Anal Bioanal Chem (2005) 382: 381–387
DOI 10.1007/s00216-004-3017-z

SPECIAL ISSUE PAPER

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Rapid voltammetric determination of nitroaromatic explosives at electrochemically activated carbon-fibre electrodes

Received: 13 October 2004 / Revised: 26 November 2004 / Accepted: 1 December 2004 / Published online: 14 April 2005

Abstract The electrochemical behaviour of some nitroaromatic explosives (2,4,6-trinitrotoluene, TNT; 2,6-dinitrotoluene, 2,6-DNT; 2-nitrotoluene, 2-NT; 2-amino-4,6-dinitrotoluene, 2-A-4,6-DNT; 3,5-dinitroaniline, 3,5-DNA; and nitrobenzene, NB) at electrochemically activated carbon-fibre microelectrodes is reported. Electrochemical activation of such electrode material by repeated square-wave (SW) voltammetric scans between 0.0 and +2.6 V versus Ag/AgCl, produced a dramatic increase in the cathodic response from these compounds. This is attributed to the increase of the carbon-fibre surface area, because of its fracture, and the appearance of deep fissures along the main fibre axis into which the nitroaromatic compounds penetrate. Based on the important contribution of adsorption and/or thin layer electrolysis to the total voltammetric response, a SW voltammetric method for rapid detection of nitroaromatic explosives was developed. No interference was found from compounds such as hydrazine, phenolic compounds, carbamates, triazines or surfactants. The limits of detection obtained are approximately 0.03 μg mL^{-1} for all the nitroaromatic compounds tested. The method was applied for the determination of TNT in water and soil spiked samples; recoveries were higher than 95% in all cases.

Keywords Nitroaromatic explosives · Activated carbon fibre · Square-wave voltammetry

Introduction

Nitroaromatic explosives, fabricated mainly for military use [1], are important pollutants of soils and waters of places where they are produced and stored [2]. Among them, TNT (2,4,6-trinitrotoluene) is the most abundant, and concentrations of up to 10,000 mg L^{-1} can be found in contaminated areas [3]. This compound has been classified as toxic by the Environmental Protection Agency, because it produces nocive effects in all lifeworks [4]. Another compound, belonging to the same family, 2,6-DNT (2,6-dinitrotoluene), is one of the volatile compounds with longer life present in explosives and their residues [5–7] and, like TNT, it is adsorbed through the skin producing adverse health effects [8, 9].

Separation and determination of TNT and related explosives in complex samples have been achieved by use of gas [10, 11], liquid [12], and supercritical-fluid [13] chromatography. Micellar electrokinetic chromatography [14] and capillary electrophoresis in non aqueous medium [15] have also been used. Electroanalytical techniques have been employed for determination of these compounds by using their reduction signal at several electrode materials [16]. Table 1 summarizes the analytical characteristics of some methods developed for TNT and related species. Amperometric detection has been shown to improve remarkably the sensitivity of these determinations with respect to conventional UV measurements. Thus the use of electrochemical detection at a glassy carbon electrode in liquid chromatography, by applying a potential of −0.80 V, enabled the achievement of a detection limit of 0.01 μg mL^{-1} TNT [17]. Gold and silver-coated gold electrodes have also been used for detection of this type of compound by capillary electrochromatography [18] and capillary electrophoresis [19], a separation microsystem with a gold-film electrode that reduces the detection limits with respect to former methods has been constructed for capillary electrophoresis [20]. Screen-printed carbon electrodes (SPCE) have also been shown to be very useful for these capillary electrophoresis microsystems [21].

The need to meet the demand for environmental safety of soils and waters leads to a requirement for rapid screening analytical methods of high sensitivity to detect the presence of nitroaromatic explosives at trace

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Table 1 Electrochemical methods for nitroaromatic explosives

Electrode	Technique	Analyte/ sample	Calibration data	LOD ($\mu g\ mL^{-1}$)	Ref.
GCE	LC–ED E_{det} −0.8 V	TNT and others	0.09–318 (L.R. TNT)	0.01 (TNT)	[17]
Au	CEC–ED E_{det} −0.7 V	TNT, DNTs/soil, water	Not given	0.075 (TNT)	[18]
Ag/AuE	CE–ED E_{det} −0.7 V	TNT, DNTs/soil, water	Not given	0.080 (TNT)	[19]
Au-filmE	CE–ED E_{det} −0.8 V	TNT, DNTs	Not given	0.024 (TNT)	[20]
SPCE	CE–ED E_{det} −0.7 V	TNT, DNTs	Not given	0.600 (TNT)	[21]
SPCE	SWV	TNT	1–10 $\mu g\ mL^{-1}$ (L.R.) $m=4.144\ \mu A\ \mu g^{-1}\ mL$	0.2	[22]
SPCE	AdsSV	2,6-DNT/saliva, water, dust wipe samples	Up to 137 $\mu g\ mL^{-1}$ (L.R.) m = 228 $\mu A\ \mu g^{-1}\ mL$	0.161	[23]
CNT-GCE	AdsSV E_p −0.50 V	TNT	0.1–1 $\mu g\ mL^{-1}$ (L.R.) $m=84.9\ \mu A\ \mu g^{-1}\ mL$	0.0006	[24]
MicroAuE	CV	TNT/air	Not given	Not given	[25]
Multiple-CFE	SWV E_p = −0.5 V	TNT/water	Up to 7 (L.R.)	0.03	[26]

SPCE, screen-printed carbon electrode; ED, electrochemical detection; CE, capillary electrophoresis; LC, liquid chromatography; CFE, carbon-fibre electrode; CNT-GCE, carbon nanotube-modified glassy carbon electrode

levels. SPCEs have provided good results for this purpose, and have been applied for the determination of TNT by square-wave voltammetry (SWV) [22] and 2,6-DNT by adsorptive stripping voltammetry (AdsSV) [23]. Recently, multiwall carbon nanotube-modified glassy-carbon electrodes (MWCNT-GCE) have been used for determination of TNT by AdsSV in sea water, with very low detection limits when the deposition time was increased to 10 min [24]. Furthermore, a sensor based on a gold microelectrode for determination of TNT in the gas phase by cyclic voltammetry [25], and a sensor for remote monitoring of this explosive in water based on detection on multiple carbon fibres [26], have also been developed. Finally, electrochemical methods have also been used for determination of explosive compounds other than nitroaromatic compounds, for example RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) [27] and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) [19].

We have recently reported that electrochemical activation of carbon fibre microelectrodes (CFMEs) by repeated SW voltammetric scanning resulted in a dramatic increase of the cathodic current of nitro derivatives [28, 29]. This was attributed to the increase of the carbon fibre surface area because of its fracture and the appearance of deep fissures along the main fibre axis. Penetration of the nitro derivatives into the microchannels of the activated fibre can be of benefit, analytically, in the design of surface-accumulation schemes for traces of these pollutants in applications in solid-phase extraction or electrochemical remediation [30]. In this paper, the voltammetric behaviour of several nitro aromatic explosives at electrochemically activated CFMEs is discussed, and the possibility of detecting these compounds at low concentrations is reported. Finally, the method for determination of TNT was applied to water and soil samples.

Experimental

Apparatus and electrodes

Voltammetric measurements were carried out with a BAS (West Lafayette, IN, USA) 100B potentiostat provided with a BAS C2 EF-1080 cell stand and a BAS PA-1 current preamplifier. A BAS VC-2 10-mL electrochemical cell was also employed. Cylindrical microelectrodes used as working electrodes were prepared from single carbon fibres (Union Carbide, Danbury, CT, USA) and were 8 μm in diameter and 8 mm in length [31]. The reference electrode was a BAS MF 2052 Ag/AgCl electrode. A Pt wire was used as auxiliary electrode.

Reagents and solutions

Stock 1000 mg L^{-1} solutions of TNT, 2,6-DNT, 2-NT (2-nitrotoluene), 2-A-4,6-DNT (2-amino-4,6-dinitrotoluene), and 3,5-DNA (3,5-dinitroaniline) in acetonitrile (Restek) and nitrobenzene (NB) (Fluka) were used. All solutions were stored at $T<4°C$ in brown glass bottles wrapped in aluminium foil. More dilute solutions were prepared from these by suitable dilution with acetonitrile (SDS, HPLC grade). A 0.1 mol L^{-1} $H_2PO_4^-/HPO_4^{2-}$ buffer solution of pH 7.0 was also used. All other solvents and chemicals were of analytical reagent grade. The water used was obtained from a Millipore Milli-Q system. All solutions used for voltammetric experiments in the cathodic range were previously deaerated by bubbling with nitrogen for 15 min.

Procedures

Activation of carbon fibre microelectrodes (CFMEs)

The procedure for the electrochemical activation of CFMEs has been reported previously [29]. Briefly, carbon fibre microelectrodes were activated by immersion in 0.05 mol L^{-1} $H_2PO_4^-/HPO_4^{2-}$ buffer solution of pH 7.0 and applying five successive SW voltammetric scans between 0.0 and 2.6 V (vs. Ag/AgCl). A square-wave amplitude, E_{sw}, of 50 mV, a step height, ΔE_s, of 4 mV, and a frequency, f, of 25 Hz were used.

Determination of TNT in water and in soil samples

A 5-mL sample (tap water or ground water) was spiked with TNT at 2.0 mg L^{-1} and diluted to 10 mL with 0.1 mol L^{-1} $H_2PO_4^-/HPO_4^{2-}$ buffer solution of pH 7.0. The solution was then transferred to the electrochemical cell and the determination of TNT was carried out by SWV (E_{sw}, 75 mV; ΔE_s, 8 mV; f, 25 Hz) by applying the standard additions method, which involved addition of 10-μL aliquots from 1000 mg L^{-1} TNT standard solution.

For analysis of soil samples, approximately 1 g soil previously spiked with TNT at the 200 µg g^{-1} level, was accurately weighed and introduced into a 30-mL centrifuge tube. Next, 2 mL acetonitrile was added and the mixture was mechanically shaken for 30 min. After centrifugation at 3500 rpm for 15 min the liquid was filtered through a Nylon syringe filter 0.2 µm in diameter. A 100-μL aliquot of this extract was diluted to 10 mL with phosphate buffer solution of pH 7.0 and the same SW voltammetric method described above for water samples was then followed.

Results and discussion

Cyclic voltammetry at activated CFMEs

Figure 1 shows cyclic voltammograms obtained from 20 mg L^{-1} solutions of TNT, 2,6-DNT, 2-NT, 2-A-4,6-DNT, 3,5-DNA, and NB at an electrochemically activated CFME in 0.05 mol L^{-1} phosphate buffer solution of pH 7.0. As can be observed, well-defined narrow cathodic peaks were always obtained; E_p values are given in Table 2. Moreover, small s-shaped waves typical of microelectrodes were observed when the cyclic voltammograms were recorded under the same conditions at a non-activated CFME (dashed curves). Similar to the behaviour of other nitro derivatives, both the very high cathodic current, considering the microelectrode dimensions, and the change in the shape of the voltammograms at the activated CFME can be attributed to fibre fracture produced by the electrochemical activation, with the subsequent appearance of deep fissures along the main fibre axis and an increase in the carbon fibre surface area. This enables penetration of electroactive species into the interior void volume, giving rise to an important contribution of adsorption and/or (according to Kuwana and co-workers [32]) thin-layer electrolysis to the total voltammetric response.

According to the currently accepted mechanism for electrochemical reduction of nitro compounds [33, 34], the cathodic responses can be attributed to four-electron reduction of the nitro group to the hydroxylamine derivative. The electrochemical reduction of polynitro aromatic compounds has been claimed to be a complex process which depends on the number of nitro groups, their relative positions on the ring, and the nature of other substituents on the aromatic system [16]. As can be observed, voltammograms from TNT and dinitro derivatives (2,6-DNT, 2-A-4,6-DNT, and 3,5-DNA) contain three reduction peaks for TNT and two reduction peaks for the dinitro compounds; these peaks correspond to reduction of each of the nitro groups present in the molecules. This type of multiple signal was also observed for TNT previously accumulated on a carbon nanotube-modified glassy-carbon electrode [24] and for 2,6-DNT adsorbed on a SPCE [23]. However, no multiple peaks were reported for SPCEs when no previous accumulation had been carried out [21] and at non-electrochemically activated carbon fibres [26].

As can be observed in Table 2, the E_p values obtained at the activated CFMEs are less negative than the $E_{1/2}$ values at the non-activated fibres. Moreover, when the E_p values are compared with those obtained at pH 5 at a glassy-carbon electrode [17], differences of up to 200 mV less negative are found at the activated CFMEs. On the other hand, reverse scans in cyclic voltammetry give small anodic signals, similar to those obtained from non-activated fibres, which can be attributed to oxidation of the formed hydroxylamine at the electrode surface [23]. The magnitude and shape of these anodic signals indicate that no accumulation of the product from nitro compound reduction occurred under the experimental conditions employed.

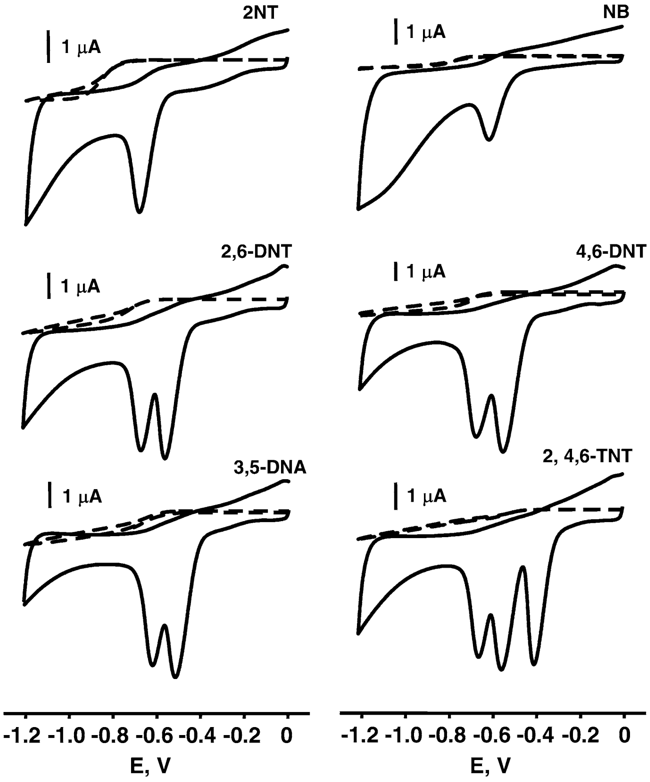

Fig. 1 Cyclic voltammograms from 20 mg L^{-1} solutions of nitroaromatic explosives at an electrochemically activated CFME in 0.05 mol L^{-1} phosphate buffer solution of pH 7.0; $v = 50$ mV s^{-1}. Dotted curves are voltammograms at non-activated CFME

Table 2 Voltammetric data for nitroaromatic explosives at a CFME

Compound	Non-activated (CV)		Activated (CV^a, SWV^b)	
	$-E_{1/2}$ (mV)	$-i_L$ (μA)	$-E_p$ (mV)	$-i_p$ or Δi_p (μA)
TNT	508	0.687	404; 551;654^a 375;517;620^b	4.95; 4.78; 4.00^a 2.35; 2.50; 3.08^b
2,6-DNT	707	1.07	555; 666^a 524; 637^b	4.69; 4.02^a 3.01; 3.70^b
2-NT	854	1.22	678^a 656^b	3.57^a 1.84^b
2-A-4,6-DNT	681	0.859	551;671^a 519; 632^b	6.57; 5.47^a 3.08; 3.67^b
3,5-DNA	633	0.979	514; 620^a 495; 604^b	5.25; 4.52^a 7.23; 7.44^b
NB	765	0.422	605^a 598^b	2.53^a 1.85^b

[a] CV data at 20 mg L^{-1}
[b] SWV data at 2 mg L^{-1} (1.2 mg L^{-1} for NB)

The effect of the potential scan rate, over the 5–1000 mV s^{-1} range, on peak current and peak potential values showed that E_p always shifts to more negative values as the scan rate increased. Moreover, linear i_p versus $v^{1/2}$ plots were obtained for low scan rates (up to 100 mV s^{-1}), corresponding to diffusion-controlled processes. However, for faster scan rates, i_p increased rapidly with increasing v and linear dependence of i_p on v was observed, which confirmed the contribution of adsorption and/or thin layer electrolysis to the voltammetric response [29].

Square-wave voltammetry at activated CFMEs

SWV was selected as the electrochemical technique to be used for determination of nitroaromatic explosives, because of its demonstrated good performance when used at electrochemically activated CFMEs [28, 29]. As an example, Fig. 2 shows net SW voltammograms for NT, 2,6-DNT, and TNT. The corresponding E_p and net current, Δi_p, values are summarized in Table 2. As expected, the same number of peaks were obtained for each compound as in CV, and the E_p values were less negative in SWV. Concerning the net currents, the values given in Table 2 correspond to a nitro compound concentration one tenth that used for CV.

Current density-to-concentration ratios were calculated using the microelectrode geometrical area, 2.0×10^{-3} cm^2. Because the electrochemically active area was not used to calculate current densities, these ratios should be considered only as approximate values for comparison purposes. The values obtained ranged between 63 A cm^{-2} mol^{-1} L for 2-NT and 218 A cm^{-2} mol^{-1} L for 2A-4,6-DNT, which are considerably higher than those reported for other compounds such as xanthine and hypoxanthine [33] at activated fibres. Moreover, the current density-to-concentration ratio for TNT, 175 A cm^{-2} mol^{-1} L is similar to that calculated from literature data using AdsSV at a multiwall carbon nanotube-modified glassy carbon electrode [24].

Penetration of nitroaromatic explosives into the microchannels of the activated fibre was demonstrated by recording SW voltammograms from a solution that contained only the buffer solution with an activated CFME previously used to obtain a SW voltammogram from a 2 mg L^{-1} TNT solution, and then thoroughly rinsed with the same buffer solution. The presence of the voltammetric signals of TNT in the first scan, which rapidly decreased in successive scans, indicated that TNT was present in the interior of the activated CFME upon removal from the initial solution, and was removed by further potential scanning. This accumulation can serve as a preconcentration step for development of sensitive methods for the determination of nitroaromatic explosives. Moreover, the accumulation process might be also used for decontamination in electrochemical remediation procedures, although a working electrode of larger surface area, for example many carbon fibres, would be required for this particular purpose.

The possibility of developing a stripping voltammetric method for TNT was evaluated with 5 mg L^{-1} TNT solution and an accumulation period of 120 s at an applied potential of 0.0 V (working conditions taken from Ref. [24]). Although a three-fold increase in the reduction current of the explosive was observed compared with the electrochemical response with no accumulation (this improvement might be even better after optimization of the accumulation potential and the period of time on the CFME), the stripping method was not further considered, because of the growing increase in background current which resulted from repeated accumulation–stripping processes. This effect was previously observed for antibacterial nitro compounds [28] and attributed to an increase in the capacitance of the activated microelectrode when the microelectrode is used continuously [35].

Determination of nitroaromatic explosives

In accordance with the discussion above, direct SW voltammetric methods were developed for determination

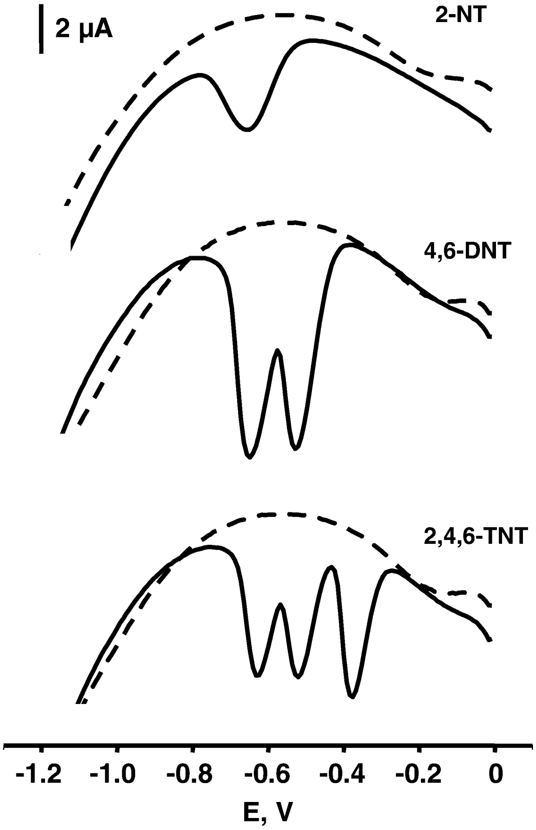

Fig. 2 SW voltammograms from 2.0 mg L^{-1} solutions of 2-NT, 4,6-DNT, and 2,4,6-TNT at electrochemically activated CFME in 0.05 mol L^{-1} phosphate buffer of pH 7.0; $E_{SW}=75$ mV, $\Delta E_S=8$ mV, $f=25$ Hz. The *dotted line* is the background electrolyte signal

of nitroaromatic explosives, and optimization of the conditions used was carried out. The influence of pH on the net peak current and the peak potential values is shown in Fig. 3 for TNT and NB. For TNT the E_p values plotted correspond to the peak appearing at more negative values. Similar behaviour was observed for both compounds, with a shift of the E_p values to more negative potentials as the pH increased. This is the expected behaviour for reduction processes involving protons, such as those of the nitro groups of the molecules tested to form the corresponding hydroxylamine [34]. The slope of the E_p versus pH plot is higher for both compounds in the range of more acidic values, which is attributed to formation of the $Ar\text{–}NO_2H^+$ protonated species which are reduced at less negative potentials [34]. Moreover, for pH values higher than 10, E_p becomes practically independent of pH. For NB, this change in the slope value coincides with the appearance of a wider second reduction signal, which is attributed to a two-step reduction mechanism [34] as follows:

a. $Ar\text{–}NO_2 + e \rightarrow Ar\text{–}NO_2^{\bullet}$
b. $Ar\text{–}NO_2^{\bullet} + 3e + 4\ H^+ \rightarrow Ar\text{–}NHOH + H_2O$

Values of i_p were practically independent of pH over the whole pH range (Fig. 3), and 0.05 mol L^{-1} $H_2PO_4^-$/HPO_4^{2-} buffer solution of pH 7.0 was selected for further work, because the same medium is used in the fibre activation step.

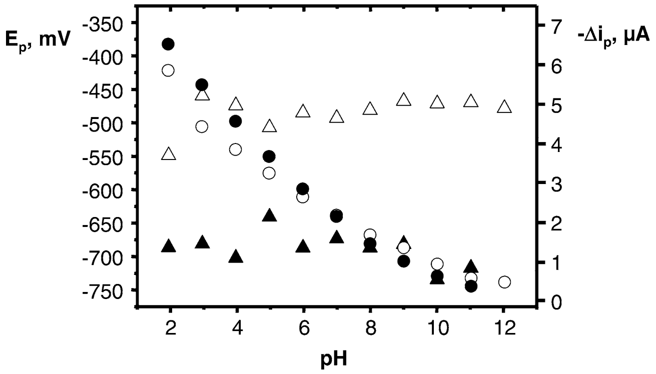

Fig. 3 Effect of pH on peak potential (*circles*) and net peak current (*triangles*) obtained by SWV at electrochemically activated CFMEs for 1.0 mg L^{-1} TNT (*solid symbols*) and 12.0 mg L^{-1} NB (*open symbols*). Conditions as for Fig. 2

The typical SWV variables (E_{SW}, ΔE_S, and f) were also optimized to obtain the best sensitivity and resolution for TNT net current responses. The values selected were: $f=25$ Hz, $\Delta E_S=8$ mV, and $E_{SW}=75$ mV.

Under these conditions linear calibration graphs were obtained by SWV for the nitroaromatic explosives tested, with the characteristics summarized in Table 3. For compounds exhibiting multiple signals, the peak appearing at the most negative potential was used as the analytical signal, because this enabled higher precision in i_p measurements. The limits of quantification and detection were calculated from the 10×standard deviation and the $3\times s_b/m$ criteria, respectively, where m was the slope of the corresponding calibration plot and s_b was estimated as the standard deviation of the signals ($n=10$) corresponding to the lowest concentration of the calibration plots (0.1 mg L^{-1}). The RSD values that appear in Table 3 correspond to 10 measurements, using a single activated microelectrode, from different solutions of the corresponding nitroaromatic compound at a concentration of 1.0 mg L^{-1}. The same single microelectrode was used for each set of experiments despite the increase in the microelectrode capacitance observed when the same microelectrode was used continuously. This is illustrated in Fig. 4, in which repeated SW voltammograms for TNT are displayed. It can be seen that although the background current increased with successive voltammograms, this did not affect the reproducibility of the voltammetric response. When these characteristics are compared with those reported for other methods (Table 1), one can deduce that detection limits are similar or even lower than those reported previously except for the CNT-modified GCE. When the comparison is restricted to voltammetric methods for TNT determination, the LOD achieved with activated CFMEs is approximately a factor of ten lower than that obtained with a SPCE using also SWV [22], and the same as that obtained using SWV at mul-

Table 3 Analytical characteristics of the calibration plots for SWV determination of nitroaromatic explosives at electrochemically activated CFMEs

Compound	Linear range (mg L^{-1})	Correlation coefficient, r	Slope ($\mu A\ \mu g^{-1}\ mL$)	Intercept (μA)	LOD ($\mu g\ mL^{-1}$)	LOQ ($\mu g\ mL^{-1}$)	RSD (%)
TNT	0.1–10	0.9994	1.42 ± 0.01	−0.05 ± 0.06	0.03	0.09	2.4
2,6-DNT	0.1–10	0.999	1.46 ± 0.02	−0.03 ± 0.07	0.03	0.09	3.1
2-NT	0.1–10	0.9996	1.52 ± 0.02	0.38 ± 0.05	0.05	0.16	3.6
2-A-4,6-DNT	0.1–10	0.998	0.51 ± 0.01	0.18 ± 0.03	0.06	0.19	4.7
3,5-DNA	0.1–10	0.9998	1.38 ± 0.01	−0.04 ± 0.03	0.02	0.08	4.1
NB	0.1–10	0.993	1.71 ± 0.09	−0.03 ± 0.04	0.03	0.08	3.7

tiple CFEs [26], although the range of linearity achieved is wider with activated CFMEs. However, as might be expected, the AdsSV method at multiwall carbon nanotube-modified glassy-carbon electrodes [24] provided a calibration plot with a remarkably higher slope value and an LOD a factor of 100 fold lower, although an accumulation period of 10 min was needed with this method. Finally, with regard to the stripping method reported for determination of 2,6-DNT [23], the higher slope of the calibration plot should be noted, as also should the lower detection limit achieved with the direct SW voltammetric method at activated CFMEs.

An important aspect of the analysis that can also be deduced from data in Table 3, is that the slope values of the calibration plots for TNT, 2,6-DNT, and 2-NT are practically the same. These nitroaromatic compounds are those usually found in contaminated samples [17], and therefore the rapid direct SW voltammetric method at activated CFMEs might be used as a screening method for overall detection of nitroaromatic explosives in these samples.

The method was also highly selective. A study of interference from other compounds, for example hydrazine, phenol, pentachlorophenol, atrazine, simazine, disulfiram, thiram, Triton X-100, and sodium dodecylsulfate (SDS), was carried out. SW voltammograms from 10 mg L^{-1} solutions of these compounds were recorded. Under the experimental conditions used, none of substances tested gave cathodic signals in the potential range between 0.0 and −1.2 V, the SW voltammograms coinciding practically with that of the supporting electrolyte solution.

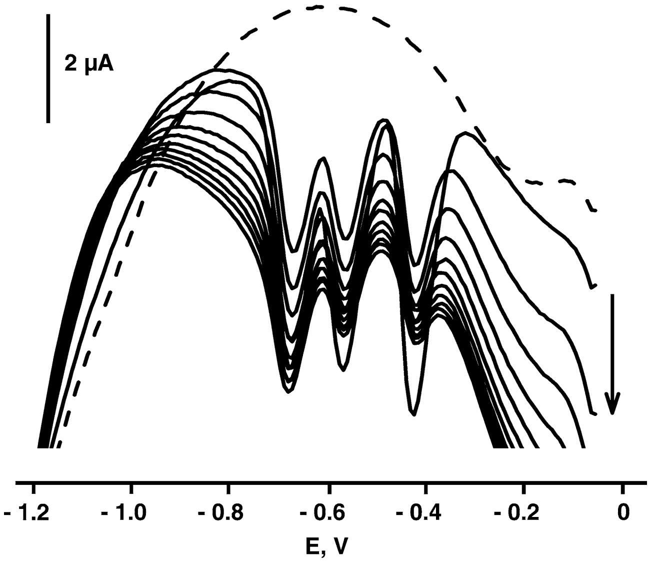

Fig. 4 Repeated SW voltammograms recorded at the same electrochemically activated carbon fibre microelectrode from 2.0 mg L^{-1} TNT solutions. Conditions as for Fig. 2. The *dotted line* is the background electrolyte signal

Determination of TNT in water and soil samples

The analytical usefulness of the voltammetric method for determination of nitroaromatic explosives was demonstrated by applying it to the determination of TNT in water and soil samples. Two water samples were

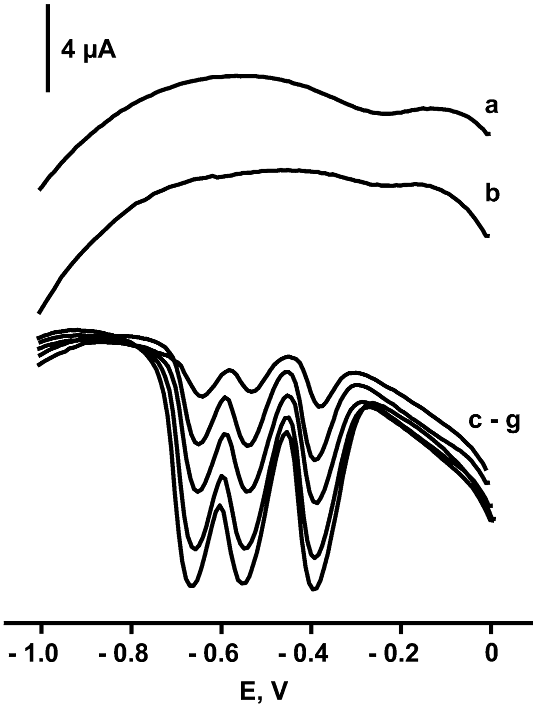

Fig. 5 SW voltammograms from the phosphate buffer solution used as supporting electrolyte (**a**), a non-spiked soil sample (**b**), a soil sample spiked at the 200 µg g^{-1} level (**c**), and successive additions of 10 μL aliquots from a 1000 mg L^{-1} TNT standard solution (**d**—**g**). Conditions as for Fig. 2

Table 4 Determination of TNT in water and soil samples

Sample	TNT added	TNT found[a]	Recovery (%)
Tap water	2 mg L^{-1}	1.95 ± 0.07 mg L^{-1}	98.4 ± 5.5
Ground water	2 mg L^{-1}	1.91 ± 0.10 mg L^{-1}	95.3 ± 5.1
Soil	200 mg g^{-1}	190 ± 19 mg g^{-1}	95.0 ± 9.8

[a] Mean value from five determinations

analysed, tap water and ground water spiked with TNT at the 2.0 mg L^{-1} concentration level. The soil sample was a reference material from agricultural land, previously homogenized, dried, and sieved, which was spiked at the 200 μg g^{-1} level. The very simple experimental procedures described in the Experimental section were applied to each sample. The absence of TNT was first verified in the non-spiked samples. As an example, Fig. 5 shows SW voltammograms for the supporting electrolyte solution (voltammogram a), for a non-spiked soil sample (voltammogram b), and for the spiked soil sample (voltammogram c) together with those corresponding to successive TNT standard additions used for quantification (voltammograms d–g). As can be observed, voltammograms a and b are practically coincident, indicating the absence of TNT from the nonspiked soil, and the voltammogram of the spiked sample and those of the standard additions show the same three reduction peaks characteristic of the analyte. Table 4 summarizes the results obtained for the three samples analysed. As can be seen, the recoveries achieved are acceptable for all the samples tested, the confidence intervals being calculated for a significance level of 0.05.

Conclusions

A simple, rapid, sensitive, and selective SW direct voltammetric method for the determination of nitroaromatic explosives, useful as a screening method for detection of these compounds in contaminated water and soil samples, has been developed. The good analytical performance of this method is because of the electrochemical activation process to which CFMEs, used as working electrodes, are subjected. Electrochemical activation by repeated SW voltammetric scans enables high cathodic currents to be obtained from nitroaromatic explosives, as a consequence of the penetration of these compounds into the microchannels of the activated fibres, which gives rise to an important contribution of adsorption and/or thin layer electrolysis to the total voltammetric response of such electroactive analytes.

Acknowledgements Financial support from the Ministerio de Ciencia y Tecnología (Projects BQU 2001–2050 and BQU 2003–00365) and Comunidad de Madrid Project No. 07G/0006/2003 are gratefully acknowledged.

References

1. Dutta SK, Hollowell GP, Hashem FM, Kuykendall LD (2003) Soil Biol Biochem 35:667–675
2. Lee KB, Gu MB, Moon SH (2003) Water Res 37:983–992
3. Altamirano M, García-Villada L, Agrelo M, Sánchez-Martín L, Martín-Otero L, Flores-Moya A, Rico M, López-Rodas V, Costas E (2004) Biosens Bioelectron 19:1319–1323
4. Talmage SS, Opresko DM, Maxwell CJ, Weish CJE, Cretella FM, Reno PH, Daniel FB (1999) Rev Environ Contam Toxicol 161:1–156
5. Hass R, Schreiber I, Low E, Stork G (1990) Fresenius' Z Anal Chem 338:41–45
6. Jenkins TF, Leggett DC, Miyares PH, Walsh ME, Ranney TA, Cragin JH, George V (2001) Talanta 54:501–513
7. Spaggord RJ, Gibson BW, Keck RG, Thomus DW, Barkley JJ Jr (1982) Environ Sci Technol 16:229–232
8. Butterworth BE (1990) Mutat Res 239:117–132
9. Hunt RH, Neubauer NR, Picone RF (1980) Am Ind Hyg Assoc J 41:592–594
10. Hable M, Stern C, Asowata C, Williams K (1991) J Chromatogr Sci 29:131–136
11. Calderara S, Gardebas D, Martínez F (2003) Forensic Sci Int 137:6–12
12. Kleibohmer W, Camman R, Robert J, Musenbrock E (1993) J Chromatogr 638:349–356
13. Wallemborg SR, Markides KE, Nyholm L (1997) J Chromatogr A 785:121–128
14. Oehrle SA (1997) Electrophoresis18:300–302
15. Lu Q, Collins GE, Smith M, Wang J (2002) 469:253–260
16. Bratin K, Kissinger PT, Briner RC, Brunlett GS (1981) Anal Chim Acta 130:295–311
17. Hilmi A, Luong JHT, Nguyen AL (1999) J Chromatogr A 844:97–110
18. Hilmi A, Luong JHT (2000) Electrophoresis 21:1395–1404
19. Hilmi A, Luong JHT, Nguyen AL (1999) Anal Chem 71:873–878
20. Hilmi A, Luong JHT (2000) Anal Chem 72:4677–4682
21. Wang J, Lu F, MacDonald D, Lu J, Ozsoz MES, Rogers KK (1998) Talanta 46:1405–1412
22. Wang J, Tian B, Sahlin E (1999) Anal Chem 71:5436–5439
23. Honeychurch KC, Hart JP, Pritchard PRJ, Hawkins SJ, Ratcliffe NM (2003) Biosens Bioelectron 19:305–312
24. Wang J, Hocevar SB, Ogorevc B (2004) Electrochem Commun 6:176–179
25. Krausa M, Schorb K (1999) J Electroanal Chem 461:10–13
26. Wang J, Bhada RK, Lu J, Mac Donald D (1998) Anal Chim Acta 361:85–91
27. Ly S-Y, Kim D-H, Kim M-H (2002) Talanta 58:919–926
28. Guzmán A, Agüí L, Pedrero M, Yáñez-Sedeño P, Pingarrón JM (2004) Electroanalysis (in press)
29. Agüí L, Guzmán A, Yáñez-Sedeño P, Pingarrón JM (2002) Anal Chim Acta 461:65–73
30. Tomaszewski W, Gun'ko VM, Skubiszewska-Zieba J, Leboda R (2003) 266:388–402
31. Agüí L, Reviejo J, Yáñez-Sedeño P, Pingarrón JM (1995) Anal Chem 67: 2195–2200
32. Kelly RS, Weiss DJ, Chong SH, Kuwana T (1999) Anal Chem 71:413–417
33. Cavalheiro ETG, Brajter-Toth A (1999) J Pharm Biomed Anal 19:217–220
34. Núñez-Vergara LJ, Bonta M, Navarrete-Encina PA, Squella JA (2001) Electrochim Acta 46:4289–4300
35. A Brajter-Toth A, El-Nour KA, Cavalheiro ET, Bravo R (2000) Anal Chem 72:1576–1579