



## ELECTROCHEMICAL DETERMINATION OF NITRO EXPLOSIVE (HNS) USING GLASSY CARBON ELECTRODE

B. Kavitha\*, H. Gurumallesh Prabu\*\*, K. N. Marimuthu\*\*\*, S. Esakku\*\*\* & N. Senthil Kumar\*\*\*

\* Department of Chemistry, Sri Ranganathar Institute of Engineering and Technology, Coimbatore, Tamilnadu

\*\* Department of Industrial Chemistry, Aligappa University, Karikudi, Tamilnadu

\*\*\* Department of Chemistry, Arignar Anna Government Arts College, Cheyyar, Tiruvannamalai, Tamilnadu

**Cite This Article:** B. Kavitha, H. Gurumallesh Prabu, K. N. Marimuthu, S. Esakku & N. Senthil Kumar, "Electrochemical Determination of Nitro Explosive (HNS) Using Glassy Carbon Electrode", International Journal of Applied and Advanced Scientific Research, Volume 1, Issue 2, Page Number 109-113, 2016

### Abstract:

A glassy carbon electrode (GC) exhibited an attractive performance for the detection and determination of a nitro compound like 1,2- Bis(2,4,6-trinitrophenyl)ethylene (HNS). Cyclic voltammetry, differential pulse and square wave voltammetry were used in a combined way to identify the electrochemical characteristics and to optimize the conditions for detection. For calibrating and estimating HNS, square-wave voltammetry was mainly used. The HNS shows a well-defined peak at in the dimethyl sulfoxide (DMSO) containing Tetrabutyl Ammonium Bromide (TBABr) medium. The existence of peak at -0.10 V showed good peak and high current response.

### Introduction:

Several analytical techniques were developed for the determination of HNS which included non-aqueous titration, thin-layer chromatography, UV spectrophotometry,<sup>1,2</sup> and high-performance liquid chromatography methods,<sup>3</sup> electrochromatography,<sup>4</sup> reverse - phase liquid chromatography-mass spectrometry<sup>5</sup> and flow-injection analysis<sup>6</sup>. HNS has been determined by gas chromatography-mass spectrometry using diazopropane.<sup>7</sup> A simple and sensitive method is therefore needed for the fast, accurate detection and estimation of HNS. In this work an electro-analytical approach was developed for the detection and determination of HNS by square-wave stripping voltammetry using a glassy carbon (GC) electrode.

### Experimental:

The high energy chemical used for this study was HNS, soluble in Dimethyl Sulfoxide (DMSO). 0.01 M stock solution of HNS was prepared using appropriate solvent. A 0.1 M TBABr in DMSO was used as supporting electrolyte. Experimental technique like cyclic voltammetry (CV), chronocoulometry (CC), differential pulse voltammetry (DPSV) and square wave stripping voltammetry (SWSV) were employed using CHI 620 A Electrochemical Analyzer Instrument.

### Results and Discussion:

Cyclic Voltammetry (CV) of 1,2- Bis (2,4,6 – trinitrophenyl)ethylene (HNS) was studied using Glassy Carbon(GC) electrode at a scan rate of 50 mV/s. Dimethylsulfoxide (DMSO) containing 0.1 M tetra butyl ammonium bromide (TBABr) solvents were used as supporting electrolyte. With GC and Pt electrodes, HNS showed three reduction peaks at potentials about -0.05 V (R-peak I), -0.81 V(R-peak II), -1.00 V (R-peak III) and two oxidation peaks at potentials of -0.66 V (O-peak I) and -0.18 V. R- peak II and O-peak I, R-peak I and O- peak II are seemed to be redox couples. The voltammogram obtained with GC electrode was in the Figure 1

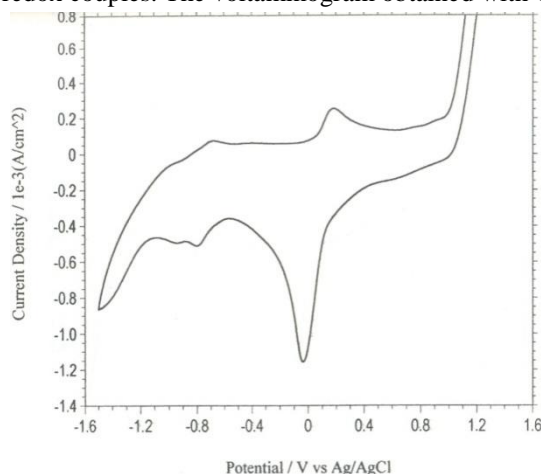


Figure 1: Cyclic Voltammogram of HNS using GC electrode in DMSO medium containing 0.1 M TBABr Medium

**Effect of Scan Rate:**

Effect of scan rate was studied in the range from 10 to 50 mV/s with GC electrode, as the scan rate was increased with the peak potential ( $E_p$ ) and half-peak potential ( $E_{p/2}$ ) values shifted towards cathodically for reduction peaks (R-peak I, R-peak II and R-peak III). The  $E_p$  and  $E_{p/2}$  values shifted anodically for oxidation peaks (O-peak II). No peak potential shift was observed for O-peak I. When the scan rate was increased, the modulus ( $|E_p - E_{p/2}|$ ) and the current values increased linearly and  $i_{p/v}$  values decreased for almost all peaks. The obtained results are given in Table 1. The plot of  $\log i_p$  against  $\log$  scan rate for different peaks in the scan rate study yielded slope values of 0.12 V (R-peak I), 0.07 V (R-peak II), 0.10 V (R-peak III), 0.15 V (O-peak I), and 0.03 V (O-peak II). These values indicate the diffusion controlled nature of the reactions. The  $i_{p/v}^{1/4}$  values showed increasing trend for R-peak I, decreasing trend for O-peak II, almost constancy for O-peak I and random variation R-peak II and R-peak III). The electron transfer co-efficient ( $\alpha_n$ ) value obtained in the scan rate study was greater than 0.5. This indicates the reversible reaction nature of the redox couple.

Table 1: Effect of scan rate in CV with GC Electrode

Peak	$v$ (mV/s)	10	20	30	40	50
	$v^{1/2}$	3.16	4.47	5.47	6.32	7.07
Reduction Peak I	$-E_p$ (V)	0.066	0.054	0.030	0.016	-0.036
	$-E_{p/2}$ (V)	0.108	0.100	0.089	0.080	0.051
	$E_p - E_{p/2}$ (mV)	42	46	59	64	87
	$i_p$ ( $\mu$ A)	12.87	17.47	24.07	28.17	39.74
	$i_p/v$	1.287	0.873	0.802	0.704	0.794
	$i_p/v^{1/2}$	4.072	3.908	4.400	4.457	5.620
	$\alpha n_a$	1.135	1.036	0.808	0.745	0.548
Reduction Peak II	$-E_p$ (V)	0.801	0.803	0.806	0.806	0.812
	$-E_{p/2}$ (V)	0.750	0.752	0.754	0.755	0.758
	$E_p - E_{p/2}$ (mV)	51	51	52	53	54
	$i_p$ ( $\mu$ A)	10.77	13.59	15.28	18.65	20.10
	$i_p/v$	1.077	0.679	0.509	0.466	0.402
	$i_p/v^{1/2}$	3.408	3.040	2.793	2.951	2.842
	$\alpha n_a$	0.93	0.93	0.91	0.90	0.88
Reduction Peak III	$-E_p$ (V)	0.930	0.933	0.936	0.940	0.943
	$-E_{p/2}$ (V)	0.900	0.901	0.903	0.904	0.906
	$E_p - E_{p/2}$ (mV)	30	32	33	36	37
	$i_p$ ( $\mu$ A)	2.56	3.80	5.68	8.09	9.48
	$i_p/v$	0.256	0.190	0.189	0.202	0.189
	$i_p/v^{1/2}$	0.810	0.850	1.038	1.280	1.340
	$\alpha n_a$	1.59	1.49	1.44	1.32	1.28
Oxidation Peak I	$-E_p$ (V)	0.69	0.69	0.69	0.69	0.69
	$-E_{p/2}$ (V)	0.77	0.77	0.77	0.78	0.77
	$E_p - E_{p/2}$ (mV)	80	80	80	90	80
	$i_p$ ( $\mu$ A)	2.26	3.00	4.12	4.86	5.45
	$i_p/v$	0.22	0.15	0.14	0.12	0.11
	$i_p/v^{1/2}$	0.71	0.67	0.75	0.77	0.77
	$\alpha n_a$	0.60	0.60	0.60	0.53	0.60
Oxidation Peak II	$-E_p$ (V)	0.13	0.14	0.15	0.16	0.18
	$-E_{p/2}$ (V)	0.09	0.10	0.10	0.11	0.12
	$E_p - E_{p/2}$ (mV)	40	40	50	50	60
	$i_p$ ( $\mu$ A)	13.87	14.88	15.90	16.76	17.71
	$i_p/v$	1.37	0.74	0.53	0.42	0.35
	$i_p/v^{1/2}$	4.34	3.33	2.91	2.65	2.50
	$\alpha n_a$	1.20	1.20	0.96	0.96	0.80

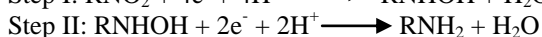
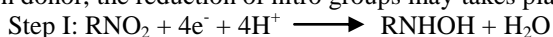
**Effect of HNS Concentration:**

Effect of HNS concentration was studied in the range from 746 to 1093 ppm at a scan rate of 50 mV/s. When the HNS concentration was increased, the peak current increased for R-peak I, R-peak II and O-peak II and decreased for R-peak III and O-peak I. The current function values ( $i_p/AC_v^{1/4}$ ) calculated showing decreasing trend for all peaks. This indicates the diffusion-controlled nature of the reaction.

### Chronoamperometry and Chronocoulometry:

Chronoamperometry of HNS was studied at a fixed final potential of -1.5 V and the initial potential was varied from +0.5 V to -0.6 V. The difference in slope (forward-Reverse) value obtained at a potential of 0.0 V showed good response. Chronocoulometry of HNS was studied at a fixed final potential of -1.5 V and the initial potential was varied from +0.5 V to -0.6 V. The difference in slope (forward-Reverse) value obtained at a potential of 0.5 V showed good response. Based on the results, a tentative reaction mechanism is proposed for HNS. The stock solutions of some high-energy chemicals were appeared as colored. In DMSO solvent medium, it showed brown color for HNS. During cyclic voltammetric scan, blue color for HNS was observed on GC electrode surface. From this it is clear that aromatic nitro compounds (HNS) produce color. The color obtained in the potential scan, thus may be due to the formation of radical anion of the compound, which is absorbed on the electrode. NO<sub>2</sub> group is electron-withdrawing in nature. The presence of two nitro groups on alternate carbon atoms may make the middle carbon atom an electron-deficient centre. An electron may add to the electron-deficient centre. The radical anion thus formed may be stabilized due to presence of nitro groups. Organic compound with stable radical anion are expected to be colored. HNS contains six NO<sub>2</sub> groups. The electron withdrawing nature of these nitro groups may make electron-deficient carbon atoms for HNS. Electron-deficient carbon atom has an affinity for the incoming electron and such addition of electron to analyte may be easy and hence the peak to appear at a lower potential. This may be the reason for the HNS reduction to take place at a lower potential.

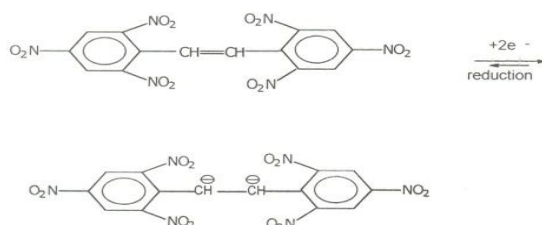
In the absence of proton donor, aromatic nitro compounds may be reduced electrochemically with 1 electron to generate the radical anion, which is stable in the solvent and hardly generates any reduction products in aprotic solvents. Formation of hydroxylamino product requires protons. Numerous studies have been reported on the electro reduction of aromatic nitro compounds in protic solvents. In them, the reduction potentials are known to be nitroso, hydroxylamino, amino, azo, azoxy and hydrazo compounds. The products formed are generally dependent on the electrolysis conditions like pH, electrode material and electrolysis etc. In presence of proton donor, the reduction of nitro groups may takes place in two steps (8). They are as follows.



Based on the cyclic voltammetric and controlled potential results, the number of electrons involved in the reaction was commuted as below.

Compound	Concentration in M	Electrolytic Potential (V)	Charge (x10 <sup>-6</sup> C)	"n" calculated
HNS	1.0 x 10 <sup>-9</sup>	- 0.10	221	2.3

Proposed Mechanism of HNS



### Stripping Voltammetry:

After completion of cyclic voltammetric study for the reaction mechanism, stripping voltammetric experiments were carried out for HNS in DMSO 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 (R-peak I) over anodic scan, stripping voltammetry was carried out in the direction only with both differential pulse and square waves modes.

### 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 1.1 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 hence optimized. Effect of pulse amplitude (PA) was carried out in the range from 0.01 V to 0.30 V. PA of 0.05 V showed good peak shape and peak current response and hence taken as optimum. Effect of potential increment (PI) was carried out in the between 0.001 V and 0.005 V. PI of 0.004 V showed good shape, peak current response and hence taken as optimum (Figure 2). Effect of pulse period (PP) and pulse width (PW) were studied simultaneously in the ranges from 0.04 to 0.20 s and 0.02 to 0.10 s respectively. PP of 0.08 s and PW of 0.04 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. When the accumulation time was increased, the peak current increased accordingly. The best optimum conditions observed in the studies are given in Table 2

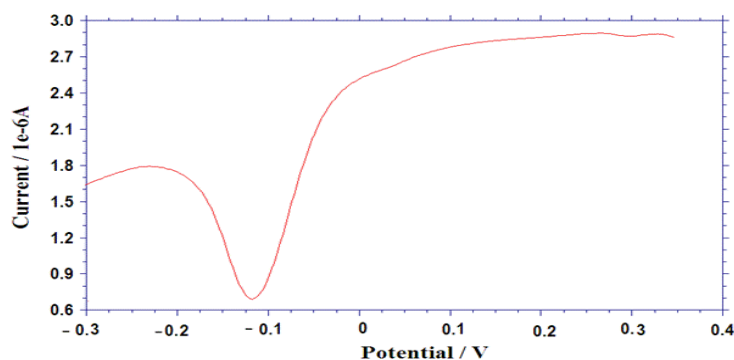


Figure 2: Differential Pulse Voltammogram of HNS using GC electrode in DMSO medium containing 0.1 M TBABr medium

Table 2: Optimum Conditions for HNS in DPSV

Parameters	Optimum Conditions
Accumulation Potential	1.1V
Initial Scan Potential	0.5V
Pulse Amplitude	0.05V
Potential Increment	0.004V
Pulse Period	0.08 Sec
Pulse width	0.04 Sec

**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 1.2 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 from 0.01 V to 0.10 V. SWA of 0.04 V showed good peak shape and peak current response and hence selected as optimum. Effect of potential increment (PI) was carried out in the between 0.001 V and 0.005 V. PI of 0.004 V showed good shape, high peak current response and hence taken as optimum. Effect of frequency (FR) was carried out in the range from 2 to 10 Hz (Figure 3). A FR of 8 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 (Table 3). As the accumulation time was increased, the peak current showed mixed responses.

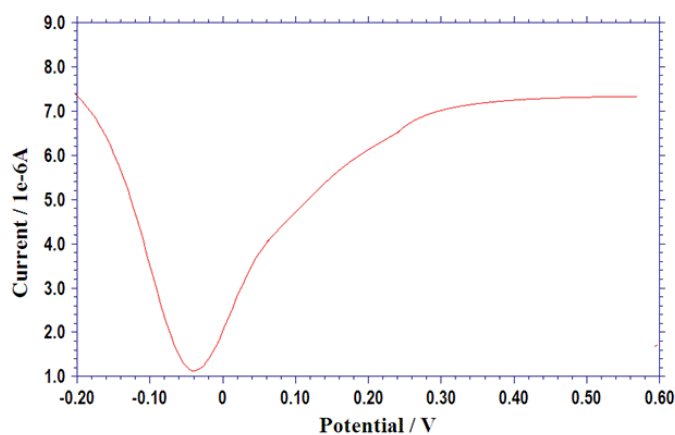


Figure 3: Square Wave Voltammogram of HNS using GC electrode in DMSO medium containing 0.1 M TBABr medium

Parameters	Optimum Conditions
Accumulation Potential	1.2V
Initial Scan Potential	0.5V
Square Wave Amplitude	0.04V
Potential Increment	0.004V
Frequency	8HZ

Table 3: Optimum Conditions for HNS in SWSV

**Conclusion:**

In the electrochemical studies, cyclic voltammetry experiment was used to propose the reaction mechanism of HNS in DMSO medium. The differential pulse and square wave voltammetry were used in a combined way to identify the electrochemical characteristics and optimize the conditions for HNS detection.

For calibrating and estimating HNS, square-wave voltammetry was mainly used. The HNS shows a well-defined peak at in the dimethyl sulfoxide (DMSO) containing Tetrabutyl Ammonium Bromide (TBABr) medium. The existence of peak at -0.10 V showed good peak and high current response. Hence it may be an alternative tool to determine nitro based explosives in contaminated soil.

**References:**

1. R. T. Sane, V. B. Tirodkar, A. J. Desai, M. K. Patel, and U. D. Kulkarni, *Indian Drugs*, 1992, 29, 489.
2. B. P. Reddy, M. V. Suryanarayana, S. Venkatraman, G. L. Krupadanam, and C. S. P. Sastry, *Indian Drugs*, 1993, 30, 176.
3. M. Sultan, G. Stecher, W. M. Stoggl, R. Bakry, P. Zaborski, C. W. Huck, N. M. ElKousy and G. K. Bonn *CurrentMedi.Chem.*, 2005, 12, 573.
4. Fanali, *J.Chromatogr.,A*, 2004, 1044, 295
5. J. B. Quintana and T. Reemtsma, *Spectrum.*, 2004, 18, 765
6. Z. Atkosar, G. Altiokka, K. Kircali, and E. harma. *Turcica*, 2001, 43, 177
7. B. K. Logan, P. N. Friel, K. L. Peterson *Predmore, J.Anal.Toxicol.*, 1995, 19, 61
8. T. Ohba, H. Ishida, T. Yamaguchi, T. Horiuchi and K. Ohkubo, *J. Chem. Soc. Chem. Commun* (1994), 263