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Determination of explosives in soil and ground water by liquid chromatography–amperometric detection

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Abstract

Electrochemical reduction of trinitrotoluene (TNT) and several nitroaromatics has been exploited toward the development of an amperometric detector for liquid chromatography (LC). Up to a ten-fold increase in sensitivity was accomplished for the explosives using amperometric detection instead of conventional UV measurement. A working glassy carbon electrode (poised at −0.80 V vs. Ag/AgCl) offered a detection limit of 9, 44 and 550 n*M* for trinitrobenzene, TNT and 1,4-dinitrobenzene, respectively. Separation of eleven TNT-related compounds in a mixture was achieved within 15 min using a C_{18} column and a mobile phase consisting of acetonitrile–50 m*M* phosphate buffer pH 5 (1:2, v/v) and 18 m*M* sodium dodecylsulfate. The LC–amperometric detection system was applicable for analyzing soil extracts and ground water and the results obtained agreed well with that of the US Environmental Protection Agency recommended procedure. Extension to analysis of HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) and RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) was accomplished with a silver working electrode instead of a glassy carbon electrode installed in a thin channel cell.

Keywords: Explosives; Soil; Water analysis; Environmental analysis; Nitrotoluenes; Nitrobenzenes

1. Introduction

Production, storage and testing of explosives have resulted in a widespread environmental problem because these mutagenic, toxic, and persistent compounds have leached from soils and accumulated in the food chain [1–3]. In response to the need for continuous measurement of explosives in the natural media, fiber-optic and immunochemical sensors [4,5] have been developed for 2,4,6-trinitrotoluene (TNT). The search for simple devices for real time and on-site detection has also led to the development of an electrochemical probe for TNT analysis in untreated river water, ground water and drinking water [6]. The TNT electrochemical probe was free of interference from organics such as benzidine, phenol, hydrazine and several metal ions but its response was suppressed by nitrophenol, nitrobenzene and dinitroaniline [6]. In addition, samples containing high levels of humic materials may require a complicated sample pretreatment involving microdialysis sampling.

The need to separate and quantitate the explosives in complex samples has sustained continuing investigations of different separation methods including capillary electrophoresis [7–9], LC [10–13], supercritical fluid chromatography [14] and gas chromatography [15,16]. In most of the published

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studies ultraviolet (UV) detection was used although UV-absorbing extractables in the sample would interfere to a significant extent [17]. Based on redox behavior of nitroaromatics, amperometric detection using pendant mercury electrodes or gold-mercury thin film electrodes, has been used together with LC for separation and determination of several explosives with various degrees of success [18–21]. The amalgamated gold electrodes represented an improvement over the pendant mercury electrodes but both types present some difficulty in practical and routine applications. Recently, the glassy carbon electrode was shown to be capable of providing part-per-billion detection limits when operated in either oxidation or reduction mode [22]. LC analysis with amperometric detection has also been applied to monitor degradation processes of explosives [23].

This article describes a LC system equipped with amperometric detection for analysis of complex explosive mixtures that contain TNT and several other related compounds. An improved LC method using sodium dodecylsulfate (SDS) in the mobile phase is also developed and optimized for separation of explosive mixtures. Both the glassy carbon and silver working electrodes are investigated for sensitive detection of the explosive compounds including RDX (hexahydro-1,3,5-trinitro-1,3,5-triazine) and HMX (octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine) in soil extracts and ground water and their sensitivity is compared with LC–UV detection.

2. Experimental

2.1. Materials

All explosives were purchased from Chem Service (West Chester, PA, USA) whereas other chemicals were obtained from Aldrich (Milwaukee, WI, USA). Fig. 1 gives the structures, common abbreviations and peak assignments for the explosives investigated in this study. The soil and ground water samples were taken from contaminated sites.

2.2. Sample preparation

Stock solutions of explosives were prepared in acetonitrile (ACN) and an appropriate volume of each component was added to ACN to obtain desired concentrations. Extraction was done by agitating 1 g of soil and 10 ml ACN in a capped container for 30 min. The supernatant from centrifugation was used as the LC sample. The ground water sample was analyzed after being filtered with a 0.45 μm disk-filter. All samples were protected from light and kept at 4°C.

2.3. Instrumentation

Cyclic voltammetry (CV) experiments perused a potentiostat/galvanostat (Model 263A, EG&G, Princeton Applied Research, Princeton, NJ, USA) to operate a three-electrode system consisting of a saturated Ag/AgCl reference electrode [RE-1, Bioanalytical System (BAS), West Lafayette, IN, USA], a platinum wire counter electrode and a working glassy carbon (BAS-MF-2012) or a silver wire electrode (Aldrich). The silver wire electrode was 0.5 mm diameter with 1 cm length immersed in the test solution.

The liquid chromatography (LC) system consisted of a pump (Model 590, Waters, Milford, MA, USA) and a 20 μl injection loop (Model 7725, Rheodyne, Cotati, CA, USA) and a C_{18} column (15 cm, packed with 5 μm spheres, Supelcosil LC-PAH, Supelco, Mississauga, Canada). The mobile phase (acetonitrile–50 m*M* sodium phosphate pH 5, 1:2, v/v, containing 18 m*M* SDS) was purged with nitrogen overnight to expel dissolved oxygen. Amperometric detection was achieved with a glassy carbon electrode (BAS-MF-1000) or a silver electrode (BAS-MF-1008) installed in a thin-layer detector (BAS-CC-5) operated with a voltammograph (BAS-CV-1). Before use, the electrode was polished with 0.05 μm alumina (No. 40-6365-006, Buehler, Lake Bluff, IL, USA). For comparison, the explosives were detected by an UV detector set at 230 nm (Waters LC spectrophotometer, model 481). Analog signals from the voltammograph or the amperometric detector were digitalized by an A/D board (DP500-AD supplied with an interface box, Labtronics, Guelph, Canada) that was installed on a PC 486 computer. The data were stored in ASCII files and converted to PRN files for treatment by a graphic program. All experiments were performed at room temperature with a mobile phase flow rate of 1 ml/min.

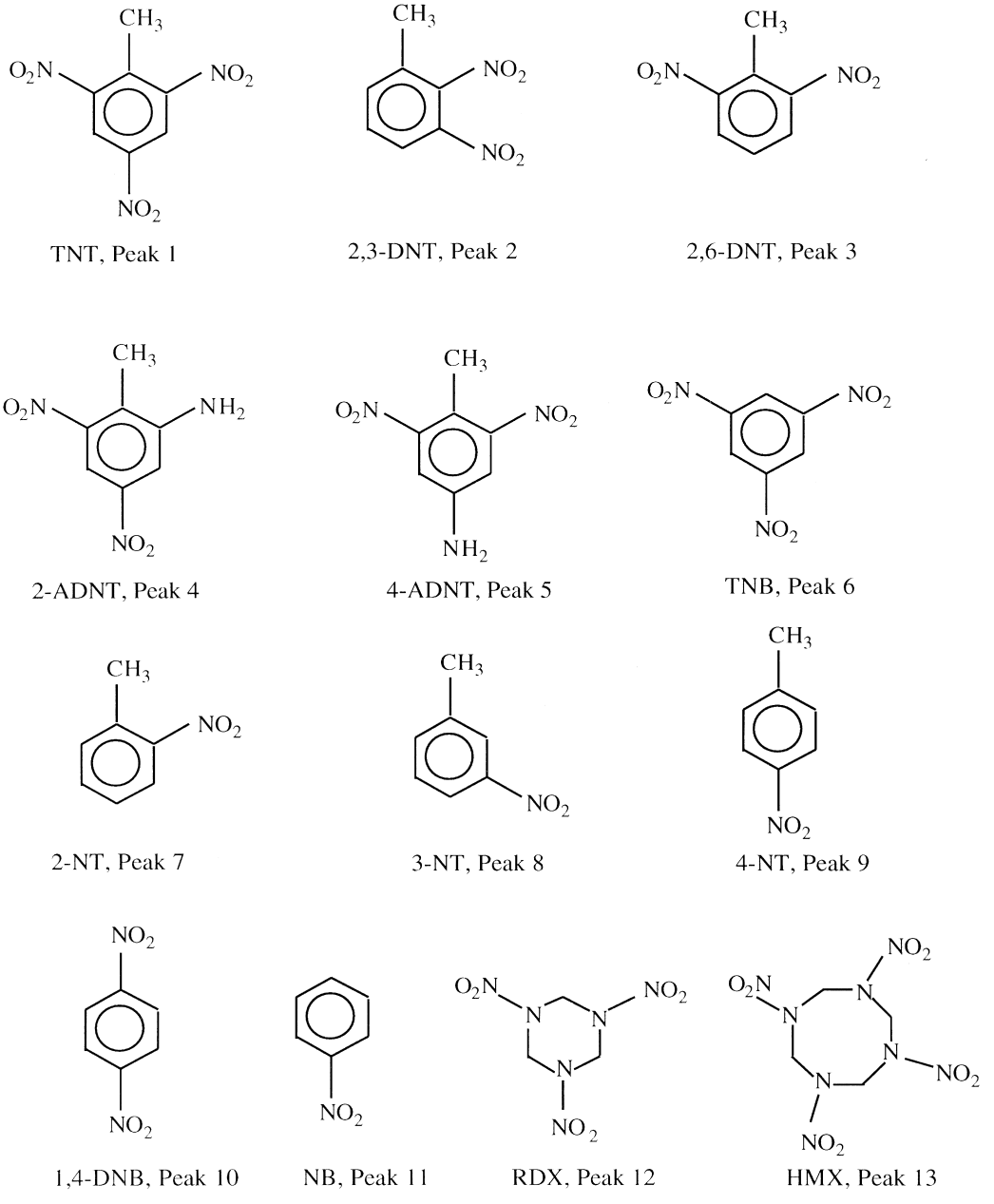

Fig. 1. Structures, abbreviations and peak assignments of the nitroaromatic, nitramine explosives, RDX and HMX.

2.4. Safety

Explosive compounds and stock solutions were handled in a ventilated hood and stored in closed glass containers. Disposable latex gloves were worn while working with explosive compounds and care was taken to dispose of waste solutions properly.

3. Results and discussion

3.1. Electrochemical reduction and oxidation of explosive compounds

Nitroaromatics including TNT are readily reduced with various mercury electrodes and the electron-

transfer process involves an initial reduction of the nitro groups to hydroxyl amines, followed by the conversion of the latter to amine groups. For TNT reduction, the glassy carbon electrode was also reported to display a single voltammetric peak at ca. −0.5 V, corresponding to the formation of the hydroxylamine moiety [6]. The second reduction step, corresponding to the transformation of the hydroxylamine product to an amine was observed at ca. −0.7 V.

Fig. 2 (curve a) presents a cyclic voltammogram obtained with a solution of TNT in acetonitrile–50 m*M* phosphate pH 5, 1:2 v/v, containing 18 m*M* SDS. The stated SDS concentration is referred to as the value in the aqueous buffer before mixing with acetonitrile. As addressed later, this mixture was found suitable as a LC mobile phase for satisfactory separation of all explosives investigated in this study. Three distinct reduction peaks (at −0.50, −0.70 and −0.90 V) were observed during the decreasing potential sweep, likely corresponding to the formation of hydroxylamine and/or amine moieties from the sequential reduction of the three NO_2 groups. However, the increasing sweep indicated only one oxidation peak at +0.1 V, far remote from the least negative reduction peak (−0.5 V). Such behavior thus implied the process responsible for the reduction peaks was irreversible and unrelated to the oxidation process. The oxidation peak at +0.1 V could correspond to further transformation of the moieties formed during the decreasing potential sweep. When the potential was maintained for a few minutes (the time for reduction) at −0.5, −0.7 or −0.9 V, the peak obtained at +0.1 V increased with increasing reduction time. Similar observations were reported by Schmelling et al. [24] although the supporting buffer was different (TNT in nitrogen-sparged buffer, pH 5.1, 100 m*M* phosphate and 8% ethanol). Thus it would be reasonable to attribute the peak at 0.1 V to the oxidation of hydroxylamine. This would

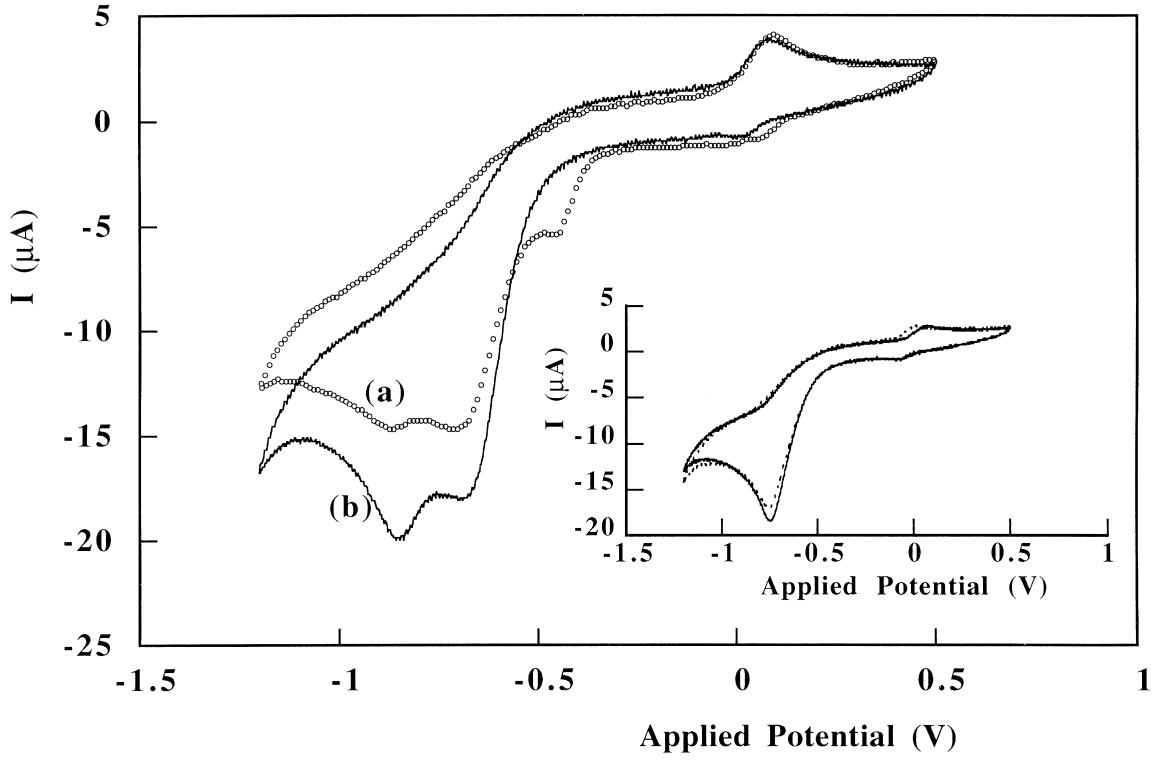

Fig. 2. Cyclic voltammograms obtained for 50 μ*M* solutions of TNT (a) and 2,6-DNT (b) in deoxygenated acetonitrile–50 m*M* phosphate pH 5 containing 18 m*M* SDS (1:2, *v*/*v*). Inset: voltammograms for 2-NT (solid) and nitrobenzene (dotted), 50 μ*M* in the same milieu. Working electrode: glassy carbon, reference electrode: Ag/AgCl and counter electrode: platinum. Scan rate=50 mV/s.

be in line with the results previously reported in the literature [25,26]

The three reduction peaks appeared to correspond to the three nitro groups of TNT because the voltammogram of 2,6-DNT displayed only two peaks at −0.68 and −0.84 V (Fig. 2, curve b). The close match of the reduction potentials for TNT with two peaks observed with 2,6-DNT also suggested the peak at −0.50 V (absent for 2,6-DNT) was due to the reduction of the nitro group at the *para*-position to the hydroxylamine product. One could be tempted to attribute one of the two peaks (at −0.68 and −0.84 V) to the reduction of the *ortho*-nitro group then the remaining peak might be assigned to the reduction of the remaining nitro group after the other (on the same 2,6-DNT molecule) has been reduced. However, the reduction potential of the NO_2 group in the *para*-position (−0.5 V) appeared to depend upon the presence of at least one NO_2 group in the *ortho*-position since 4-NT displayed a peak at −0.74 V (figure not shown). Moreover, neither of the peaks at −0.68 and −0.84 V could be assuredly assigned to the reduction of an *ortho*-nitro group since 2-NT actually exhibited a peak at −0.74 V (Fig. 2, inset, solid line). The peaks at −0.68 and −0.84 V might be related to further reduction of the hyroxylamine moiety but the available evidence would not permit a confirmation.

Nitrobenzene also exhibited one reduction peak at −0.75 V (Fig. 2, inset, dotted line) and each compound in this study displayed a number of reduction peaks corresponding to its number of nitro groups (data not shown). From the voltammograms obtained for both 2-NT and nitrobenzene one may conclude that the presence of the methyl group in the aromatic ring did not appear to affect the reductive potential of the *para*-nitro group. Nevertheless, all reduction peaks appeared at potentials more positive than −0.8 V, this reductive potential was therefore selected for detection of the explosives in LC analysis.

3.2. Improved LC–amperometric detection of explosive mixtures

Water–methanol is the mobile phase used in the LC Method 8330, drafted by the US Environmental Protection Agency (EPA), for analysis of explosives in aqueous samples including extracts from soils. Variations of this method have also been used in several studies reported in the literature with improved results. Since this mobile phase could not resolve some explosive compounds, organic modifiers such as ACN and tetrahydrofuran, have been investigated and the best resolution was obtained with isopropanol [27], although the elution time was longer. Initial experiments in this study confirmed the resolving power of water–methanol and water–isopropanol as the mobile phase. Cyclic voltammetry performed with these two solvent mixtures, with phosphate added as the supporting electrolyte, yielded irreproducible voltammograms (data not shown) which implied the unsuitability of these two modifiers in this study. On the contrary, the reproducibility of voltammograms obtained in the above ACN–phosphate buffer suggested the suitability of this solvent mixture as a mobile phase for LC with amperometric detection, as confirmed by the chromatogram presented in Fig. 3A. Repeated runs using this mobile phase produced a peak height variation of less than 3% for every peak, but resolution of the analytes was not achieved even by increasing the ACN content of the mobile phase (from 10 to 75%). NB, 1,4-DNB and TNB co-eluted (peaks 6,10,11) whereas TNT (peak 1) essentially moved together with 4-NT (peak 9) and 3-NT (peak 8). In addition, a slight peak tailing was also noted in the amperometric detector. Such behavior could be related to the irregularity of packing of the stationary phase, dead volume or adsorption of the analytes on the electrode surface, but the extent was not pronounced.

It was apparent that some analytes exhibited the same interaction with the stationary phase. Consequently, another separation mechanism had to be introduced to the LC system to resolve such compounds. Improved separation could be provided by adding a detergent or surfactant to the mobile phase and the separation mechanism has been known as micellar liquid chromatography. Although surfactants such as cetyltrimethylammonium bromide (CTAB), polyoxyethylene and lauryl ether have been used in LC [28], SDS is the most common. For example, a C_{18} stationary phase and a 3% acetic acid, 3% propanol mobile phase containing 0.1 *M* SDS were used to resolve five organotin compounds [29]. SDS has been used to accomplish baseline separation of ten positional explosive isomers in a

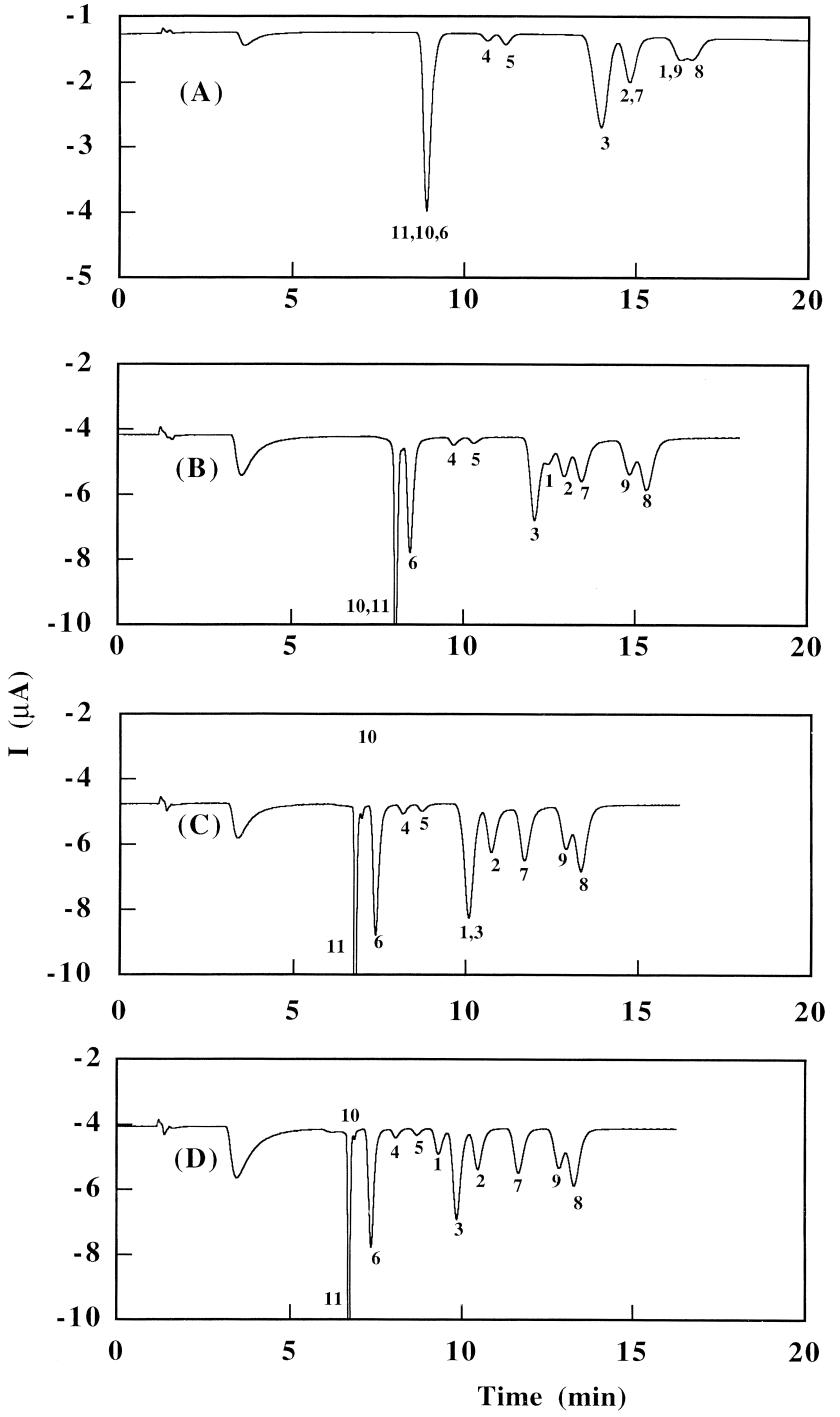

Fig. 3. Chromatograms (C_{18} column) obtained with acetonitrile–50 m*M* phosphate (1:2, v/v), pH 5 with different SDS contents (A): 0, (B): 8, (C): 15, (D): 18 mM. Concentration of each compound is given in Table 1. Amperometric detection with glassy carbon electrode poised at −0.8 V vs. Ag/AgCl in thin channel. Mobile phase flow rate: 1 ml/min.

mixed-mode scheme of capillary electrokinetic separation [30]. The critical micellar concentration (CMC) of SDS in water is about 8 m*M*, however, the addition of an organic solvent, up to 10–20% may deteriorate micelles or inhibit micellar formation [31,32]. For the case at hand, the effectiveness of SDS was evident, however it must be stated that there were no independent results such as the pyrene 1:3 ratio method in fluorescence spectroscopy to indicate any micellar formation [29]. In this study, the quantity of added SDS in the mobile phase was 18 m*M* which was significantly higher than the CMC level of this surfactant, in water (8 m*M*). However, based on a recent report by Luong and Guo [29], micellar formation was very likely inhibited by high ACN (33%) used in the mobile phase. The explosives were expected to associate with hydrophobic chains of the surfactant in the aqueous/ACN solution and in turn altered the interaction between the analytes and the C_{18} stationary phase. The chromatogram was clearly improved with the addition of 8 m*M* SDS (Fig. 3B) and good resolution was achieved at 18 m*M* SDS (Fig. 3D). Among the studied analytes, TNT was most affected by the addition of SDS. Without SDS this compound co-eluted with 4-NT but increasing SDS content accelerated its elution (Fig. 3C) and resolved it from 2,3-DNT (Fig. 3D). The elution order somewhat corresponded with the solubility of the analytes as exemplified by NB, TNB and TNT (solubility of 1:500, 1:3000 and 1:10 000 g/g of water, respectively). However 1,4-DNB (solubility 1:12 500 g/g) eluted before TNB and TNT. Therefore, both the chemical structure and hydrophobicity played an important role to control the interaction between the explosive and the C_{18} column in the presence of SDS. The chromatogram also showed that the major analytes including TNT were well resolved. Only 4-NT and 3-NT (peaks 8 and 9), TNT-manufacturing by-products, were incompletely resolved. This will not be problematical in any practical assays since 2-NT and 4-NT are rarely, if ever, found in TNT-contaminated sites. Successive injections (10 times) produced peak heights and elution times varying $<2\%$, confirming the stability of the electrode response and the absence of electrode poisoning.

Notice that increasing SDS content was also beneficial in augmenting the reduction peaks of NB, TNB, 2,3-DNT and 2,6-DNT. The shortening of elution times was an unexpected advantage of adding SDS, but 18 m*M* was the optimum level since the runs at 22 and 30 m*M* yielded peak clustering. Peak heights were proportional to the concentrations between 0.4 and 140 μ*M* for most components except NB and 1,4-DNB. The peak height of each compound was within 5% of the value obtained when a sample containing the same concentration of the single compound was analyzed. This observation signified the absence of interference among the analytes. The detection limit for each component is presented in Table 1 where the limits obtained with UV detection are also included to show a 3–12-fold sensitivity improvement attained by amperometric detection. As seen in this table, amperometric detection was most sensitive to the determination of TNB (9 n*M*) whereas its sensitivity for DNB was considerable lower (535 n*M*).

DNB (peak 10) displayed a troublesome response. A sample containing only DNB yielded a single peak at 7.0 min which was the same retention as seen in Fig. 3D for this analyte. The peak heights obtained with varying DNB concentrations, in single component samples, revealed a linear response range between 0.5 and 300 μ*M*. However, DNB in a mixture yielded greatly diminished peaks, up to three-times less than a corresponding single component sample, and linearity was not achieved. Experimental data further revealed that the DNB response was adversely affected by nitrobenzene with respect to peak height, peak area and linearity. Such interference could be caused by the electrode poisoning effect of NB or chemical interaction between NB and DNB. The data obtained in this study could not elucidate the mechanism. In practical applications, it would be important to recognize that DNB determination would not be feasible in NB-containing samples.

3.3. Analysis of explosives in contaminated soil and ground water

The potential advantage of amperometric detection over UV detection was proven by the analysis of a soil sample containing a high level of humic materials. Humic materials are mixtures of humic acid, ulmic acid and fulvic acid. They are microbial

Table 1
Detection limit of the explosive compounds attained by amperometric detection.

	Concentration[a]	Detection limit (n*M*)		
		Amperometric[b]	UV[c]	Ratio
Nitrobenzene (NB)	120	120	1000	9
1,4-Dinitrobenzene (DNB)	15	550	1800	3.3
1,3,5-Trinitrobenzene (TNB)	1	9	–	–
2-Amino 4,6-dinitrotoluene (2-ADNT)	13	100	700	7
4-Amino 2,6-dinitrotoluene (4-ADNT)	13	100	700	7
2,6-Dinitrotoluene (2,6-DNT)	140	200	1300	6
2,3-Dinitrotoluene (2,3-DNT)	70	190	880	4
2-Nitrotoluene (2-NT)	125	400	1500	4
Trinitrotoluene (TNT)	44	45	500	12
4-Nitrotoluene (4-NT)	125	400	1600	4
3-Nitrotoluene (3-NT)	125	400	1600	4
HMX	5	100	800	8
RDX	5	110	800	8

[a] Individual concentration (μM) in sample to yield chromatograms in Fig. 3. Detection limit is the concentration to give a response three time the noise level, determined with solution of one analyte.
[b] Amperometric detection with glassy carbon at −0.8 V vs. Ag/AgCl.
[c] UV detection at 230 nm.

transformation products of organic matter, commonly found in soils that have supported vegetation. With UV detection, the non-contaminated sample already exhibited several peaks (Fig. 4A, dotted line). The three added nitroaromatics (TNT, 2,6-DNT and 3-NT) eluted in the same separation window and were completely masked (Fig. 4A, solid line). As expected, amperometric detection did not detect the presence of the humic substances (Fig. 4B, dotted line) while the spiked sample yielded well-defined peaks that could be assigned accordingly (Fig. 4B, solid lines). UV detection displayed a large peak at 7 min (Fig. 3A) while amperometry registered a peak at 3.1 min (Fig. 4B). The UV detected peak could be due to many absorbing (but non-electroactive) compounds that were present in the soil and oxygen was responsible for the peak at 3.1 min. It is very difficult, virtually impossible to eliminate oxygen in samples to be injected with a syringe, but the oxygen peak at 3.1 min did not interfere with the analysis.

Amperometric detection was very suitable and convenient for analyzing slightly contaminated soils. The chromatogram obtained with an extract from such a sample (soil 1 — Fig. 5A) showed identifiable sharp peaks, closely matching elution times of standard mixtures. Individual peak heights were used in conjunction with the calibration correlation for each compound to calculate the explosive contents in the soil. The obtained results agreed well with the values obtained by the standard EPA procedure (Table 2).

A highly contaminated soil sample (soil 2) was extracted and analyzed to yield the chromatogram represented in Fig. 5B. Spiking with individual analytes revealed that the peak at 12.6 min was due to 2,4-dinitrotoluene (DNT). Furthermore, it was confirmed that a sample containing 2,4,6-trinitrobenzoic acid (TNBA) gave a cluster that appeared between 1.0 and 3.0 min, excluding peak at 3.5 min that was very likely due to oxygen. The peak heights of this cluster increased with the time that the solution was allowed to stand before analysis, clearly indicated the instability of this product. TNBA has been identified as an intermediate in the pathway for photocatalytic transformation of TNT [33], and it is likely responsible for the cluster observed in Fig. 5B. The two peaks (2-NT at 10.25 min and 3-NT at 11.33 min) were then identified by spiking but they did not match their respective elution times as found in Fig. 3C. The shift in elution times could be due to

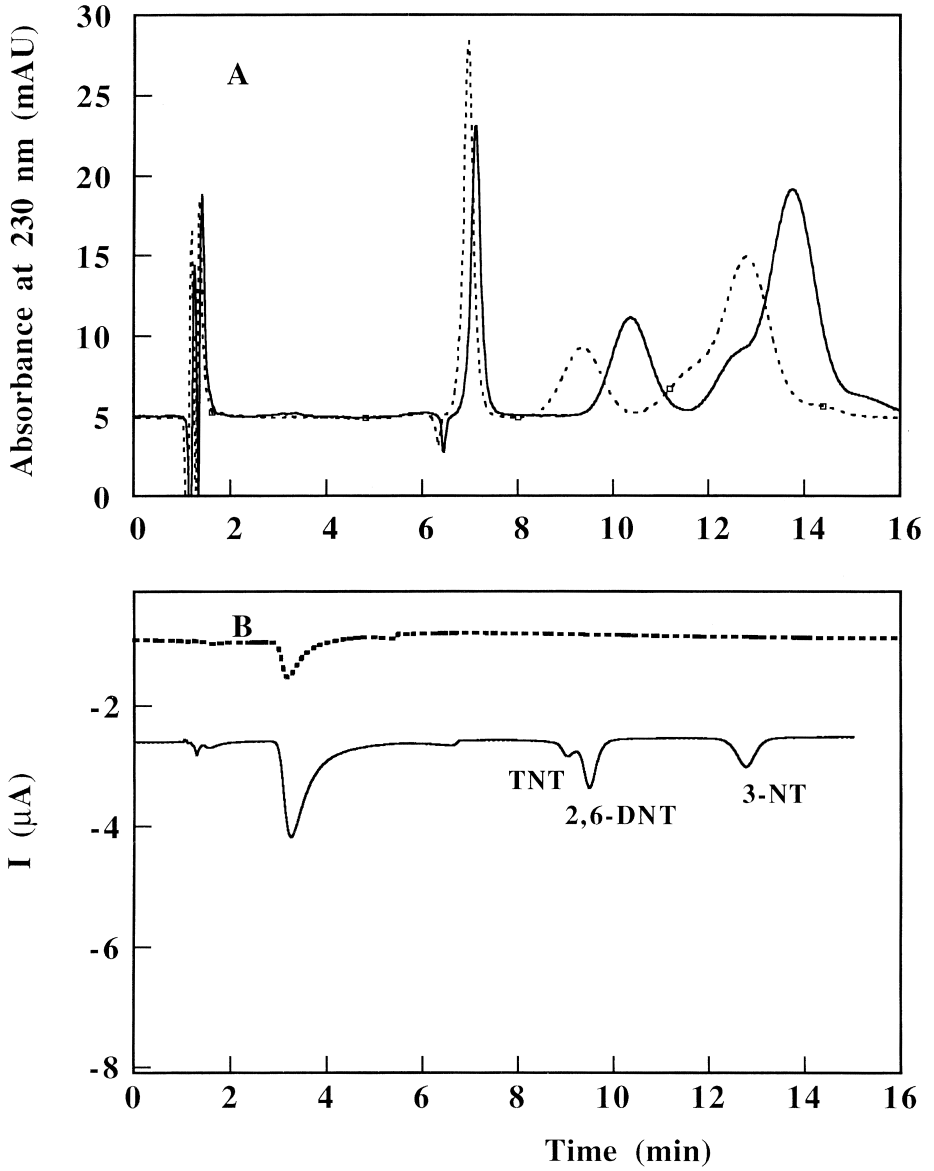

Fig. 4. Chromatograms (C_{18} column) of a garden soil extract (dotted) and a spiked extract (solid) as detected by UV at 230 nm (A) and amperometry (B). Mobile phase as in Fig. 3D and amperometric detection conditions are same as in Fig. 3.

the influence that unknown components exerted on the interaction between the analytes, the mobile phase, and the stationary phase. This effect was much less pronounced as the extract was diluted 30-fold to yield a chromatogram (Fig. 5C), showing better matched elution times, which allowed peak identification for TNT and 2,6-DNT. Peak heights were also used to determine the explosive contents, in good agreement with the values determined by the EPA method (Table 2). Simple filtration of a ground

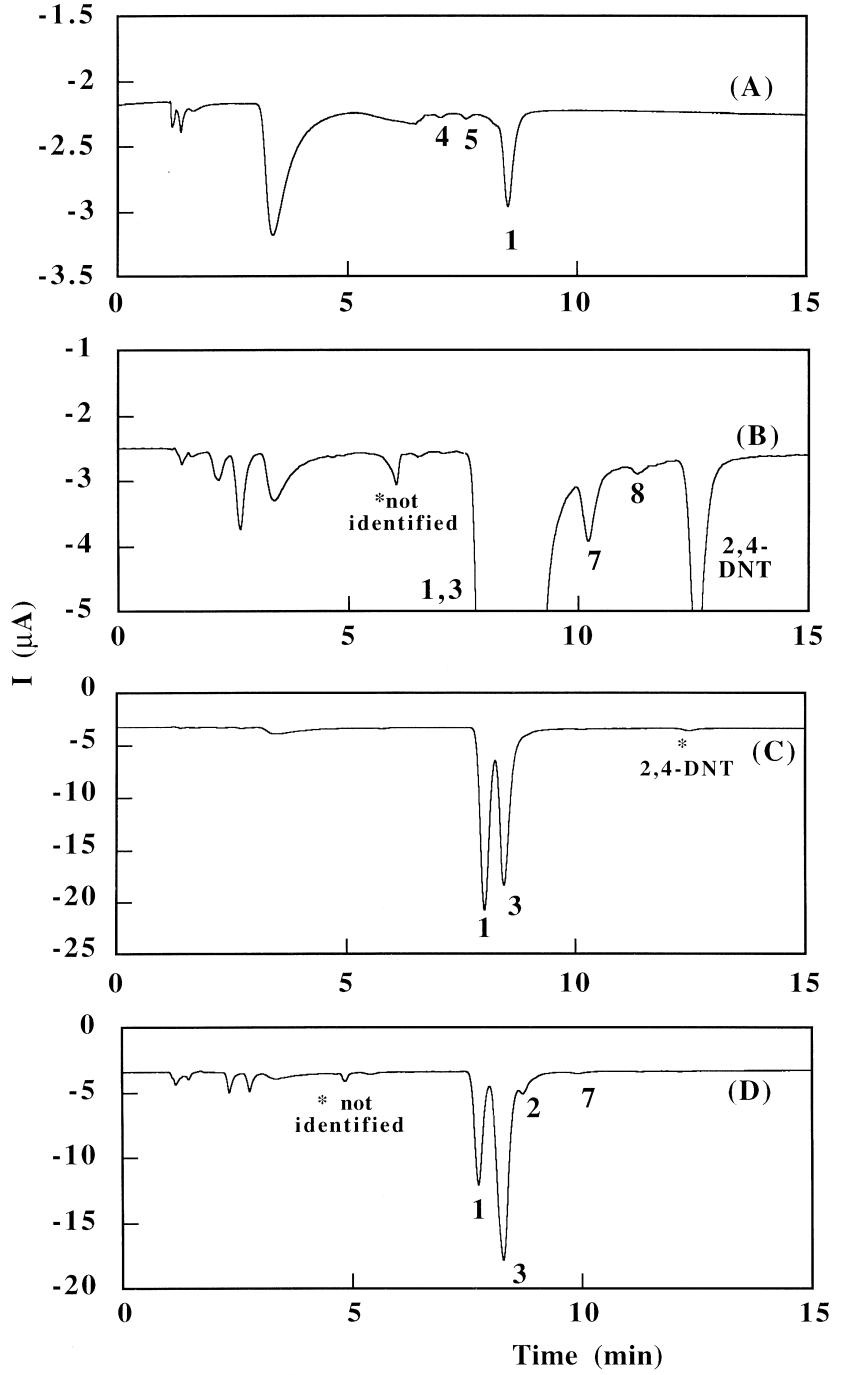

Fig. 5. Chromatograms (C_{18} column) of extracts; (A): slightly contaminated soil; soil 1 (B): highly contaminated soil; soil 2 (C) sample in (B) diluted 30-fold in acetonitrile–50 m*M* phosphate pH 5 containing 18 m*M* SDS (1:2, v/v) (D): chromatogram of a ground water sample. Mobile phase and detector are same as in Fig. 3D.

Table 2
Determination of the explosives in contaminated soil and ground water samples.[a]

Analytes	Concentration (μM)		
	Soil 1	Soil 2	Ground water
TNT	18.5 (18)	12 800 (12 800)	220 (210)
2-ADNT	3 (2.8)	–	–
4–ADNT	4 (4.3)	–	–
2,6-DNT	–	26 000 (26 000)	840 (850)
2,3-DNT	–	–	110 (120)
2-NT	–	110 (110)	4.5 (4.7)
3-NT	–	27	–

[a] Values in parentheses were obtained with the EPA method 8330.

water sample was sufficient to yield an appropriate sample leading to a chromatogram (Fig. 5D) that permitted concentration determination (Table 2). The same extraneous peaks appear to be the same as those observed with soil extracts.

3.4. Improvement of amperometric detection for HMX and RDX

Of comparable importance is the applicability of amperometric detection in LC for two other common

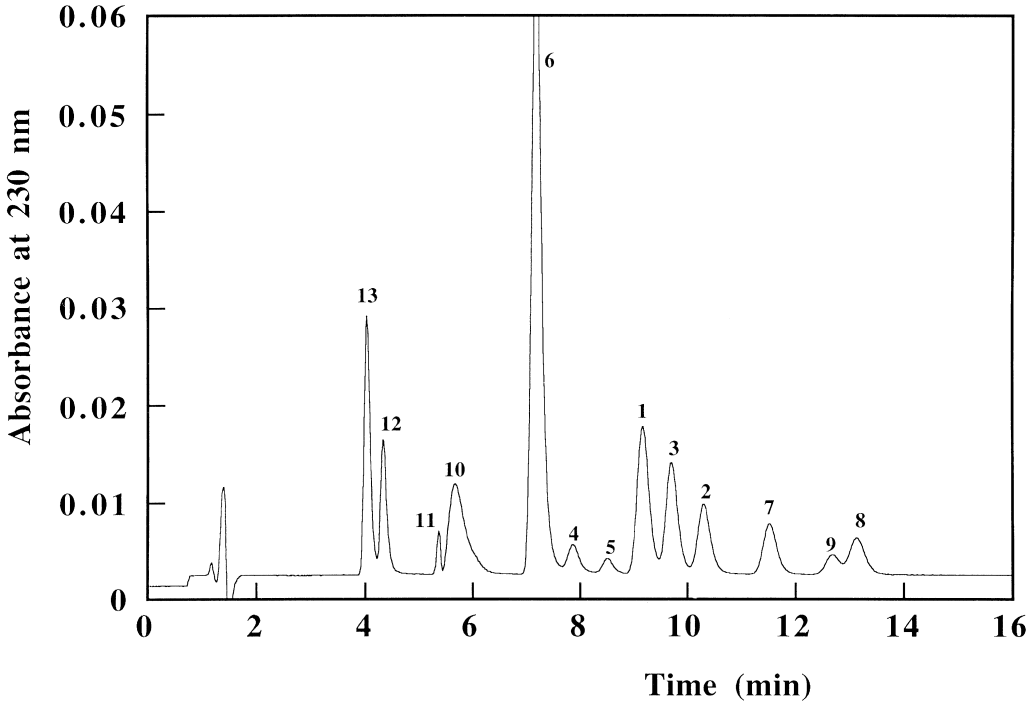

Fig. 6. Chromatogram (C_{18} column) of a solution containing eleven nitroaromatics and nitramines, HMX and RDX. Column and mobile phase as in Fig. 3D. UV detection at 230 nm.

explosives: HMX and RDX. An initial attempt using LC–UV detection revealed that the above ACN–phosphate buffer containing SDS could satisfactorily resolve both HMX and RDX from the other 11 nitroaromatic and nitramine explosives (Fig. 6). However, the LC system equipped with amperometric detection failed to detect the presence of HMX and RDX even at high concentrations (data not shown).

A series of experiments was then conducted to study the electrochemical reductive characteristics of these two compounds. As shown in Fig. 7A, the glassy carbon surface only yielded a reduction current at potentials more negative than −1.0 V for RDX or HMX and similar behavior was also observed for the platinum or gold working electrode. Evidently, an applied potential at −0.8 V was not sufficient for detection of either RDX or HMX using the glassy carbon electrode whereas a lower negative potential (−1 V) was not applicable in the LC–amperometric detection because this operating condition would entail the formation of hydrogen gas (from H^+ ions) to overlap any reduction activities. Further studies revealed that the cyclic voltammo-

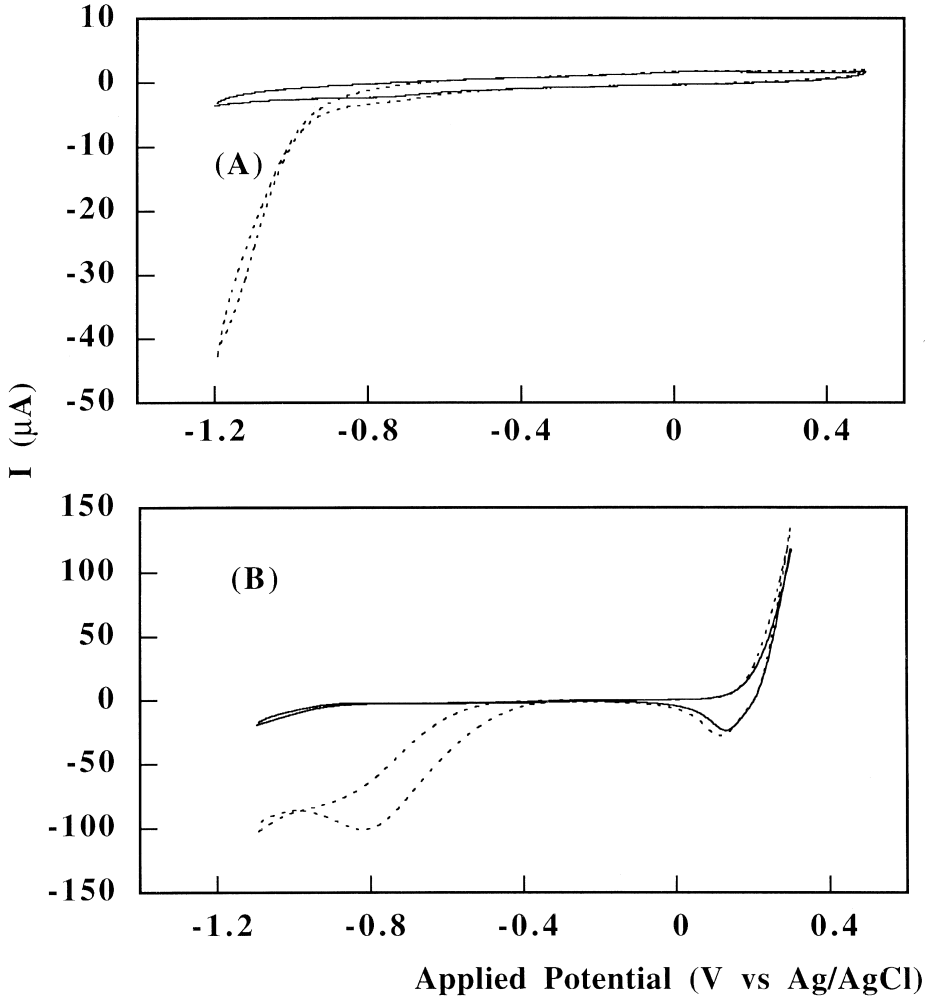

Fig. 7. Cyclic voltammograms (scan rate of 50 mV/s) obtained with deoxygenated 1:2 (v/v) acetonitrile–50 m*M* phosphate pH 5 containing 18 m*M* SDS (solid curves) and with the same milieu containing 1.9 m*M* RDX (dotted curves) as monitored with glassy carbon working electrode (A) and silver wire (B). Reference and counter electrodes are Ag/AgCl and Pt, respectively.

gram obtained with the silver electrode exhibited a pronounced reduction peak at −0.8 V vs. Ag/AgCl (Fig. 7B). The silver electrode exhibited the same stability and reproducibility as noted for glassy carbon and was used to analyze samples from contaminated sites and remediation processes. With silver as the working electrode in the LC–amperometric detection, all thirteen components including RDX and HMX were detected. However, this electrode material was less applicable for the analysis of 1,4-DNB since the low sensitivity of this target analyte obtained with the glassy carbon electrode became even more pronounced.

The sample and the mobile phase were well deaerated with nitrogen to expel oxygen, however, a series of repeated experiments confirmed that the silver electrode exhibited a high background current (baseline) in comparison to the glassy carbon electrode. There was also a periodic noise associated with the silver electrode and this baseline fluctuation did not correspond to the pump cycle and was not due to any defect of the LC system as confirmed by a separate run using the glassy carbon electrode. Polishing and conditioning the silver electrode (by maintaining at −0.7 V for 20 min while the mobile phase is flowing) initially eliminated the baseline fluctuation, however, this fluctuation was noted again after 30 min of operation. A mathematical filter inserted into the plotting software could easily eliminate the baseline fluctuation, but the raw data are presented in Fig. 8 to draw attention to this peculiar behavior. The first peak was attributed to oxygen, even nitrogen sparged samples would produce that peak because oxygen elimination could be achieved only with a closed-loop transfer. This peak was noted to diminish by adding phosphate buffer to the sample. Such a sample matrix effect normally manifested when the solvent front reached the detector (at 1.7 min in this case) and since no difficulty was encountered, the reason for the delay was not investigated.

4. Conclusions

Various electrode materials were studied to demonstrate the suitability of glassy carbon and the superior performance of silver for detecting explosives as separated by LC. The separation was improved significantly with the addition of SDS in

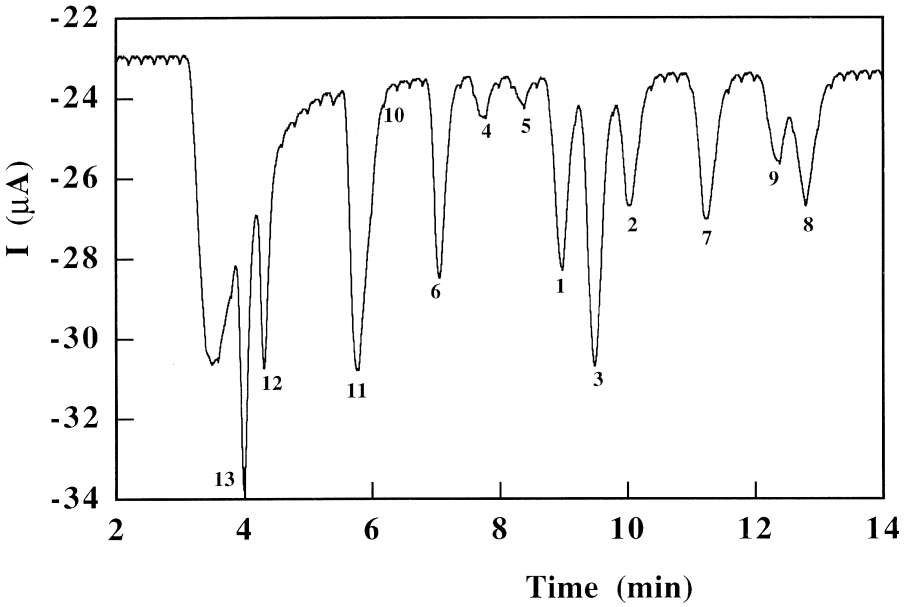

Fig. 8. Chromatogram (C_{18} column) of a solution containing eleven nitroaromatics and nitramines, HMX and RDX. Mobile phase as in Fig. 3. Amperometric detection with silver electrode poised at −0.8 V vs. Ag/AgCl in thin channel.

the mobile phase. Amperometric detection is better than UV detection for analyzing samples that contain UV-absorbing humic materials that are often found in soils that have supported vegetation. Liquid chromatography with amperometric detection using glassy carbon electrodes were able to detect explosive components in aqueous samples having low to mid-ppb concentrations. The procedure was demonstrated as suitable for direct application on ground water as well as simply extracted soils. The inability to detect HMX and RDX was remedied by using silver instead of glassy carbon as the detecting electrode. Amperometric detection as developed in this study offers better sensitivity compared with UV absorption, it could be useful for determining explosive concentrations in complex mixtures, to monitor leaching from soil, contamination of water ways and remediation processes.

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