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TRACE LEVEL DETECTION OF N-METHYL-N-2, 4, 6-TETRANITROANILINE, A NITRO EXPLOSIVE MATERIAL USING ADVANCED ELECTROCHEMICAL TECHNOLOGY

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Abstract:

Explosives and their byproducts must be monitored in soil and surrounding water ways since these are mutagenic, toxic and persistent pollutants that can leach from the contaminated soil to accumulate in the food chain. In this study, a voltammetric method has been developed for the determination of Tetryl secondary explosive. The electrochemical redox behavior of Tetryl was studied through cyclic voltammetry using Glassy Carbon electrode (GC). Tetryl exhibited one predominant reduction peak at a potential of -0.18V and a small reduction peak at -0.40V in acetonitrile buffer containing 0.1M TBABr. Only cathodic peaks were observed indicating the irreversibility of the electrochemical reaction. Differential pulse and square wave voltammetry techniques were used for quantitate determination of Tetryl. Calibration curves were drawn and were linear in the range 50ppm to 100 ppm with a detection limit of 14ppm for Tetryl. This methods can be applied to determine the contaminations in soil/water samples etc.

Key Words: Explosive, Tetryl & Voltammetry

1. Introduction:

Explosives and their byproducts must be monitored in soil and surrounding water ways since these are mutagenic, toxic and persistent pollutants that can leach from the contaminated soil to accumulate in the food chain (1). The sources of these explosive contaminants include the manufacturing, testing and disposal of explosives by defense establishments. Nitro explosives like TNT, Tetryl are major ingredients in nearly every ammunition formulation and are the secondary explosives used in the greatest quantities. In practice, explosive contaminants in soil and water may undergo metabolic transformation, photo catalytic degradation and biodegradation by processes like oxidation, dehydrogenation, reduction, hydrolysis, exchange reactions (2). Hence, trace level detection of theses explosives in the complex environmental matrixes by classical methods is difficult and will require development of new analytical methods. Techniques such as spectrometric (3-7), Gas chromatography (8-9), Liquid Chromatography (10-11), HPLC (12), Electrophoresis (13), Reverse - phase liquid chromatography-mass spectrometry, flow-injection analysis and electrochemical methods with various detection techniques that are coupled with several different separation methods such as Gas, liquid chromatography (14-15). Voltammetric and amperometry methods are used in qualitative and quantitative determination of trace levels of pollutants in various environmental components over a wide range of concentrations. These techniques are sensitive to oxidation and reduction and thus offer a promising analytical method for ordnance compounds (16-17). The objective of this study is to develop a voltammeric method for the determination of Tetryl explosive in acetonitrile buffer containing 0.1M TBABr. In this study, Cyclic voltammetry and Chronocoulometry are used to identify the reaction mechanism and Stripping voltammetry methods (DPSV & SWSV) are used to develop an analytical procedure for the determination of Tetryl at trace level.

2. Experimental:

Apparatus and Technique: Voltammetric experiments were performed using CH Instrument- 620A Electrochemical Analyzer. The electrochemical cell with glassy carbon as working, Silver-Silver chloride and platinum foil as reference and counter electrodes respectively was employed for the electrochemical studies.

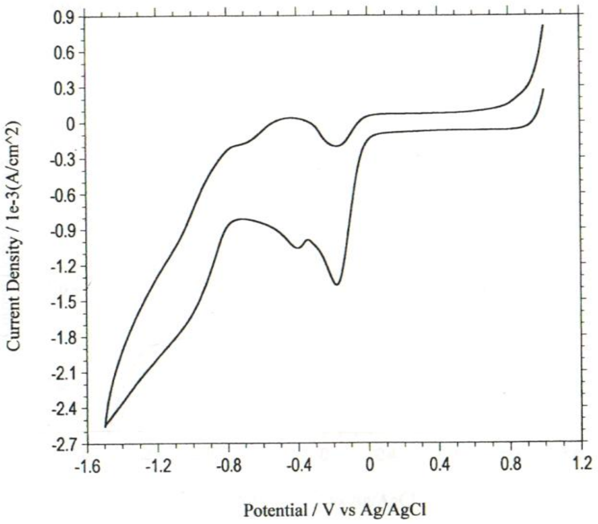
Electrode Pretreatment: The GC electrode was policed with a suspension of alumina powder and then rinsed thoroughly with deionized water to remove any alumina residue. Electrochemical pretreatments were done in a 50mM $(NH_4)_2SO_4$ solution, pH 3.0 being adjusted with sulfuric acid. The pretreated electrodes were allowed to stay for 10min in deionized water before measurements to improve the stabilization of the voltammetric response.

Electrochemical Studies: The electrochemical redox behavior of Tetryl (N-methyl-N-2,4,6-tetranitroaniline) was studied using cyclic voltammetry technique which provides a basis for Differential pulse stripping voltammetry (DPSV) and square wave stripping voltammetry (SWSV) techniques. A stock solution of 0.01M concentration of Tetryl was prepared in acetonitrile. Five milliliter of 0.1M tetrabutyl ammonium bromide (TBABr) in acetonitrile solution was used as supporting electrolyte. DPSV and SWSV were performed for different volumes of analyte concentrations to obtain the calibration plots after optimizing the instrumental parameters individually.

3. Results and Discussions:

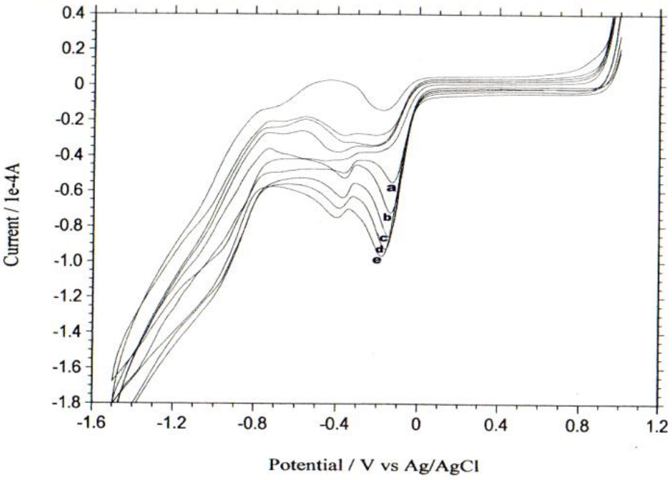
Cyclic Voltammetry: In cyclic voltammetric analysis, potential was stepped from + 1.0 V and scanned at a rate of 50mV/s to a potential of -1.5 V and reversed. During cathodic scan of potential, Tetryl exhibited a predominant peak at a potential of -0.18 V (Peak I) and a small reduction peak at -0.40V (Peak II). Only cathodic peaks were observed in the forward sweep, but no anodic peak was observed in the reverse sweep indicating the irreversibility of the electrochemical reaction (Figure 1).

Figure 1: Cyclic voltammogram of Tetryl using GC electrode in acetonitrile containing 0.1M TBABr



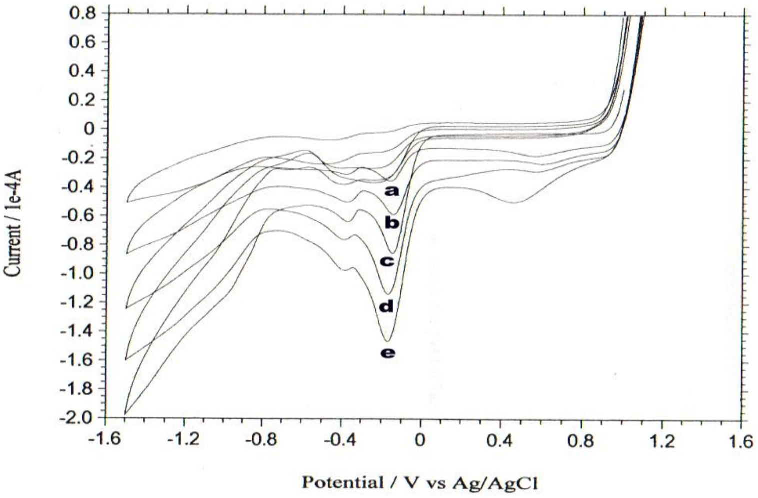
Effect of Scan Rate: The effect of voltammetric scan rate was studied in the range from 10 to 50 mV/s . As the scan rate was increased, the peak potential shifted towards more cathodic direction and the peak current increased linearly for both reduction peaks. Plot of peak current (i_P) against square root of scan rate($\nu^{1/2}$) showed linear trend for both peaks. As the scan rate was increased, the $i_P / \nu^{1/2}$ values decreased for both peaks. From the plot of log i_P against log ν, the slope values of 0.35 and 0.49 are obtained for peak I and peak II respectively (Figure 2).

Figure 2: Cyclic Voltammograms of Tetryl at different Scan rates (a=10, b=20, c=30 d=40 f=50mV/s)



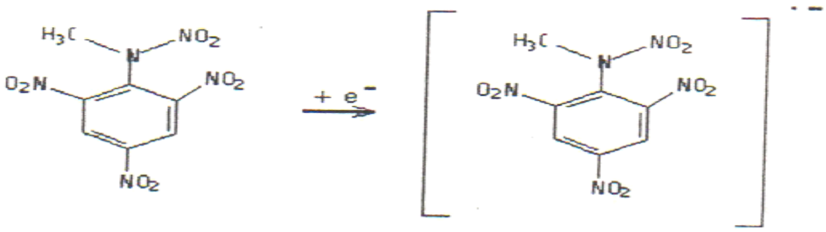
Effect of Concentration: The effect of Tetryl concentration was studied in the range between 110 and 487 ppm at a constant scan rate of 50mV/s. For this study, only the peak I was considered due to higher peak current response. As the concentration was increased, the peak current increased linearly which indicates the peak current was dependent on the Tetryl concentration. All the results indicate the diffusion controlled reduction of Tetryl (Figure 3).

Figure 3: Cyclic Voltammograms of Tetryl at different concentrations (a=110, b=212, c=307 d=395 f=487 ppm)



Calculation of "n" Using Chronocoulometry: Chronocoulometric experiment was carried out for Tetryl with GC electrode. The potential of the GC electrode was stepped from an initial potential where no redox reaction occurs to a final potential where the reaction of interest does occur. Instead of measuring current directly, it is integrated and the charge is measured in this technique. The number of electrons involved in the electrochemical was derived from the forward slope charge value (Q_d) of Anson's plot (Q against $t^{1/2}$) obtained in this experiment using the following equation ($Q_d = 2nFAD^{1/2}Ct^{1/2} / \pi^{1/2}$), where n = eq./mole, F= the Faraday constant, A=area of the electrode (0.0707 cm^2), D=diffusion coefficient in cm^2 /s, C= bulk concentration in mol/cm^3 and t =time in seconds. The charge value (Q_d) was calculated from the Anson's plot and used for the calculation of the number of electrons involved in the reduction process. The number of electrons transferred for initial reduction was calculated to be one when potential was stepped from 0.1V to -0.2V at a Tetryl concentration of 0.01 x 10^{-3} M. Based on the literature details and also from the cyclic voltammetric and chronocoulometric results obtained in the present study, possible reduction mechanism has been proposed. Tetryl may form radical anion, which in turn take up protons from the solvent and convert into corresponding amine (Scheme I).

Scheme I:



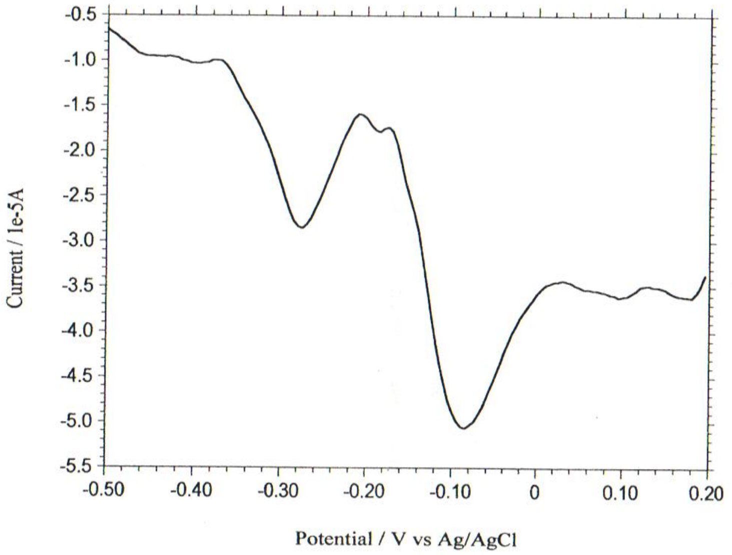
Tetryl Tetryl Radical Anion

Stripping Voltammetry:

After completion of cyclic voltammetric and chronocoulometric study for the reaction mechanism, stripping voltammetric experiments were carried out for Tetryl in acetonitrile containing 0.1 M TBABr medium for the analytical procedure development. Owing to sharp and intense peak nature obtained in the cyclic voltammetric cathodic scan (Peak I) over anodic scan, stripping voltammetry was carried out in the direction only with both differential pulse and square waves modes. The DPSV and SWSV analysis at trace levels normally involves very small current response. For that reason, it is important to optimize all parameters to a high degree of precision.

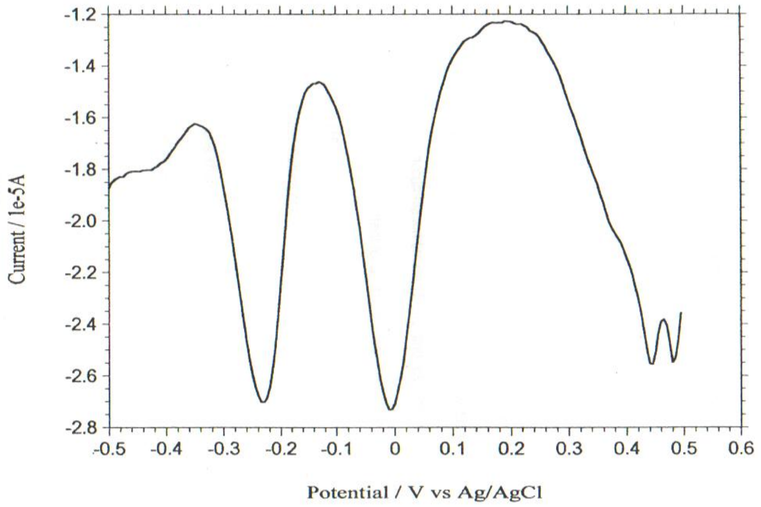
Differential Pulse Stripping Voltammetry: Effect of accumulation potential (E_{acc}) was carried out in the range between -1.5 V and +1.5 V . E_{acc} of 1.5 V showed good peak characteristics and hence as optimum. Effect of initial scan potential (E_{is}) was carried out in the range from 0.5 V to 0.1 V. E_{is} of 0.2 V showed good peak shape response and hence optimized. Effect of pulse amplitude (PA) was carried out in the range from 0.01 V to 0.50 V. PA of 0.03 V showed good peak shape and peak current response and hence taken as optimum. Effect of potential increment (PI) was examined between 0.001 V and 0.005 V. PI of 0.005 V showed good shape, peak current response and hence taken as optimum. Effect of pulse period (PP) and pulse width (PW) were studied simultaneously in the ranges from 0.04 s to 0.20 s and 0.02 s to 0.10 s respectively. PP of 0.12 s and PW of 0.06 s were selected as optimum values due to their better response of peak current and sharp peak shape. Effect of accumulation time (t_{acc}) was carried out from 20 to 100 s. An accumulation time of 20s was selected as optimum due to higher peak response. A typical stripping voltammetric response obtained under optimum differential pulse experimental conditions for a Tetryl concentration of 14 ppm is given in Fig 4.

Figure 4: DPSV under optimized conditions at a Tetryl concentration of 14 ppm



Square Wave Stripping Voltammetry: Effect of accumulation potential (E_{acc}) was carried out in the range between -1.5 V and +1.5 V. E_{acc} of 1.3 V showed good peak characteristics and hence as optimum. Effect of initial scan potential (E_{is}) was carried out in the range from 0.5 V to 0.1 V. E_{is} of 0.5 V showed good peak shape response and optimized. Effect of square wave amplitude (SWA) was carried out in the range from 0.01 V to 0.05 V. SWA of 0.03 V showed good peak shape and peak current response and hence selected as optimum. Effect of step increment was examined between 0.001 V and 0.005 V. A step increment of 0.005 V showed good shape, high peak current response and hence taken as optimum. Effect of frequency (FR) was studied in the range from 2 to 10 Hz. A FR of 6 Hz showed good peak shape and peak current response and hence taken as optimum. Effect of accumulation time (t_{acc}) was carried out from 20 to 100 s. An accumulation time of 20s was selected as optimum due to higher peak response. A typical stripping voltammetric response obtained under optimum square wave experimental conditions for a Tetryl concentration of 14 ppm is given in Fig 5.

Figure 5: SWSV under optimized conditions at a Tetryl concentration of 14 ppm



4. Conclusions:

In this electrochemical studies, cyclic voltammetry and chronocoulometry experiments were used to propose the reaction mechanism of Tetryl in acetonitrile medium. The differential pulse and square wave stripping voltammetry were used to identify the electrochemical characteristics and optimize the conditions for

Tetryl determination. Tetryl shows a well defined peak at a potential of -0.18V in acetonitrile containing TBABr. Hence these techniques can be used for the qualitative and quantitative determination of Tetryl in soil. In particular, these techniques can be applied for the development of electrochemical sensor systems for the determination of explosives contamination in soil matrix.

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