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Determination and characterization of organic explosives using porous graphitic carbon and liquid chromatography–atmospheric pressure chemical ionization mass spectrometry

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Abstract

A new LC–MS method for the determination and characterization of three groups of commonly used organic explosives (nitroaromatic compounds, cyclic nitroamines and nitrate esters) was developed using a porous graphitic carbon (PGC) (Hypercarb) column. Twenty-one different explosive-related compounds – including 2,4,6-trinitrotoluene, its by-products and its degradation products – were chromatographically separated in a single analysis. This efficient separation facilitates the identification of the manufacturer of the explosive using the identified analytes as a fingerprint. A final, conclusive identification of the analytes can be obtained using LC–MS equipped with an atmospheric pressure chemical ionization (APCI) interface. Solvent effects on chromatographic behaviour were investigated, as were the effects of solvent mixtures and mobile phase additives. The number and the relative positions of the nitro groups within analyte molecules influence their order of elution; these effects were investigated. The data thus generated can be interpreted to support a hypothesis concerning the retention mechanism of nitro-containing compounds when using PGC. Limits of detection ranged from 0.5 to 41.2 ng. The new methodology described herein improves the sensitivity and selectivity of explosive detection. The effectiveness of the method is demonstrated by the analysis of soil samples containing explosives residue from test fields in Sweden and Afghanistan.

Keywords: Explosives; Porous graphitic carbon; LC–MS; APCI; TNT; RDX; HMX; CL20; PETN; HNS; Hypercarb

1. Introduction

Hazardous site characterization, forensic investigations, acts of terrorism or detection of landmines and unexploded ordnance (UXO) are scenarios that require the use of adequate analytical methods for the analysis of traces of energetic materials. Explosives can be classified in many ways, according to different criteria. Thus, explosives have been divided into high and low explosives, the former used as detonating charges and the latter as propellants. Explosives have also been classified according to their chemical structure. Most organic explosives contain nitro groups and are subdivided into nitroaromatic compounds, nitrate esters and nitroamines (respectively, Fig. 1A–C).

Common analytical techniques for the analysis of explosives include gas chromatography with electron capture [1], nitrogen phosphorus detection [2] or mass spectrometry [3] and high-performance liquid chromatography with ultraviolet or MS detection [4–10]. Other approaches, like amperometric gas-phase sensing [11] or optical techniques [12,13] have also been employed.

Explosives are unstable compounds and their polarity varies from moderate to high due to their nitro groups. These properties impose certain limitations on techniques used for their analysis, since explosives may be decomposed during the analysis or result in poor chromatographic retention, as well. Gas chromatography (GC) is suitable for the analysis of nitroaromatic compounds, but not for nitrate esters and nitroamines, which undergo thermal decomposition under these conditions. High-performance liquid chromatography (HPLC) would be a better alternative for the more unstable and polar explosives. However, the use of conventional stationary phases,

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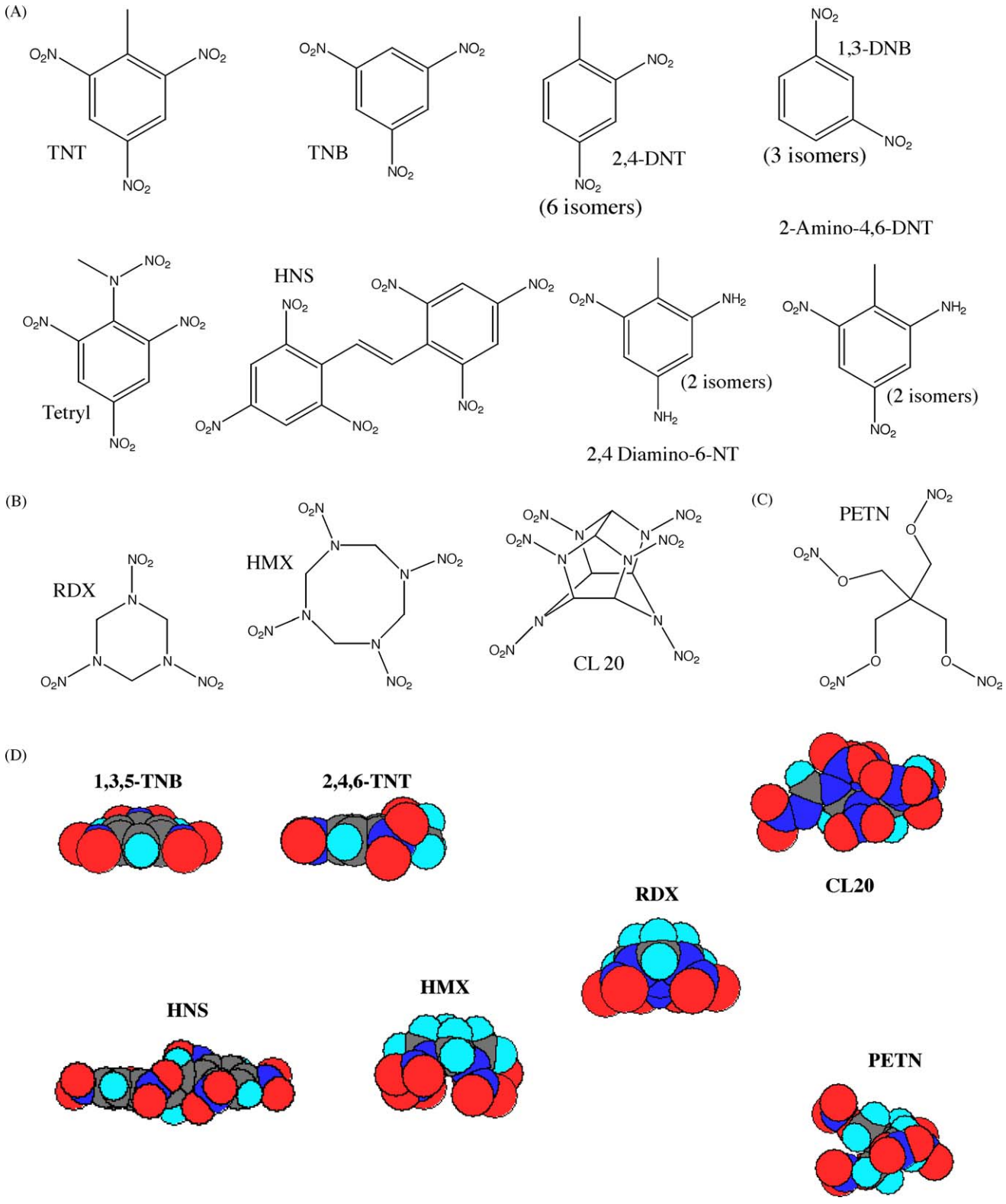

Fig. 1. Target analytes: (A) nitroaromatics; (B) cyclic nitroamines; (C) nitrate esters and (D) geometry of selected analytes as calculated using MOPAC.

e.g. C18, results in little or no retention of the most polar explosives. Additional difficulties may arise with the chromatographic behaviour of individual analytes when attempting analysis of a large number of individual explosive-related compounds.

Since its first description as a stationary phase for liquid chromatography [14,15], porous graphitic carbon (PGC) has been shown to have remarkable and attractive properties. This material is well known as a chemically stable and inert stationary phase [16]. Its ability to retain polar small molecules is superior

to that of silica-derivatized sorbents, [17–22] and it is suitable for use across the entire pH range. The retention mechanism of PGC differs from that of conventional reverse phase columns. The graphitic surface interacts with the analyte through π interactions and polar interactions with the lone-pair electrons available on the molecules. The extremely strong interactions between certain solutes and the rigid planar graphite surface are mainly due to specific interactions with the π electrons. Stereochemical differences between the analytes can give rise to great differences in the strength of these interactions. Another well-known characteristic of PGC is its utility in separating isomers that are difficult to separate with conventional reversed phase columns [23–28].

The suitability of this material for the use with supercritical phases has been investigated and applications have recently been developed [2,29,30]. The conductive properties of this material have been exploited to develop electrochemically modulated liquid chromatography (EMLC). This facilitates the manipulation of the donor acceptor character of PGC by changing the applied potential, resulting in a very powerful tool for the separation of organic and inorganic compounds [31–35]. A drawback of using EMLC is the requirement of more complex instrumentation.

In spite of these attractive qualities, PGC is not frequently used. This may be because it is difficult to predict the chromatographic behaviour of a given solute [17,36,37], and the retention mechanisms are not yet fully understood [38]. This can necessitate extensive optimisation of the mobile phase composition in order to separate mixtures of compounds when using PGC.

Fullerene-based columns have been used to analyse explosives and their performance was compared to that of an RP-C18 column [39]. This stationary phase exhibits chromatographic behaviour similar to PGC. On the other hand, this stationary phase consists of derivatised silica and therefore suffers from the effects of underivatized silanol groups as well as decreased pH and thermal stability relative to PGC.

Very recently, several authors have investigated certain anomalous behaviours of PGC [40,41] and have to some extent elucidated the redox chemistry responsible for these apparently non-reproducible chromatographic behaviours.

Due to the difficulties in using GC–MS, several research groups have been using atmospheric pressure ionization techniques in order to unambiguously identify explosives. Since the pioneering study using thermospray [42], LC–MS has proven to be a suitable technique for the analysis of explosive materials [6,8,43].

The objective of this work was to develop an analytical method suitable for most of the commonly used explosives and their derivatives. The target analytes included members of the major explosive subgroups, i.e. nitroaromatic compounds, cyclic nitroamines and nitrate esters. Using LC–APCI-MS with a PGC column, 21 different explosive-related compounds, exhibiting a wide range of polarity and thermal stability could be analyzed in a single procedure. The optimized method has been applied to soil samples from test fields in Sweden and Afghanistan.

2. Experimental

2.1. Chemicals and reagents

The chemicals and reagents used were water (HPLC isocratic grade), acetonitrile (HPLC isocratic grade), methanol (HPLC isocratic grade) and tetrahydrofurane (HPLC isocratic grade) supplied by J.T. Baker (Deventer, The Netherlands); Toluene (Chromasolv) by Riedel-de Haen (Seelze, Germany); trifluoroacetic acid (99.5%) by Apollo scientific limited (Derbyshire, UK); dichloromethane (LiChrosolv) and 1 M NaOH solution by Merck (Darmstadt, Germany).

Three groups of explosives were chosen for use as probe compounds: (I) *nitroaromatic compounds*: 1,3,5-trinitrobenzene (CAS 99-35-4) (TNB), 2,4,6-trinitrotoluene (CAS 118-96-7) (TNT), tetryl 2,4,6,*N*-tetranitro-*N*-methylaniline (CAS 479-45-8) (TNMA), 1,3,5-Trinitro-2-[2(2,4,6-trinitrophenyl)-vinyl]benzene (CAS 20062-22-0) (HNS), 1,2-dinitrobenzene (CAS 528-29-0) (1,2-DNB), 1,3-dinitrobenzene (CAS 99-65-0) (1,3-DNB), 1,4-dinitrobenzene (CAS 100-25-4) (1,4-DNB), 4-amino-2,6-DNT (CAS 19406-51-0), 2-amino-4,6-DNT (CAS 35572-78-2), 2,4-diamino-6-NT (CAS 6629-29-4), 2,6-diamino-4-NT (CAS 59229-75-3), 2,3-DNT (CAS 602-01-7), 2,4-DNT (CAS 121-14-2), 2,5-DNT (CAS 619-15-8), 2,6-DNT (CAS 606-20-2), 3,4 DNT (CAS 610-39-9), 3,5-DNT (CAS 618-85-9); (II) *cyclic nitroamines*: octogen or 1,3,5,7-tetranitro-1,3,5,7-tetrazacyclooctane (CAS 2691-41-0) (HMX), CL-20 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazatetracyclo[5.5.0.0^{5,9}.0^{3,11}]dodecane (CAS 135285-90-4) and hexogen or 1,3,5-trinitro-1,3,5-triazacyclohexane (CAS 121-82-4) (RDX); (III) *nitrate esters*: pentaerythritol tetranitrate 1,3-bis-nitrooxy-2,2-bis-nitrooxymethyl-propane (CAS 78-11-5) (PETN).

All the standards were supplied by Promochem Standard AB (Wesel, Germany), except for HNS, TNT, Tetryl, Pentyl, RDX, HMX, CL20, PETN supplied by FOI (Tumba, Sweden) and 1,2-DNB, 1,3-DNB, 1,4-DNB supplied by Merck (Darmstadt, Germany).

It was observed that when using a solvent containing an alcohol or a ketone, TNT was degraded. This phenomenon was not instantaneous, which is the case when a base is present in the solvent, but the degradation was significant after a few days. For this reason, reference compounds were dissolved in acetonitrile to a concentration of 0.1 μmole/ml. An external reference standard was obtained by injecting 25 μl of this solution. MOPAC PM3 was used for the geometry studies at the PM3 level of theory on RDX, TNB, TNT and HNS (Fig. 1D). CS ChemDraw Ultra 5.0 by Cambridge SoftCorporation (Cambridge, MA, USA).

2.2. High-performance liquid chromatography-MS and UV systems

A 2695 Quartenary HPLC System by Waters (Milford, MA, USA) was used to deliver the solvent mixture. The complete separation of all the analytes, including the DNT isomers, was carried out on a (250 mm × 4.6 mm I.D., 5 μm particles) Thermo

Table 1
Liquid chromatography gradient and APCI interface gas flow parameters used for the complete separation of DNT and DNB isomers

Full isomer separation gradient system				
Time	Flow rate (ml/min)	Solvent A%	Solvent B%	Solvent C%
0	0.9	37	63	0
5	0.9	37	63	0
10	0.9	28	72	0
25	0.9	0	98	2
30	1.1	0	50	50
31	1.1	0	0	100
34	1.4	0	0	100
42	1.4	0	0	100
42.5	1.4	0	100	0
43.5	1.4	37	63	0
43.5	0.9	37	63	0
50	0.9	37	63	0

Quest (Cheshire, UK) Hypercarb PGC column using a gradient mobile phase.

The compositions and flow rates of the mobile phases used during gradient elution are reported in Table 1, being (A) 49.5% water, 9.9% methanol, 39.6% acetonitrile and 1.0% dichloromethane; (B) 73% methanol, 25% acetonitrile and 2% toluene; (C) 25% acetonitrile and 75% toluene.

Fast analysis can be carried out using the conditions described in Table 2. A shorter column was used in this case 100 mm × 3 mm I.D. (5 μm). Under these conditions, good separation was obtained for all the analytes except for 3,4-DNT, 2,3-DNT, 1,3-DNB and 1,4 DNB.

In both cases, the temperature of the column was kept at 30 °C using a Waters temperature control module.

When injecting dirty samples such as soil extracts, it was necessary to periodically (every 50–100 soil samples) clean the PGC column to maintain chromatographic performance. First the column was flushed with a mixture of 100 ml THF (tetrahydrofuran)/water (1:1) containing 0.1% trifluoroacetic acid (TFA). It was then, flushed with 100 ml THF/water (1:1) containing 0.1% NaOH. Thereafter, the column was flushed with 100 ml THF/water (1:1) containing 0.1% TFA. Finally, it was flushed with 100 ml methanol/water 95:5.

Table 2
Liquid chromatography gradient and APCI interface gas flow parameters used for the fast analysis of explosives

Fast analysis gradient conditions				
Time	Flow rate (ml/min)	Solvent A%	Solvent B%	Solvent C%
0.00	0.65	32	68	0
3.20	0.65	32	68	0
5.20	0.8	22	78	0
6.00	0.8	22	78	0
8.00	0.8	0	40	60
8.40	0.9	0	0	100
12.00	0.9	0	0	100
12.20	0.65	32	68	0
17.00	0.65	32	68	0

Column characteristics and the composition of phases A–C are reported in Section 2.

The mass spectrometer used was a Bruker Esquire 3000+ ion trap mass spectrometer by Bruker Daltonics (Bremen, Germany) equipped with an APCI interface. APCI Interface conditions were set to the following values: drying temperature 225 °C, vaporizer temperature 300 °C, HV 4000 V.

The nebulizer gas pressure (NG) and drying gas flow rate (DG) were varied during gradient elution as follows: from 0 to 29.41 min, NG 70 psi, DG 3.0 l/min; from 29.41 to 45 min, NG 70 psi, DG 1.0 l/min; from 45 to 50 min, NG is 70, DG 3,0. For the fast analysis gradient from time 0 to 8.74 min, NG 60 psi, DG 1.0 l/min; from 8.74 to 15.69 min, NG 25 psi, DG 1.0 l/min; from 15.69 to 17 min, NG is 60 psi, DG 1.0 l/min.

UV detection was conducted by using a Waters UV Detector Model 996 photodiode array detector. The best signal-to-noise ratio was found at 290 nm.

The software used to control the HPLC pumps, UV detector and the LC–MS detector was Hystar, Hyphenation Star NT Version 2.2 by Bruker Daltonics.

2.3. Soil samples extraction

Microwave-assisted extraction (MAE) of nitroaromatics from soil samples was done with an Ethos E, Touch Control Microwave Solvent Extraction Labstation by Milestone (Bergamo, Italy). The solvent used for MAE was 25 ml of 0.1 M sodium phosphate pH 8 buffer. This is well suited for inducing vibrations in substances since water is highly dipolar. The extraction conditions were optimized using a factorial design with a model treating three components: temperature, energy and time [44]. Optimal conditions involved an initial ramp of 4 min duration using a maximum of 400 W to reach the extraction temperature of 80 °C. The temperature was then held for 5 min at 80 °C using a maximum of 300 W. The extract from the MAE was filtered through a 5 μm porous polytetrafluoroethylene (PTFE) filter.

Solid-phase extraction (SPE) was used in a clean-up and concentration step following MAE. The adsorbent, Abselut NEXUS from Varian (Walnut Creek, CA, USA), a patented copolymeric SPE material with a combination of hydrophilic and lipopholic moiety, was purchased as single pre-packed 30 mg adsorbent cartridges with 10 ml reservoirs. The phase was washed by rinsing with 10 ml of acetone and then 5 ml of buffer before the sample was applied. After sample application the phase was rinsed with heated buffer (65 °C) and then dried under a gentle stream of nitrogen, with vacuum applied to the column for 10 min. The nitroaromatics were then eluted with portions of toluene at 50 °C, to give a total volume of 2 ml; the SPE cartridge was maintained at 50 °C during this elution. The SPE was then allowed to cool down to room temperature and a total volume of 1 ml of acetone was added in portions. The elution was performed with no vacuum applied until only the solvent adsorbed onto the phase remained. The remaining solvent was then eluted under vacuum until the solid phase was dry. The acetone was evaporated from the toluene/acetone mixture using a gentle stream of nitrogen. Fifty microliters of ethylene glycol was added to the toluene extract and then evaporated in the same way until only the keeper remained in the vial. The residue

was dissolved in 200 μl of acetonitrile. Finally 100 μl of this solution was injected into the LC–MS system. The recovery for all nitroaromatics was almost 100%, except for the two most polar compounds, 2,6-diamino-4-nitrotoluene and 2,4-diamino-6-nitrotoluene, which exhibited a recovery of approx. 60%. To determined the extraction efficiency, the soil sample was spiked with a nitroaromatic standard solution and analyzed with GC ($n = 10$, RSD < 10%).

3. Results and discussions

3.1. Retention mechanisms and the influence of the solvents in the chromatographic behaviour of PGC

Chromatography of explosive nitro compounds is of great interest due to the insights it affords into the retention mechanisms of PGC. In the case of the nitroaromatics, the presence of different numbers of nitro groups attached to the aromatic ring, along with varying substitution pattern and their electronic and structural properties generate a very interesting class of polar non-ionic species. They can be used to clarify the role of the so-called "polar retention effect" on PGC. The retention mechanism of PGC based on chromatographic results has been discussed by several authors for a variety of compounds and conditions [17,24,36,45–48].

Many factors seem to influence the chromatographic behaviour of PGC; these can be summarized as follows: (1) solvophobic effects and dispersion forces – these dominate with non-polar compounds, and cause the PGC to behave as a reversed phase. (2) The polar retention effect on graphite (PREG) – this is observed with polar compounds and results in increased retention as polarity increases. (3) Steric effects arising from the interaction of the compounds with the flat graphitic surface – these facilitates separation of closely related species. (4) The presence of ionic species in the mobile phases – these have been shown to have significant effects on the chromatographic behaviour of ionic species and molecules containing certain functional groups.

There are three principal factors affecting retention of nitro compounds: charge-induced interactions between the nitro groups and the PGC surface, steric effects in the specific molecule, and solvent effects. RDX and TNB have similar structures, with three nitro groups organized into a six-membered ring. The major difference between the two is that TNB is aromatic while RDX is not. TNB exhibits a much higher retention due to the flatness of the aromatic ring, which allows strong interactions between the nitro groups and the graphitic surface [49,50] (Fig. 1D). This difference in geometry also explains the short retention times for the other non-aromatic analytes in this investigation, i.e. HMX, PETN and CL 20. The impact of the steric hindrance regarding the retention on PGC is illustrated by TNB and TNT. Both are aromatic compounds with a similar structure, except for one methyl group attached to the TNT molecule. Steric clashing between the methyl group and

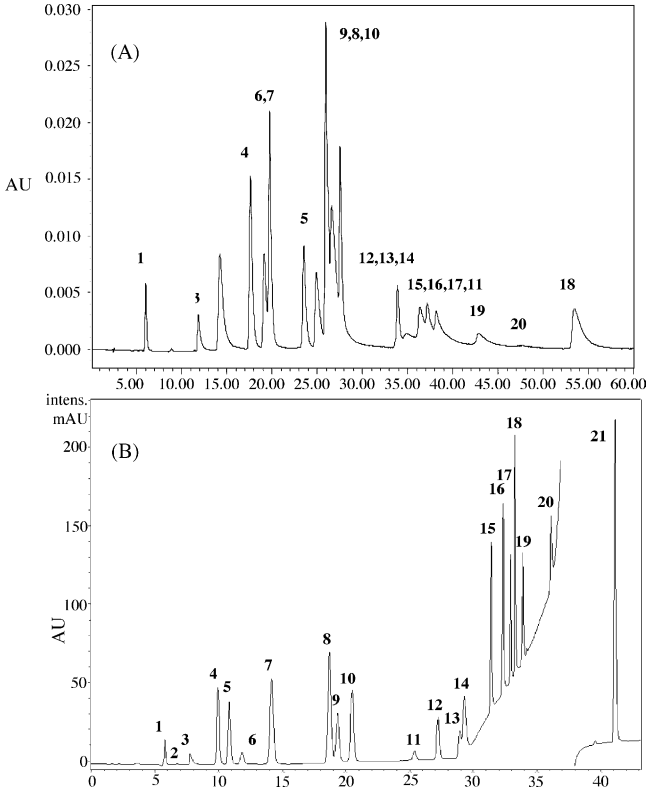

Fig. 2. Effects of toluene on peak shape and retention times of organic explosives using a PGC column (UV detection 290 nm). (A) Gradient elution using a water–acetonitrile–methanol system: (1) RDX; (2) PETN [not injected in (a)]; (3) HMX; (4) 1,2-DNB; (5) 2,4-diamino-6-NT; (6) CL 20; (7) Tetryl; (8) 2,6-DNT; (9) 3,4-DNT; (10) 2,3-DNT; (11) 2,6-diamino-4-NT; (12) 4-amino-2,6-DNT; (13) 1,3-DNB; (14) 1,4-DNB; (15) 2,5-DNT; (16) 2,4-DNT; (17) TNT; (18) 2-amino-4,6-DNT; (19) 3,5-DNT; (20) TNB; (21) HNS [not eluted in (A)]. (B) Gradient elution using a mobile phase containing toluene (see Section 2). Numbering same as in (A).

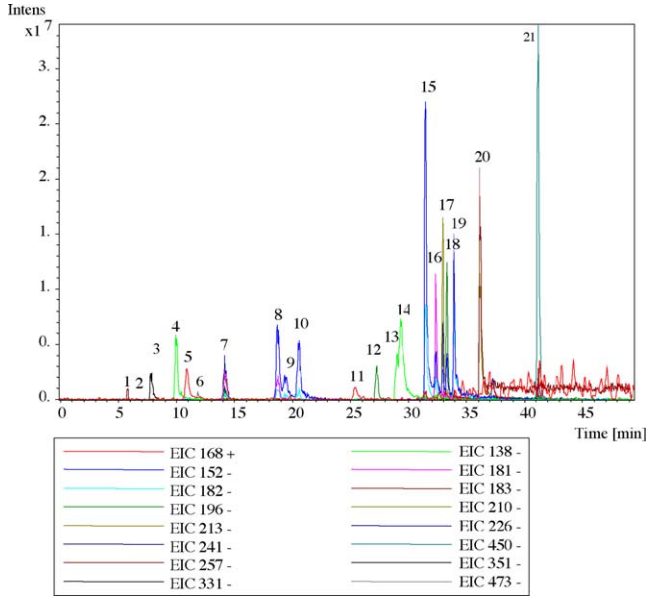

Fig. 3. LC–MS extracted chromatographic profiles of common organic explosives on PGC column (1.5–3.3 nmol injected). (1) RDX; (2) PETN; (3) HMX; (4) 1,2-DNB; (5) 2,4-diamino-6-NT; (6) CL 20; (7) Tetryl; (8) 3,4-DNT; (9) 2,3-DNT; (10) 2,6-DNT; (11) 2,6-diamino-4-NT; (12) 4-amino-2,6-DNT; (13) 1,3-DNB; (14) 1,4-DNB; (15) 2,5-DNT; (16) 2,4-DNT; (17) TNT; (18) 2-amino-4,6-DNT; (19) 3,5-DNT; (20) TNB; (21) HNS.

the two adjacent nitro groups of TNT weakens the solute's interaction with the graphitic surface, decreasing the retention time of TNT. Solvent effects are also important. Using acetonitrile and methanol as the organic modifier, these compounds elute poorly and with unacceptable peak shapes (Fig. 2A). In our previous studies, it was necessary to add small amounts of ionic species [9] or toluene [10] to elute TNT and related compounds from the PGC column. In this study an increasing amount of toluene was used in order to improve the peak shape and elute the most strongly retained compounds (Fig. 2B). In order to elute HNS when using a PGC column, a very high percentage of toluene (75%, v/v), in the mobile phase is required. This is necessary because HNS is scarcely soluble and is a planar molecule with two aromatic rings in a conjugated aromatic system with six electron-withdrawing nitro groups. The planar structure allows this very electron-poor aromatic system to form very strong interactions with the graphite surface.

The retention of the much more polar degradation products of TNT, such as amino and diamino derivatives, is another interesting feature of PGC. These compounds, especially the diamino derivatives are retained poorly under conventional RP conditions but are strongly retained by PGC. Adding toluene weakened these retaining interactions, allowing elution of these basic compounds with a symmetric peak shape. This effect can be seen in Fig. 2, where the addition of toluene inverts the order of elution of TNB and 2-amino-4,6-DNT.

Raising the temperature improved the peaks' shapes but had a negative effect on the separation of DNT and DNB isomers. Under the optimized conditions, all the target analytes were separated.

A faster analysis can be performed using the conditions reported in Table 2. Under these conditions, 1,3-DNB and 1,4-DNB completely co-elute. 3,4-DNT and 2,3-DNT also overlap but these isomers can nevertheless be distinguished because they ionize in different ways (see Table 3 and Section 3.2) and generate different *m*/*z* signals.

A useful feature of PGC is that large volumes of organic solvents can be injected, which can improve the limit of detection. In this study, very large amounts of methanol or acetonitrile could be used – with the soil extracts, 100 μl of acetonitrile was injected without any peak broadening.

For purity test of common analysis it is possible to use UV detection and confirmatory analysis by LC–MS. Limits of detection by UV at 290 nm are also reported in Table 3. The ability to effect chromatographic separation of all the isomers of the TNT by-products is important in characterizing a batch of explosives and can assist in identifying its producer.

3.2. LC–APCI-MS and UV analysis of explosives

Negative APCI is commonly used for the detection of nitroaromatic compounds and the fragmentation patterns of several explosives have been reported [5,6,51,52]. As previously observed by other authors [8,53], ionization of nitroaromatic compounds using LC–APCI-MS interface can occur via an electron-capture mechanism rather than a dissociative mech-

Table 3
Retention times, ionization mode, "in source" fragmentation and limits of detection using APCI LC–MS and UV

RT (min)	Analyte	M.W.	Ionization	Detected ions using negative APCI (relative abundance)	LODs MS (ng inj.)	LODs UV (ng inj.)
5.9	RDX	222.12	Cl^- adduct	259 (40), 257 (100)	3.2	11.0
6.9	PETN	316.00	Cl^- adduct	353 (29), 351 (100)	41.2	141.0
7.9	HMX	296.16	Cl^- adduct	333 (35), 331 (100), 147 (5)	0.7	20.0
10.0	1,2-DNB	168.11	–	168 (7), 138 (100), 108 (18)	11.1	2.9
10.9	2,4-Diamino-6-NT	167.17	+	168 (100)	12.4	3.6
11.9	CL 20	438.19	Cl^- adduct	475 (36), 473 (100), 235 (17), 233 (31)	2.6	20.4
14.2	Tetryl	287.14	–	288 (16), 241 (100), 237 (28), 226 (30), 213 (56), 196 (18), 181 (49), 169 (6), 151 (6), 135 (11), 107 (4)	5.6	2.7
18.7	3,4-DNT	182.13	–	182 (11), 181 (49), 152 (100), 122 (8)	10.3	2.3
19.4	2,3-DNT	182.13	–	182 (20), 152 (100), 122 (12)	15.2	2.7
20.6	2,6-DNT	182.13	–	182 (27), 152 (100), 122 (25)	7.3	4.2
25.5	2,6-Diamino-4-NT	167.17	+	168 (100)	37.3	21.3
27.2	4-Amino-2,6-DNT	197.15	–	197 (32), 196 (100), 167 (64), 149 (10)	39.0	5.9
29.0	1,3-DNB	168.11	–	168 (46), 138 (100), 108 (4)	32.8	9.2
29.3	1,4-DNB	168.11	–	168 (43), 138 (100), 108 (7)	17.7	3.7
31.4	2,5-DNT	182.13	–	182 (32), 152 (100), 122 (6)	3.7	0.7
32.3	2,4-DNT	182.13	–	182 (21), 181 (100), 165 (64), 152 (36), 137 (31, 135 (31), 107 (7)	34.7	2.4
33.0	TNT	227.13	–	227 (50), 226 (50), 210 (100), 197 (69), 180 (5), 167 (15), 152 (13), 137 (9), 124 (3), 109 (3)	4.0	3.1
33.9	3,5-DNT	182.13	–	182 (82), 152 (100), 122 (5)	7.2	1.5
33.3	2-Amino-4,6-DNT	197.15	–	196 (100), 180 (23), 179 (5), 178 (13), 167 (12), 165 (8), 152 (9), 150 (17), 136 (3)	7.3	4.1
36.0	TNB	213.10	–	213 (86), 183 (100), 167 (2), 125 (4)	11.4	8.1
41.1	HNS	450.23	–	450 (100), 241 (6)	0.5	1.6

anism (most commonly deprotonation). Under operating conditions, this phenomenon occurred mainly with HNS, TNB and 3,5-DNT. It has been observed that ionisation of non-aromatic nitrates in the presence of dichloromethane gives rise to chlorinated adducts. After the addition of dichloromethane to the mobile phase, the non-aromatic nitrates form a number of chloride and nitrate adducts. The use of at least 1% of dichloromethane is necessary in order to obtain chloride adducts exclusively and thus simplify the spectra. The use of larger amounts of dichloromethane does not improve the ionization of non-aromatic nitrate compounds and negatively affects the ionization of the aromatic. Because of these reasons and because these species are eluted rapidly, dichloromethane was added only to phase A. In Table 3, the relative abundance of adducts and fragments obtained in the experimental conditions are reported and used to identify the target analytes.

Positive ionization was used only to ionize the most basic compounds such as the di-amino species. Simultaneous acquisition of positive and negative ionization chromatograms was possible without significant loss of sensitivity and with acceptable peak definition (Fig. 3).

Analyses were performed at various APCI ion source temperatures to determine the optimal ionisation temperature. TNT, HMX, CL20, HNS, Tetryl, 4-amino 2,6-DNT, 2-amino-4,6-DNT ionized most efficiently between 350 and 375 °C. All the other analytes in this investigation were ionized between 225 and 300 °C, due to their lower thermal stability. An acceptable ionisation temperature for use in a general analytical method using APCI was found to be 300 °C. The presence of water in the first part of the gradient necessitated the use of an elevated nebulizing pressure and drying gas flow rate. In the second part of the gradient, these values were reduced in order to improve the sensitivity. When the toluene content was increased in the last part of the gradient, the gas flow rate was further reduced.

3.3. Linearity, reproducibility and detection limits

The linearity and reproducibility of the MS detection were investigated by consecutively injecting the analyte mixture at five different concentrations (with a duplicate at each point). The linear range for all the analytes was in the range of 0.03–2.5 nmol. The correlation coefficient varied in the range of 0.980–0.9999 for all the investigated analytes, except for HMX which exhibited a correlation factor (r^2) of 0.9770.

The robustness of this method has been verified over a period of several months. Reproducibility of the retention times was determined with 10 ($n = 10$) injections. The RSDs of the peaks retention times were in the range of 1–10%. After injection of large amount of real soil samples, differences in the retention times were observed. This problem was solved by changing the pre-column after about 50 injections. After a long-time usage a washing procedure was applied as described in the experimental

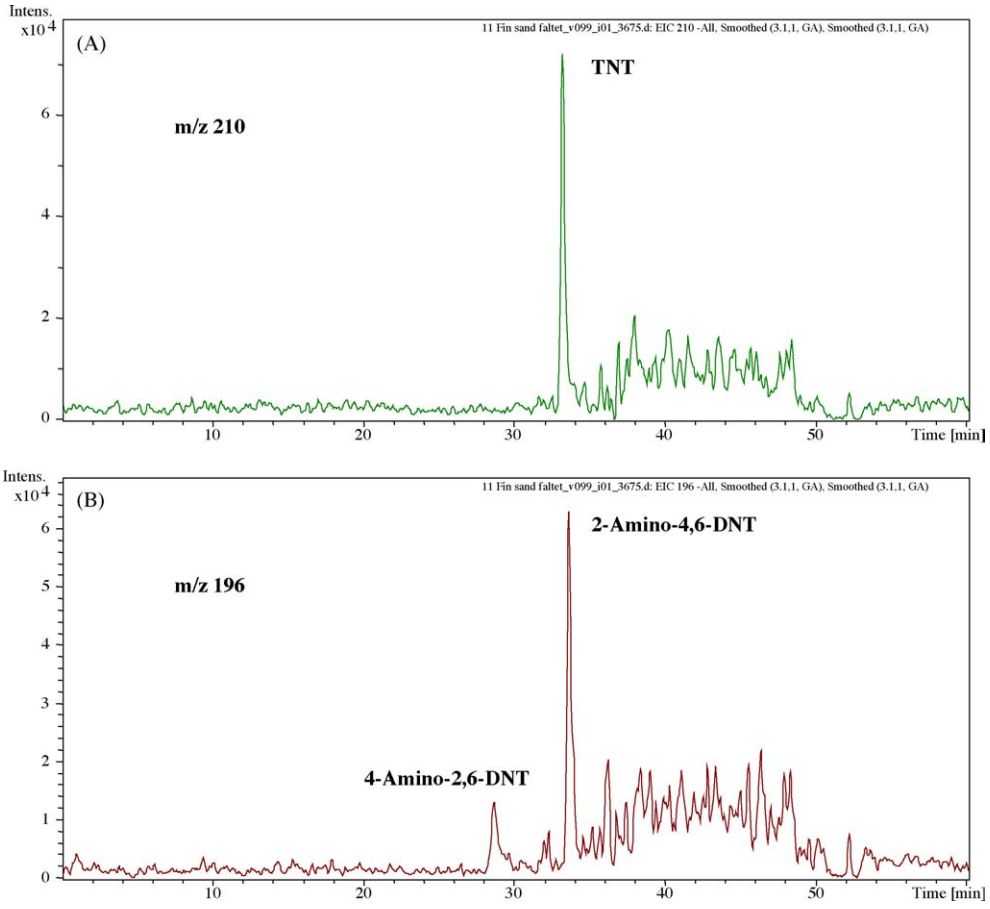

Fig. 4. Analysis of soil sample extracts from a test field in Sweden. Amount detected: TNT 23 ng; 4-amino-2,6-DNT 10 ng; 2-amino-4,6-DNT 9 ng.

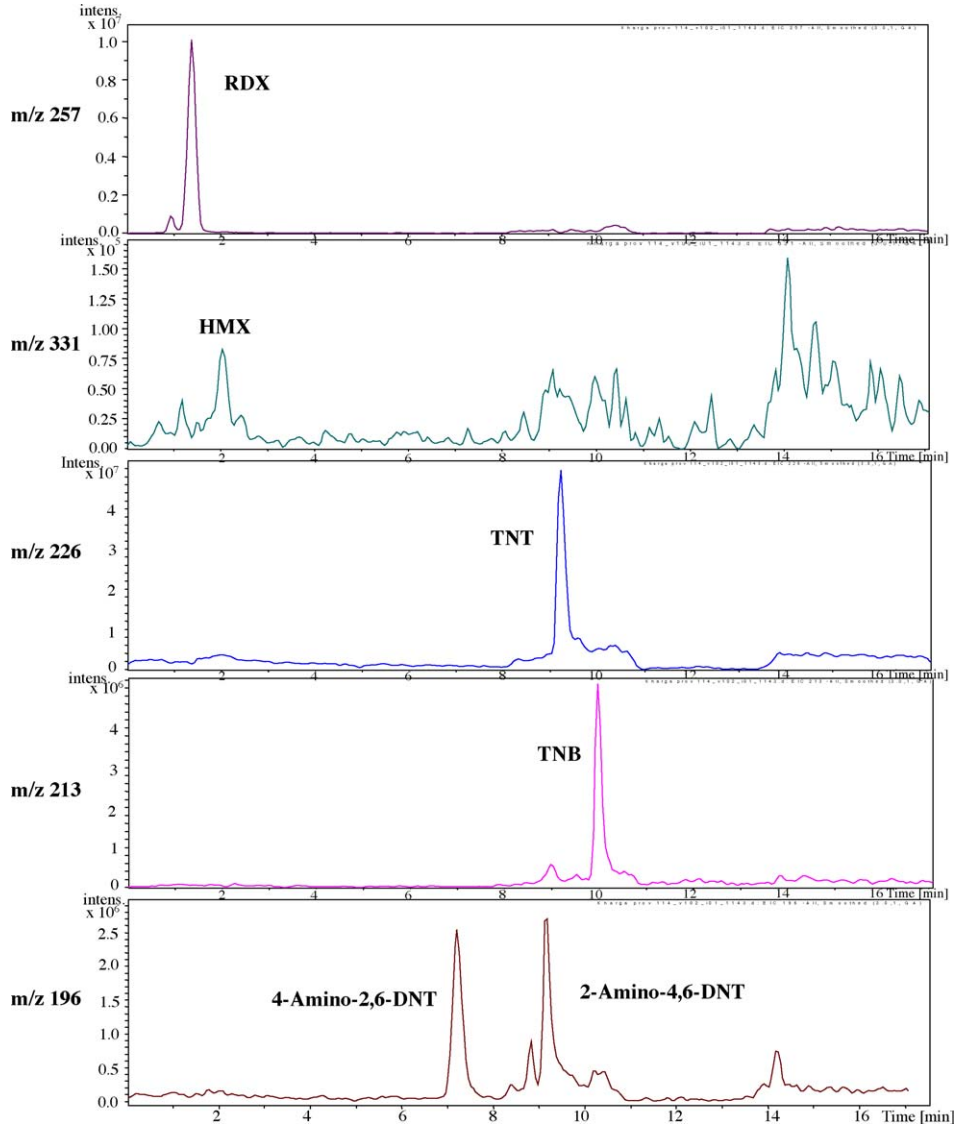

Fig. 5. Analysis of soil sample extracts from a landmine test field in Afghanistan. Amount detected: RDX 200 ng; HMX 10 ng; TNT 6000 ng; TNB 200 ng; 4-amino-2,6-DNT 770 ng; 2-amino-4,6-DNT 170 ng.

section. After the washing, chromatographic performances of PGC were fully reestablished.

The LOD for each analytes was calculated as the amount that produces a signal which is three times the standard deviation of the noise signal and is reported in Table 3.

3.4. Real soil samples

The applicability of the overall method was demonstrated by the analysis of real soil samples from test fields in Sweden and Afghanistan. In such cases it was necessary to analyse many samples, and it was more important that the analysis be fast and cheap than that it be able to effect complete resolution of various DNT isomers. Where this is the case, a shorter gradient program can be applied using a shorter column, as described in Section 2.

The chromatogram shown in Fig. 4 shows the analysis of the soil sample from Sweden and the peaks corresponding to 4-amino-2,6-DNT, 2-amino-4,6-DNT and TNT. This soil sample was collected from the surface soil, 10 cm above the buried charge, containing TNT. The charge has been in the soil for 3 years; therefore, two degradation products could be detected.

The chromatogram in Fig. 5 comes from the analysis of a soil sample extract collected in a test field in Afghanistan, used for training mine dogs. This chromatogram demonstrates the presence of TNT, HMX, RDX, 4-amino-2,6-DNT, 2-amino-4,6-DNT and TNB in the same soil sample.

4. Conclusions

The analytical methodology developed in this study demonstrates the efficiency of PGC in separating the most commonly used explosives and related compounds, assisting the identification of these analytes in a number of different matrices. Because retention by PGC arises from a combination of different interactions, it can be tuned by adjusting the composition of the mobile

phase. The use of LC–MS in combination with PGC represents an improved alternative to existing analytical methods based on derivatized silica reversed phase columns. The use of a high percentage of toluene in the mobile phase allows the elution of the most strongly retained compounds from the PGC surface and improves APCI-MS detection. The robustness, reproducibility and sensitivity have all been tested and found to give excellent results.

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