Analysis for explosives in contaminated soil using the electrochemical method

Suw Young Ly★

Biosensor Research Institute, Seoul National University of Technology
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폭발물 오염토양에서 전기화학법을 이용한 RDX 흔적량의 분석

이 수 영★

서울산업대학교 바이오센서연구소
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Abstract: Cyclic voltammetry (CV) and square wave stripping voltammetry (SW) analysis of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) using the double-stranded ds calf thymus (DNA) mixed in carbon nanotube paste electrode (PE) were provided. The optimum analytical conditions were determined and the peak potential was 0.2 V vs. Ag/AgCl. The linear working ranges of CV (50-75 ug/L) and SW (5-80 ng/L) were obtained. The precisions of RSD in the 10 ug/L was 0.086% (n=15) and the detection limit was 0.65 ng/L (2.92×10^{-12} M) (S/N=3) with 300 s adsorption time at the optimum condition. The method was used to determine the presence of explosive chemicals in contaminated soil samples.

요 약: 순환전압전류법과 벗김전압 전류법을 사용한 폭발물(hexahydro-1,3,5-trinitro-1,3,5-triazine, RDX)의 흔적량 분석을 위하여 double-stranded ds calf thymus (DNA)와 카본 나노튜브 혼합 전극을 사용하였으며. 최적 분석 조건을 시험한 결과 0.2 V vs. Ag/AgCl 전위에서 봉우리 전류를 발견하였다, 이 전위를 사용하여 선형분석 농도 범위: 50-75 ug/의 순환전압전류법과, 5-80 ng/L의 벗김 전압 전류법에 도달하였으며, 10 ug/L의 농도에서 15번 반복 측정한 상대 표준편차는 0.086% 이었다. 또한 300초의 벗김 분석 조건에서 0.65 ng/L (2.92×10^{-12} M) (S/N=3)의 검출 한계에 도달 하였으며, 이 조건에서 폭약에 오염된 토양중의 RDX 흔적량을 분석 응용하였다

Key words : voltammetry, DNA, carbon nanotube, RDX

1. Introduction

For many years, abandoned explosives of RDX (MW: 222.12, $C_3H_6N_6O_6^{3-}$: hexahydro-1,3,5-trinitro-1,3,5-triazine) were disposed, burned, or detonated in remote areas, causing hazardous and serious

★ Corresponding author
Phone : +82-(0)2-970-6691   Fax : +82-(0)2-973-9149
E-mail : suwyoung@snut.ac.kr

environmental contamination problems.[1] These mixtures were absorbed into the soil, ultimately leaking into underground water, posing a serious threat to living species. Many explosives are toxic and contain carcinogens.[2] Due to their potential to contaminate the environment and damage the viability of farm fields, the importance of detecting these explosive substances has become urgent. RDX is a popular explosive substance,[3,4] although impurities or byproducts of RDX were found as a new possible source of energy.[5] Explosives and other contraband material contain various chemical elements, such as hydrogen, carbon, nitrogen, and oxygen in distinct quantities and ratios. To detect RDX, a variety of methods, including using an immunosensor,[6] gas chromatography,[7] liquid chromatography,[1] pulsed fast-thermal neutron,[8] and remote electrochemical sensor[9] have been reported. Moreover, ion mobility spectrometry systems[10] and amperometric gas sensor[11] have been developed. A reversed-displacement immunosensor in seawater was used to detect 2,4,6-trinitrotoluene (TNT), and analytical limits were set at 2.5 ng/mL or part-per-billion (ppb) in saline buffer and 25 ppb in seawater with a 10 min analysis time.[6] Land mine detections in soils may be collected and assayed for traces of nitroaromatic, nitramine and nitrate ester explosives.[7] Gas chromatography and an electron capture determination in soil showed a concentration range between 0.4 μg/ml and 8,000 μg/ml as nitro-metabolite in animal liver tissue.[4] Another method of pulsed fast-thermal neutron analysis is a technique based on the neutron which uses the microgram working ranges reactions to identify and quantify a great number of elements.[8] However, in scientific analysis, a simpler and low-level detection method is required. The voltammetry method is useful in detecting specific substances such as RDX, as well as serving as a general-purpose sensor for environmental analysis.[12-16] It is a system that is compact and does not need pretreatment. Stripping techniques are very sensitive and dependent on the working electrode system, so carbon nanotube was determined in many previous experiments as an effective method.[17-19] Since DNA has a unique sensitivity, it is immobilized onto the carbon nanotube electrode for detection.[20] In this study, the DNA and carbon nanotube were combined with paste electrode, and the peak current was obtained at the 0.2 V peak potential[1] within the ppt ranges. Optimum results were attained under very low analytical working ranges compared to other common voltammetry methods. Hence, while this efficient method was used in contaminated soil samples, it can also be useful in other environmental assays at low-range detection.

2. Experiment

2.1. Apparatus, Reagents, and Procedure

A CHI660A instrument electrochemical workstation from voltammetry systems (CH Instruments Inc., Cordova, TN, USA) was used in all the experiments. A three-electrode system was applied to the CV and SW signals, with saturated Ag/AgCl/KCl as the reference electrode and a PE working electrode. Platinum wire was also used as an auxiliary electrode. Throughout the experiments, all the electrolyte solutions were used with double-distilled water (18 M ohm/Cm). All required reagents were arranged from analytical level chemicals (Aldrich). The 0.1 M ammonium phosphate solution was prepared as the most suitable supporting electrolyte. The concentration of the electrolyte solution within the range of 0.01-0.3 M was performed, and 0.1 M $NH_4H_2PO_4$ concentration found to be effective for RDX. The carbon nanotube (Nanostructured & Amorphous Materials, Inc.) and double-stranded calf thymus DNA (double-stranded and prepared from calf thymus sigma), and a mineral oil ratio (%) of 40:40: 20 were used. All other reagents were prepared from Aldrich, which were homogenized in a mortar for 30 min. This mixed paste was inserted into a plastic syringe needle with a diameter of 3.0 mm. A copper wire was then connected to the electric system. A CV scan was examined for the peak potential with various scan rates in a 0.1 ammonium phosphate solution ranging from -0.1 to 0.1 V, finally appearing at the 0.5 V/s scan rate. The experiments were performed at room temperature
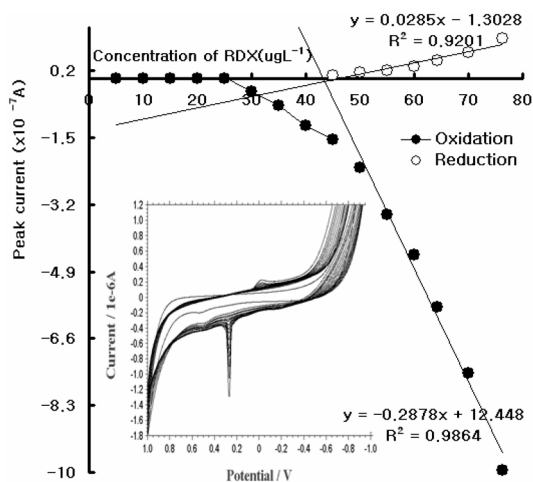
Fig. 1. The cyclic concentration effects of 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, and 75 ug/L for RDX, with 0.5 V/s scan rate in 0.1 M ammonium phosphate solutions.

without removing oxygen.

3. Results and Discussion

3.1. Cyclic Voltammetry

Firstly, various acid and base electrolyte solutions were examined, with the 0.1 M ammonium phosphate solution yielding good results. With this solution, peak potential was determined. *Fig.* 1 shows the result for various concentration effects. With the blank solution, a simple sigmoid curve appeared and noise signal was not obtained, the initial and switching potential of -1 V through 1 V with wide potential ranges was used for the peak search in the scan rate of 0.5 V/s. Then, the electrolyte solution was fixed with 0.5 mg/L RDX spike to get the peak potential, obtaining a 0.25 V oxidation peak. More increases in concentration were conducted to calibrate the spikes. At the range of 5-25 ug/L, small signals appeared. Subsequently, 30-45 ug/L showed no linear increase, and at the range of 50-75 ug/L, the usable linear equation of y= −0.2878x+12.448 with R^2 =0.9864 was obtained, showing a sharp increase. Under these conditions, other reduction peaks appeared with a poor potential of -0.1 V. Thus, the anodic reaction can be used to more sensitive
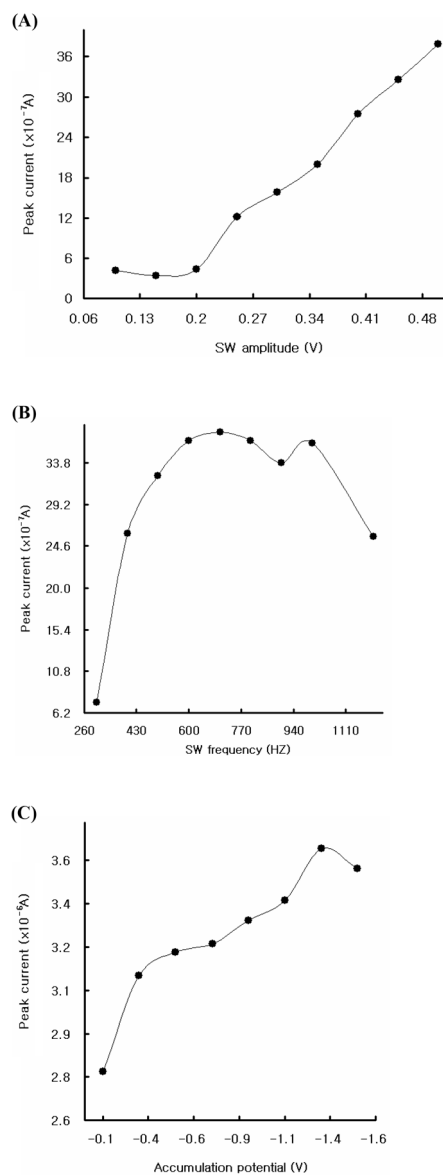

Fig. 2. (A): The peak currents in SW amplitude of 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, 0.4, 0.45, and 0.5 V, (B): SW frequency of 300, 400, 500, 600, 700, 800, 900, 1,000, and 1,200 HZ. (C): Accumulation potentials of -0.1, -0.3, -0.5, -0.7, -0.9, -1.1, -1.3, and -1.5 V, at 10 u/gL RDX.

working ranges, and various accumulation parameters were examined.

3.2. SW stripping voltammetric parameters

In SW, stripping voltammetry was examined for

low-range detection. *Fig.* 2(A) shows the various SW amplitude potential at the fixed concentration of 10 ug/L RDX, ranging from 0.1 to 0.5 V. Peak currents are increased linearly, with a maximum peak current of 37.85×10^{-7} A responding at the 0.5 V amplitude. At this condition, peak width increased; thus, the 0.5V amplitude was used in other conditions. At this state, various SW frequencies on the oxidation peak height of RDX were measured at the range of 300-1200 Hz. *Fig.* 2(B) shows the peak signals were increased from the frequency range of 300 to 700 Hz. At 700 HZ, and maximum peak current was obtained with 37.18×10^{-7} A peak height, showing similarity with SW amplitude results. The peak currents were decreased until they reached the range of 900 Hz. They were changed again between the range of 900 and 100 Hz. Finally, the peak current was decreased rapidly in the range of 1200 Hz with 25.64×10^{-7} A peak height. *Fig.* 2(C) shows the effects of the square wave accumulation potential of the peak current within the range of -0.1 through -1.5 V. The responses were increased nonlinearly. The peak currents from the range of the -0.1 V through -0.3 V increased sharply, and then from the range of the -0.5 to 0.7, the peak currents were decreased. Nevertheless, it increased again at the range of -0.7 to -1.3 V. Maximum peak appeared at -1.3 V with 3.6×10^{-6} A height, showing that it is more sensitive than the SW amplitude and frequency results. Also, other influence parameters of accumulation times were examined for the range of 50-300 s with 6 points, and other parameters of electrolyte hydrogen ionic strength of the 2.47-7.31 pH ranges were examined with 8 points. Optimum conditions were 300 s accumulation time with 6.82×10^{-5} A, and 6.11 pH solution with 8.40×10^{-5} A peak height (results not shown). At this condition, hydrogen ionic strength is more sensitively influenced than other parameters. Finally, all these conditions were applied in various possible interference species with metals, and other explosive analogies were examined with a fixed concentration of 1 mg/L RDX, ten hold concentration of 10 mg/L of Co(III), Ge(lV), dinitrobenzene, and dinitrotoluen was spiked and

interference was not obtained. On the other hand, 10 mg/L of Ba(II), Cr(III), Hg(II), Bi(II), and Cd(II) yielded 108.9%, -49.70%, 65.93%, 7.28%, and 10.35% interference, respectively. The% indicates depression in the RDX peak current. Other interference ions can be corrected using standard addition methods.

Under optimum conditions, usable analytical working ranges are determined. Initially, the ppm range of 2-32 mg/L with 16 points was obtained, with equations of y=2.036x+2.72 and precisions of R^2=0.9913. Narrow peak width appeared, then more sensitive ranges of 5-75 ug/L SW with 15 points were obtained with the linear equation of y=1.1669x-6.069 and precision of R^2=0.9888. The results are usable in analytical application (not shown here). Finally various sensitive working ranges were determined. In this experiment, environmental noise signal was excluded with the steel cage. *Fig.* 3(A) shows the results of the nanogram range of 5-80 ng/L with 16 points for the RDX and the raw voltammograms of *Fig.* 3(B). At these ranges, the slop ratio of x/y=0.3375 and Y axis intercept of -0.1466, relative standard deviation of R^2=0.99964, with sharp peaks appearing, were obtained. The result can be useful in low-range detection of RDX. With these conditions, statistical analysis yielded relative standard deviation (RSD) posted for 15 determinations of the 10 ug/L RDX solution with 300 s accumulation time was 0.086%, and the estimated detection limit was 0.65 ng/L (2.92×10^{-12} M) based on the signal-to-noise ratio (S/N=3). Analytical application was performed with conta-minated soil samples from a shooting range in clay soil in a northeastern suburb in Seoul, and were examined using the standard addition method following the procedure of Gauger, *et al.*[8] and Suw Young *et al.*[3] Contaminated soil sample (5 g) was collected and ground in mortar, then mixed with 100 mL reagent acetone. The supernatant was filtered using 0.45 micron filter paper, and the solution was examined using standard addition methods. *Fig.* 3(C) shows the results of the blank solution represented by the first curve and the diluted soil sample and continuous 10.0, 20.0, 30.0 ng/L RDX
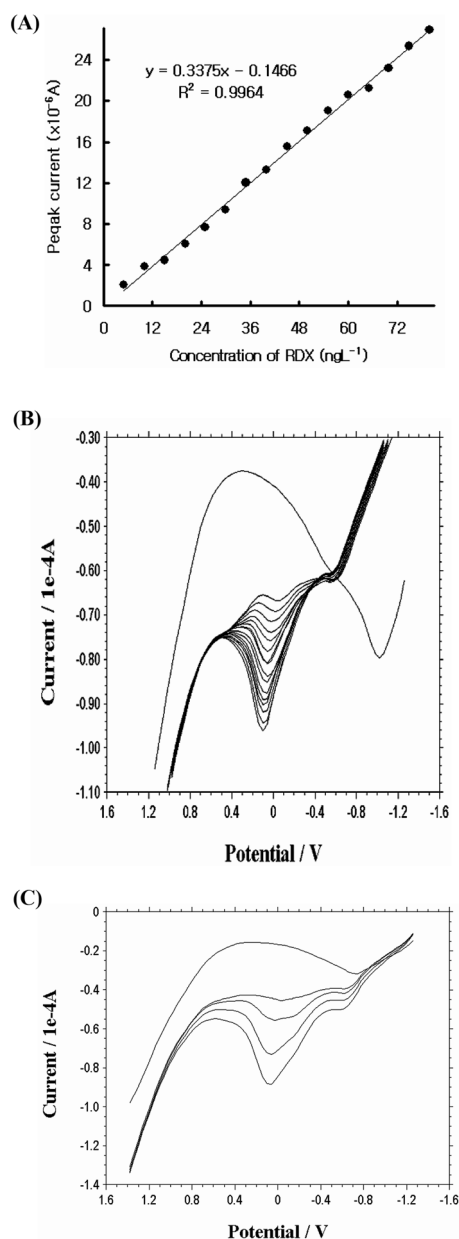
(A)

(B)

(C)

Fig. 3. (A): analytical linear ranges; and (B): raw voltamm-ograms of 5, 10, 15, 20, 25, 30, 35, 40, 45, 50, 55, 60, 65, 70, 75, and 80 ng/L RDX in a 0.1 M NH₄H₂PO₄ electrolyte solution; (C): analytical application of the contaminated soil sample, each curve shown for the electrolyte blank solution, 0.05 mL soil solution spike, and standard for 10, 20, 30 ng/L RDX spike in a pH 6.1, in a 0.1 M NH₄H₂PO₄, initial potential of -1.3 V, final potential of 1.4 V, SW frequency of 700 Hz, SW amplitude of 0.5 V, increment potential of 40 mV, and accumulation time of 300 s. Other parameters were used in Fig. 2.

standard spiking represented by the second curve. The results indicate that RDX concentration in the particular soil sample found was at 90 ng/g soil and the contaminated value in the soil varied widely depending on the location of the sampling sites. More expanded applications of commercial RDX of N company sample were tested for the known contents of 1000 mg/L using the standard addition method. It was found that such RDX was five times under optimal conditions, yielding good results with a 98% (n=5) recovery.

4. Conclusion

In this study, DNA was mixed in carbon nanotube paste electrode to determine RDX. Optimum conditions were reached to very low detection limits at ppt levels, proving to be more sensitive in various analytical conditions. This analytical application showed good performance of DNA mixed on the surface of carbon nanotube paste for the RDX. This indicates that DNA PE (detection limit: 0.65 ng/L (2.92×10^{-12} M)) is more sensitive compared to other methods[6,7,4] for trace assay of RDX. It can also be used to analyze other kinds of environmental contamination.

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