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# Voltammetric determination of nitroaromatic and nitramine explosives contamination in soil

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## Abstract

The contamination of soil by nitroaromatic and nitramine explosives is widespread during the manufacture, testing and disposal of explosives and ammunitions. The analysis for the presence of trace explosive contaminants in soil becomes important in the light of their effect on the growth of different varieties of plants and crops. 2,4,6-Trinitrotoluene (TNT), cyclotrimethylene trinitramine (Research Department explosive, RDX) and cyclotetramethylene tetranitramine (high melting point explosive, HMX), other related explosive compounds and their by-products must be monitored in soil and surrounding waterways 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 explosive such as RDX, HMX and TNT. The electrochemical redox behavior of RDX, HMX and TNT was studied through cyclic voltammetry and quantitative determination was carried out by using square wave voltammetry technique. Calibration curves were drawn and were linear in the range of 63–129 ppm for RDX with a detection limit of 10 ppm, 49–182 ppm for HMX with a detection limit of 1 ppm and 38–139 ppm for TNT with a detection limit of 1 ppm. This method was applied to determine the contaminations in several soil samples that yielded a relative error of 1% in the concentrations.

*Keywords:* Explosives; Soil analysis; Trace levels determination; Voltammetry

## 1. Introduction

Contamination of soil by Research Department explosive (RDX), high melting point explosive (HMX), trinitrotoluene (TNT) and other nitroaromatic and nitramine explosive compounds is a significant worldwide problem. The sources of these explosive contaminants include the manufacturing, testing and disposal of explosives by defense establishments. These compounds are mutagenic, toxic and have the tendency to persist in the environment [1–3]. TNT, RDX and HMX are major ingredients in nearly every ammunition formulation and are the secondary explosives used in the greatest quantities. These explosives are environmentally harmful compounds as they are toxic in nature harming marine and terrestrial species· In practice, explosive contaminants in soil may undergo metabolic transformation, photo catalytic degradation and biodegradation by processes like oxidation, dehydrogenation, reduction, hydrolysis, exchange reactions.

Therefore, trace level detection of these explosives in the complex environmental matrixes by classical methods is difficult and will require development of new analytical methods.

Various methods for detection of explosive substances have been reported. These are mostly spectrometric [4,5,7,13] and electrochemical methods [6,14–19] with various detection techniques that are coupled with several different separation methods such as extractions [10–12], gas [7,8] and liquid [9,10,15] chromatography and electrophoresis [14,16].

Voltammetric [6,14–16] and amperometry methods [17–19] are used in qualitative and quantitative determination of trace levels of pollutants in various environmental components over a wide range of concentrations. Some of the main features of modern voltammetric methods are their sensitivity, selectivity and specificity. These techniques are sensitive to oxidation and reduction reactions and thus offer a promising analytical method for ordnance compounds.

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The objective of this study is to develop a voltammetric method for the determination of explosive contamination in soil. The reduction potential provides the method selectivity for a specific explosive and the current generated during electrochemical reaction determines the concentration of the targeted explosive contaminant in soil matrix. Development of an electroanalytical procedure for the determination of nitroaromatic and nitramine explosive contamination in soil such as trace levels of RDX, HMX and TNT using the square wave voltammetry (SWV) method is presented.

## 2. Experimental

### 2.1. 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.

### 2.2. Electrode pretreatment

The GC electrode was polished with a suspension of alumina powder (1 μm), and then rinsed thoroughly with deionized water to remove any alumina residue [20]. Electrochemical pretreatments were done in a 50 mM $(NH_4)_2SO_4$ solution, pH 3.0, being adjusted with sulfuric acid. The pretreated electrodes were allowed to stay for 10 min in deionized water before measurements; this procedure improved the stabilization of the voltammetric response. Before each series of measurements, pretreated electrodes were calibrated with a standard solution.

### 2.3. Electrochemical studies

The electrochemical redox behavior of RDX, HMX and TNT was studied using cyclic voltammetry technique, which provides a basis for SWV detection. Individual standard stock solution of 0.1 M concentration of RDX, HMX and TNT were prepared in acetonitrile. Five millilitre of 0.1 M tetrabutyl ammonium bromide (TBABr) in acetonitrile solution was used as supporting electrolyte. The peak potential, half peak potential, peak current values and the number of peak details were assessed. SWV analysis was performed for different volumes of these concentrations to obtain the calibration plots. Calibration curves were made by taking analyte concentration versus peak current ($i_p$).

### 2.4. Soil samples

Explosives contaminated soil samples were collected from four different locations based on their extensive use for processing, testing and disposal of explosives and ammunitions. Two types of soil samples one from the soil surface and another from 10 to 15 cm deep were collected with the help of screw auger. Four locations of which two were chosen for specific contamination by HMX where HMX manufacturing was going on. The other two locations are disposal and testing grounds for explosives by open burning or detonation was suspected of being contaminated with various explosives.

The collected soil samples were then subjected to air-drying at room temperature (20–25 °C). After 10 days, soil samples were ground well and sieved through 600 μ SS sieve and explosive contaminants were extracted as per American Society for Testing of Materials (ASTM) method [21]. Two grams of each sample was weighed and 20 ml of acetonitrile was added. The suspension was subjected to shaking for 1 min and placed in ultrasonic bath for 6 h. Ten millilitre of the extract and 10.0 ml of aqueous $CaCl_2$ (5 g/L) solution as a flocculating agent were

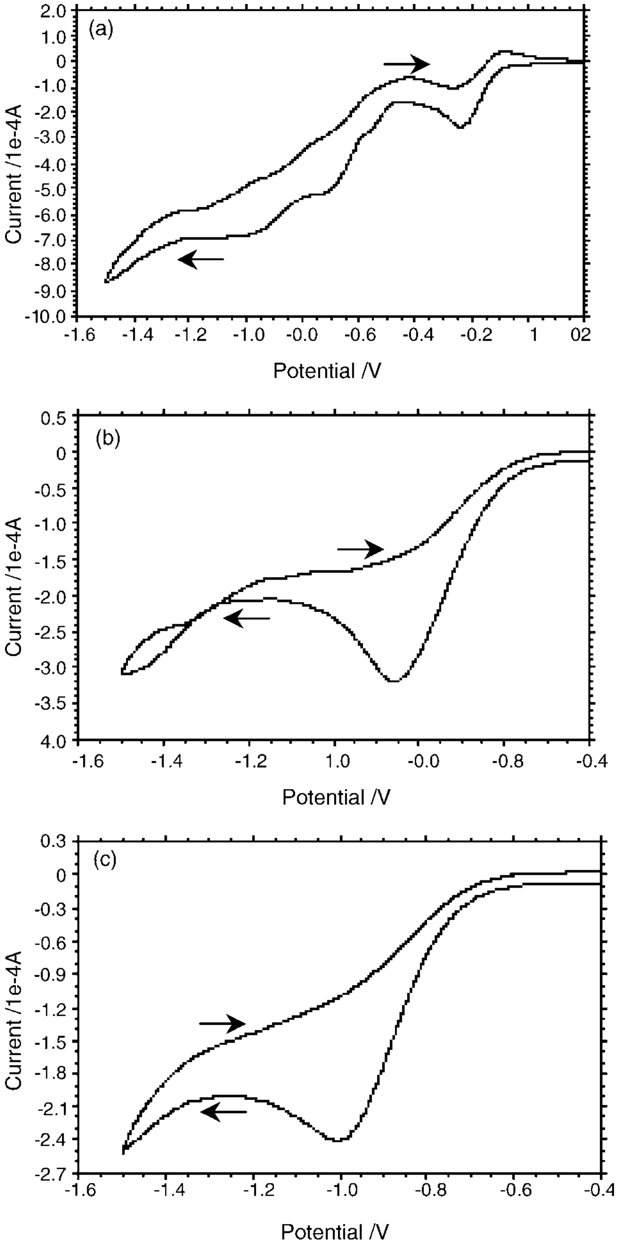


Fig. 1. Cyclic voltammograms obtained for 0.1 M solution of TNT (a) RDX; (b) and HMX (c) in deoxygenated acetonitrile–0.1 M tetrabutyl ammonium bromide solution; working electrode: glassy carbon, reference electrode: Ag/AgCl and counter electrode: platinum. Scan rate: 50 mV/s.

added and filtered through 0.2 μm filter. Five millilitre of 0.1 M TBABr supporting electrolyte solution was taken into the cell, to that 1 ml of the soil extract was added and SWV analysis was performed. Peak potential, half peak potential, half peak width, peak current and peak area values were determined from the voltammograms.

## 3. Results and discussions

### 3.1. Cyclic voltammetry

In cyclic voltammetric analysis, potential was stepped from +1.0 V and scanned at a rate of 50 mV/s to a potential of −1.5 V and reversed. During cathodic scan of potential, TNT exhibited a predominant peak at a potential of −0.24 V with shoulder peaks at −0.54, −0.70 and 0.97 V. During reverse scan, TNT showed a peak at potential of −0.2 V (Fig. 1a).

RDX and HMX exhibited one predominant peak each at potentials of −0.86 V (Fig. 1b) and −1.0 V (Fig. 1c), respectively during cathodic scan of potential. On the other hand, no peaks were noticed in both cases on the reverse sweep indicating the irreversibility of the electrochemical reaction. These results demonstrate that RDX, HMX and TNT are electroactive and undergo electrochemical reduction reaction. The energy required for the reaction is in the order of TNT (−0.2 V) < RDX (−0.86 V) < HMX (−1.0 V). It is apparent that TNT undergoes reduction at lower potential while HMX undergoes reduction at higher potential in this medium (Table 1).

Krausa and Schorb [17] have studied CV behaviour of various niroaromatic explosives such as TNT, 2,4-DNT, 2,6-DNT and 1,3-DNB and reported that the potential difference between the oxidation peaks of TNT and other nitoarmoatic explosives were too small for quantitative distinction. Therefore, nitroaromatics will be determined as a total parameter. Similarly the difference between peak potential of nitramine explosives such as RDX and HMX were very low (0.14 V). Hence, nitramine explosives will be determined as a total parameter. While the potential difference between reduction peaks of TNT and nitramine explosives (RDX and HMX) allow the distinction between nitroaromatic and nitramine explosives. Hence, it can be possible for the quantitative determination.

The effect of scan rate ($\nu$) on the peak current for the reduction of explosives were examined. The plot of $i_{pc}$ versus $\nu^{1/2}$ for RDX, HMX and TNT showed linear response in the range 10 ± 200 mV/s, indicating that the reduction involves diffusion. In addition, the peak potential ($E_p$) shifts more negative with increasing scan rate in all the three cases, which confirms the irreversible tendency of the reduction process. The effect of the pH of the acetate buffer on the reduction process of RDX, HMX and TNT were studied in a pH range of 4–8. In all the cases, the peak current increased slowly with increasing pH up to 4.5, remaining constant in the pH range of 4.5–6, then decreases gradually in a range of 6–8 with increasing pH. Thus, pH 4.5 was chosen for the further analysis.

### 3.2. Calculation of “n” using chronocoulometry

Chronocoulometric experiments were carried out for these explosives with glassy carbon working electrode [22]. 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 electrochem-

Table 1
Cyclic voltammetric studies of explosive compounds

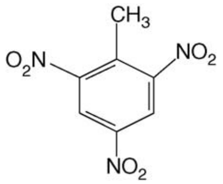
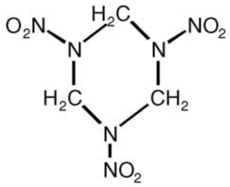
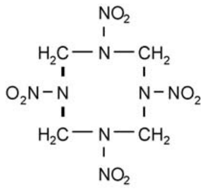
| Name of the explosive | Nature of explosive | Structure | Nature of $NO_2$ groups | No. of peaks | $-E_p$ (V) |
|---|---|---|---|---|---|
| 2,4,6-Trinitrotoluene (TNT) | Nitroaromatic |  | 3 C-$NO_2$ | 1 | 0.24 |
| Cyclotrimethylene trinitramine (RDX) | Nitramine |  | 3 N-$NO_2$ | 1 | 0.86 |
| Cyclotetramethylene tetranitramine (HMX) | Nitramine |  | 4 N-$NO_2$ | 1 | 1.0 |

Table 2
Calculation of "*n*" using chronocoulometry

| Analyte | Concentration ($\times 10^{-3}$ M) | Stepping potential (V) | | $D$ value ($\times 10^{-6}$ cm$^2$/s) | Charge obtained ($\times 10^{-4}$ C) | "*n*" value calculated |
|---|---|---|---|---|---|---|
| | | From | To | | | |
| Tetryl | 0.010 | 0.1 | −0.2 | 5.1 | 1.009 | 0.82 |
| TNT | 0.010 | 0.0 | −0.3 | 5.8 | 1.311 | 0.99 |
| PETN | 0.010 | −0.6 | −1.3 | 4.9 | 2.572 | 2.1 |
| RDX | 0.025 | −0.6 | −1.3 | 5.9 | 4.685 | 1.4 |
| HMX | 0.025 | −0.6 | −1.3 | 5.0 | 4.869 | 1.6 |

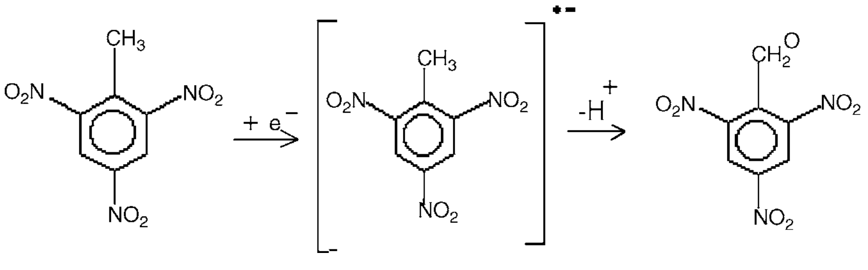
ical reaction was derived from the forward slope charge value ($Q_d$) of Anson's plot ($Q$ against $t^{1/2}$) obtained in this experiment using the following equation [$Q_d = 2nFAD^{1/2}Ct^{1/2}/\pi^{1/2}$], where, $n$ = eq./mole, $F$ = the Faraday constant (96500), $A$ = area of the electrode (0.0707 cm$^2$), $D$ = diffusion coefficient in cm$^2$/s, $C$ = bulk concentration in mol/cm$^3$ and $t$ = time in seconds.

For each chemical, the charge ($Q_d$) 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 for trinitrophenylmethylnitramine (Tetryl), TNT and two for pentaerythritoltetranitrate (PETN), RDX, HMX. The "*n*" values calculated from chronocoulometry experiments are tabulated in Table 2.

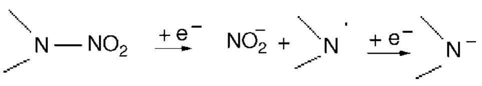
### 3.3. Probable reaction mechanism based on cyclic voltammetry and chronocoulometry experimental results

Based on these literature details and also from the cyclic voltammetric and chronocoulometric results obtained in the present study, possible reduction mechanism has been proposed.

TNT may form free radical on reduction at lower potential and then eliminate a proton.



RDX and HMX may undergo two-electron reduction in aprotic solvents (addition of first electron is synchronous with cleavage of the nitrogen–nitrogen bond to form nitrite ion and a nitrogen radical in step 1, and then the radical accepts the second electron in step 2).



The stock solutions of HMX and RDX were colorless, while that of TNT was light yellow in color. During the cyclic voltammetric scan, a pink color for TNT was formed on working electrode as well as counter electrode surfaces. RDX and HMX did not produce any color during the potential scan. From the structural aspects, it is understandable that aromatic nitro compound (TNT) produce color, while cyclic nitramines (RDX and HMX) do not. It is reported that organic compounds, which form stable radical anion undergo color change. The color obtained during the potential scan may be due to the formation of radical anion of the compound, which is adsorbed on the electrode surface [23].

### 3.4. Effects of other ions

Possible interference of several metal ions with RDX, HMX and TNT determination was tested individually with a concentration of 1 mg/L. The ions such as Pb(II), Fe(II), and Bi(II) at 1 mg/L level did not present any interference with RDX, HMX and TNT. On the other hand, the ions such as Zn(II), and Hg(II) (1.0 mg/L) showed interference with enhancement in the peak current. However, the interference of the Zn (II) and Hg (II) ions can be easily eliminated by applying the standard addition method.

### 3.5. Effect of analyte concentration in square wave voltammetry

The SWV 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. Hence, the effect of analyte concentration was studied at following optimized experimental conditions (initial scan potential 0.5 V, final scan potential −1.5 V, increment 0.004 V, amplitute 0.025 V, frequency 15 Hz) for all compounds at the scan rate of 60 mV/s

Table 3
Dependencies of peak current and peak potential on RDX, HMX and TNT

| Compound | Conc. in ppm | $-E_p$ (V) | $-E_h$ (V) | $H_{pw}$ (V) | $i_p$ (μA) | $A_p$ (μVA) |
|---|---|---|---|---|---|---|
| RDX | 63 | 0.780 | 0.688 | 0.176 | 7.51 | 1.411 |
| | 83 | 0.804 | 0.712 | 0.176 | 10.80 | 2.074 |
| | 98 | 0.772 | 0.688 | 0.176 | 12.97 | 2.430 |
| | 111 | 0.792 | 0.700 | 0.180 | 14.75 | 2.848 |
| | 121 | 0.812 | 0.716 | 0.188 | 17.11 | 3.430 |
| | 129 | 0.812 | 0.716 | 0.188 | 17.75 | 3.570 |
| HMX | 49 | 0.772 | 0.664 | 0.212 | 2.54 | 0.558 |
| | 85 | 0.744 | 0.636 | 0.216 | 4.609 | 1.039 |
| | 111 | 0.748 | 0.632 | 0.216 | 6.605 | 1.479 |
| | 132 | 0.744 | 0.632 | 0.212 | 8.368 | 1.855 |
| | 148 | 0.756 | 0.644 | 0.212 | 9.608 | 2.139 |
| | 161 | 0.766 | 0.652 | 0.212 | 10.74 | 2.417 |
| | 173 | 0.780 | 0.664 | 0.216 | 12.35 | 2.788 |
| | 182 | 0.784 | 0.664 | 0.220 | 12.97 | 2.972 |
| TNT | 38 | 0.280 | 0.204 | 0.144 | 10.95 | 1.685 |
| | 65 | 0.268 | 0.196 | 0.140 | 20.81 | 3.274 |
| | 85 | 0.260 | 0.192 | 0.132 | 25.91 | 3.543 |
| | 101 | 0.252 | 0.184 | 0.132 | 30.54 | 4.150 |
| | 114 | 0.248 | 0.180 | 0.132 | 34.92 | 4.760 |
| | 124 | 0.244 | 0.176 | 0.132 | 36.78 | 5.07 |
| | 139 | 0.244 | 0.172 | 0.136 | 40.22 | 5.59 |

$E_p$, peak potential; $E_h$, half peak potential; $H_{pw}$, half peak width; $i_p$, peak current; $A_p$, peak area.

and with the sensitivity of $1 \times 10^{-3}$ A/V. Analyte concentrations ranging from 6 to 129 ppm for RDX, from 5 to 182 ppm for HMX and from 4 to 139 ppm for TNT were investigated by SWV analysis and the results are given in Table 3. RDX and HMX exhibited one predominant cathodic reduction peak each at potentials about −0.7 (Fig. 2) and −0.9 V (Fig. 3), respectively. TNT exhibited two cathodic reduction peaks at potentials about −0.2 and −0.6 V (Fig. 4).

Calibration curves were plotted peak current against concentration ranging from 63 to 129 ppm for RDX, 49 to 182 ppm for HMX and 38 to 139 ppm for TNT. The linear regression analysis of calibration curves in Fig. 5 yields the correlation coefficient $R^2 = 0.9934$, 0.9931, 0.9857 for TNT, RDX and HMX, respectively. The correlation coefficient values reveal that all these compounds showed good linearity between concentration and current responses.

The repeatability (on the same day) and interday reproducibility of both peak potentials and peak currents reported in Table 4 are based each on five experiments using the solution of RDX, MNX and TNT. Behavior of these compounds in the electrolytes was tested using SWV technique. Repetition of sample analysis after 72 h period did not show any significant change in results of analyses.

### 3.6. Soil analysis

The explosive contaminants were extracted by using modified version of a field method described by Jenkins and Walsh

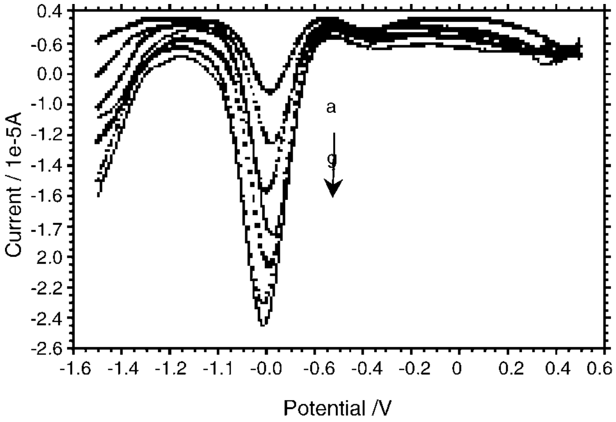


Fig. 2. Square wave stripping voltammograms for a solution containing RDX with different concentration (a) 37; (b) 63; (c) 83; (d) 98; (e) 111; (f) 121 and (g) 129 ppm; initial scan potential: 0.5 V, final scan potential: −1.5 V, increment: 0.004 V, amplitute: 0.025 V, frequency: 15 Hz.

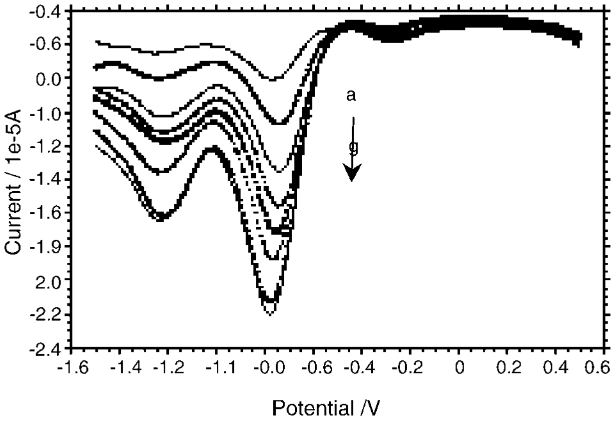


Fig. 3. Square wave stripping voltammograms for a solution containing HMX with different concentration (a) 49; (b) 85; (c) 111; (d) 132; (e) 148; (f) 161; (g) 173 and (h) 182 ppm; initial scan potential: 0.5 V, final scan potential: −1.5 V, increment: 0.004 V, amplitute: 0.025 V, frequency: 15 Hz.

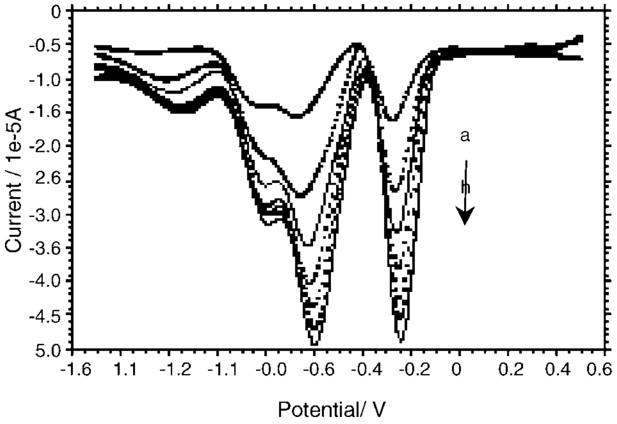


Fig. 4. Square wave stripping voltammograms for a solution containing TNT with different concentration (a) 38; (b) 65; (c) 85; (d) 101; (e) 114; (f) 124 and (g) 139 ppm; initial scan potential: 0.5 V, final scan potential: −1.5 V, increment: 0.004 V, amplitute: 0.025 V, frequency: 15 Hz.

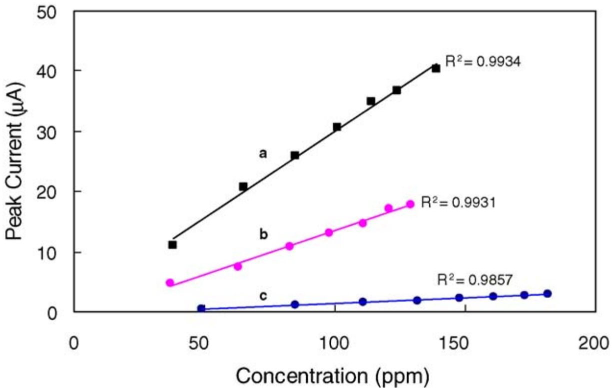


Fig. 5. Calibration plot (peak current vs. concentration) for (a) TNT; (b) RDX and (c) HMX.

[24]. The typical procedure is outlined. Approximately, 5.0 g of soil were placed into an amber screw-top vial and extracted by shaking using 20 ml of reagent-grade acetone for 3 min. The sediment in the extracts was allowed to settle out of suspension. The supernatant was filtered through a disposable 0.45 μm syringe tip filter and stored in a certified clean vial under refrigeration until analysis.

Table 4
Regression data of the calibration lines for quantitative determination of RDX, HMX and TNT and using SWV

| | RDX | HMX | TNT |
|---|---|---|---|
| Linearity range (ppm) | 63–129 | 49–182 | 38–139 |
| Correlation coefficient (*R*) | 0.9931 | 0.9851 | 0.9934 |
| R.S.D. of the slope | 1.34 | 1.04 | 1.12 |
| R.S.D. of the intercept | 0.98 | 0.92 | 1.02 |
| Number of data points | 7 | 8 | 7 |
| LOD (ppm) | 10 | 1 | 1 |
| LOQ (ppm) | 20 | 10 | 10 |
| Repeatability of peak current (R.S.D. %) | 0.52 | 0.62 | 0.78 |
| Repeatability of peak potential (R.S.D. %) | 0.11 | 0.09 | 0.13 |
| Reproducibility of peak current (R.S.D. %) | 1.21 | 1.68 | 1.55 |
| Reproducibility of peak potential (R.S.D. %) | 0.32 | 0.58 | 0.42 |

Table 5
Amount of explosive contamination in soil determined through SWV technique

| Sample location | Contaminant | Nature of contaminant | Conc. in soil (μg/g) |
|---|---|---|---|
| Location 1 | | | |
| Surface soil | RDX/HMX | Nitramine | 365 |
| Deep soil | RDX/HMX | Nitramine | 686 |
| Location 2 | | | |
| Surface soil | RDX/HMX | Nitramine | 624 |
| Deep soil | RDX/HMX | Nitramine | 350 |
| Location 3 | | | |
| Surface soil | TNT | Nitroaromatic | 177 |
| | RDX/HMX | Nitramine | 565 |
| Deep soil | TNT | Nitroaromatic | 280 |
| | RDX/HMX | Nitramine | 245 |
| Location 4 | | | |
| Surface soil | RDX/HMX | Nitramine | 399 |
| Deep soil | RDX/HMX | Nitramine | 135 |

SWV technique was used to analyze the explosive contaminants in the soil samples. One millilitre of the soil extract was added to known volume of supporting electrolyte solution and the potential was initiated at +0.5 V and scanned at a rate of 60 mV/s to a potential of −1.5 V. The peak current values obtained for the soil samples were compared with the standard calibration curves obtained from the concentration study. The explosive concentration in soil on μg/g basis is calculated by using following equation

$$\text{explosive contamination}\,(\mu\text{g/g}) = \frac{\text{solution conc.}\,(\mu\text{g/ml}) \times 20(\text{ml})}{\text{wt. of soil sample}\,(\text{g})}$$

The calculated values of RDX/HMX and TNT concentration in soil extracts are given in Table 5. The nature of explosive contaminants found and the concentrations are varied with type of location from which the samples were collected. For soil samples collected at locations such as HMX manufacturing facility mainly contains the mixture of nitramine explosives (RDX and HMX) and the mixture of nitroaromatic and nitramine explosives contaminants was found in highest concentration at disposal and testing grounds.

## 4. Conclusion

Voltammetric methods such as CV and SWV techniques can be used for the qualitative and quantitative determination of nitroaromatic and nitramine explosives 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. In this study all the parameters and experimental conditions are optimized for the determination of nitroaromatic and nitramine explosives in soil. The potential difference between reduction peaks of TNT and nitramine explosives (RDX and HMX) allow the distinction between nitroaromatic and nitramine explosives and therefore, the selectivity of these techniques can be enhanced. This method is accurate, precise and the instrumentation is of low cost. This study reveals that the selected locations are contaminated with explosive compounds such as RDX, HMX and TNT ranging. Analysis of 10–15 cm deep soil confirms the leaching of explosive contaminants from surface.

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