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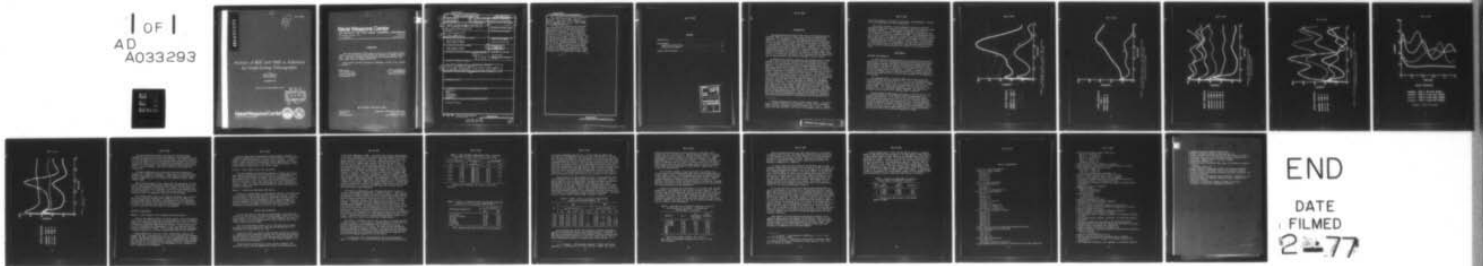
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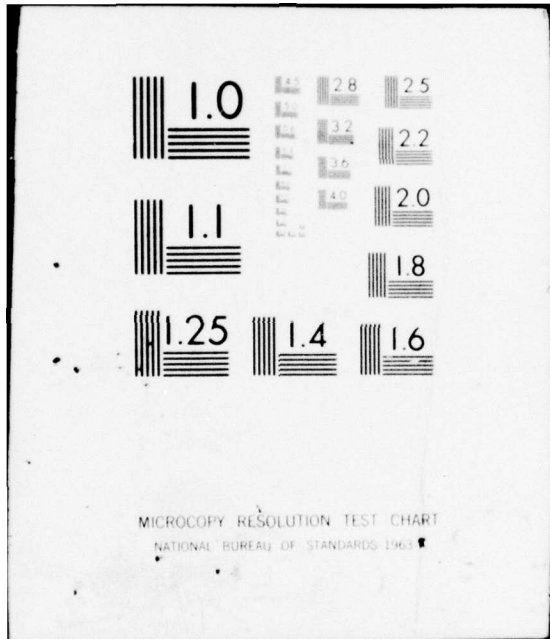
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Analysis of RDX and HMX in Admixture by Single-Sweep Polarography

by
Gerald C. Whitnack
Research Department

DECEMBER 1976

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R. G. Freeman, III, RAdm., USN Commander

G. L. Hollingsworth Technical Director

FOREWORD

The work described in this report is part of a continuing research project entitled "Applied Polarography for Analysis of Ordnance Materials." This work is supported by the Naval Sea Systems Command, Code 0332, under Task Area Number SF57572301.

This report has been reviewed for technical accuracy by Dr. Arnold T. Nielsen.

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(U) *Analysis of RDX and HMX in Admixture by Single-Sweep Polarography*, Gerald C. Whitnack. China Lake, Calif., Naval Weapons Center, December 1976. 20 pp. (NWC TP 5898, publication UNCLASSIFIED.)

(U) This report presents and describes a new polarographic analytical procedure that should prove useful in the direct analysis of RDX and HMX in admixture. The single-sweep technique is rapid and sensitive to about 50 parts-per-billion of either RDX or HMX alone or in admixture in effluent or natural water. The method can also be used to analyze for HMX as an impurity in manufactured RDX or for RDX that may be present in manufactured HMX. A determination can be made in 5 min on a 2-ml aliquot of water to within $\pm 10\%$ of the actual amount of explosive present. No separation or concentration of the explosives from the water sample is needed prior to the analysis in most cases.

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INTRODUCTION

Cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetra-nitramine (HMX) are used on a large scale today as nitramine-type explosives in the manufacture of propellants and ordnance-related materials. The production, use, and demilitarization of these materials is associated with an urgent need for better methods of analysis for RDX and HMX, respectively, in admixture. Reliable techniques that can determine either RDX or HMX alone and in admixture over a range in concentration from parts-per-billion to assay percentages in the solid manufactured material are lacking. In addition, precise, rapid, and sensitive procedures are needed for the analysis of RDX and HMX, respectively, in the effluent and natural water connected with the manufacturing of these explosives and pollution abatement control studies.

Although several methods of analysis have been developed for RDX and HMX,¹ few of these can determine both RDX and HMX in parts-per-billion directly in aqueous solution and in the manufactured solid material. In addition, most of the techniques measure either RDX or HMX in the matrix and the remainder is a value obtained by difference. The methods are not too reliable and are time-consuming; they suffer, in general, from lack of inexpensive apparatus for the analysis, and specificity, sensitivity, or simplicity in the analysis. For example, in chromatographic procedures, where electron capture detectors (nickel-63) are used for increased sensitivity, the detector is not very durable for field use, does not have long-term stability needed for continuous automatic operation, and is not amenable to temperature programming. This type of detector is also very sensitive to trace quantities of water and can be easily fouled by large quantities of other material that might occur in the system. Flame ionization detectors, although more reliable, many times suffer from lack of sensitivity. Both liquid and gas chromatography are currently being used to determine RDX and HMX in the manufactured material. Most of the methods of analysis in use today for the nitramine-type explosives also require a separation and/or preconcentration step of the explosive from the matrix before

¹ Defense Documentation Center, Defense Supply Agency. *Analytical Study of RDX-HMX Mixtures*, by H. Schubert, F. Volk, and H. Roszinski. Cameron Station, Alexandria, Virginia, December 1971. 20 pp. (Translation from *Explosivstoffe*, Vol. 14, No. 12, December 1966, pp. 265-73.)

doing the analysis by gravimetric procedures, chromatography, colorimetry, spectrophotometry, or X-ray diffraction.

This report presents a new polarographic analytical procedure developed at NWC that should prove useful in the direct analysis of RDX and HMX in admixture. A single-sweep polarographic procedure is described that can analyze for HMX as an impurity in manufactured RDX or for RDX as an impurity in manufactured HMX. The polarographic procedure is also rapid and sensitive to about 50 parts-per-billion of either RDX or HMX alone or in admixture directly in effluent or natural water. A determination can be made in 5 min to within $\pm 10\%$ of the true amount of explosive present in a water sample. In many cases, no separation or concentration step of the explosive from the water sample is needed prior to analysis and an analysis can be made on a 2-ml aliquot of water.

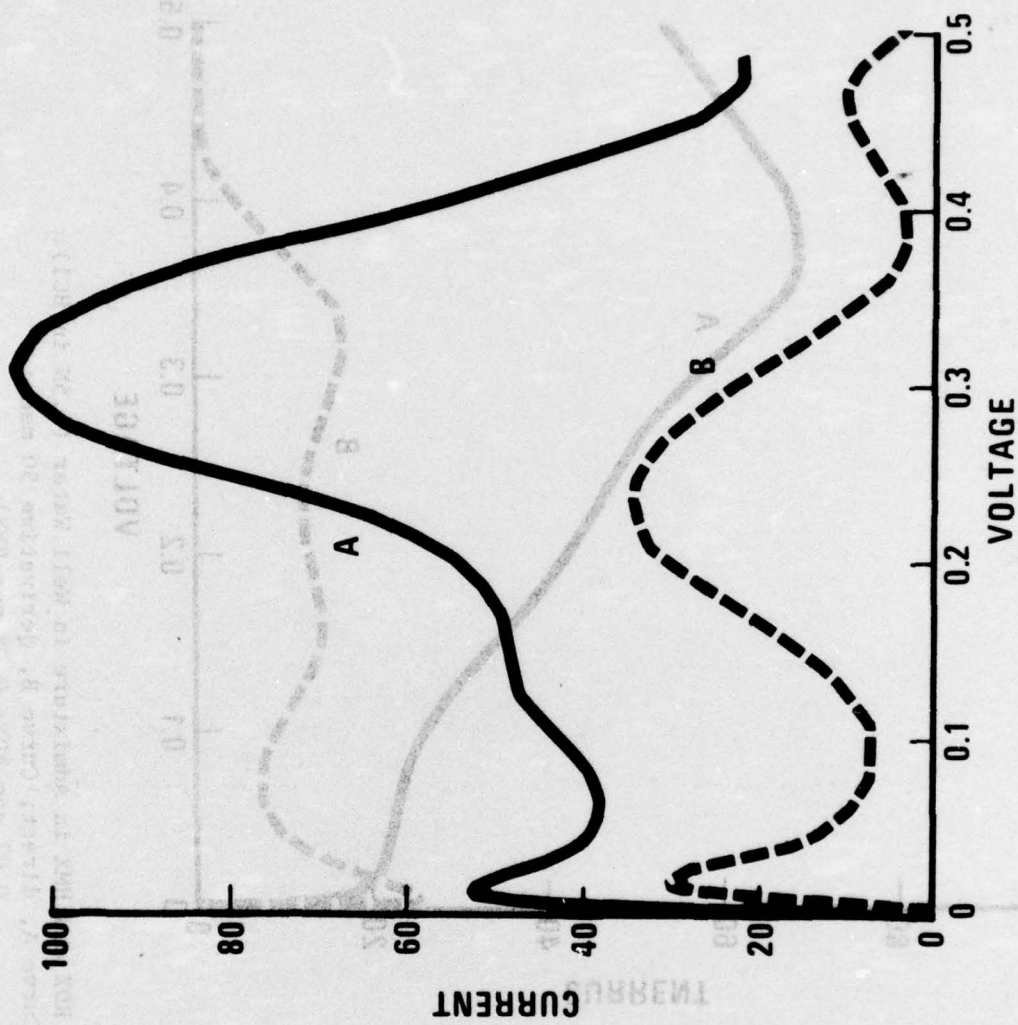
EXPERIMENTAL

APPARATUS AND MATERIALS

A single-sweep polarograph known as the A-1660 Davis differential cathode-ray *Polarotracer* and manufactured by Southern Analytical Instruments Company, England, was used to establish the optimum analytical conditions for the analysis and then to perform the analysis of both RDX and HMX in solution. A Moseley 2D X-Y recorder was used to record the data obtained with the *Polarotracer*. Figures 1 through 6 show typical current voltage curves for HMX and RDX in various supporting electrolytes obtained with the *Polarotracer* and recorded with the Moseley 2D X-Y recorder.

The dropping mercury electrodes (DME) used in this study were conventional type with drop times of 7 to 10 sec in distilled water at a mercury height of 43.18 cm; $m = 5$ to 7 mg per drop of mercury. Redistilled mercury was used for both the anode (mercury pool) and the cathode (DME). The current peak potentials (i_p) are referred to the mercury pool or to a saturated calomel electrode. pH values were obtained on all solutions with a Beckman Model G pH meter.

The polarographic measurements were made at $25^\circ\text{C} \pm 0.10^\circ$ on 2 ml of solutions placed in a 5-ml capacity quartz polarographic cell. Samples containing 10^{-3} to 10^{-5} g/ml of the explosive were diluted before making the analysis with the *Polarotracer*. Standard solutions and sample preparation of the explosives were made in spectroquality acetone obtained from Matheson, Coleman and Bell. The standards were prepared in the 10^{-4} to 10^{-5} g/ml range and then microaliquots (0.01 to 0.05 ml) of these solutions were added directly to the polarographic cell solution with a 50- μ l Hamilton hypodermic syringe.



START POTENTIAL

CURVE A = -0.35 V

CURVE B = -0.40 V

FIGURE 1. RDX and HMX in 1N HCl. (Curve A, RDX = 2.01 ppm, HMX = 4.00 ppm; Curve B, HMX only = 2.00 ppm)

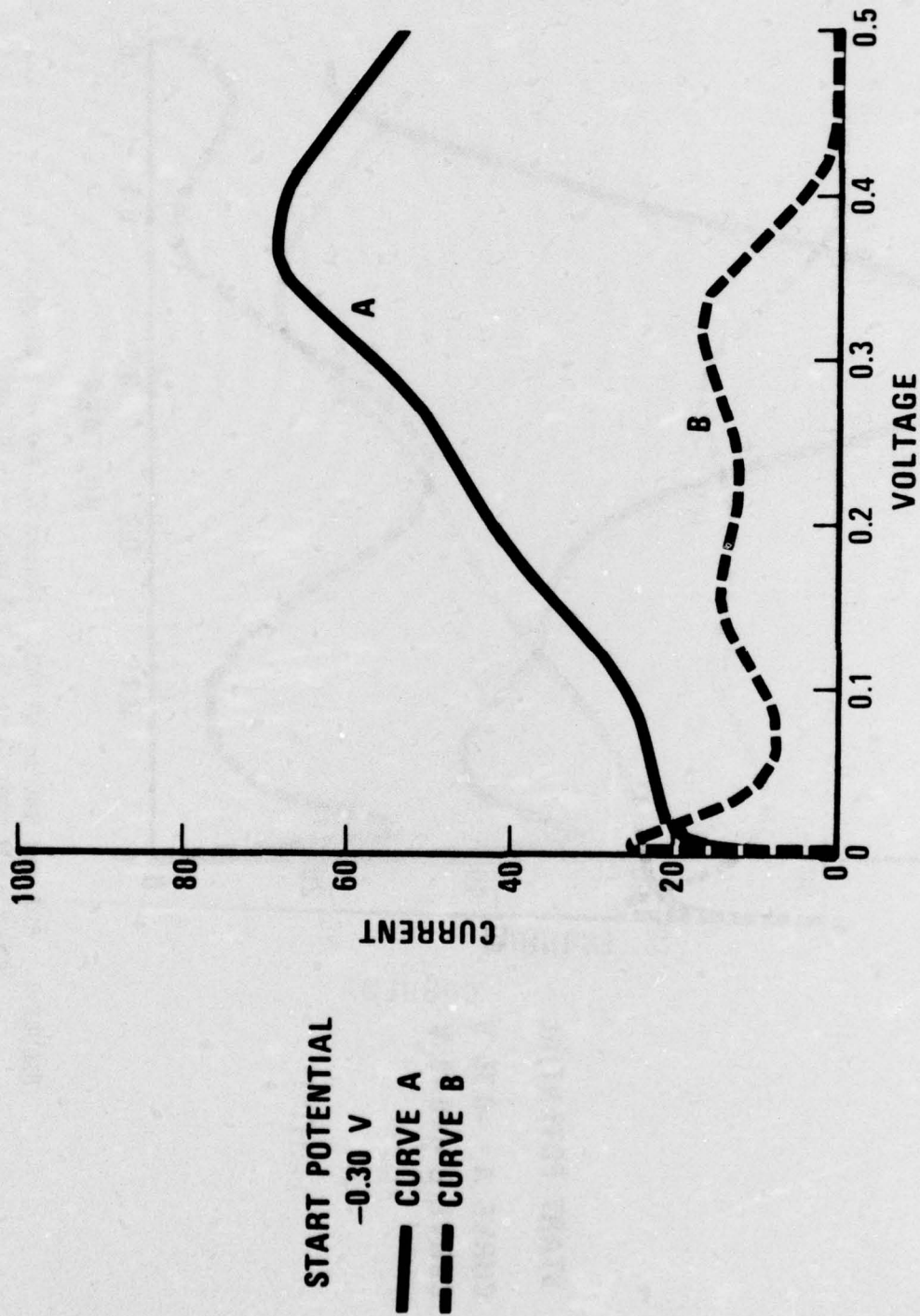
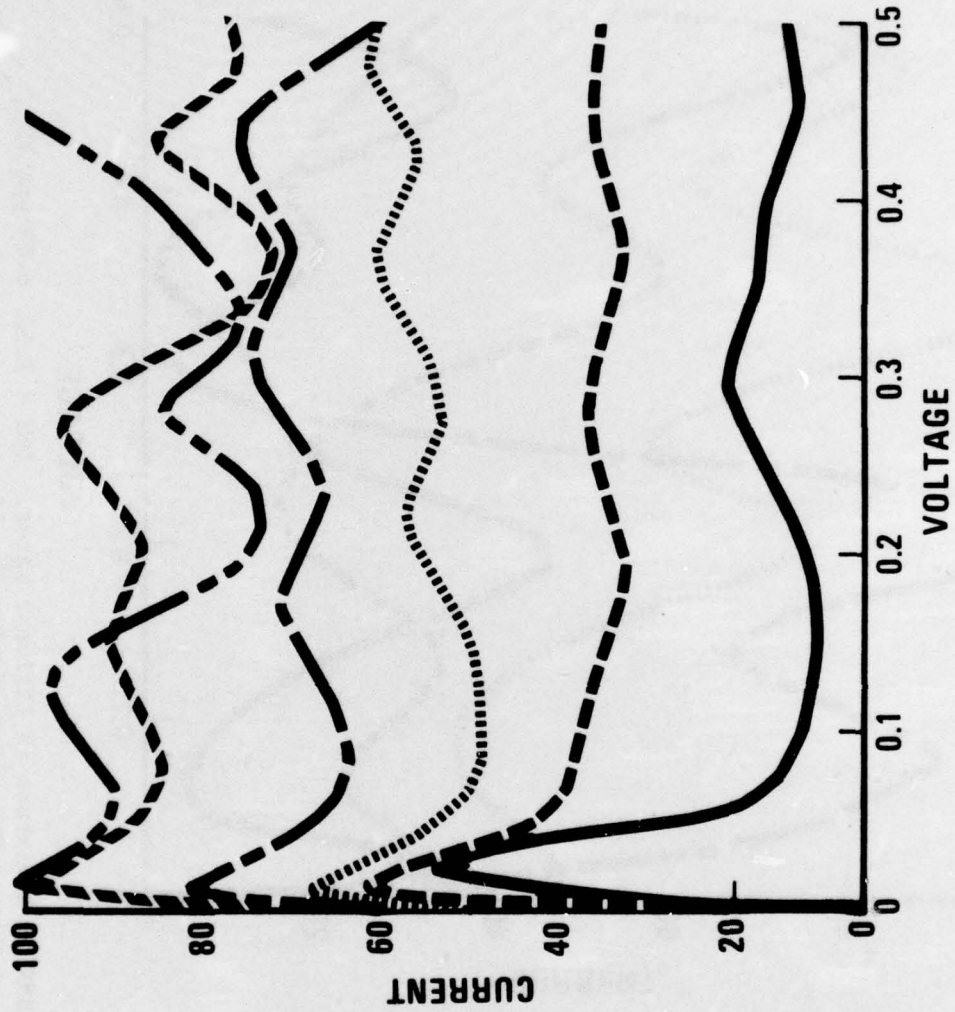


FIGURE 2. RDX and HMX in Admixture in Well Water (1.5N in HCl).
(Curve A, direct; Curve B, derivative 50 msec;
0.07 ppm RDX; 0.08 ppm HMX)



START POTENTIAL

- — — — — -0.35 V
- - - - - -0.60 V
- -1.00 V
- · - · - 1.05 V
- /// - - - - 1.20 V
- - - - - 1.35 V

FIGURE 3. RDX and HMX in Effluent Water.
 (pH 7.50, 0.8 ppm each added,
 derivative 50 msec)

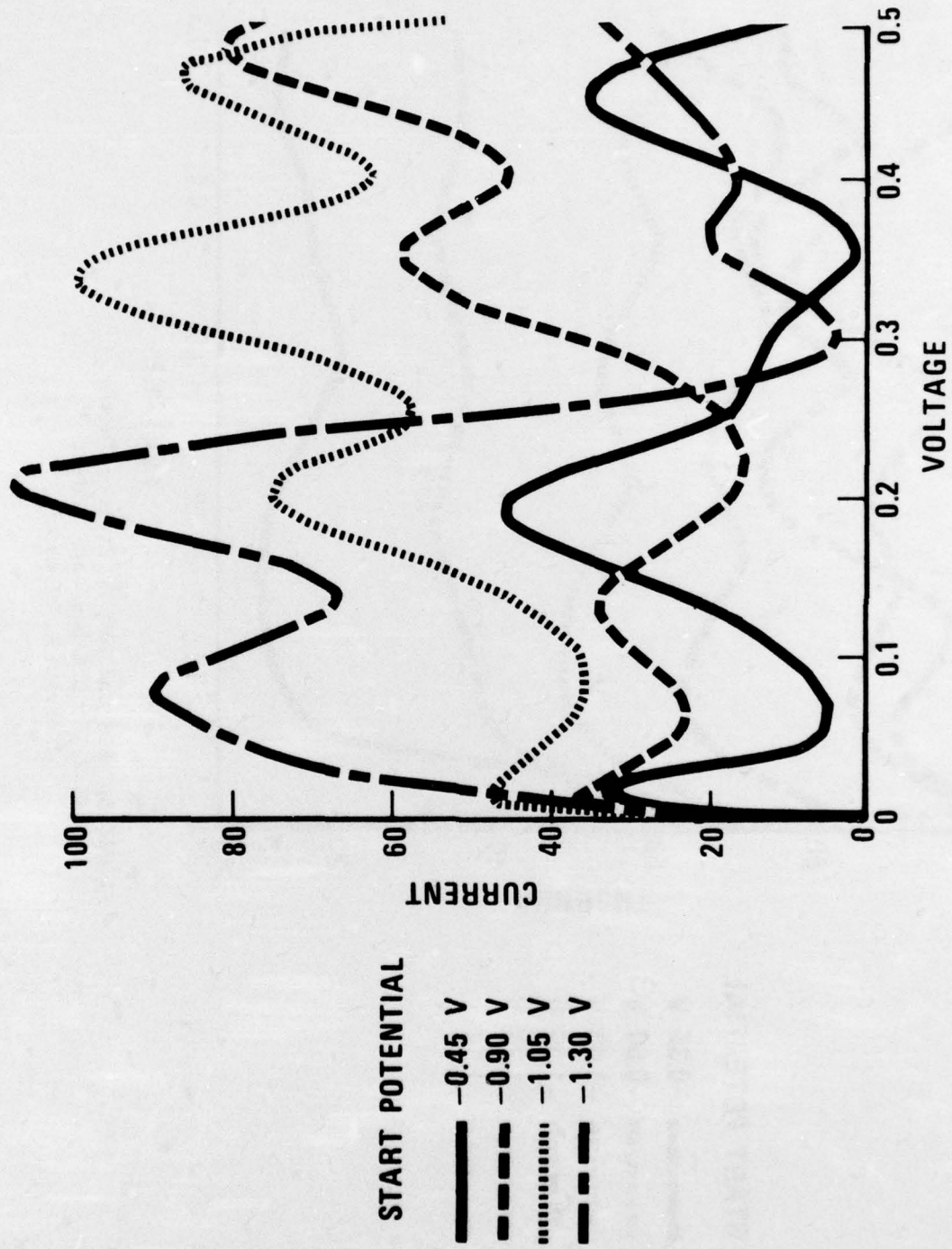
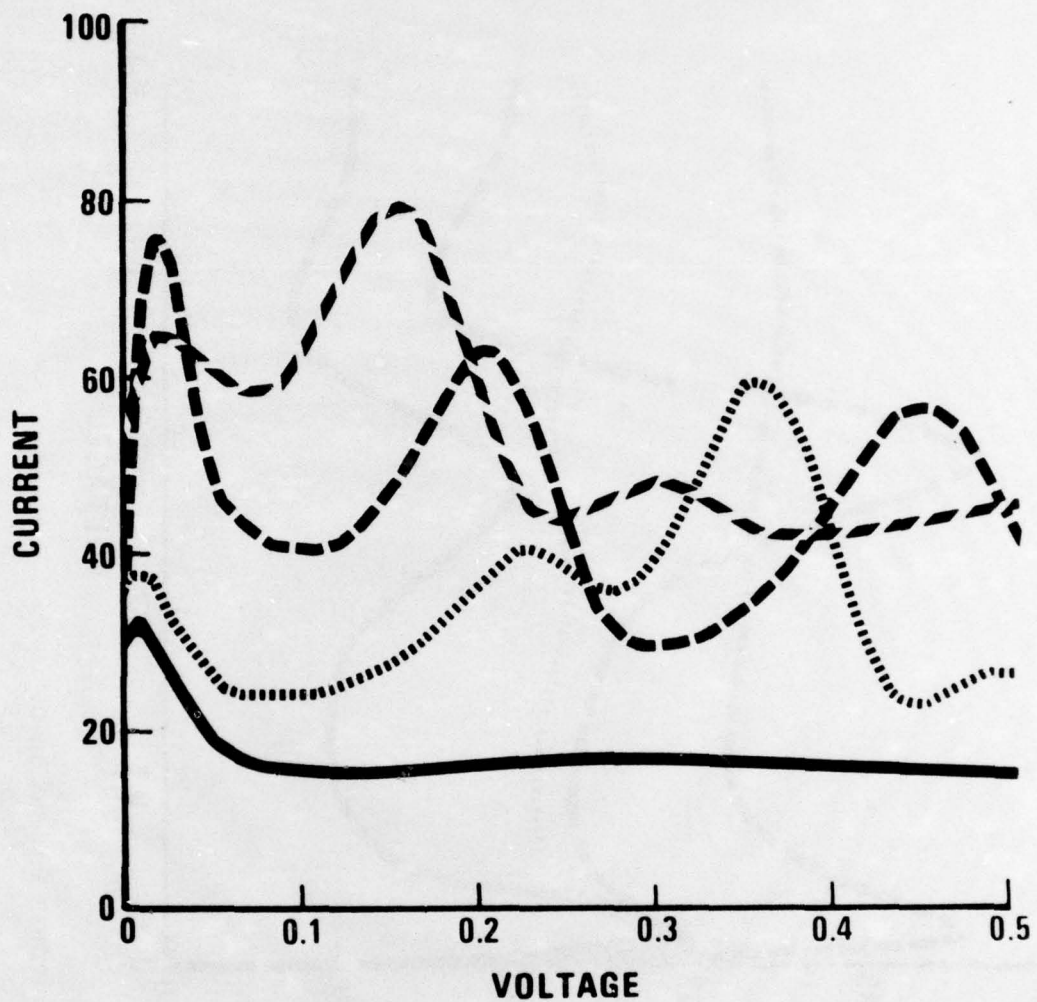


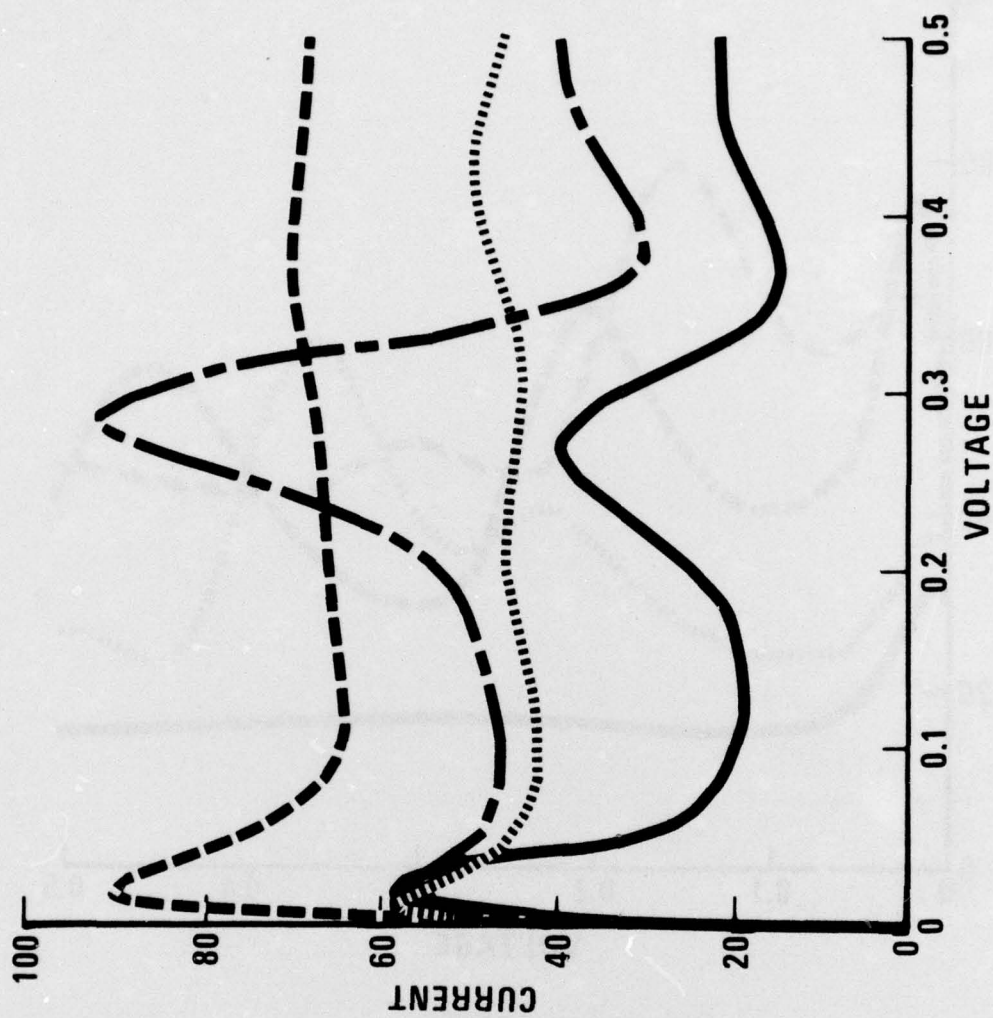
FIGURE 4. RDX and HMX in Admixture in Effluent Water. (pH = 7.50, 6.03 ppm RDX, 4.00 ppm HMX added, derivative 50 msec)



START POTENTIAL

- — — — — -0.40 V, NO RDX ADDED
- - - - - -0.40 V, 4 ppm RDX ADDED
- -1.00 V, 4 ppm RDX ADDED
- / - / - / - / - -1.20 V, 4 ppm RDX ADDED

FIGURE 5. RDX in 0.5 M NaCl.



START POTENTIAL

- — — — — -0.40 V
- - - - - -0.65 V
- -0.80 V
- . - . - . -1.20 V

FIGURE 6. HMX in 0.5 M NaCl.
(4.00 ppm)

Britton and Robinson buffer solutions were prepared double strength (2X), and then the buffer was added to the polarographic cell with varying amounts of the explosive solutions. The final concentration of the buffer was 0.1 M, with sodium chloride added when necessary to carefully control the ionic strength of the solution in the polarographic cell for analysis. Dissolved oxygen was removed from all solutions in the polarographic cell prior to analysis with oxygen-free nitrogen gas.

The RDX and HMX used in this work were obtained from Holston Defense Corp., Kingsport, Tennessee. The purity of the RDX was about 93% RDX and 7% HMX as established by an NWC carbon-13 nuclear magnetic resonance (NMR) analysis. The purity of the HMX was 99.9% as established by NMR.

Most solutions used in these studies had cell resistances of less than 500 ohms (as determined with a Wheatstone bridge) and the IR correction was negligible in computing the i_p values. The potential of the mercury pool was fairly constant in the Britton and Robinson buffer solution through the 3 to 7 pH range, and the i_p values are referred to the mercury pool for comparative purposes in this pH range.

The effluent water used in this study was obtained from a process which used activated carbon-filled columns to effect the removal of soluble organic matter and many of the inorganic ions from wastewater. This water had a pH of 6 to 8 and contained enough ionic conductivity to serve as an excellent electrolyte for polarography. No interference from ions such as Cu^{2+} , Pb^{2+} , and Cd^{2+} was observed.

ANALYTICAL PROCEDURES

Method A. Water Samples Direct (Effluent and Natural Water)

Place a 2-ml sample of water in a 5-ml capacity quartz polarographic cell to which has been added some redistilled mercury. Pass a stream of oxygen-free nitrogen gas through the solution in the cell for 2 or 3 min to remove any dissolved oxygen from the solution. Set the start potential of the single-sweep polarograph at -1.10 V (vs. mercury) and the current on derivative, 50 msec. After several sweeps by the polarograph a current-voltage curve is drawn on graph paper with the X-Y recorder.

Peaks observed at -1.25 and -1.38 V, respectively, indicate the presence of RDX. A peak seen at -1.50 to -1.53 V indicates the presence of HMX. The amount of RDX and HMX can then be calculated from a standard curve for RDX and HMX, respectively, or by a standard addition technique with the addition of microaliquots of standard solutions of RDX and HMX, respectively, to the solution in the polarographic cell, followed by a direct comparison of waveheights.

Typical single-sweep polarograms for RDX and HMX in admixture in a sample of effluent water (pH 7.50) are shown in Figure 3. The concentration of RDX and HMX added to the water is 0.8 ppm each. A large number of waves are seen, representing a rather complex series of electrode reactions taking place at the DME, as the start potential of the voltage sweep is varied over a 0 to -1.35 V range.

Method B. Water Sample Direct (HCl Acidified)

The same procedure as described in Method A is used, only 1 ml of water sample is mixed with 1 ml of 3.0N HCl in the polarographic cell. After the dissolved oxygen is removed, the start potential of the polarograph is set at -0.10 to -0.20 V, and a peak observed at -0.48 V shows the presence of RDX. The start potential of the polarograph is then set at -0.30 to -0.40 V and a peak seen at -0.58 V indicates the presence of HMX. The amounts of RDX and HMX can then be determined as described in Method A.

Method C. Manufactured RDX and/or HMX (Solid)

Dissolve a weighed sample of approximately 100 mg of solid material in spectroquality acetone and dilute to 100 ml with acetone. Place a 0.01-ml aliquot of the acetone solution (hypodermic syringe) into 2 ml of 1N HCl solution in the polarographic cell. Treat the sample the same as described in Method B and determine the amount of HMX as an impurity in RDX or the amount of RDX as an impurity in HMX by either the method of standard addition or the use of a standard curve.

RESULTS AND DISCUSSION

Data on the effect of the mercury column height on the diffusion current (i_d) for each wave observed for RDX and HMX, respectively, indicate diffusion controlled processes at the DME throughout the entire pH range studied, i.e., the limiting current varies with the square root of the corrected mercury height.

Over the concentration range of 10^{-3} to 10^{-9} g/ml the i_d values for most of the waves observed for both RDX and HMX appeared to be proportional to concentration ($i_d = KC$).

Since the current i_p values for RDX and HMX, respectively, depend on concentration and become more negative with increasing concentration, and since plots of $\log i/(i_d - i)$ do not give a linear relationship, the overall reduction process occurring at the DME (cathode) appears to be irreversible for each compound.

With solutions containing two or more organic compounds, the possibility exists that one compound may affect the diffusion process

of the other compound at a DME. In strong acid solutions small amounts of RDX can be determined in the presence of larger amounts of HMX (Figure 1, curve A) on derivative current. When the ratio of these compounds exceeds 3:1 there is difficulty in measuring the RDX wave. The HMX wave is only slightly more negative than that for RDX (Figure 1, curve B) and the waves overlap on direct current (Figure 2, curve A). The resolving power of the A-1660 polarograph (40 mV) allows for good definition of the HMX wave on derivative current (50 msec) and precise measurement of very small concentrations of HMX in the presence of RDX (Figure 2, curve B). When 10 to 50 parts-per-billion of standard HMX solution is added to a solution containing a large concentration of RDX, only the waveheight of the more negative current (due to HMX) increases proportionally to the amount added. The waveheight of the more positive current (due to RDX) is unaffected by the addition of this microquantity of HMX to the solution. When 10 to 50 parts-per-billion of standard RDX solution is added to a solution containing a large concentration of HMX, there appears to be no effect on the HMX wave, and the more positive wave due to RDX is easily measured.

The effect of hydrochloric acid concentration on the i_p and i_d values of RDX and HMX, respectively, is shown in Table 1. Only one wave is observed with HMX throughout the entire HCl normality range studied. RDX appeared to exhibit two waves in 0.1N through 3.0N HCl solution with the more negative waveheight decreasing with increasing HCl concentration. In strong HCl solution (6N) only one wave is seen for both RDX and HMX. In strong acid solution a highly protonated species of each compound should predominate, and very little of the unprotonated molecule should be present. In 6N HCl solution a shift of i_p values to more positive values for both RDX and HMX would seem to indicate a direct reaction of a proton to form an intermediate species which is reduced more easily. In the weaker HCl solutions the i_p values for the compounds are more negative, indicative of a species which reduces with more difficulty. In strong HCl solution the RDX protonated species appears to be slightly easier to reduce at the DME than the HMX species.

The effect of different acids on the i_p values of both RDX and HMX is shown in Table 2. The presence of chloride has very little effect on the wave separation of the compounds from a comparison of the i_p values of each compound in 0.5 M NaCl. The waves for RDX and HMX are also more negative in sulfuric, phosphoric, and tartaric acid solutions, respectively, than in hydrochloric acid. These data show good evidence for protonated species of both RDX and HMX existing in strong HCl acid solution with greater separation of the i_p values.

It is known that with a weak ampholyte such as nitroguanidine ($pK_a = 12.2$ and $pK_b = 14.5$) different ionic and molecular species exist

TABLE 1. RDX and HMX in Hydrochloric Acid, 4 ppm Each.
(Derivative, 50 msec, SSF = X1-2.5, ASF = X-10)

i_p (vs. Hg pool), V		Hydrochloric acid (normality)	i_d , Waveheight ^a	
1st	2nd		1st	2nd
-0.66	-0.83	RDX, 0.1	14.0	26.0
....	-0.83	HMX, 0.1	56.0
-0.50	-0.65	RDX, 1.0	23.0	6.0
....	-0.64	HMX, 1.0	32.0
-0.48	-0.58	RDX, 3.0	30.0	5.0
....	-0.58	HMX, 3.0	32.0
-0.48	RDX, 6.0	56.0
....	-0.55	HMX, 6.0	40.0

^a Graph paper divisions, 10 x 10 to 1.25 cm (X-Y recorder).

TABLE 2. Effect of Different Acidic and Neutral Supporting Electrolytes on i_p Values of RDX and HMX.

Supporting electrolyte	i_p (vs. Hg pool), V	
	RDX	HMX
0.5 M NaCl ^a	-0.60	-0.67
1N HCl-0.5 M NaCl	-0.48	-0.64
1N H ₂ SO ₄	-0.82	-0.93
2N H ₂ SO ₄	-0.75	-0.94
0.1N H ₃ PO ₄	-0.93	-1.08
0.1N C ₄ H ₆ O ₆	-0.93	-1.05

^a More negative waves also observed in this solution.

in solution depending upon the pH.² In this study two waves were observed with nitroguanidine in 0.1N through 2.0N HCl while in 6N HCl only one wave was observed. The waveheight of the second and more negative nitroguanidine wave also became less as the acid concentration was increased, while the height of the first wave increased until the second wave could no longer be seen. Thus, RDX behaves the same in HCl solutions as nitroguanidine, but HMX exhibits only one wave, which has an i_p value the same as the second wave seen for RDX in 0.1N HCl through 3.0N HCl; only in the strong HCl (6N) does HMX seem to show an i_p value indicative of a protonated species. Here the i_p value is about 250 mV more positive and within about 70 mV of the i_p value for RDX (Table 1).

Similar behavior of RDX and HMX solutions to nitroguanidine solutions throughout the pH range studied was seen in this work. Thus, it would seem that, like nitroguanidine, the number of waves observed for RDX and HMX at different potentials in different pH media can be explained by the fact that different ionic and molecular forms of RDX and HMX exist in solution. These present a complex system to study in the neutral and alkaline pH region. The reduction mechanism in neutral and alkaline solution appears to be complicated and even n-values are of little help in elucidating the overall process in such media. The effect of pH on the i_p values of RDX and HMX is shown in Table 3.

TABLE 3. Effect of pH on i_p Values of RDX and HMX.
(Britton and Robinson Buffers, 2X)

pH	RDX					HMX			
	i_p (vs. Hg pool), V					i_p (vs. Hg pool), V			
	1st	2nd	3rd	4th	5th	1st	2nd	3rd	4th
2.00	-0.96	-1.12	-1.36	-1.46	-1.15
3.15	-0.96	-1.12	-1.28	-1.45	-1.05	-1.28	-1.44
5.20	-0.89	-1.15	-1.37	-1.48	-0.99	-1.48	-1.67
7.01	-0.81	-1.15	-1.35	-1.44	-0.92	-1.48	-1.67
9.10	-0.68	-0.93	-1.11	-1.29	-0.76	-1.17	-1.34	-1.58
12.00	-0.30	-0.58	-0.72	-0.95	-1.07	-0.39	-0.78	-1.09	-1.27

Acid solutions are the best for analytical purposes, although it appears that in effluent water, where the pH is near 7, the amount of HMX can be determined directly in the presence of RDX by using the wave HMX produces in this solution at -1.50 V (vs. mercury pool). RDX can best be determined directly in effluent water, with a pH near 7, by

² G. C. Whitnack. "Polarographic Behavior of Nitro and Nitrosoguanidine," *J. Electrochem. Soc.*, Vol. 106, No. 5 (1959), pp. 422-27.

using the waves RDX produce in the solution at -0.85 and -1.25 V, respectively (vs. mercury pool). RDX and HMX were added to a typical effluent water and the results are shown in Figures 3 and 4. Similar polarograms are shown in Figure 5 for RDX and in Figure 6 for HMX, respectively, in 0.5 M NaCl solution of pH 6. A study of the effect of RDX on the HMX wave and vice versa in effluent water with a pH near 7 showed that in the part-per-billion range there is rarely an interference problem and the waveheights for RDX and HMX, respectively, are linear with concentration.

If 2,4,6-TNT, 2,4-DNT, or their derivatives are present in an effluent water containing RDX and/or HMX, then the HCl supporting electrolyte cannot be used. The polarograms from these explosives overlap in HCl media and an analysis for RDX or HMX cannot be made. Neutral, slightly alkaline, or weakly acidic electrolytes are best for the analysis of RDX, HMX, and TNT or DNT derivatives in admixture. Although many waves are seen in these solutions a separation of the waves allows for some characterization and measurement.

A mixture containing parts-per-million of 2,4,6-TNT, RDX, and HMX, respectively, was studied in a pH 7 buffer solution (Table 4). TNT produces three well defined waves that are all more positive than those for either RDX or HMX. TNT can be determined from these waves without interference from either RDX or HMX. Both RDX and HMX can then be determined separately in this media from their respective waves, which are more negative than those for TNT, and are separated enough from each other to allow for good measurement.

TABLE 4. RDX, HMX, and 2,4,6-TNT in Admixture in Britton and Robinson pH 7.10 Buffer. (2.01 ppm RDX, 2.00 ppm HMX, 1.04 ppm TNT)

Explosive	i_p , V	i_h , Graph paper divisions ^a	Start potential, V
2,4,6-TNT	-0.37	17.0	-0.10
2,4,6-TNT	-0.56	31.0	-0.20
2,4,6-TNT	-0.70	36.0	-0.40
RDX	-1.02	5.0	-0.80
RDX	-1.38	8.0	-1.15
HMX	-1.35	6.0	-1.15
HMX	-1.58	3.5	-1.15

^a Derivative current, 50 msec; SSF = X1-2.5, ASF = X-10. Graph paper divisions, 10 x 10 to 1.25 cm (X-Y recorder).

Once the explosive mixture has been characterized in an effluent or natural water solution, the supporting electrolyte which allows for the best separation of the waves with definity for precise measurement is used for the polarographic analysis. References by Hetman³ and Whitnack,⁴ respectively, suggest useful supporting electrolytes for mixtures of explosives in solution.

If a water sample contains inorganic contaminants such as some metallic cations that may interfere in the analysis of HMX or RDX by the described polarographic procedure, they can be removed by the addition of a chelating agent such as EDTA to the water sample. An interfering anion, such as iodide or iodate, may be removed by the addition of a reducing or oxidizing agent to form another chemical species that does not interfere. When the interferences cannot easily be removed, then the RDX and/or HMX must be extracted from the water sample with pure organic solvents such as benzene or n-hexane. The solvent is then evaporated off and the sample is taken up with HCl or a suitable electrolyte for the final polarographic analysis.

In strong acid (HCl) solution the single-sweep polarographic procedure is sensitive to the detection of 50 parts-per-billion of either RDX or HMX in effluent water and to the analysis of mixtures of RDX and HMX at the part-per-billion level. A second (more negative) wave, which appears to be less than the height of the first wave, is seen for HMX in 1N to 3N HCl solutions. This wave (Figure 1, curve B), about -0.86 V (vs. mercury pool), can be used to characterize the presence of HMX but is too close to the reduction of H^+ to be useful in the quantitative analysis of HMX. The second HMX wave may be due to a nitroso species of HMX in solution which is formed in the reduction of the nitro group ($NO_2 \rightarrow NO$) of the HMX at the DME in the first step. A nitroso species is generally reduced at a more negative potential than a nitro species of the same compound and is likely to undergo decomposition by acid more readily in solution.

Some samples of Holston-manufactured RDX were analyzed by the suggested single-sweep polarographic method (Method C above) for the amount of HMX produced as an impurity in the product. The data showed the HMX content of this manufactured RDX to be 7.0% by weight. The percent of HMX found in these samples checked very well with that obtained by an NMR analysis on the same samples.

³ J. S. Hetman. "Polarography of Explosives," *Z. Anal. Chem.*, Vol. 264 (1973), pp. 159-64.

⁴ G. C. Whitnack. "Single-Sweep Polarographic Techniques Useful in Micropollution Studies of Ground and Surface Waters," *Anal. Chem.*, Vol. 47 (1975), pp. 618-21.

A known weighed amount of pure (99.9%) HMX was added to a weighed sample of RDX that had been analyzed for its HMX content by NMR analysis. A total weighed sample of about 200 mg of the RDX-HMX mixture was then dissolved in 5.0 ml of acetone. The acetone solution contained 46 mg of added HMX (by weight). One milliliter of this solution was diluted to 100 ml with acetone for the polarographic analysis. Recovery data for the HMX content of this sample with the described polarographic procedure is given in Table 5. The data indicate that a small amount of HMX can be determined in admixture with a large amount of RDX to within ± 5 to 10% of the actual amount of HMX present in the sample. A small amount of RDX in the presence of a large amount of HMX can be determined by the same polarographic procedure within the same limits of precision.

TABLE 5. Recovery of Added HMX in Solid RDX
(Single-Sweep Polarographic Analysis).

Sample no.	HMX added, g	HMX ^a found, g	Recovery, %
1	0.0460	0.0434	94.3
2	0.0460	0.0476	103.5
3	0.0460	0.0470	102.2

^a Corrected for HMX content of 200 mg RDX sample (7% HMX).

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