ORIGINAL RESEARCH PAPER
Volume - 15 | Issue - 05 | May - 2026 | PRINT ISSN No. 2277 - 8179 | DOI : 10.36106/ijsr
INTERNATIONAL JOURNAL OF SCIENTIFIC RESEARCH

VOLTAMMETRIC DETERMINATION OF DINITROTOLUENE USING PENCIL GRAPHITE BLEND ELECTRODE

Chemistry

Y. Madhu Kiran Electroanalytical Lab, Department of chemistry, Sri Venkateswara University, Tirupati - 517502, Andhra Pradesh, India

M. Sunil Kumar Electroanalytical Lab, Department of chemistry, Sri Venkateswara University, Tirupati - 517502, Andhra Pradesh, India

N.Y.Sreedhar* Electroanalytical Lab, Department of chemistry, Sri Venkateswara University, Tirupati - 517502, Andhra Pradesh, India *Corresponding Author

ABSTRACT

Pencil graphite paste blend electrode fabricated from HB and 4B graphite was efficiently used in the sensitive sensing of dinitrotoluene (DNT). The modified electrode was characterised using cyclic voltammetry and differential pulse voltammetry for DNT reduction. Differential pulse voltammetry was used to optimise the parameters involved and to develop analytical method for DNT with detection limits of 2.5 nM. The voltammetric method was then applied to ground water samples and validated by determining recoveries of DNT in the range of 86.0 - 97.5 % with corresponding RSD values (3.4 - 4.6 %).

KEYWORDS

Pencil graphite paste electrode, Dinitrotoluene (DNT), Voltammetry, Ground water samples

INTRODUCTION

2,4-dinitrotoluene (DNT) is quite an important nitroaromatic compound with two nitro groups present in ortho and para positions on the toluene nucleus. It is a precursor of the explosive TNT and used in the manufacture of drugs, dyes and other special chemicals. As it is an active explosive constituent and carcinogenic, the analytical methods for DNT in environmental samples are quite significant and in high demand.

A number of analytical methods were reported for its determination using GC, HPLC and optical methods. Nitroaromatic compounds were extracted using stir bar sorptive extraction (SBSE) followed by determination using gas chromatography and mass spectrometry [1] A novel technique was developed based on the determination of nitro organic explosives using gas chromatography- pyrolysis with UV detection [2]. Further nitroaromatic explosives were detected by employing gas chromatography with electron capture detector in soil samples [3]. A dispersive liquid-liquid extraction was reported with subsequent gas chromatography for the analysis of explosives in water samples [4].

The origin and characterisation of 2,4,6 - trinitro toluene was investigated through its by-products by making use of liquid chromatography - atmosphere pressure chemical ionisation mass spectrometry [5]. Dinitrotoluene compounds were extracted using solid phase extraction with liquid chromatography – mass spectrometry [6]. High performance liquid chromatography based methods were meticulously reviewed in the analysis of explosives with clear merits [7]. Explosives in environmental waters were determined using solid phase micro extraction based liquid chromatography [8]. Dinitrotoluenes were determined using electrospray high resolution mass spectrometry and laser electrospray mass spectrometry [9-10]. Raman spectroscopy and SERS were employed in determination of explosives [11-13].

Voltammetry offers quite a considerable number of analytical methods for the sensitive determination of DNT [14-17]. Modified pencil graphite electrode was used in the determination of important analytes [18-21]. There is always a demand for simple, cheap and efficient voltammetric sensors for sensitive determination of DNT. The aim of the present work is to develop a pencil graphite blend paste electrode and a novel differential pulse voltammetry (DPV) method for sensitive determination of DNT in ground water samples.

EXPERIMENTAL:

MATERIALS AND METHODS

All the materials used were procured from Sigma-Aldrich, USA and the Faber - Castell pencil graphite of HB and 4B grades were purchased from local stationery and ground water samples were collected from Tirupati, AP, India.

All voltammetric measurements were done using CHI 660D instrument completely controlled by CHI software. Pencil graphite paste electrode as working electrode, platinum wire as counter electrode and Ag/AgCl, 3M KCl as reference electrode were used. The recordings of buffer pH were done using Elico Li-120 pH meter.

Pencil graphite paste electrode (PGPE) fabrication

Pencil graphite of grade HB (85%) and 4B (15%) were pulverised and mixed with mineral oil to get a homogenised paste. The paste was then neatly packed in teflon tube of 2 mm id and then given a copper wire for voltammetric measurements. The smooth surface of the electrode was obtained by touching with soft tissue, washed with double distilled water and N_2 gas dried. Other paste electrodes such as pencil graphite paste with HB and 4B grades were fabricated separately for comparative voltammetric analysis.

DPV method for 2, 4 - DNT

The electrolytic cell of voltammetry consisted of 1 mL of DNT solution (100 nM) and 9 mL of BR buffer of pH 2.0 with total volume, 10 mL. The solution was first degassed with N_2 gas for 10 min and DPV measurements were carried out. Similarly DPV curves for different concentrations of dinitrotoluene were recorded including blank buffer sample (Figure 1).

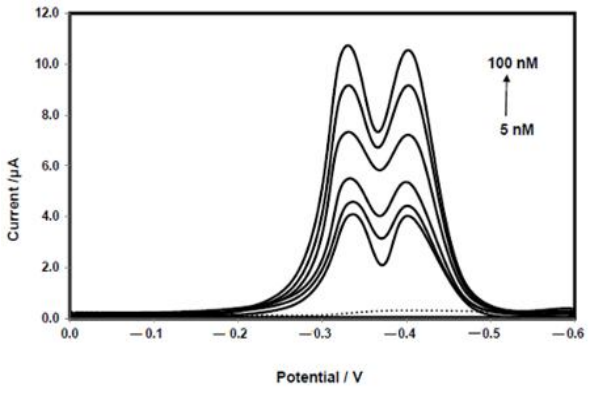


Figure 1: DPV curves of DNT (5 -100 nM) at PGPE with blank buffer (pH 2.0) in dotted line

RESULTS AND DISCUSSION:

Cyclic voltammetry studies of 2, 4- DNT at pencil graphite paste electrode

By using the fabricated paste electrode, CV studies were carried out between the potential range 0.8 to -1.0 V vs. Ag/AgCl/KCl (3M) at a scan rate of 100 mV/s for DNT solution (100 µM). The CV curves were recorded with two irreversible reduction peaks of the two nitro groups to hydroxyl amine groups involving $4e^-$ and $4H^+$ at -0.33 and -0.41 V. In the reverse scan oxidation and reduction peaks were obtained related to oxidation of -NHOH to -NO group and the corresponding re-formation of -NHOH from -NO group in the cathodic scan (Figure 2). The effect

of scan rate on the first reduction peak current of DNT was studied using cyclic voltammetry over the range 50 - 500 mV/s. The peak current varied linearly with scan rate indicating the reaction was found to be adsorption-controlled.

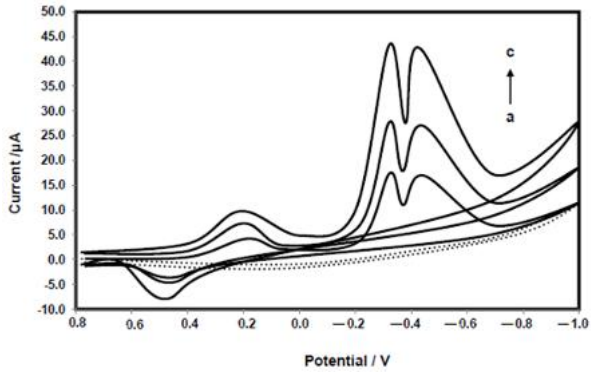


Figure 2: CV curves of DNT (100 µM) at PGPE,(85% HB & 15% 4B (a)) along with PGPE, (4B(b)) and PGPE (HB(c)) with blank BR buffer of pH 2.0 in dotted form

Effect of pH

The role of pH was quite important and studied over the pH range 2 - 10 on the first irreversible reduction peak of DNT using DPV technique. On increasing the pH from 2 to 10, the DNT peak current decreased, indicating the involvement of hydrogen ions in the reduction reaction (Figure 3). Further peak potential increases in cathodic direction with increasing pH, confirming the role of H^+ ions in the reduction.

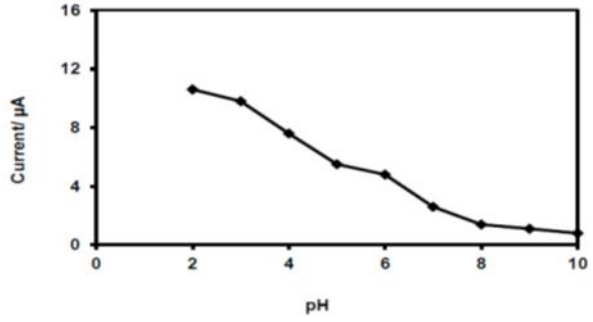


Figure 3: Effect of pH on the peak current of DNT (100 nM)

Effect of accumulation potential (E_{acc})

The role of accumulation potential (0 to -1.4 V) was studied on the reduction peak current of DNT using differential pulse voltammetry. The peak current reached its maximum for potential -0.2 V where the analyte got accumulated at the electrode interface. Thus a potential of -0.2 V was selected as optimum accumulation potential for DPV measurement (Figure 4).

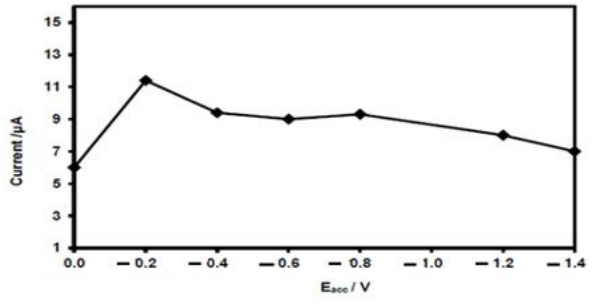
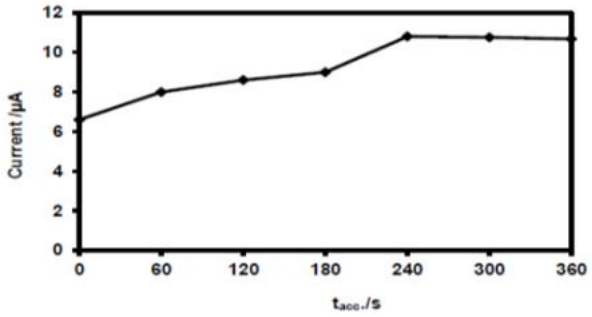


Figure 4: Effect of accumulation potential (E_{acc}) on peak current of DNT (100 nM)

Effect of accumulation time (t_{acc})

The effect of accumulation time (0 - 360 s) was determined on the first reduction peak current of DNT. The peak current reached maximum for accumulation time, 240s where the analyte, accumulated at the paste electrode interface. This value was chosen as optimal value for the DPV determination of dinitrotoluene (Figure 5).

Figure 5: Effect of accumulation time (t_{acc}) on peak current of DNT (100 nM)



Pencil graphite composition

The percentage composition of 4B pencil graphite in the range 5 - 25 % was tested using the peak currents of DNT. Maximum peak currents were obtained for pencil graphite 4B, 15 % (W) with pencil graphite HB, 85 % (W), used in the fabrication of paste electrode. The optimal working parameters for DPV were enlisted in Table 1.

Table -1 Optimisation of DPV parameters

S.No.	Parameter	Value
1	pH	B.R: 2.0
2	Accumulation potential(E_{acc})	-0.2 V
3	Accumulation time(t_{acc})	240 s
4	Pulse amplitude	25 mV
5	Pulse width	10 ms
6	Step potential	50 mV
7	Quiet time	2 s
8	Scan rate	100 mV/s

Application of the DPV method

The developed method was directly applied for ground water samples towards DNT determination. The ground water samples of 100 mL were filtered and spiked with known concentration of DNT over the concentration range 20 - 100 nM. The DPV protocol was carried out for the spiked water samples and good recoveries were obtained in range 86.0 - 97.5 % with corresponding RSD values of 3.4 - 4.6 % as presented in Table 2.

Table-2 Recovery studies for DNT in ground water samples

S.No.	Added (nM)	Measured (nM)*	Recovery (%)	RSD(%)
1	20	17.2	86.00	3.4
2	40	36.3	90.75	3.7
3	60	58.5	97.50	4.6
4	80	77.2	96.50	4.3
5	100	96.8	96.80	3.9

***Average of 5 determinations**

Linear curve

A calibration line was obtained for the DNT concentration range, 5 - 100 nM and peak currents were determined by differential pulse voltammetry using standard addition method. The equation of the line was Ip(µA) = 0.072 C(nM) + 3.508 with R^2 = 0.999 and the detection limits were 2.5 nM based on $3S_b/m$ where m is the slope of calibration line and S_b is the standard deviation of the blank sample (Average of 10 determinations).

Stability, reproducibility of the DPV method

The stability of the electrode signal was determined by measuring the variation of peak current of DNT for 30 days. The electrode showed a decrease in peak signal of 84 %. Intra-day and Inter-day reproducibility of the peak signals was determined by carrying out 10 determinations on the same day and 10 replicate determinations on consecutive days. The RSD values were 2.8 and 3.9 % respectively. This indicated that the electrode exhibited good stability and reproducibility.

Interference studies

The effect of phenol, p-nitrophenol, p-nitroaniline and other inorganic ions such as Ca^{2+}, Na^+, K^+, Mg^{2+}, SO_4^{2-}, PO_4^{3-}, NO_3^-, NO_2^- at the concentration of 1000 fold was investigated. The decrease in peak signal was < 8 %. But picric acid and TNT at 200 fold concentration seriously interfered with DNT determination. Hence these two compounds were to be isolated before carrying out DNT measurement. This indicated good selectivity of the developed method.

CONCLUSION

The developed pencil graphite paste electrode produced significantly good peak signals for the determination of DNT. The method could be readily applied for the determination of DNT in ground water samples with excellent recoveries. The advantages of the present method are its simplicity, rapidity with good sensitivity and selectivity with few sample preparation steps. The present pencil graphite paste electrode combined with other carbon nanomaterials such as graphene and nanotubes could be considered as future research for new sensors.

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