sweep Voltammograms of (a) Blank Solution; (b) Otto Fuel, Diluted 10^5:1; (c) Otto Fuel Solutions after Standard Addition of 14 ppm PGDN.

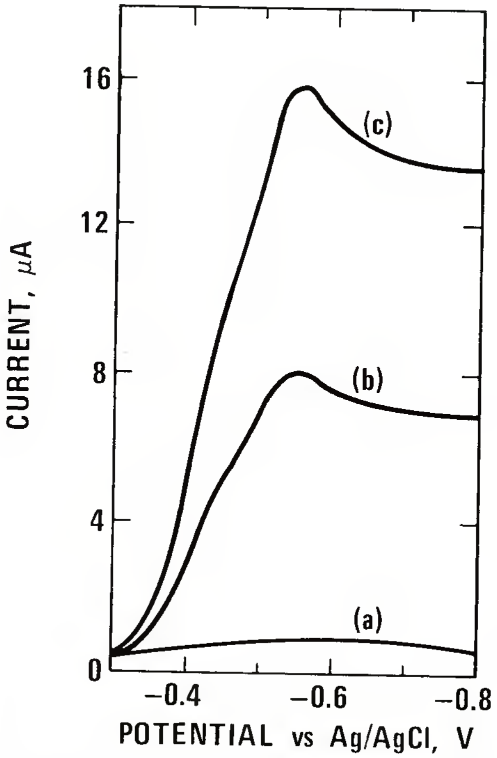

FIGURE 13. Linear Sweep Voltammograms of (a) Blank Solution; (b) Sump Water from NWS, Yorktown, after Processing by Oily Water Separator; (c) Same Sump Water Sample, after Standard Addition of 12 ppm PGDN.

a value far above the acceptable limit. Figure 14 shows the voltammogram of a sample of sump water from NUSC after passage through the carbon columns. Comparison with the traces obtained from a standard addition of 4 ppm and from a solution of 1 ppm PGDN indicates that if any PGDN is present in the treated water, the concentration falls well below the acceptable limit.

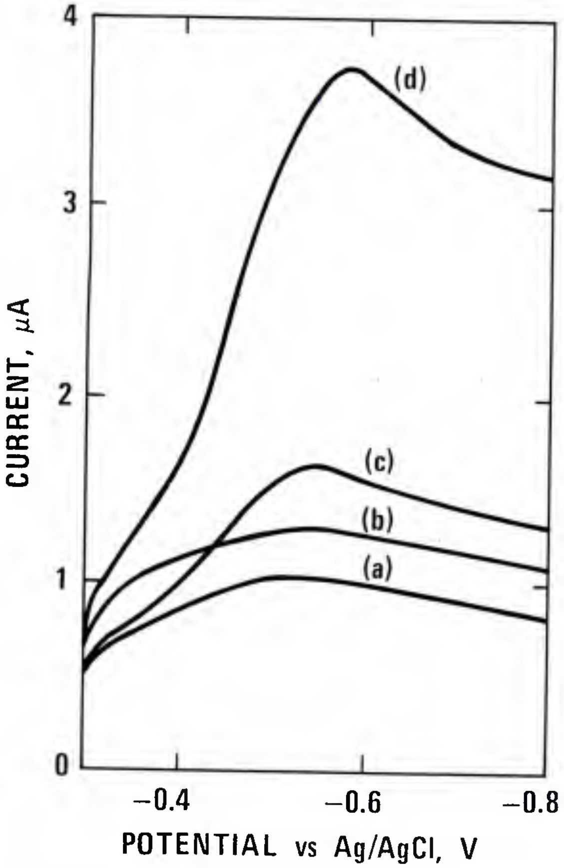

FIGURE 14. Linear Sweep Voltammograms of (a) Blank Solution; (b) Treated Water from NUSC, After Passage Through Carbon Columns; (c) Solution Formed by Addition of 1 ppm PGDN to Blank Solution; (d) Solution Formed by Addition of 4 ppm PGDN to Treated Water Sample.

PORTABLE VOLTAMMETER

A suitable electrode having been found, the next problem was to devise and build an inexpensive, compact, and simple voltammeter for use in conjunction with the electrode. A voltammeter meeting these standards was constructed at NWC. Details of the instrument construction will be published in Part 2 of this report.

The instrument measures 18 x 13 x 5 inches and fits into an aluminum carrying case. It plugs into any 115 V AC outlet. Cables which connect to the electrodes plug into the instrument panel. The voltammeter has three mode settings according to whether a blank, standard or test solution is being run. The solution is salted, placed in the electrode-containing cell and deaerated. Pressing of a button on the instrument panels actuates a cycle of three fast cleaning scans followed by a slow measuring scan. A microcomputer stores the maximum current value observed in a preset potential "window" area during the measuring scan. After runs have been made on blank, standard, and test solutions, the computer calculates the concentration of the test solution, prints out the result, and displays it. If the operator wishes to see the complete voltammogram, the instrument can be connected to an X-Y recorder.

Voltammograms obtained by the instrument are shown in Figures 15-18. They compare well with voltammograms obtained on the PAR 174. The ability of the instrument to detect the presence of Otto fuel is demonstrated in Figure 15.

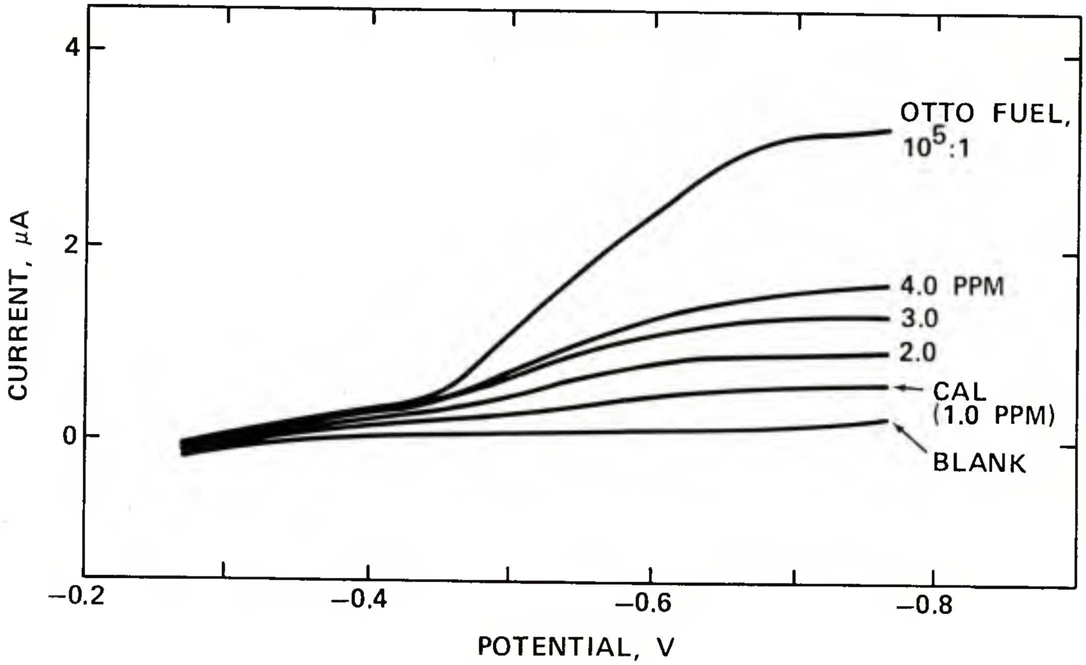

FIGURE 15. Recorder Traces from Runs on Portable Voltammeter. PGDN Solutions.

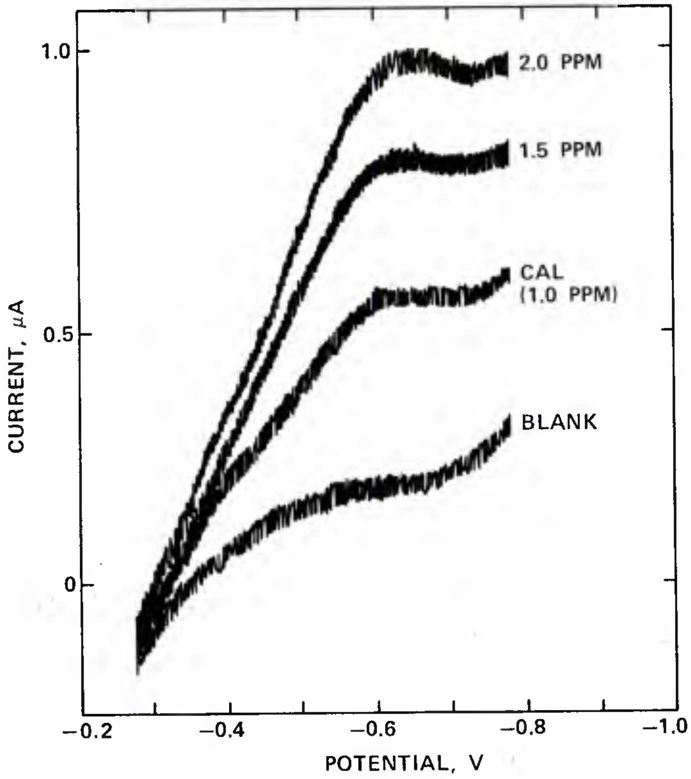

FIGURE 16. Recorder Traces from Runs on Portable Voltammeter, NG Solutions (Using Expanded Y Scale).

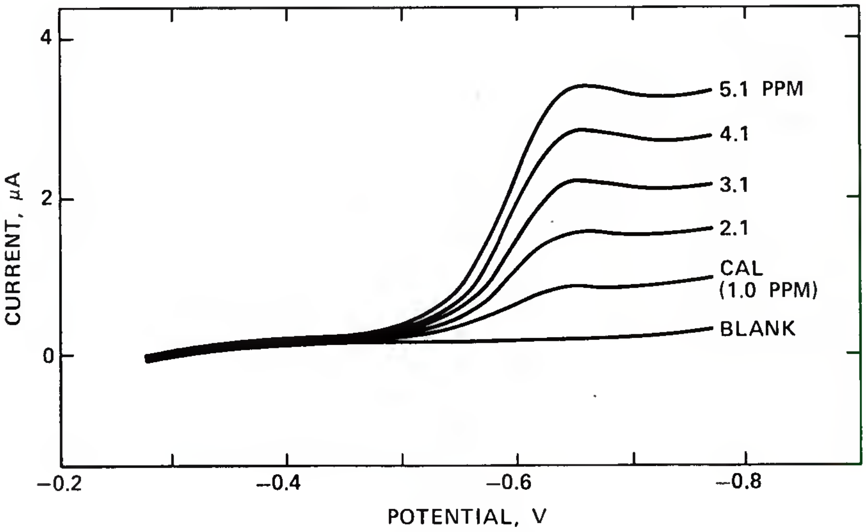

FIGURE 17. Recorder Traces from Runs on Portable Voltammeter, 2,6-DNT Solutions.

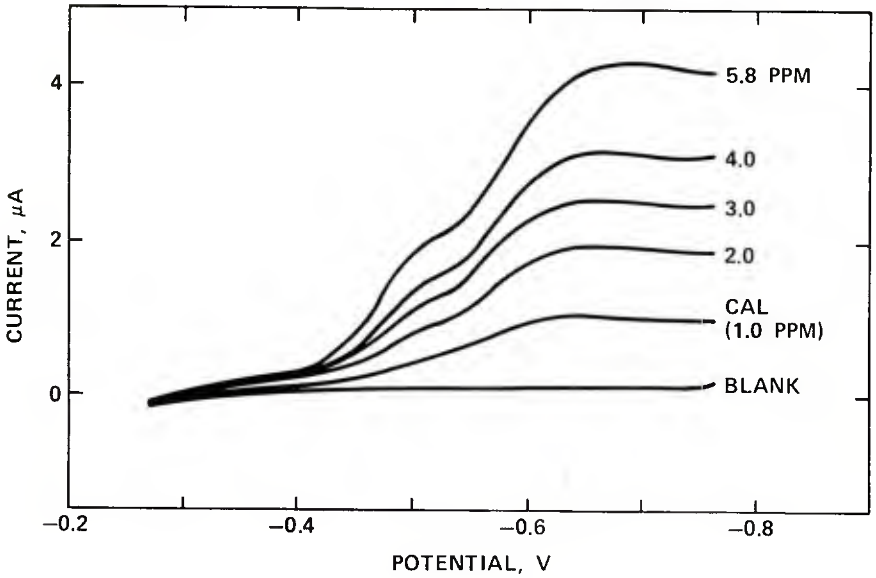

FIGURE 18. Recorder Traces From Runs on Portable Voltammeter, TNT Solutions.

SUMMARY AND CONCLUSIONS

The ability of the silver wire electrode to detect low concentrations of nitrate esters and other nitro compounds of importance to ordnance facilities has been demonstrated. Concentrations as low as 0.5 ppm can be detected and quantitated.

For situations in which only one such compound is present or dominant, use of the electrode in conjunction with the portable voltammeter provides a convenient means of monitoring effluent water and checking the efficiency of the purification process. Facilities concerned with more complicated matrices might make use of the electrode in conjunction with a separation technique such as liquid chromatography.

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