

Assay of Dinitrotoluene on a Contaminated Soil Sample with an Anodic Stripping Peak Current

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This report presents a voltammetric assay of dinitrotoluene using a DNA immobilized onto a carbon nanotube paste electrode (PE). The cyclic voltammetry (CV) and square wave (SW) stripping voltammetry parameters of the optimized conditions were obtained. An anodic peak current appeared at 0.3 V (versus Ag/AgCl) in a 0.1-M $\text{NH}_4\text{H}_2\text{PO}_4$ electrolyte solution. The detection limit was found to be 0.6 ngL^{-1} ($\text{S/N} = 10$), within a deposition time of 100 sec.

Key Words : Voltammetry, DNA, Dinitrotoluene, Anodic

1. Introduction

Dinitrotoluene (DNT) is produced by mixing toluene with nitric acid [1] in the presence of sulfuric acid, which will result in the formation of 80% 2, 4- DNT and 20% 2, 6- DNT [2]. 2,4- DNT is very explosive and highly reactive, whereas 2,6- DNT does not evaporate [2]. DNT is one of the most widely produced military explosives [3,4,5 and 6] all over the world, and it has a particularly well-developed market due to the importance of explosive compounds of 2,4,6-TNT, 2,4- DNT and 2,6- DNT [7-8]. As its development grew, the problems it might cause have elicited increasing concerns. Explosive compounds remain in the environment [5, 6 and 9], especially in the physical and chemical properties of soil [10, 11 and 12]. There has been a growing concern that contamination from firing ranges can adversely affect the health of people [13-14]. DNT is also easily adsorbed through the skin, thus exposing humans to its harmful health effects [9]. Detection of DNT is being developed with a variety of sensors, as a result of which the concentrations of DNT are approximately 25 times higher than those of TNT {148 parts-per-billion (ppb) compared to 6 ppb} [15]. To detect DNT, a few methods

have been used, including the THz(terahertz) time-domain spectroscopy (THz-TDS), Fourier transform infrared spectroscopy (FTIR) [11 and 16], and high-performance liquid chromatography (HPLC) [17 and 18]. An FTIR spectroscopic investigation of 2,4-DNT in the 0.2-19.5 THz range was performed [11]. The objective of the study was to detect 2,4- and 2,6- DNT in contaminated soil using the voltammetric method. At first, contaminated soil was collected at a firing range. The DNT concentration in the soil was 1 g in 100 mL of distilled water (previous results). there have been a few reported studies on DNT chemical voltammetric methods. Therefore, the authors used chemical voltammetric methods to determine the presence of DNT in the soil sample at a simple methods and obtained successful results, which had a very low detective limit at the ppt level.

Carbon nanotubes have been developed due to their electronic and chemical properties, [19-20]. Since the unique electrical properties of nanotubes—i.e., high conductivity [20-22], chemical inertness, and mechanical strength and stability [23] in harsh chemical environments [21] for biosensors [24], have been reported, excellent improvements have been demonstrated [24-25]. Carbon nanotubes enable highly sensitive detection of DNT The study presented here describes the use of carbon nanotube paste electrodes (CNTPE) mixed with DNA(Deoxyribonucleic acid) to determine

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the electrochemical behavior [25] of dinitrotoluene. The combination of CNT with DNA has been gaining increasing attention recently due to its capacity to reach a lower detection limit [20 and 23]. Therefore, the authors researched on the peak current of dinitrotoluene using the CNT-mixed-with-DNA method and successfully lowered the detection limit of DNT to 0.6 ngL^{-1} . The method can be applied to the soil assay related to explosive materials.

2. Experiment

2.1. Apparatus, Reagents, and Procedure

All voltammetric experiments were performed using a CHI660A instrument electrochemical workstation (from CH Instruments, Inc., Cordova, TN, USA).

To prepare the PE 40% nanotube graphite powder (from Nanostructured & Amorphous Materials, Inc.) and 40% DNA (double-stranded and prepared from calf thymus sigma) was mixed with 20% mineral oil. The mixture was homogenized in a mortar for 30 minutes. The mixed paste was inserted into a plastic syringe needle using a 3-mm-diameter, then copper wire was connected to the electrochemical measurements systems.

A three-electrode system was used to detect the voltammetric signal. The PE electrode was used with saturated Ag/AgCl/KCl as the reference electrode, and with a platinum auxiliary electrode. The experimental solution was prepared using double-distilled water ($18 \text{ Mega Ohm.Cm}^{-1}$). The standard and other reagents obtained from Aldrich(analytical reagent grade) were diluted as needed. The electrolyte solutions of the acid and base buffer (all in 0.1 M) were initially examined to search for a possible supporting electrolyte solution. As a result, a 0.1-M phosphate buffer solution was found to be the most suitable. Its ionic strength was examined within the range of 0.01-0.3 M. The 0.1-M ionic solution was found to have the most suitable concentration. To determine the peak potential, cyclic voltammograms were conducted at a scan rate of 0.5 Vs^{-1} . An oxidation peak potential of 0.3 V was obtained, at which condition various stripping parameters were sought to determine the more sensitive detection ranges. The cyclic voltammetry potential range of -1.1 V at the scan rate of $0.5(\text{V}/\text{sec})$ with 14 repeats was scanned

for the immobilization of DNA onto the carbon nanotube surface. The three-electrode system was then immersed in a 15-mL cell.

3. Results

3.1. Concentration effects of cyclic voltammetry

First, in cyclic voltammetry, various concentration ranges were tested with a scan rate of 0.5 Vs^{-1} , an initial potential of -1.0 V, and a switching potential of 1.0 V using a 0.1-M ammonium phosphate electrolyte solution so that analytical peak potentials could be examined with a wide potential window. Fig. 1 shows the test results. As no signals appeared in the blank electrolyte solution, a small amount of 2-ugL^{-1} dinitrotoluene was spiked at these conditions and a small oxidation peak was obtained at 0.3 V, but the reduction peak was hardly found. Thus, more increased concentrations were spiked from 2 to 40 ugL^{-1} of dinitrotoluene, and a linearly increasing working curve was obtained with a slop sensitivity of $\Delta x/\Delta y = 0.1119$ and a precision of $R^2 = 0.992$ ($N = 14$). Under optimum conditions, the anodic maximum peak current was found to be $4.71 \times 10^{-7} \text{ A}$ at a dinitrotoluene concentration of 40 ugL^{-1} . This result can be applied in the analytical field.

3.2. Optimizations of SW Parameters

Fig. 2 (A) shows the various SW frequency parameters used, from 300 to 1,000 Hz. From 300 to 400 Hz, the peak current increased, after which the

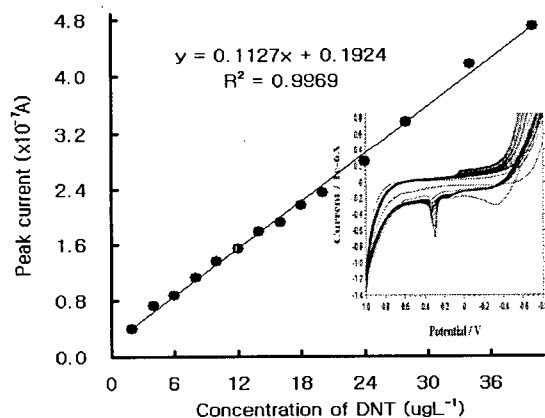


Fig. 1. The working curve and its voltammogram using cyclic voltammetry according to dinitrotoluene concentrations of 2, 4, 6, 8, 10, 12, 14, 16, 18, 20, 24, 28, 24.47 and 40 ugL^{-1} in a 0.1-M $\text{NH}_4\text{H}_2\text{PO}_4$ solution at the scan rate of 0.5 Vs^{-1} .

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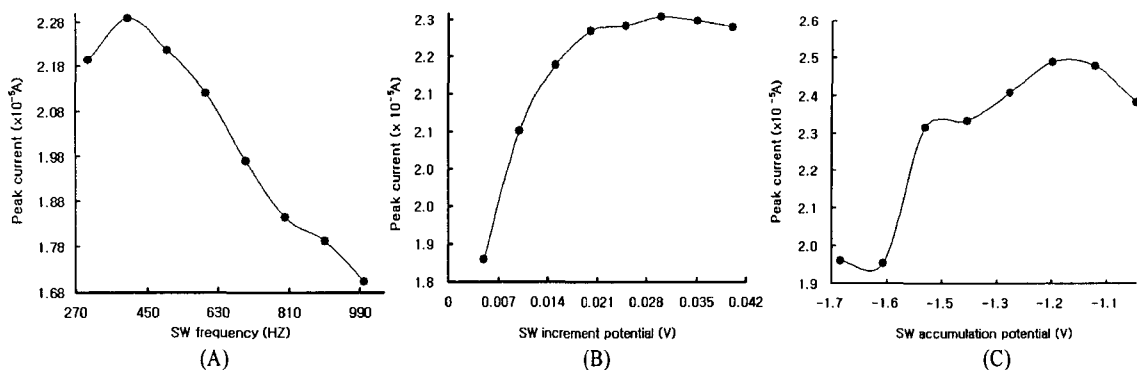


Fig. 2. Oxidation square wave (A) frequencies of 300, 400, 500, 600, 700, 800, 900 and 1,000 Hz. (B) Increment potentials of 0.005, 0.01, 0.015, 0.02, 0.025, 0.03, 0.035 and 0.04 V. (C) Initial potentials of -1.0, -1.1, -1.2, -1.3, -1.4, -1.5, -1.6 and -1.7 V. Other parameters were of Fig. 4.

peak current sharply decreased up to 1,000 Hz. Thus, at 400 Hz, the maximum response of 2.2289×10^{-5} A appeared. In this test, the amplitude and the increment were pegged at 0.45 and 0.04, respectively. In Fig. 2 (B), the SW stripping increment potentials were examined at the 0.005-0.04V range with 8 points. The signal shown in the voltammogram (not shown in this figure) constantly increased. The maximum peak current of 0.03 V was obtained at 2.264×10^{-5} A, after which it decreased slowly up to 0.04 V. Fig. 2 (C) showed an initial potential from -1.0 to -1.7 V, manifesting irregular changes. Beginning with -1.0 V, the peak current gradually increased to -1.2 V, then decreased to -1.6 V. Between -1.5 V and -1.6 V, the peak current was very rapidly indicated. At -1.2 V, the 2.49×10^{-5} A peak current reached its maximum peak. Although not presented in this study, the SW

amplitude was examined to determine the peak current ranging from 0.1 to 0.45 V. The maximum peak was obtained at 18.4×10^{-6} A in 0.45 V, which was more sensitive than any other parameter and which showed a constantly increasing peak width.

3.3. SW accumulation times and electrolyte pH effects

Fig. 3 (A) shows the experimental results of this study's test of the stripping voltammetric parameters of various accumulation times in the range of 50-400 sec. The experimental peak current increased linearly; and at 400 sec, a maximum peak current of 13.8×10^{-5} A was obtained, which was more sensitive than the pH effects, whereas the peak widths were constant and narrowly appeared. Other experiments, however, used a short 100-sec accumulation time to save time. Fig. 3 (B) shows the stripping voltammetric peak current in

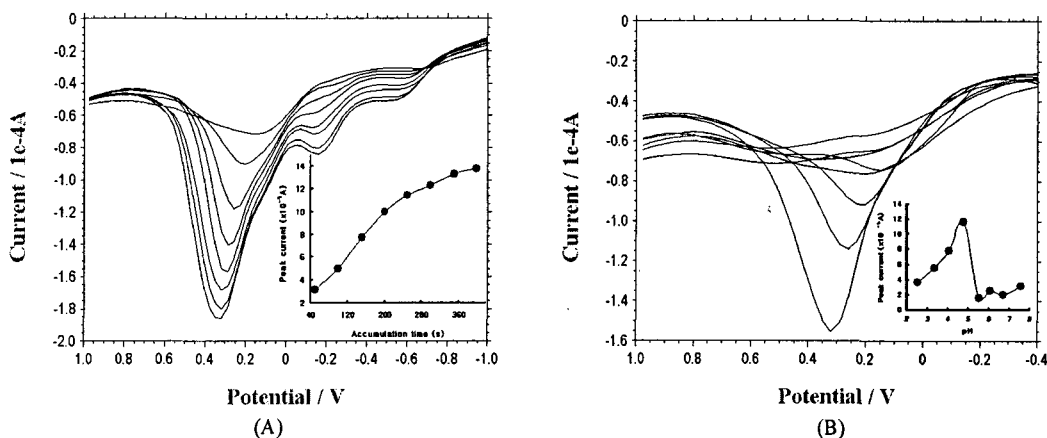


Fig. 3. (A) SW stripping anodic accumulation peak currents for 50, 100, 150, 200, 250, 300, 350 and 400 sec. (B) Various pH peak currents (2.54, 3.36, 4.06, 4.77, 5.54, 6.08, 6.71 and 7.59) in 22-mgL^{-1} dinitrotoluene. Other parameters were of Fig. 4.

2 mgL⁻¹ of concentrated dinitrotoluene within the pH range of 2.54-7.59. This pH accumulation peak current non-linearly appeared with a wide peak width. At the pH range of 2.54-4.77, a linearly increasing working curve was indicated, after which all of a sudden, it started to fall down very sharply. Other ranges repeatedly increased and decreased, and the maximum peak current of 4.77 × 10⁻⁵ A at the pH of 4.77 appeared. Thus, all other SW parameters were used with a 4.77 pH strength.

3.4. Analytical applications and Statistics

Finally, the optimized parameters were used to detect the working concentration range of 2-19.5 ngL⁻¹ of dinitrotoluene. At these conditions, the linear equation $y = 0.5261x + 0.7816$ and the precision of $R^2 = 0.9947$ were calculated, and showed a gradually increasing linear curve. As shown in Fig. 4 (A), its voltammogram illustrated regular changes in its peak sharp, the response of which was very sensitive with a narrowed peak width. The maximum peak current of 10.72 × 10⁻⁶ A at 20 ngL⁻¹ of concentrated dinitrotoluene was obtained, and its peak increased sharply. At these conditions, the relative standard deviation (RSD) was found to be 0.9947 at a 100-s⁻¹ accumulation time, and the estimated detection limit was 0.6 ngL⁻¹ on the basis of the signal-to-noise ratio (S/N = 3). Then the analytical application of the sand from the firing range was examined for the known concentration of the 0.1-mL

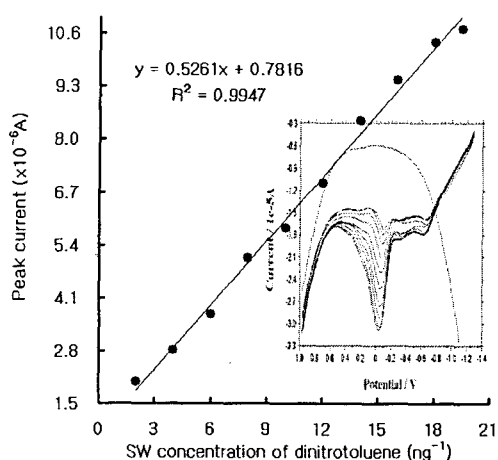


Fig. 4. (A) SW concentration effect of a stripping voltammogram and its working curve for 2-, 4-, 6-, 8-, 10-, 12-, 14-, 16-, 18- and 20-ngL⁻¹ dinitrotoluene in 0.1 M of NH₄H₂PO₄ at a deposition time of 100 sec. Other parameters were of optimum paramitters.

soil solution, and using the standard addition method, the results was calculated with a 0.6-mgL⁻¹/1g soil sample. This application test was carried out five times under optimum conditions. The results were satisfactory at 0.59 mgL⁻¹, with a 95.5% (n = 5) recovery. Several other interferences were also examined, such as metal ions and their similar kinds of explosion materials, under these optimized conditions. At the spike of 1 mgL⁻¹ of dinitrotoluene, the existence of 10 mgL⁻¹ of Ba(II), Cr (III), Co(III), Hg(II), Bi(I), Cd(II), Ge(IV), RDX, dinitrobenzene, and 99% dinitrotoluene resulted in 218.28%, -67.98%, 10.95%, 171.86%, 14.07%, 10.87%, 10.55%, 0.23%, 498.52%, and 43.88%, respectively. The results showed that dinitrobenzene in similar explosive materials responded most sensitively. The presence of other interference ions was also effectively corrected using standard addition methods.

4. Conclusion

This paper describes the identification of optimized conditions for determining dinitrotoluene in contaminated soil sample using the voltammetric method. This method was found to be viable and stable in various analytical conditions for SW, and to be more sensitive than other common voltammetric methods. The results presented lower detection limits in nanogram ranges. This indicates that the voltammetric method could be usable to assay in environmental materials and could be applicable in other fields that requiring explosive analysis

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