Talanta 115 (2013) 768–778

Contents lists available at SciVerse ScienceDirect

Talanta

journal homepage: www.elsevier.com/locate/talanta

Determination of nitroaromatic and nitramine type energetic materials in synthetic and real mixtures by cyclic voltammetry

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ARTICLE INFO

Article history:
Received 31 January 2013
Received in revised form
21 June 2013
Accepted 25 June 2013
Available online 29 June 2013

Keywords:
Cyclic voltammetry
Nitro explosives analysis
TNT
DNT
RDX
HMX

ABSTRACT

Nitro-explosives contain reducible aromatic –NO_2 groups or cyclic $>$N–NO_2 bonds that may undergo reductive cleavage. This work reports the development of a cyclic voltammetric (CV) assay for nitroaromatics (trinitrotoluene (TNT), dinitrotoluene (DNT)) and nitramines (1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)) using a glassy carbon electrode. This determination was first used for these energetic materials by resolving current responses of reduction potentials primarily due to one constituent but partly contributed by other constituents. Calibration curves of current intensity versus concentration were linear in the range of 30–120 mg L^{-1} for RDX with a limit of detection (LOD) of 10.2 mg L^{-1}, 40–120 mg L^{-1} for HMX (LOD = 11.7 mg L^{-1}), 40–120 mg L^{-1} for TNT (LOD = 11.2 mg L^{-1}), and 40–140 mg L^{-1} for DNT (LOD = 10.8 mg L^{-1}). Results showed that the CV method could provide a sensitive approach for the simultaneous determination of RDX and TNT in synthetic and real mixtures. Deconvolution of current contributions of mixtures at peak potentials of constituents was performed by multiple linear regression. The proposed method was successfully applied to the analysis of military explosives comp A5 and octol, and method validation was performed both against HPLC on a comp B (TNT+RDX) sample and against GC–MS on real post-blast residual samples containing both explosives.

1. Introduction

The relatively heterogeneous distribution of explosives in contaminated and remediated land makes field analysis techniques important in exploring the nature and distribution of these contaminants. In-field observations enable more effective operation of out-field stationary laboratories using more robust analytical techniques. Stationary laboratories accommodate sophisticated instrumental techniques such as gas chromatography (GC), high performance liquid chromatography (HPLC), and ion mobility spectrometry (IMS) equipped with mass spectrometric (MS) detectors which unfortunately have high cost and complexity. In this regard, voltammetry may be a cheaper and more portable alternative [1]. The advantages of electrochemical systems for on site/in situ measurements of explosives rely on high sensitivity and selectivity, reasonable linear concentration ranges, minimal space and power requirements, and low-cost instrumentation. Different electrode materials found application for electrometric estimation of nitroaromatic and nitramine explosives, including mercury, various forms of carbon (fiber, diamond, glassy carbon) and gold/amalgam [2–4]. Relatively high negative potentials are necessary for reduction in voltammetric determination of nitramines and nitrate esters [5]. Generally trinitro compounds (e.g., TNT and picric acid) are more readily reducible than the corresponding dinitro and mononitro analogs. The most important advantage of electrochemical techniques over UV spectrophotometry is the higher selectivity [6]. Nevertheless, chemical contamination can sometimes affect the analytical results. For example, in TNT determination, results can be influenced by nitrobenzene, nitrophenol and nitroaniline derivatives present in the media. Since electrochemical techniques are performed in the liquid phase, nitro-explosives (mostly water-insoluble) should be dissolved in a suitable organic solvent. Additionally, electrodes may lose their efficiency because of contamination over time. Electrode effectiveness can be enhanced by the selection of suitable electrodes such as nanocomposite-coated electrodes used for electrochemical detection of TNT and several other nitroaromatics [5]. Inorganic film-modified electrodes have also found increasing use in technical applications [7]. When a polyphenol-coated screen-printed carbon electrode was used for sensitive voltammetric measurement of TNT in the presence of surface-active substances, it was observed that the protective polyphenol coating on the electrode offered resistance to surfactant

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http://dx.doi.org/10.1016/j.talanta.2013.06.047

(e.g., gelatin, humic acid and sodium dodecyl sulfate) fouling while allowing facile transport of the target TNT [8]. A chemically modified gold electrode, based on thiolated α-cyclodextrin (α-CD) self-assembled monolayer, was used for the sensitive determination of nitroaromatic explosive compounds (basically TNT). For example, as opposed to most electroanalytical techniques merely reporting single constituent determination, Profumo and coworkers successfully eliminated the interference of DNT and picric acid (at mass concentration ratios of 10:1 and 1:1, respectively) to TNT determination on a bare gold electrode showing memory effects [9] by modification of the electrode surface with α-CD, leading to the resolution of well-distinguished peaks for the three nitroaromatic compounds [9].

Square-wave voltammetry applied with a Hg electrode in the absence of O_2 enabled nitro-explosive determination in water samples at the order of 0.2 μg L^{-1} TNT and 15 μg L^{-1} RDX/HMX [10]. Saravanan et al. studied the electrochemical behaviour of nitro-explosives with CV and carried out separate quantitative determination of TNT and RDX/HMX (at the order of several tens-hundreds mg L^{-1}) by using square-wave voltammetry, however it is not clear how they performed synthetic/real mixture analysis [11]. A remote sensing technology developed for TNT detection in marine environment relied on using a carbon fiber as the working electrode, involving the application of a rapid and sensitive square-wave voltammogram for scanning; the detection scheme was based upon stepwise reduction of the nitro aromatic groups first to hydroxylamines and then to amine groups [12]. A rotating disc gold electrode, bare or modified with an alkanethiol self-assembled monolayer, was used to measure the simultaneous square-wave voltammetric differential current response of the electrochemical reduction of TNT and DNT, but on bare electrodes, background currents limited detection sensitivity down to ppm levels [13]. Square-wave cathodic stripping voltammetric analysis of RDX using mercury-film plated glassy carbon electrode enabled RDX deposition at −0.15 V (vs Ag/AgCl) for 120 s, then reduction at −0.7 V, with 9.8% RSD at 2 mg L^{-1} RDX levels [14]. The electrochemical behaviour of some nitroaromatic explosives such as TNT, DNT and 2-nitrotoluene at electrochemically activated carbon-fibre microelectrodes required electrochemical activation of such electrode material by repeated square-wave voltammetric scans between 0.0 and +2.6 V vs Ag/AgCl, producing an increase in the cathodic response from these compounds [15].

Carbon nanotube-modified glassy carbon electrode for adsorptive stripping voltammetric determination (at 10 min deposition time) of ultratrace TNT has been claimed to reach sub-μg L^{-1} levels of detection with linear response between 0.1 and 1 mg L^{-1} [16]. Fast electrochemical detection of nitro-aromatics in soils of former explosive factories (detection level 50 mg kg^{-1}) was accomplished by a cyclic voltammetric sensing system, where the TNT reduction peak at approx. 0.2 V produced a higher and concentration-dependent current intensity than the oxidation peak at approx. 0.7 V; however the reduction peak could not be utilized as a sensor signal because oxygen was also reduced at the Au-electrode surface at approx. 0.35 V [17].

The major drawbacks of electrochemical sensors are limited sensitivity, mobile electrolyte requirement and electrode fouling, while the antibodies used in selective explosive recognition in immunosensors are not reusable, hindering their utility in airport security screening applications, as indicated in a comprehensive review by Singh [18]. In most literature studies on electroanalytical techniques, the analysis of nitro-explosive mixtures – with reference to standard or real samples having the same matrix – was basically unattempted, with a few exceptions. For example, Polsky et al. combined square-wave voltammetry with partial least squares (PLS) regression analysis only to differentiate 2,4- and 2,6-dinitrotoluene in synthetic mixtures, but no military-purpose real mixtures (i.e., composite explosives) were analyzed [19]. Qualitative and limited quantitative analysis of synthetic mixtures, as well as of composite explosives like comp B, pentolite and tetrytol, were performed by coupling CV measurements with advanced chemometric data processing (involving multivariate calibration equipped with artificial neural networks), however, statistical comparison of results (through *t*- and *F*-tests and coefficients of variation) for expected and found component analysis of composite explosives were not reported [20]. In general, effective sensing methods reported in the literature do not demonstrate the ability to sense explosive compounds simultaneously in natural mixtures such as groundwater, because overlap regions of electroactivity in nitro-explosive compounds results in cross-contribution of current from one compound to another, requiring deconvolution of contributions from each compound of structural similarity [13]. Thus, the aim of this study is to develop simple, sensitive and selective cyclic voltammetric techniques for the simultaneous quantitative estimation of nitroaromatic and nitramine type energetic materials in the same matrix media such as composite explosives. In this regard, the voltammetric behaviour of military-purpose explosives, namely TNT, RDX, HMX and DNT, was investigated on a glassy carbon working electrode. CV was applied to nitro-explosive solutions (alone or in admixture) in the environmentally relevant concentration range for hazardous waste characterization.

2. Experimental

2.1. Chemicals, solutions and instruments

The explosive materials; TNT (trinitrotoluene), RDX (1,3,5-trinitro-1,3,5-triazacyclohexane), HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazosin), comp B composite explosive (containing 60% RDX, 39% TNT, and 1% wax), Comp A5 (99% RDX and 1% filler material), and octol composite explosive (containing 70% HMX and 30% TNT) were kindly supplied by Makine Kimya Endustrisi Kurumu (MKEK: Machinery & Chemistry Industries Institution) through the supervision of Milli Savunma Bakanligi, Teknik Hizmetler Daire Baskanligi (Ministry of National Defence, Office of Technical Services) of Turkey. All other reagents were from E. Merck (Darmstadt, Germany), Sigma-Aldrich (Deisenhofen, Germany) and Fluka (Neu-Ulm, Germany). The solvent used in preparation and dilution of explosive solutions was HPLC-grade extra pure acetonitrile (E. Merck). The alumina slurry used for electrode cleaning was from Baikowski International Corp. (0.05 μm, Baikalox 0.05CR). The supporting electrolyte for conductivity was TBAB: tetrabutylammonium bromide (Sigma Aldrich). The organic solvent was dried with molecular sieves (Aldrich, 4 Å beads, 8–12 mesh). For electrode cleanliness, isopropyl alcohol (Sigma Aldrich), acetone and ethanol (both technical grade) were used. For removing impurities and oxygen from commercial nitrogen gas, a KOH solution of pyrogallol (20 g KOH and 20 g pyrogallol were separately dissolved in 45 mL water each, and the solutions were mixed) and concd. sulfuric acid for humidity absorption were used in separate wash-bottles.

The standard stock solutions of individual explosive materials and military-purpose explosive mixtures (comp B, comp A5 and octol) at 1000 mg L^{-1} concentrations were prepared in extra pure acetonitrile. The working solutions to be tested with the developed voltammetric method were prepared from these stock solutions by dilution with pure acetonitrile which was dehumidified (i.e., moisture removed) with molecular sieves.

Voltammetry experiments were performed with a Princeton Applied Research Potentiostat model 2263 potentiostat/galvanostat interfaced to a PC computer and controlled PowerSuite software. Glassy carbon (BASi stationary voltammetry electrodes; ∅ 1.6 mm, area 0.02 cm^2) was used as the working electrode, silver wire as pseudo-reference electrode, and platinum wire as auxiliary electrode. The pseudo-reference electrode was calibrated externally using a 5 mM solution of ferrocene/ferrocenium$^+$ (Fc/Fc^+) couple in the electrolyte, and the potentials were reported versus Ag/AgCl. This couple was not present in the reaction mixture (analyte solution), but instead, as a rule after each measurement, the silver electrode was checked with (Fc/Fc^+) solution, and then potentials were corrected with reference to the potential that should be observed with the Ag/AgCl electrode. For validation of the proposed assay against HPLC on a comp B sample (containing both RDX and TNT), a Perkin Elmer Series 200 HPLC chromatographic instrument equipped with a Hypersil C18 (5 μm), 250 mm × 4.6 mmID reversed phase (RP)-column was used in conjunction with a UV (254 nm) detector, and a 40% MeOH+60% H_2O (v/v) mixture was used as the mobile phase at a flow rate of 1 mL min^{-1}. The injection volume was 25 μL.

For validation of the proposed assay against a GC–MS system, real post-blast residual samples were analyzed with the use of a Thermo Scientific Trace gas chromatograph coupled with a DSQII mass spectrometer containing positive ion chemical ionization and quadrupole analyzer. GC was equipped with a Thermo 5 MS column (30 m × 320 μm × 0.25 μm). Calibration samples for GC–MS analysis were prepared from the 1000 mg L^{-1} stock solutions of TNT and RDX in acetonitrile with the use of the standard reference samples of ULTRA EPA-1243 TNT and Cerilliant RDX. The working solutions of TNT at 3–10 mg L^{-1} and RDX at 5–40 mg L^{-1} were prepared from the indicated stock solutions using acetonitrile as diluent.

2.2. *Optimization of voltammetric method*

Electrode type, scan rate, supporting electrolyte and concentration, electrode cleanliness and gaseous nitrogen purging time parameters have been individually examined. A glassy carbon (GC) electrode was selected as the working electrode, by which a substantial signal can be produced (as current intensity) at sufficiently separated reduction potentials. A scan rate of 50 mV s^{-1} was chosen, and tetrabutyl ammonium bromide (TBAB) was preferred as the supporting electrolyte. The electrolyte concentration was determined with the solubility test which was repeated with vacuum dried (at 50 °C temperature and 90 kPa pressure) substance, and 0.04 M was found as optimal concentration.

As the non-aqueous medium should be free of moisture and oxygen, concentrated sulfuric acid and KOH solution of pyrogallol should be used as washing solutions to ascertain N_2 purity during nitrogen purging for 5 min.

2.3. *Glassy carbon electrode pre-treatment*

The GC electrode was polished with a suspension of alumina powder in the presence of pure water on a smooth polishing cloth [21] by circular movements for a few minutes, then washed with distilled water, and sonicated for 5 min in bidistilled water. Sonication of the electrode was repeated for another 5 min in isopropyl alcohol–acetonitrile (1:1, v/v) mixture. The efficiency of this procedure for electrode cleanliness was confirmed by not observing the presence of any baseline (blank) peak during CV scan.

2.4. *Electrochemical studies of energetic materials*

A 5-mL solution of the sample was taken and dissolved in an ultrasonic bath. CV was performed in a potential range of 0.2 V–(−1.6 V), and the characteristic peak potentials for each nitrocompound were determined. The individual nitro-explosive quantification was made by linearly correlating peak current (at the characteristic potential) to concentration and the calibration lines (as current vs. concentration) were drawn for standard solutions of dried energetic materials. Then, mixture constituents were quantified using the same procedure after necessary deconvolution of current contributions from each compound. Measurements were carried out in RDX solutions in the concentration range of 30–120 mg L^{-1}, TNT and HMX solutions of 40–120 mg L^{-1}, and DNT solutions of 40–140 mg L^{-1}.

2.5. *Study of synthetic and real mixtures with decovolution of current contributions from each constituent at peak potentials*

CV was applied to synthetic {TNT+RDX} mixture solutions of nitroaromatics and nitramines by fixing the concentration of one component while changing the other, i.e., while fixing the concentration of the TNT component at 40, 60, 80, or 100 mg L^{-1} in a binary mixture, the concentration of RDX component was varied as 40, 60, 80, 100 ve 120 mg L^{-1}, making 20 synthetic mixtures altogether. The same procedure was repeated by fixing the concentration of RDX in the mixture while changing the concentration of TNT in the defined range (i.e., by fixing RDX at 40, 60, 80, 100 ve 120 mg L^{-1} and changing TNT at 40, 60, 80, 100 ve 120 mg L^{-1}, making 25 synthetic mixtures altogether); the current intensities at the characteristic peak potentials of TNT and RDX of the described mixtures were recorded.

Real mixture solutions were prepared by mixing 1000 mg L^{-1} stock solutions (five different samples for each run with the same concentration) and diluting with acetonitrile to yield final concentrations of 100 mg L^{-1} Comp A5 and 150 mg L^{-1} octol. Real mixtures were finally analyzed by the recommended voltammetric procedure for the determination of nitro-aromatic and nitramine explosives.

For deconvolution of current contributions at peak potentials, a multiple linear regression approach was followed. The simple linear regression equation ($Y = A + BX$) can be extended to represent the linear relation between one dependent variable, Y, and more than one independent variables, $X_1, X_2, \ldots, X_k$. The general form for the multiple linear regression (MLR) equation is; $Y = B_0 + B_1 \times_1 + B_2 \times_2 + \ldots + B_k X_k$ and its estimate is obtained by finding the least squares estimates (LSEs) of the B_is. The estimated (fitted) multiple regression equation is given by; $\tilde{Y} = b_0 + b_1 \times_1 + b_2 \times_2 + \ldots + b_k x_k$ which is represented, using the scatter diagram, by a regression plane in $k+1$ dimensions. The regression parameters (b_is) are referred to as the estimated partial regression coefficients. Fixing any $k-1$ of the independent variables and keeping only one free to vary culminates in a simple partial linear regression equation given the specified numerical values for all of the fixed independent variables [22]. The partial least squares (PLS) method was recommended for the computer-aided evaluation in voltammetric analysis when there is no way of chemically addressing overlapping signals [23]. Because of their relevance in the application to electroanalytical data, chemometric techniques such as multiple linear regression (MLR) and partial least squares (PLS) analysis were discussed in detail in a review [24]. The MLR analysis of electroanalytical data was processed with a stepwise forward selection method. Then, the peak current intensity (I) yielded by a mixture at a characteristic potential can be expressed as a linear combination (with coefficients m and n) of the concentrations (C) of TNT and RDX such that; $I = m\, C_{TNT} + n\, C_{RDX} + constant.$

2.6. *Validation of the CV method against HPLC using comp B composite explosive reference sample*

The CV and HPLC results were compared with for validation, as described in literature [25]. For method validation, standard solutions of 10–100 mg L^{-1} TNT and 5–100 mg L^{-1} RDX in acetonitrile were assayed by both the voltammetric method and HPLC to construct the calibration graphs. The HPLC calibration curve was constructed by recording the peak areas versus concentration. As the reference material, 25.0 mg samples ($N=5$) of comp B composite explosive (containing 39% TNT and 60% RDX) were dissolved in 25 mL acetonitrile, 2.5 mL of this stock solution (containing 1000 mg L^{-1} comp B) was diluted with acetonitrile to a final volume of 25 mL to yield 100 mg L^{-1} comp B solutions (theoretically containing 39 mg L^{-1} TNT and 60 mg L^{-1} RDX) to be assayed with HPLC. For testing the working solutions of comp B with method under the same conditions employed for TNT and RDX standards, the recommended procedure was followed. The statistical comparisons between the findings of the recommended and reference methods were made with the aid of *t*- and *F*-tests.

2.7. Validation of the CV method against GC–MS using real post-blast debris samples

The real post-blast residual samples were collected (by macroscopic examination of the debris for detecting any visible residues of particulate matter that can be analyzed directly) from the resulting craters after detonations of TNT and RDX individually, and of a 40–60% (w/w) mixture of TNT and RDX corresponding to the composition of comp B. Prior to detonation, samples of range soil were collected and analyzed as blank. After detonation of each explosive, 10 g samples of soil from the resulting craters were appropriately collected, leached with 50 mL acetonitrile for 15 min in a stoppered flask, allowed to settle for 10 min, and filtered through a 0.45 μm filter. The samples were analyzed using the proposed voltammetric and reference GC/MS methods, directly in the leachate and in 10-fold acetonitrile – diluted solution, respectively.

The literature GC–MS conditions [26] were used as starting parameters. Splitless injection was done with hold time of 2 min and injection volume of 0.5 μL. Injector temperature was 170 °C. The starting temperature of the oven was set to 70 °C, and it was held for 3 min, followed by a temperature increase to 185 °C at a rate of 8 °C $\min^{-1}$ and a subsequent increase to 250 °C at a rate of 25 °C $\min^{-1}$. The final temperature was held for 5 min. GC–MS interface temperature was 260 °C, MS source temperature 200 °C, and scan *m*/*z* range was 60–500. Carrier gas was methane, and its flowrate was 1.2 mL $\min^{-1}$. The statistical comparisons between the findings of the proposed voltammetric and reference GC/MS methods were made with the aid of *t*- and *F*-tests after normalization of initial concentrations of samples.

3. Results and discussion

The tested nitro-aromatic and nitramine compounds were all redox-active, and the relevant reduction reactions for these compounds hypothesized to occur during CV scans in the negative potential range are listed in Table 1. In acidic media, nitroaromatics are stated to be electrochemically reduced stepwise through hydroxylamine intermediates to the corresponding amines, whereas nitramines are reduced through *N*-nitroso intermediates to *N*-amines [27]. Galik and coworkers obtained electrochemical signatures of explosive mixtures on screen-printed electrodes using a novel cyclic square-wave voltammetric (C-SWV) approach, e.g., for comp B, where the reduction signals at −0.9, −1.3 and −0.7 V (versus Ag/AgCl) pointed out to the presence of TNT, RDX and both components, respectively [27]. Chua and Pumera studied the redox properties of mono-, di- and tri-nitroaromatic compounds with cyclic voltammetry (CV) at a glassy carbon electrode, and showed that the presence of a methyl group in the aromatic system leads to more negative reduction potentials, i.e., the ease of nitro group reduction varied in the order of *meta* > *para* > *ortho* positions relative to a methyl group [28]. Involvement of a TNT-methyl radical followed by carbanion formation (i.e., $Ph(NO_2)_3–CH_3+e^- \rightarrow Ph(NO_2)_3–CH_3{}^-–H^+ \rightarrow Ph(NO_2)_3–CH_2{}^{2-}$) in the reduction of TNT during CV scan [10] was not possible in our case, as the pink colour of the hypothetical methyl radical adsorbable on the working electrode was not experimentally observed.

3.1. Cyclic voltammetric response of TNT

The cyclic voltammograms recorded for different concentrations of TNT are shown in Fig. 1. The characteristic potentials of TNT appeared at −0.28, −0.7 and −1.0 V. and the maximum potentials −0.28 and −1.0 V gave (linear) concentration-dependent peak currents.

Calibration of TNT was based on peak currents at −1.0 V. and a linear dependence was found as follows;

$$I_{-1.0\ \mathrm{V}} = 0.2701C_{TNT} + 6.096 (r = 0.9977)$$

where $I_{-1.0\ \mathrm{V}}$=peak current intensity (μA) at −1.0 V; C_{TNT}=TNT concn. (mg l^{-1})

The linear calibration equation for the second peak of TNT at −0.28 V was:

$$I_{-0.28\ \mathrm{V}} = 0.1057C_{TNT} + 3.0656 (r = 0.9962)$$

where $I_{-0.28\ \mathrm{V}}$=peak current intensity (μA) at −0.28 V potential.

3.2. Cyclic voltammetric response of RDX

Cyclic voltammograms within 30–120 ppm concentration range of RDX are shown in Fig. 2. Current values at −0.78 V were found to increase linearly with concentration.

Calibration of RDX was based on peak currents at −0.78 V and a linear dependence was found as follows;

$$I_{-0.78\ \mathrm{V}} = 0.1801C_{RDX} + 5.7824 (r = 0.9987)$$

where $I_{-0.78\ \mathrm{V}}$=current intensity (μA) at −0.78 V; C_{RDX}=RDX concn. (mg l^{-1})

3.3. Cyclic voltammetric response of HMX

Voltammogram of HMX at different concentrations obtained by cyclic voltammetry (CV) can be seen in Fig. 3. A calibration curve was drawn between current values and concentrations based on the characteristic peak current of HMX at −0.9 V.

Linear calibration equation of HMX was found as:

$$I_{-0.9\ \mathrm{V}} = 0.1096C_{HMX} + 3.9596 (r = 0.9958)$$

where $I_{-0.9\ \mathrm{V}}$=peak current intensity (μA) at −0.9 V; C_{HMX}= concn. of HMX (mg l^{-1}).

3.4. Cyclic voltammetric response of DNT

Cyclic voltammograms within 40–140 ppm concentration range of DNT are shown in Fig. 4. Current values at −0.45 and −0.86 V increased linearly with concentration.

Linear working curve for DNT was:

$$I_{-0.86\ \mathrm{V}} = 0.1841C_{DNT} + 3.9596 (r = 0.9981)$$

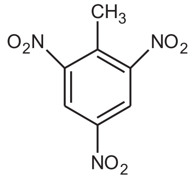
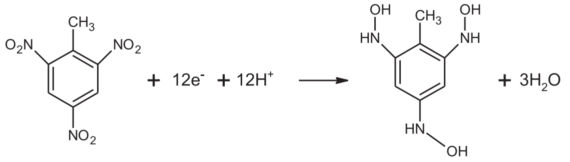
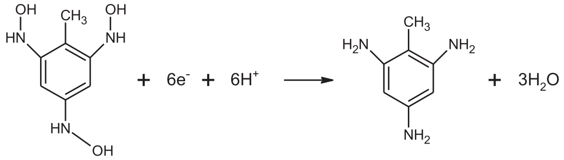
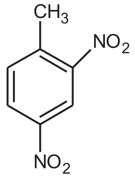
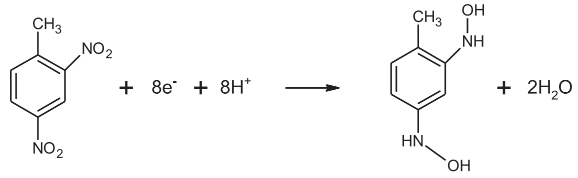
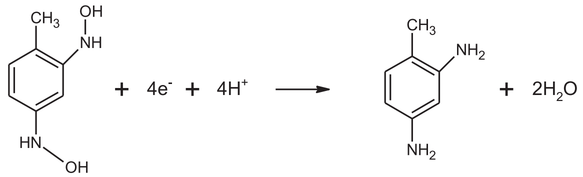
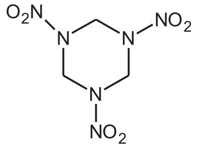
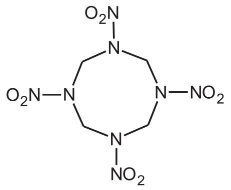
$I_{-0.86\ \mathrm{V}}$=peak current intensity (μA) at −0.86 V; C_{DNT}=concn. of DNT (mg l^{-1}).

The calibration equation for the second peak potential at −0.45 V was:

$$I_{-0.45\ \mathrm{V}} = 0.1288C_{DNT} + 2.4878 (r = 0.9978)$$

with less sensitivity (i.e., lower slope) and slightly lower linearity than the values obtained for the peak at −0.86 V. Three readings were made for each concentration, and the relative standard

Table 1
The hypothetical reduction reactions for TNT and DNT [2], RDX and HMX [2,10].

Compound	Hypothetical reduction reaction
 **TNT**	 
 **DNT**	 
 **RDX**	$>\text{N–NO}_2+6e^- \rightarrow >\text{N–NH}_2$ or $>\text{N–NO}_2+e^- \rightarrow \text{NO}_2^- + >\text{N}+e^- \rightarrow >\text{N:}^{(-)}$ (nitrite was detected in reductive hydrolysis processes of nitramines)
 **HMX**	$>\text{N–NO}_2+6e^- \rightarrow >\text{N–NH}_2$ or $>\text{N–NO}_2+e^- \rightarrow \text{NO}_2^- + >\text{N}+e^- \rightarrow >\text{N:}^{(-)}$ (nitrite was detected in reductive hydrolysis processes of nitramines)

deviation (RSD, %) of a given set of readings varied in the range 1.0–2.51% for DNT, depending on the concentration. Further quantitative evaluation of DNT was made at -0.86 V.

The calibration curve for the analyte is drawn as response (y) versus concentration (x). The minimum detectable response (y_{LOD}) corresponding to the detection limit concentration (x_{LOD}) is equal to the mean of blank responses ($\overline{y}_{bl}$) exceeded by (ks_{bl}), where s_{bl} is the standard deviation of the blank and k is a factor strongly recommended by IUPAC to be equal to 3 such that $y_{LOD}=\overline{y}_{bl}+ks_{bl}=\overline{y}_{bl}+3s_{bl}$. Thus, the calibration curve is intersected at the response value of y_{LOD} from the vertical axis and the corresponding concentration value (x_{LOD}) is read from the horizontal axis to obtain the detection limit [29]. In this work, LOD was assessed by calculating the peak current intensity at three standard deviations above the mean current intensity given by repeated ($N=10$) measurements of a reagent blank solution containing no explosive (analyte). The same procedure at ten standard deviations above the mean of blank intensity was performed for LOQ calculation. LOD and LOQ values and relative standard deviations (RSD, %) of analytical results are given in Table 2.

3.5. *The validation of the voltammetric method against HPLC for TNT and RDX determination in comp B samples*

The voltammetric determination was validated against HPLC on five samples of comp B (declared to contain 39% TNT and 60% RDX), each diluted to a final concentration of 100 mg L^{-1} (Table 3). The calibration lines for HPLC determination of pure TNT in the concentration range of 10–100 mg L^{-1} and RDX in the concentration range of 5–100 mg L^{-1} were as follows:

$$\textit{Peak Area}=8.19\times10^{4}C_{TNT(mg/L)}+1.29\times10^{5}(r=0.9991)$$

$$\textit{Peak Area}=3.61\times10^{4}C_{RDX(mg/L)}–4.79\times10^{4}(r=0.9998)$$

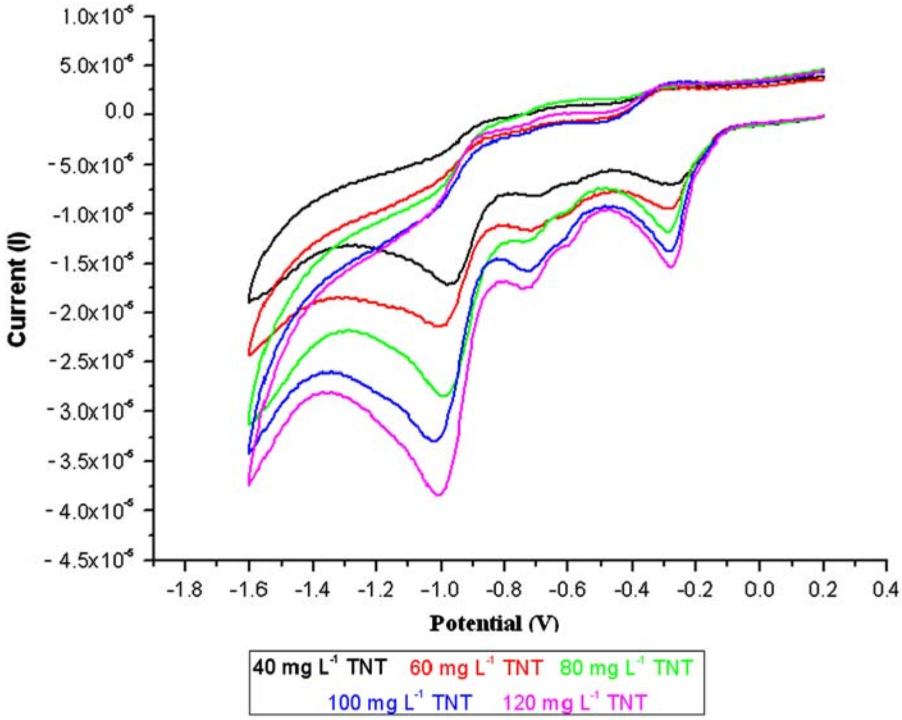


Fig. 1. Cyclic voltammograms of TNT at 40–120 ppm in 0.04 M TBAB containing acetonitrile solution at a scan rate 50 mV s^{-1}.

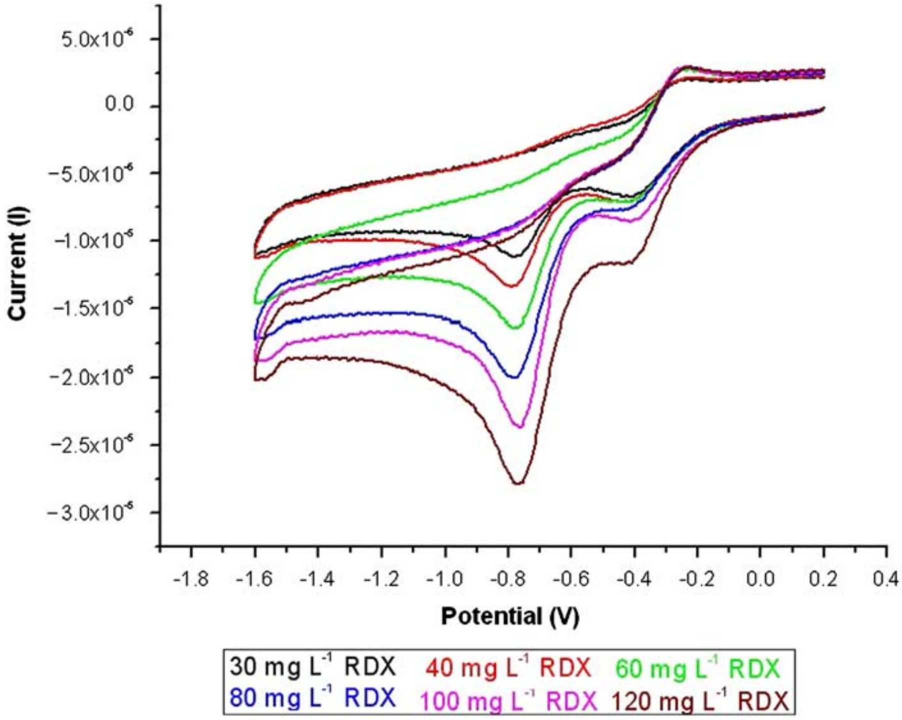


Fig. 2. Cyclic voltammograms of RDX at 30–120 ppm in 0.04 M TBAB containing acetonitrile solution at a scan rate 50 mV s^{-1}.

Statistical analysis was made on paired findings analyzed by CV and HPLC (N=5 each) using the one-way ANOVA (ANalysis Of Variance) approach with the aid of t- and F-tests [30]. The ‘null hypothesis’ was tested at different confidence levels, essentially showing no significant difference between the means and variances of results (Table 3). The confidence levels of validation were 95% for TNT and RDX using both t- and F-tests.

3.6. Analytical results for synthetic and real mixtures of nitro-explosives

For varying concentrations of RDX in admixture with a fixed concentration of TNT at 40 mg L^{-1}, TNT's peak current at −0.7 V gave an additive response with RDX's peak current values at −0.78 V. However, when a certain peak current of TNT was

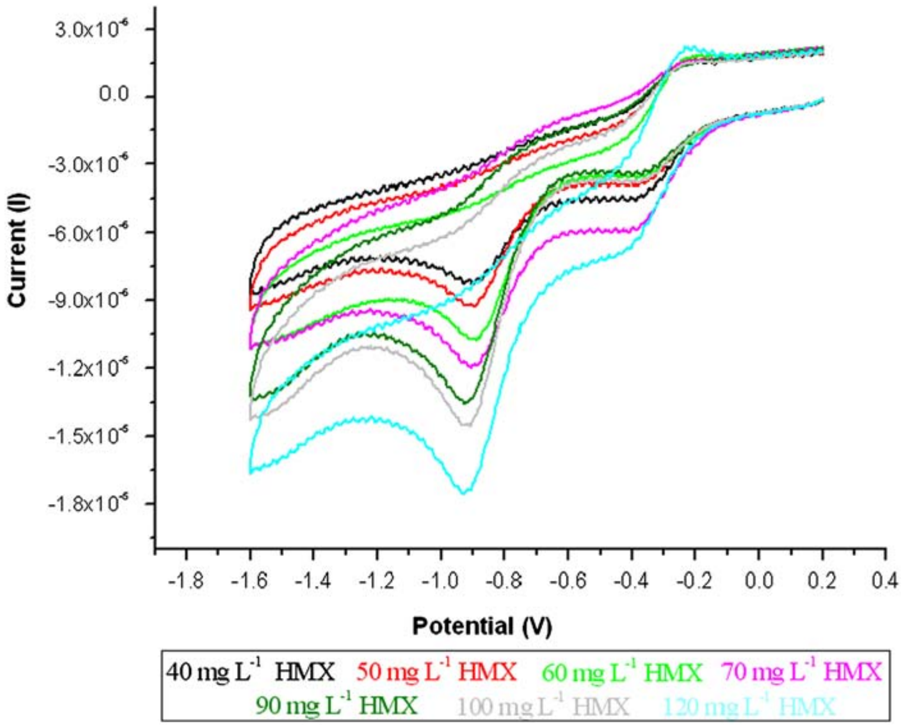


Fig. 3. Cyclic voltammograms of HMX at 40–120 ppm in 0.04 M TBAB containing acetonitrile solution at a scan rate 50 mV s^{-1}.

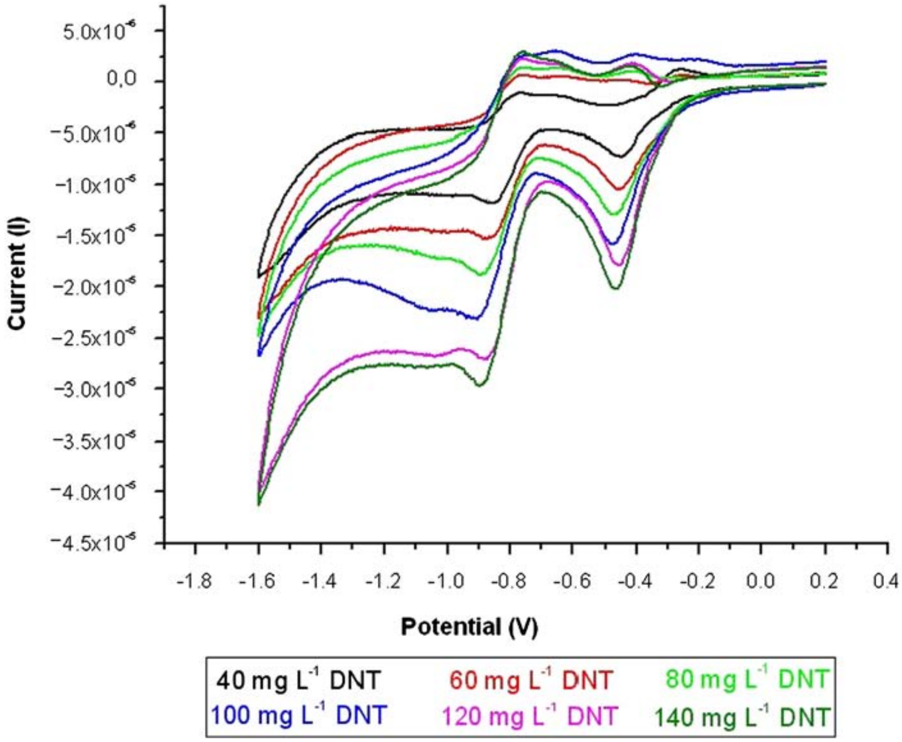


Fig. 4. Cyclic voltammograms of DNT at 40–140 ppm in 0.04 M TBAB containing acetonitrile solution at a scan rate 50 mV s^{-1}.

subtracted from those of RDX to construct a calibration curve, precise analytical determinations could not be performed. Likewise, RDX's peak current at −0.78 V was found to cause an increase in the characteristic current intensities of TNT at −1.0 V. The incremental changes (due to increasing concentrations of RDX at 40, 60, 80, 100, and 120 mg L^{-1} values) on the peak current of TNT at −1.0 V were roughly 2, 4, 6, 8, and 10 μA, respectively. Using the simple additivity assumption, it was not possible to resolve the current intensities at −0.78 and −1.0 V characteristic potentials of RDX and TNT, respectively, because the calculated concentrations of constituents of unknown mixtures did not match with the actually prepared concentrations. Thus, it was necessary to treat the whole voltammetric data by a PLS-MLR approach. The ideal analyte reduction signatures well separated to enable direct determination of the concentration of each nitro-explosive from its peak current (or from the integrated peak area) does not apply to real cases where the electroactive structural regions of the concerned compounds partly overlap [12]. Therefore, cross-contributions of current at characteristic potentials from concomitant species were mathematically deconvoluted to yield simple linear equations (e.g., with two unknowns for a TNT +RDX mixture) so as to comprise the whole CV data.

Table 2
LOD and LOQ values and relative standard deviations (RSD, %) of analytical results for the tested nitro analytes.

	TNT	RDX	HMX	DNT
LOD[a]	11.2	10.2	11.7	10.8
LOQ[a]	23	20.6	29.6	26.7
RSD,%[b]	0.99–1.39	0.74–1.66	1.66 0.63–2.26	1.0–2.51

[a] In mg L^{-1} units; LOD and LOQ were assessed by calculating the peak current intensity at three and ten standard deviations above the mean current intensity, respectively, given by repeated ($N=10$) measurements of a reagent blank solution containing no explosive (analyte).

[b] Determined for a given set of readings in which three readings were made for each concentration.

A single set of measurement data (pertaining to constant 80 ppm TNT+varying concentrations of RDX) was left out because of systematic error. Treatment of approximately ≥90% of data yielded the two equations for calculating RDX and TNT components of synthetic mixtures measured at the reduction potentials of −0.78 and −1.0 V, respectively.

$$I_{-0.78\ \mathrm{V}}-3.58=0.161C_{RDX}+0.143C_{TNT} \tag{1}$$

$$I_{-1.0\ \mathrm{V}}-3.58=0.108C_{RDX}+0.262C_{TNT} \tag{2}$$

When the above equations were applied to unknown solutions with peak currents measured at the indicated potentials, the relative errors in calculation of TNT and RDX constituents varied

Table 3
Statistical comparison of the proposed voltammetric method with HPLC and GC–MS for the determination of TNT and RDX constituents of Comp B sample.

Sample/analyte	Method	Mean concn., mg L^{-1}	Std. dev. (σ)	S[a,b]	t[a,b]	t_{table}[b]	F[b]	F_{table}[b]
Comp B/TNT	Voltammetric	39.2	0.46	–	–	–	–	–
Comp B/TNT	HPLC	38.6	0.83	0.67	1.33	2.306	3.22	6.39
Comp B/RDX	Voltammetric	57.6	1.99	–	–	–	–	–
Comp B/RDX	HPLC	59.3	1.16	1.63	1.68	2.306	2.98	6.39
TNT and RDX mixture of real post-blast residue/RDX	Voltammetric	28.1	0.83	–	–	–	–	–
TNT and RDX mixture of real post-blast residue/RDX	GC–MS[c]	28.0	0.46	0.67	0.31	2.306	3.31	6.39
TNT and RDX mixture of real post-blast residue/TNT	Voltammetric	19.3	0.24	–	–	–	–	–
TNT and RDX mixture of real post-blast residue/TNT	GC–MS[c]	19.7	0.26	0.25	2.21	2.306	1.17	6.39

[a] $S^2=\{(n_1-1)s_1^2+(n_2-1)s_2^2\}/(n_1+n_2-2)$ and $t=(\bar{a}_1-\bar{a}_2)/\{S(1/n_1+1/n_2)^{1/2}\}$, where S is the pooled standard deviation, s_1 and s_2 are the standard deviations of the two populations with sample sizes of n_1 and n_2, and sample means of $\bar{a}_1$ and $\bar{a}_2$, respectively (t has (n_1+n_2-2) degrees of freedom); here, $n_1=n_2=5$.

[b] Statistical comparison made on paired data produced with proposed and reference methods; the results given only on the row of the reference method.

[c] Leachate analysis results of post-blast residual samples were compared on a normalized concentration basis, since GC–MS determinations were made in 1:10 (v/v) acetonitrile-diluted leachates.

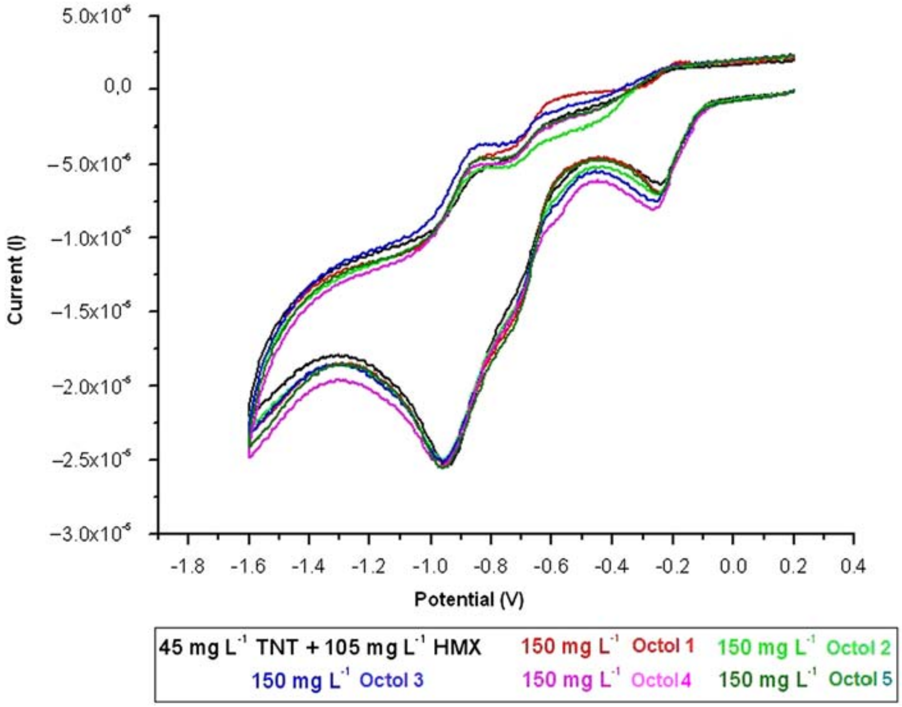


Fig. 5. Cyclic voltammograms for 150 mg L^{-1} octol (30% TNT+70% HMX) and for a synthetic mixture prepared to contain 45 mg L^{-1} TNT+105 mg L^{-1} HMX in 0.04 M TBAB containing acetonitrile solution at a scan rate 50 mV s^{-1}.

in the ranges of 3–7 and 5–10%, respectively. The TNT contribution to RDX peak current at the characteristic potential of −0.78 V was found to produce a more adverse effect in calculations than that of RDX to TNT peak current at −1.0 V. Preliminary experiments showed that dicyclohexylamine (DCHA) addition to mixtures to produce a charge-transfer complex with TNT (but not with RDX) [31] could partly overcome this adverse effect and increase the sensitivity of RDX determination (i.e., increase the coefficient of C_{RDX} in Eq. (1)) in mixtures, but this measure should be further worked out as it caused a shift in the potential of RDX at −0.78 V to more negative potentials (between −0.80 and −0.85 V) dependent on concentration.

When octol samples at a concentration of 150 mg L^{-1} (prepared from $N=5$ different stock samples of octol, declared to contain 30% TNT+70% HMX) were CV scanned, additive response for the two constituents at −0.95 V (originally HMX at −0.9 V and TNT at −1.0 V) was obtained, and resolution into two distinct peaks was not possible due to the closeness of characteristic

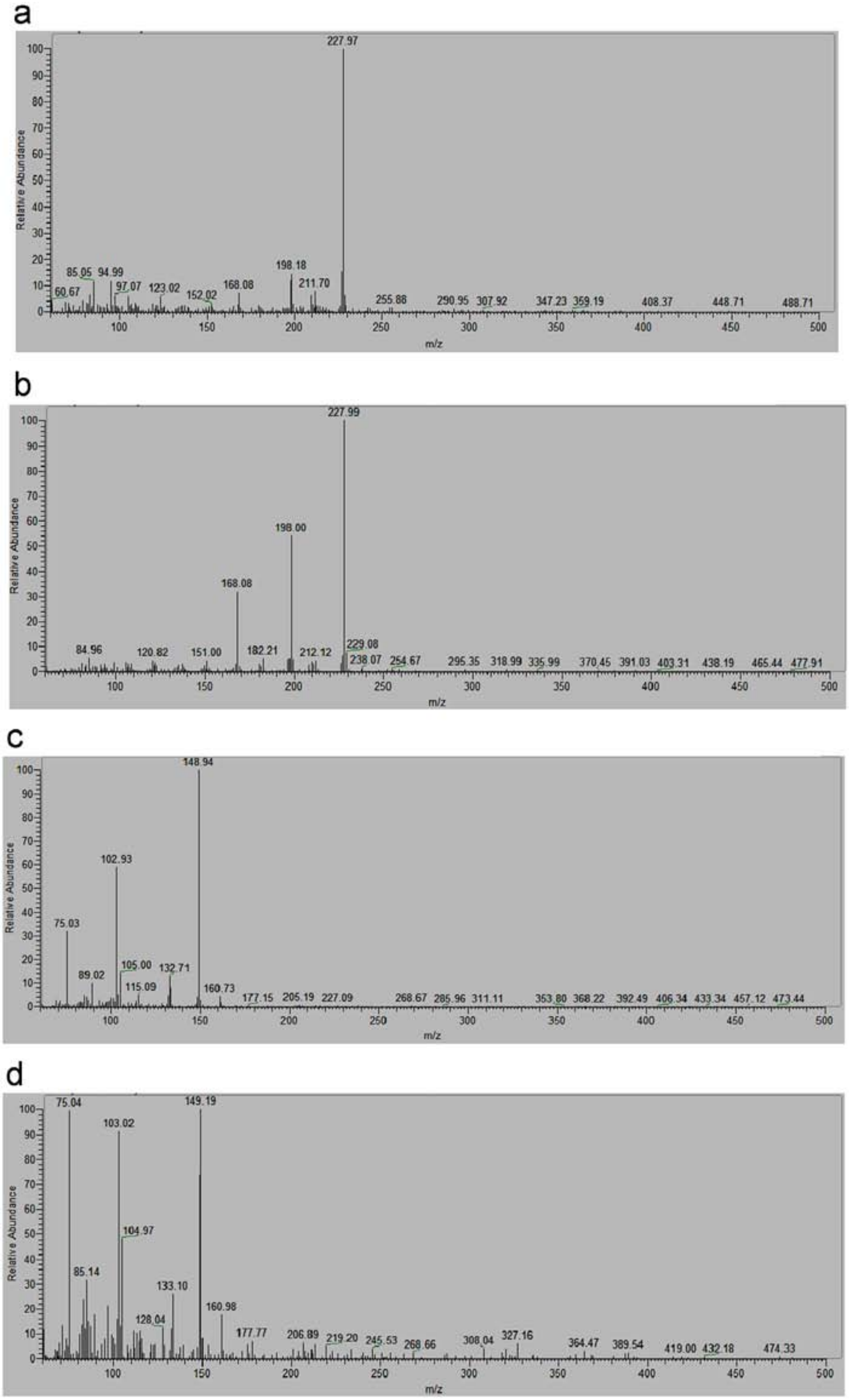


Fig. 6. The MS spectra of TNT and RDX in standard and post-blast residual samples after GC–MS analysis.

potentials of constituents. In this respect, two voltammograms (on N=5 repetitive samples) were recorded; one for 150 mg L^{-1} octol (30% TNT+70% HMX) and the other for a synthetic mixture prepared to contain 45 mg L^{-1} TNT+105 mg L^{-1} HMX (Fig. 5). Comparison of the two (almost coincident) voltammograms in Fig. 5 depicted statistically identical scans.

Finally, CV recording on $N=5$ different stock samples of Comp A5 (containing 99% RDX) at 100 mg L^{-1} final concentration yielded current intensities applicable to the calibration line of pure RDX, and the calculated concentrations showed recoveries between 93.9 and 99.2%. Since this composite explosive was almost composed of a single constituent (RDX), deconvolution of current intensities at a characteristic potential was not necessary.

3.7. Analytical results for real post-blast debris samples

In gas chromatograms, the standard TNT peak of the pure sample emerged at a retention time of 12.92 min, but for real post-blast debris, this peak emerged at 16.84 min, and the characteristic ions produced from the analyte had *m/z*: 85, 168, 198, 228 and 256 in the mass spectra (Fig. 6). The RDX peak of the pure sample emerged at a retention time of 15.86 min, but for real post-blast debris, this peak emerged at 18.76 min, and the characteristic ions produced from the analyte had *m/z*: 75, 103, 105, 133 and 149 in the mass spectra (Fig. 6). The differences in retention times of a given constituent in pre- and post-blast samples may have arisen from the polarity variations of standard and real samples, however, both the *m/z* values and the relative peak heights in pre- and post-blast samples (Fig. 6) confirmed the existence of TNT and RDX in complex samples identical with MS library references. TNT and RDX were analyzed from 3–10 to 5–40 mg L^{-1} working solutions, respectively, and quantitative analysis for each sample was performed using full scan mode.

For each sample, the mean value of three repetitive GC injections was used for calculations. The calibration equations for TNT and RDX between *Peak Area* and concentration were:

$$Peak\ Area = 8.66 \times 10^4 C_{RDX} - 1.30 \times 10^5 (r = 0.9992)$$

$$Peak\ Area = 2.76 \times 10^5 C_{TNT} - 5.21 \times 10^5 (r = 0.9990)$$

The leachate from post-blast debris sample was either directly analyzed (voltammetry) or diluted (GC–MS); measurement of RDX with the proposed voltammetric method and with GC–MS in the 1:10 (v/v) acetonitrile-diluted leachate gave 35.2 ± 1.3 and 36.8 ± 0.8 mg L^{-1} (normalized) concentrations, respectively, in the main solution (N=5 repetitive measurements for each method). When the same measurement was repeated for TNT, the post-blast debris leachate gave 28.0 ± 1.0 and 29.4 ± 0.6 mg L^{-1} (normalized) concentrations with voltammetry and GC–MS, respectively. Since 10 g post-blast soil sample was leached with 50 mL acetonitrile, the nitro-explosive contents of the original solid samples could be traced back to yield 180 ± 4 and 144 ± 3 mg kg^{-1} RDX and TNT, respectively. There was no potential shift for the voltammetric determination of RDX and TNT in the post-blast sample leachates.

After detonation of a comp B sample having a composition {40% TNT+60% RDX} (w/w), the post-blast debris was analyzed by the proposed voltammetric method using Eq. (1) and Eq. (2) and by the reference GC–MS method (mass spectra given in Fig. 6). Statistical comparison between the results of the proposed and reference GC–MS procedures applied to post-blast residues of {RDX+TNT} mixture in acetonitrile was made on $N=5$ repetitive analyses, essentially showing no significant difference between results (Table 3).

4. Conclusion

In this study, the voltammetric responses to analyte solutions containing individual or mixture energetic materials (including real samples of nitro-explosives) were investigated. Although cyclic voltammetry having portable and simple equipment has been used for individual determination of energetic materials, selective nitro-explosive determination in mixtures was rarely performed. The CV method using a glassy carbon electrode was developed for nitro-explosives analysis capable of simultaneous determination of TNT and RDX in synthetic and real mixtures (e.g., comp B, octol, and real post-blast debris). The voltammetric method was statistically validated against HPLC and GC–MS on real samples. Cross-contributions of current at characteristic potentials from concomitant species in mixtures were mathematically deconvoluted to yield simple linear equations (e.g., with two unknowns for a TNT+RDX mixture) so as to comprise the whole CV data of mixture solutions containing greatly varying concentrations of constituents. This robust method offers good prospects for use in criminology, monitoring land remediation of explosive-contaminated sites, and kinetic munition modeling during shelf life.

Acknowledgements

The authors wish to express their gratitude to the Ministry of National Defence, Office of Technical Services, to Machinery & Chemistry Industries Institution (MKEK) for the donation of nitro- and composite explosive samples, Additionally, the authors thank the Turkish Republic Ministry of Science, Industry and Technology – General Directorate of Science and Technology (T.C. Bilim, Sanayi ve Teknoloji Bakanlığı – Bilim ve Teknoloji Genel Müdürlüğü) for the San-Tez Project 00601.STZ.2010-1. The Ministry wishes to declare that none of the ideas (originally belonging to the authors) presented in this article represents their official view. All authors wish to repeat their thanks to MKEK for their general support by taking part in the indicated San-Tez Project. The authors extend these thanks to Istanbul University Research Fund for the support given to Normal Project-12110 and 14412. One of the authors (Dr. Erol Erçağ) extends his thanks to Istanbul University Research Fund for the support given to UDP Project-22511, which enabled him to present a part of this work in the 15th International Seminar on New Trends in Research of Energetic Materials in Pardubice, Czech Republic. Two authors (Ş. Sağlam and Y. Tekdemir) wish to thank the Turkish Academy of Sciences (TUBA) for research expenses support conveyed by Dr. Reşat Apak (Academy member).

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