POLAROGRAPHIC ANALYSIS OF PBX'S

B. D. Faubion

DEVELOPMENT DIVISION

APRIL - JUNE 1976

Normal Process Development
Endeavor No. 223

MASTER

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operated for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
under
U. S. GOVERNMENT Contract DA-11-173-AMC-487(A)

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ABSTRACT

Four plastic bonded explosives containing HMX and one containing RDX were run on the polarographic analyzer to determine if these explosives could be analyzed without separation using this technique. A sample of pure HMX was also analyzed for comparison. Only one of the explosives, LX-09, could not be analyzed by this method due to the interference of the PDNPA and FEFO.

The other explosives can be analyzed; however, quantitation based on calibration with pure HMX is not satisfactory. It is recommended that a calibration using standards containing all of the components in a particular PBX be used or that a standard addition method be employed in order to obtain accurate quantitative results.

INTRODUCTION

The polarographic method has been used for the quantitative analysis of RDX and HMX(1,2,3).

The method is based on the apparent two-electron reduction of the nitro-group according to the reaction

in protic solvent systems. The reduction potential is dependent on the chemical environment of the nitro group(s) and is characteristic for the material in a given solvent system. In systems containing more than one type of nitro group, the reduction potentials may be so close together that it is not possible to separate the waves.

By measuring the diffusion current (i_d) the concentration of the material containing the electroactive element (in this case the nitro group) can be determined. If a fixed height pulse is superimposed on a linearly increasing dc ramp applied to the chemical cell and the current is sampled just before and near the end of the pulse, a curve approximating the derivative of the polarographic wave is obtained. This technique is called differential pulse polarography and offers a significant improvement in sensitivity over the classical DC polarogram. The clearly defined sharp peaks allow precise measurement of peak height and location of peak potential.

In practical applications, a series of calibration standards are run and a plot of peak height versus concentration constructed. The concentration of the material in an unknown sample can be determined by measuring the peak height for this sample run under the same conditions.

(1) D. T. Lewis, *Analyst*, 79 (1959) 644.

(2) J. S. Hetman, *Anal. Chem.*, 32 (1960) 1699.

(3) B. D. Faubion, *MHSMP-73-35*.

EXPERIMENTAL

The polarographic analysis was carried out using a P.A.R.^a, model 174 polarographic analyzer operating in the differential pulse mode. A constant drop time of 0.5 sec was maintained by using the 174/70 drop timer. The potential was scanned from -1.2 V to -0.45 V vs. S.C.E.^b at a scan rate of 5 mV/sec. A current range was selected to give the best peak representation.

All the samples were run in a 20% acetone/80% 0.05 M sodium sulfite-borate buffer solution. With this system there is no interference by dissolved oxygen and deoxygenation by bubbling nitrogen through the solution is not necessary. The PBX solutions were prepared by dissolving approximately 10 mg (weighed accurately) of explosive in 20 ml of acetone and diluting to 100 ml with the buffer. Three solutions of the pure HMX were prepared in a similar manner using 5, 10, and 20 mg of explosive.

RESULTS AND DISCUSSION

A typical differential pulse polarogram of HMX in 20% acetone/80% 0.05 M sodium sulfite-borate buffer is shown in Fig. 1. The primary reduction peak for HMX in this solvent system occurs at -0.863 V vs. S.C.E. Fig. 2 shows the plot of the height of this peak in μ A vs. the concentration of HMX in ppm. The plot is linear up to 22 ppm. The reduction potential for HMX in the PBX's was shifted slightly due to the presence of the other components. Table I lists the reduction potentials observed for HMX in the various PBX's. One PBX containing RDX was also analyzed. In this system RDX is reduced at -0.735 V vs. SEC.

The HMX peak in LX-09 was not resolved. It coalesced with a peak or peaks at a more negative potential which probably results from the reduction of the nitro-groups in PDNPA and FEFO, the two other constituents of this explosive.

A shoulder of a peak at a more negative potential was also observed in the polarogram of LX-14. Additional scans were made on this material starting at -1.7 V vs. SEC. This additional peak observed at -1.44 V results from the reduction of estane and also possibly from the additional reduction of HMX. The contribution of the estane was established by running a sample of estane by itself. It showed a peak at -1.375 V. The HMX standards were also scanned in this region and showed a peak at -1.425 V, but it was not linear with concentration. Additional studies will have to be made in order to establish the source of this peak.

^aPrinceton Applied Research Corporation, Princeton, New Jersey

^bSaturated Calomel Electrode

Fig. 1. Differential Pulse Polarogram of 22 ppm HMX in 20% Acetone/80% Sodium Sulfite - Borate Buffer

Fig. 2. Polarographic Reduction of HMX in 20% Acetone/80% Sodium Sulfite - Borate Buffer at -0.863 V vs. S.C.E.

Table I. Polarographic Reduction Potentials for HMX in Various PBX's Dissolved in 20% Acetone/80% Sodium Sulfite-Borate Buffer

<u>PBX</u>	<u>Reduction Potential V vs S.C.E.</u>
LX-04	-0.855
LX-14	-0.853
9404	-0.855
LX-09	Peak not resolved

Quantitative analysis based on the calibration for pure HMX was not satisfactory. The percentage of HMX in the LX-04 came out greater than 100% because of the contribution of the peak at a more negative potential. The percentage of HMX in the LX-14 and PBX 9404 was only 93% of the expected values. Since there are no interfering peaks in the polarograms of these materials, it is speculated the other components of these PBX's have a suppressing effect on the current. This can be rationalized on the basis that any material which changes the viscosity of the solution would effect the diffusion coefficient and likewise the diffusion current. Additional studies will be required in order to develop a method for quantitative analysis of these PBX's. One method would be to calibrate using standards containing all of the components in the PBX's. The standard addition method could also be used for these samples. If a known volume of a standard solution of HMX is added to the unknown, the concentration in the unknown can be calculated from:

$$C_u = \frac{i_1 v C_s}{i_2 v + (i_2 + i_1) V}$$

where

C_u = unknown concentration
 C_s = standard concentration
 i_1 = original peak height
 i_2 = peak height after addition of standard solution
 V = original sample volume
 v = volume of standard added

This technique could possibly also be used for analysis of the LX-04.

CONCLUSIONS

The differential pulse polarographic technique should be a useful tool for the analysis of PBX's containing HMX with the exception of those containing other materials with electroactive groups which would be reduced at a potential close to the HMX reduction potential.