



High performance liquid chromatography of 1,1-diamino-2,2-dinitroethene and some intermediate products of its synthesis

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ABSTRACT

1,1-Diamino-2,2-dinitroethene (DADNE, FOX-7) is a novel explosive with low sensitivity and high performance. The unique combination of the valuable properties is a result of the structure of the compound. The molecular packing of DADNE consists of layers with strong intermolecular hydrogen bonds which stabilize the molecule.

In the paper, the results of research the purity of DADNE in different recrystallization conditions and some intermediate products of its synthesis were presented. High performance liquid chromatography (HPLC) method based on the porous graphitic carbon (PGC) column packing material has been developed. Two variants of mobile phases in different pH values: acetonitrile–water and methanol–water with ammonia (NH₃) and with trifluoroacetic acid (TFA) were used. The probable mechanism of interaction between the analyte, the stationary phase, and the mobile phase was suggested.

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1. Introduction

The purpose of the ongoing research on energetic materials is to produce more powerful, safer and environmentally friendlier explosives that fit into the new action plan of the defense forces. This directs the research towards compositions with lower sensitivity, which improves the ammunition safety and might be use in international operations.

1,1-Diamino-2,2-dinitroethylene (DADNE, FOX-7) is an explosive that has rendered much interest. The interest in the substance, from both theoretical and practical standpoints, lies in its applicability in several areas thanks to its low sensitivity combined with its relatively high performance [1,2]. It is characterized as a promising high energy density material with low shock sensitivity and better thermal stability (decompose only above 220 °C) [3]. DADNE has the same molecular stoichiometry as hexogen (RDX) and octogen (HMX) that are among the most effective and widely used explosives and monopropellants. Consequently, DADNE would yield the same high value of gaseous products per gram of compound upon complete decomposition as RDX and HMX (Fig. 1).

DADNE was first synthesized in 1998 by Latypov et al. [4–6]. Until now three different routes to prepare DADNE have been disclosed. There are a few excellent recent reviews on its synthesis [7].

The main aim of the present work was to find a methodology of qualitative and quantitative analysis of compounds that could be used to control DADNE synthesis. Unfortunately, it is impossible to find information about separation of DADNE in the literature. Most organic explosives contain nitro groups and are subdivided into nitroaromatic compounds, nitrate esters and nitroamines. Due to these nitro groups explosives are unstable compounds and their polarity varies from moderate to high. 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 [8–10], 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 [11]. However, the use of conventional stationary phases, e.g. C18, results in little or no retention of the polar DADNE and related explosives.

In the present method a new packing material based on porous graphitic carbon (PGC Hypercarb) is used as the stationary phase for the liquid chromatographic separation of compounds under investigation. The properties of Hypercarb have been utilized to provide

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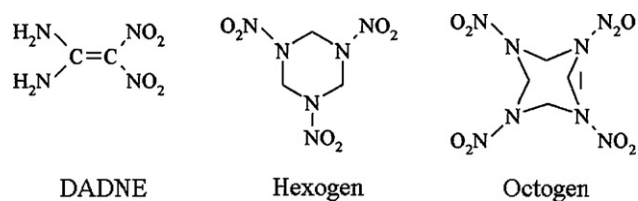


Fig. 1. Structure of DADNE, RDX (hexogen) and HMX (octogen) molecules.

solutions to a wide range of analytes which might normally be considered as problematic in HPLC separations [12–14]. Hypercarb provides unique retention and separation of very polar compounds. The surface of Hypercarb is stereoselective with the capability to separate geometric isomers and other closely related compounds. Hypercarb is stable throughout the entire pH range 1–14, and is not affected by aggressive mobile phases. Its compatibility with all solvent systems enables separation of a wide range of polarities within a single chromatographic run.

PGC retention mechanism is different from conventional reverse-phase (RP) columns [15] and this paper studies the mechanism of interaction between the DADNE in different recrystallization conditions and some intermediate products of its synthesis with the PGC stationary phase.

2. Experimental

2.1. Chemicals

The names and structures of DADNE and its intermediate products used for the studies presented in this paper are shown in Table 1. Compounds were kindly donated by Institute of Chemistry, Military University of Technology, Warsaw, Poland. Acetonitrile (ACN, HPLC grade) and methanol (MeOH, HPLC grade) were obtained from Merck (Darmstadt, Germany). Trifluoroacetic acid (TFA) and ammonia (NH₃, 25%) were analytical reagent grade and were obtained from POCh (Gliwice, Poland). Ultra-pure water was

prepared by ultrafiltration with a Mili-Q water purification system from Millipore (Bedford, MA, USA).

Mobile phase was filtered through 0.2 μm membrane filters from Phenomenex (Torrance, USA, CA). Fresh mobile phase was prepared daily.

The stock standard solutions of analytes (ca. 2 mg mL⁻¹) were prepared in 0.1% NH₃ and 0.1% TFA solutions (v/v). Working standard solutions of this compound, at concentrations range of 0.01–0.02 mg mL⁻¹, were obtained by dilution with the same solution. The stock solutions were stored at 4–8 °C.

2.2. HPLC apparatus

HPLC analyses were performed using a Hewlett–Packard 1050 Liquid Chromatograph consisting of a gradient pump, and equipped with UV 1100 detector set at λ = 250 nm. The Agilent Chem-Station software was utilized for instrument control, data acquisition, and analysis. Hypercarb PGC 100 mm × 1 mm ID (5 μm particle size) column was used during the method development. The injection valve was Rheodyne 7125 with a 20 μL injection sample loop.

2.3. Separation conditions

The analyses were performed at ambient temperature. The mobile phases were: A, water; B¹, ACN/0.1% NH₃ (90:10, v/v); B², MeOH/0.1% NH₃ (90:10, v/v); B³, ACN/0.1% TFA at a flow-rate of 0.1 mL min⁻¹.

The mobile phase initially consisted of 100% A over 2 min. The gradient was linearly changed to 100% B¹ or B³ over the next 8 min, then held constant for 3 min. The solvent ratio was returned to the initial conditions over 2 min and held for an additional 10 min before injection of the next sample. The total run time including conditioning time was 25 min.

Retention factor (*k*) was used for retention measurements and defined as $k = (t_R - t_0)/t_0$, where *t_R* and *t₀* were the retention time for the solute under investigation and the dead time, respectively.

Table 1
Names, structures, and molecular weights of investigated compounds.

Compound	Abbreviation	Structure	Molecular weight	Empirical formula
FOX-7 (H ₂ O)	FH		148.1	C ₂ H ₄ N ₄ O ₄
FOX-7 (DMF)	FD			
FOX-7 (acetone)	FA			
1,1-Diamino-2,2-dinitroethylene	DADNE			
2-Methylpyrimidine-4,6-dione	MPD		126.1	C ₅ H ₅ N ₂ O ₂
2-Methyl-5-nitropyrimidine-4,6-dione	MNPD		170.1	C ₅ H ₄ N ₃ O ₄
2-Dinitromethylene-5,5-dinitropyrimidine-4,6-dione	NMNPD		306.1	C ₅ H ₂ N ₆ O ₁₀

The dead time was determined as the concentration of solvent peak when pure MeOH was injected [16].

2.4. Method validation procedure

The external standard method of calibration was used for this analysis. At least five standard solutions containing DADNE were analyzed, and calibration curve of the peak height as a function of the concentrations of analyte was plotted. The injection was performed three times for each standard solution to test reproducibility. Limits of detection (LOD) and quantification (LOQ) were determined as signal-to-noise ratios equal to 3 and 9, respectively.

3. Results and discussion

A challenging chromatographic separation problem was encountered while developing analytical methods for the purity of DADNE in different recrystallization conditions and some intermediate products of its synthesis. All the analyzed compounds (presented in Table 1) have different numbers of nitro and amino groups in the molecule, and their varying substitution pattern, electronic and structural properties generate a very interesting class of polar non-ionic species.

Typical alkyl-bonded reversed-phase columns (C18 and C8) do not always offer the necessary selectivity needed to separate complex mixtures. In many cases, challenging method development procedures such as gradients, high or low pH mobile phases and ion-pairing reagents may be required to obtain critical separations. Compounds like these are usually very difficult to retain in conventional RP conditions without ion-pairing reagent. As expected, when using C18 column under standard conditions DADNE eluted in the dead time. So PGC stationary phase seems and is the best choice for analyzing these compounds.

3.1. Properties of PGC and compounds under investigation

Porous graphitic carbon as a stationary phase in HPLC was developed by Knox and coworkers [17,18] to provide a reversed-phase stationary phase that would not suffer from the disadvantages of silica-based sorbents. Hypercarb media is 100% porous graphitic carbon. The particles are spherical and fully porous. The surface of PGC is composed of flat sheets of hexagonally arranged carbon atoms as in a very large polynuclear aromatic molecule. The surface is crystalline and highly reproducible, with no micropores or chemically bonded phase. The surface of PGC differs from the brush type surface associated with C18 silicas. The flat rigid surface of PGC and the fact that is highly adsorptive allows for unique stereoselectivity of solutes. PGC is extremely unreactive. Its high chemical stability over the full pH range allows separation with strongly acidic and basic mobile phases [19]. Many subsequent studies have shown that the carbon columns have exclusive properties compared to silica-based packing materials [20,21].

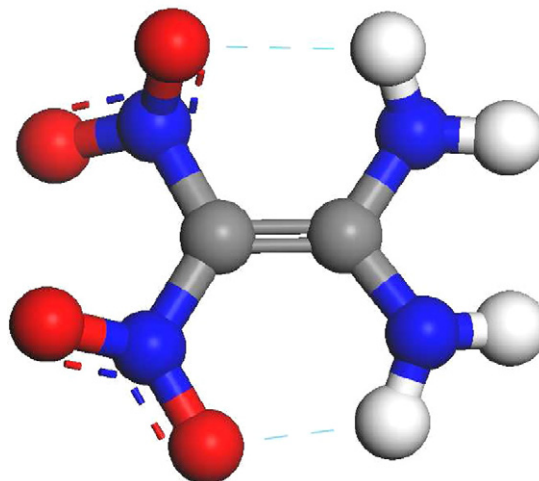


Fig. 2. DADNE molecule.

Compared with typical C–H–N–O explosives, DADNE is a small and relatively symmetric energetic molecule (Fig. 2) and consists of nitro ($-\text{NO}_2$) and amino ($-\text{NH}_2$) functional groups attached to a carbon (C–C) 'backbone'. The crystal structure of DADNE consists of four molecules aligned end-to-end in infinite two-dimensional wave-shaped layers (Fig. 3) [22].

This type of packing structure maximizes hydrogen bonding between the amine groups of one molecule and the nitro groups on its nearest neighbour, and also increases the probability of hydrogen transfer between the two molecules. The close proximity of amino hydrogens to nitro oxygens has prompted speculation that the stability of DADNE is due to hydrogen bonding within the molecule [23,24]. However, part of the increased stability can be attributed to other electronic effects. It is well known that the presence of amino groups tends to desensitize nitroaromatic molecules to shock or impact initiation. This increase in stability is attributed to 'push-pull' electron delocalization which allows partial charge transfer between 'electron-withdrawing' nitro groups and 'resonance donating' amine groups. The nearly planar configuration of DADNE indicates that it has an electronic structure with delocalized electrons. A theoretical study by Politzer et al. [25] confirmed the presence of 'push-pull' electron delocalization in DADNE. By comparing various amino/nitro derivatives of ethylene, Politzer et al. conclude that the stability DADNE is due to more to resonance effects than to hydrogen bonding.

There is evidence to suggest that intermolecular hydrogen transfer occurs via vibration-assisted bond cleavage during thermolysis of DADNE. The reported temperature of ignition for DADNE is 215 °C, while differential scanning calorimetry (DSC) shows initiation of reaction at 238 °C [24]. In isolated DADNE, several vibrational modes associated with the motion of terminal hydrogens are activated at temperatures between 110 and 270 °C. These terminal

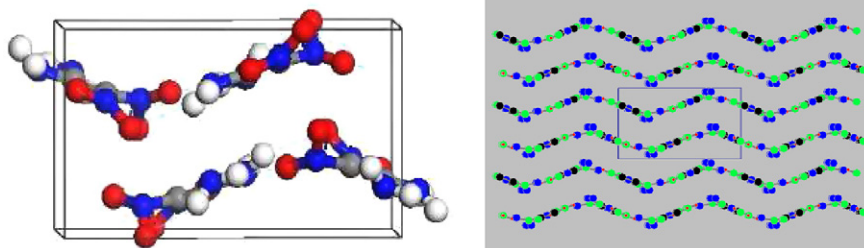


Fig. 3. Unit cell of DADNE and crystal structure of DADNE.

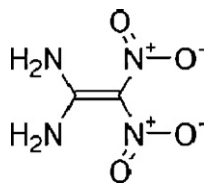


Fig. 4. Structure of DADNE molecule with charges in nitro groups.

hydrogens lie closest to neighbouring molecules in the solid, and participate in hydrogen bonding, which further weakens the N–H bond. It is therefore likely that heating DADNE excites vibrations of terminal hydrogens to the point of N–H bond cleavage, thereby liberating the hydrogen for further reactions with neighbouring molecules. Possible mechanisms for initiation of reaction in solid DADNE include (1) intra or intermolecular hydrogen transfer, (2) nitro–nitrite isomerisation and (3) C–nitro bond cleavage [22].

The carbon, hydrogen, and nitro-N atoms carry a lot of positive charges, while the oxygen and amino-N atoms bear lots of negative charges (Fig. 4). Due to the large negative charges on oxygen atoms, electronic repulsion between the adjacent nitro oxygen atoms of the same molecule is significant, which makes them deviate out of the C–C–N plane.

3.2. Dependence of $\log k$ on the mobile phase nature

The correlations between the logarithm of the retention factor ($\log k$) values and the percent of organic modifier acetonitrile and

methanol in the mobile phase are shown in Figs. 5 and 6 for the four compounds (DADNE, MPD, MNPD and NMNPD) and PGC stationary phase. The relationships are linear but with different slopes so that the higher the k values the greater the difference in retention. However, due to the different slopes of the relationships, the difference in retention depends on the analyte hydrophobicity. It is much lower with low polarity analytes. Each compound exhibited the classical RPLC hydrophobic behavior, that is, retention time decreased linearly as the concentration of the organic modifier increased because the stationary phase was saturated by organic modifier over the mobile phase composition region investigated.

Figs. 5 and 6 also demonstrate solvent strength and selectivity differences between methanol and acetonitrile mobile phases on PGC phase, and how such differences affect the separation of polar compounds. Despite the similar elution strength of the two solvents (24% acetonitrile and 32% methanol), all of the compounds elute later when acetonitrile is used. This is evidence of additional interactions leading to increasing retention.

These interactions affect varies analytes differently. This is shown by the elution order change between the three intermediate products of DADNE synthesis. When concentration of ACN in mobile phase exceeds 25% the elution orders are MPD, MNPD, and NMNPD. In the case of MeOH, when the organic exceeds 32%, MNPD elutes first, next NMNPD, and MPD.

Structures of the MPD, MNPD, and NMNPD differ in the number of nitro groups, from none, through one to four, respectively. The retention increased due to these numbers and it could be explained by stronger and stronger interactions between the nitro groups and

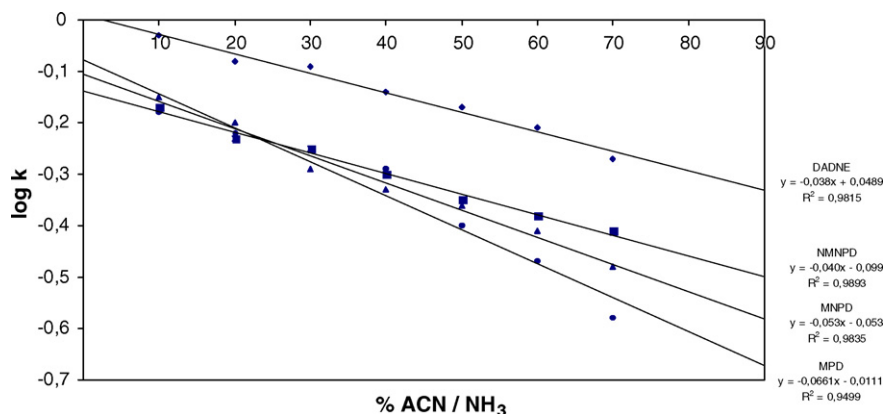


Fig. 5. Relationship between retention factor k values and the percent of component B¹ in the mobile phase [A, water; B¹, ACN/0.1% NH₃ (90:10, v/v)] obtained using PGC Hypercarb column for DADNE, MPD, MNPD and NMNPD.

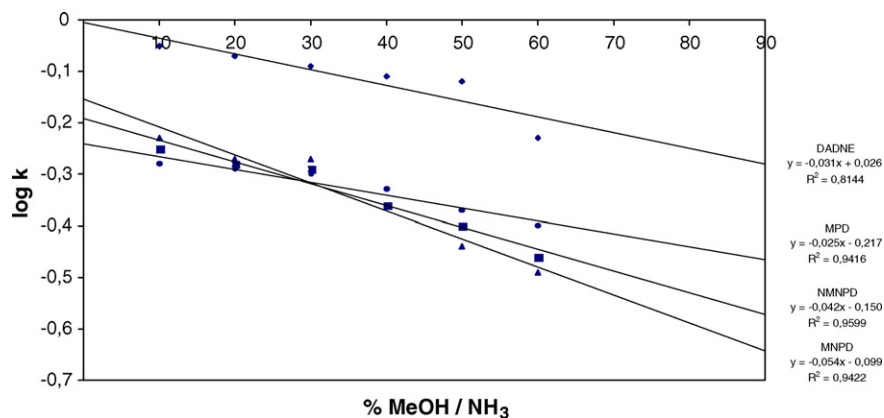


Fig. 6. Relationship between retention factor k values and the percent of component B² in the mobile phase [A, water; B², MeOH/0.1% NH₃ (90:10, v/v)] obtained using PGC Hypercarb column for DADNE, MPD, MNPD and NMNPD.

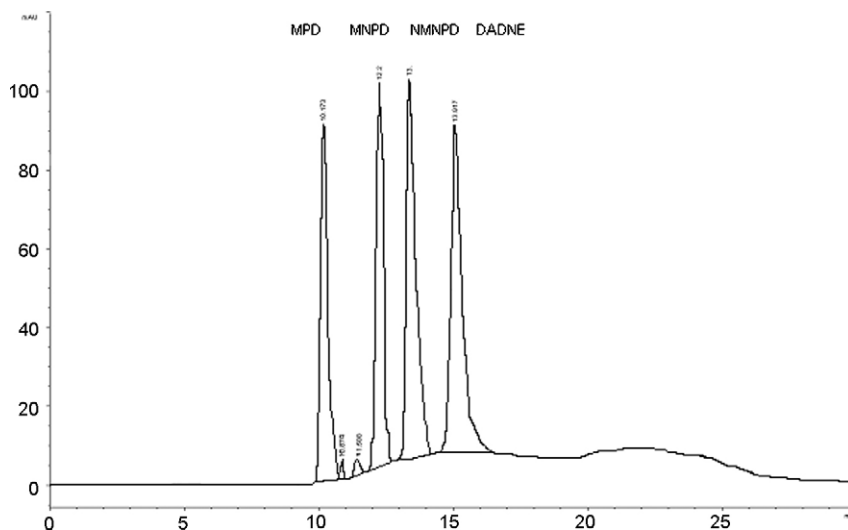


Fig. 7. Chromatogram of DADNE (1), MPD (2), MNPD (3) and NMNPD (4); mobile phase: A, H₂O; B¹, ACN/0.1% NH₃ (90:10, v/v); gradient mode.

the graphitic surface. This observed behavior is an effect of specific interactions between the π -electron systems of the solutes on the one hand and the stationary phase on the other hand. The solutes are substituted with electron-drawing nitro groups.

In this evaluation, the comparison of organics in the mobile phase suggest that methanol contributes to an increase in the π - π interactions of the carbon-phase, thus allowing improved selectivity for a diverse mix of analytes. Both the methanol and acetonitrile containing mobile phases were adjusted to equal elutropic strength. Further, the use of different organic mobile phases allows users to activate (methanol) or suppress (acetonitrile) such interactions. Modulating such interactions can selectively change the retention of a specific compound in a mixture, resulting in improved resolution. Such flexibility and utility make PGC phase powerful method development tool for separations where C18 columns fail to provide the desired separation.

3.3. Effects of ion-pair

The development of a gradient elution method for the separation of DADNE and some intermediate products of its synthesis

was accomplished after extensive investigation of various elution modes, types of gradient profiles and mobile phases. This method was then optimized further by the choice of an addition of an ion-pair reagents: TFA and NH₃. These compounds act as electronic modifiers and compete with analyte molecules for possibility of interactions with PGC π electrons.

Fig. 7 shows a chromatogram of the mixture using a mobile phase consisting of A, H₂O and B¹, ACN/0.1% NH₃ (90:10, v/v) in a gradient mode that yielded the best separation of the four compounds on the PGC column. In Fig. 8 a chromatogram of the same mixture using a mobile phase consisting of A, H₂O and B³, ACN/0.1% TFA is shown.

Three things are apparent from an examination of these two chromatograms. First, the mixture is completely separated by the two different ion-pairing reagents in mobile phase. Second, the efficiency of the PGC column is approximately the same for these two mobile phases, which implies that differences in the resolution of the mixture for these two mobile phases is due to differences in chromatographic selectivity. Third, the elution order is the same in these two cases, but the retention time of each compound is greater when TFA is used in mobile phase.

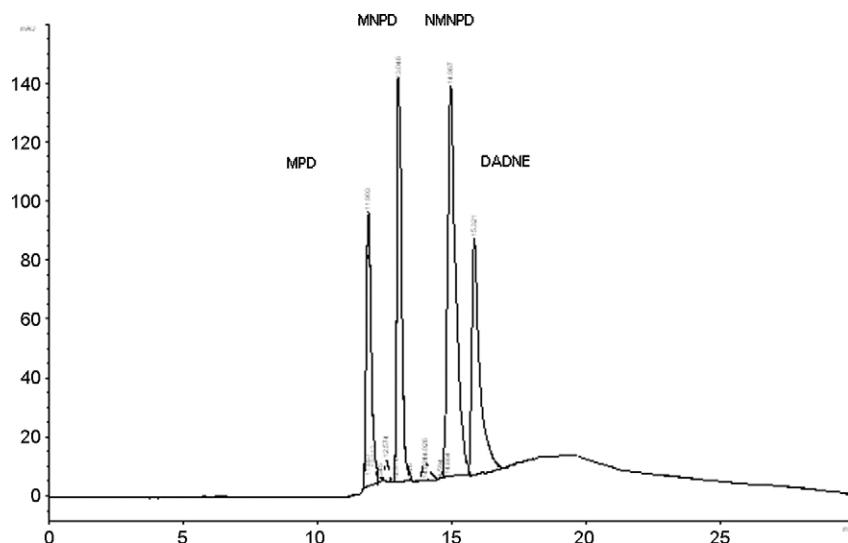


Fig. 8. Chromatogram of DADNE (1), MPD (2), MNPD (3) and NMNPD (4); mobile phase: A, H₂O; B³, ACN/0.1% TFA; gradient mode.

Retention of polar compounds and ions on Hypercarb is due to specific interactions between solutes and delocalized electrons on the graphite surface, which behaves both as an electron donor and electron acceptor. The type and concentration of electronic modifiers in the mobile phase can have a noticeable effect on the retention, selectivity and also on the peak symmetry of solutes separated on Hypercarb columns.

The use of an ion-pair reagent for improved compound selectivity and in order to prolong their retention time often has an unfavorable impact on various factors such as slow column equilibration and method ruggedness, however it is still one of the favored ways to increase the selectivity factor (α) of ionizable compounds in RP-HPLC [26].

The most commonly used electronic modifier, trifluoroacetic acid, can act as a competitive modifier which reduces polar retention. When separating ionizable acidic solutes, very often it is essential to use TFA in order to obtain elution in a reasonable run time. TFA competes with the acidic solutes for the graphite surface, preventing very strong retention of these. When analyzing ionizable basic solutes TFA behaves as an ion-pairing agent which improves peak shape at the same time as it increases retention; in this case, TFA forms an ion-pair with the analyte increasing retention moderately but also improving resolution and peak shape via electronic interactions with the graphite surface.

Ammonia (NH_3) also behaves as an electronic modifier and is very useful when strong retention on the graphite surface results in broad, asymmetrical peaks or very late eluting peaks, for basic or acidic analytes. In the separation of basic analytes NH_3 can produce sharp symmetrical peaks. It is thought that NH_3 competes with the basic analytes for the surface of the graphite, and thus reduces retention. For acidic analytes, this modifies electronic interaction with the graphite surface will improve resolution and peak shape.

A relatively low shift in retention time of DADNE in different recrystallization conditions was observed in the presence of an ion-pair reagents (data not presented). It could be due to a lower ion-pair reagent affinity to the PGC column packing material, differences in the mobile phase, or differences in the gradient elution. The ion-pairing process relies on an equilibrium between ion-pairing reagent free in mobile phase and that which is adsorbed on the stationary phase. The equilibrium is rather slow. Anything that upsets the equilibrium can change retention times. For example, a change in the column temperature or percent of organic in mobile phase will affect the partition of the ion-pairing reagent between the stationary and mobile phases. However, the exact reasons remain unknown and were beyond the scope of this investigation.

3.4. π - π interactions as a separation force in HPLC using PGC

The retention mechanism is very different from that observed with the other types of reversed-phase sorbents. It has been pointed out that one basic difference is that solute-stationary phase interactions play an important role with carbon-based sorbents. This is due to its crystalline structure made of large graphitic sheets held together by weak Van-der-Waals forces. The delocalization of the π -electrons in the large graphitic bands and the high polarizability of the carbon are responsible for the strong dispersion interactions in addition to strong solvophobic interactions. When polar analytes are of interest, the electronic interactions were shown to be more important than the hydrophobic interactions in the retention mechanism [27].

The π - π interaction is a type of electron donor–electron acceptor interaction, originating from π -electron systems in two unsaturated functional groups through either intermolecular or intramolecular interactions. In a chromatographic system, these interactions can occur between π -electrons of the stationary phase

and the analyte species [28,29]. An interaction between π -electron of PGC stationary phase, is favored when one compound is electron-rich and one is electron-poor such as the analyte.

In this work, the authors investigated the unique selectivity power of π - π interactions occurring in a challenging chromatographic separation of DADNE. A retention mechanism has been proposed, based upon π - π interactions occurring between the different analyte molecules and the PGC stationary phase. There are no ion-exchange sites on PGC; therefore the retention was due to charge transfer interactions between the negative charge of the analyte and the graphitic surface of the stationary phase. Therefore, the retention and separation on PGC are due to the successful competition of electronic interaction between the carboxylate anion of the mobile phase and the solute with delocalized electron on the PGC surface. In ion-pair chromatography, the retention was governed by hydrophobic interactions between the ion-pair and the stationary phase. With the PGC system, on the other hand, the retention was governed by electronic interactions between the anionic solute and the PGC phase that depend on the separation and resolution of these solutes [30].

In summary, the flat, highly crystalline Hypercarb surface leads to retention mechanisms which are different from those observed on silica-based bonded phases. Many factors are influenced the chromatographic behavior between PGC and nitro compounds; 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 (charge-induced interactions between the nitro groups and the PGC surface);
- (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 behavior of ionic species and molecules containing certain functional groups.

The strength of analyte interactions with the Hypercarb is also largely dependent on the molecular area in contact with the graphite surface and on the type and positioning of the functional groups in relation to the graphite surface, at the points of contact.

3.5. Method validation procedure

The limit of detection (LOD) and the limit of quantification (LOQ) values at $\lambda = 250 \text{ nm}$ for both mobile phases were summarized in Table 2. The LOD were calculated as the minimum concentration providing a chromatographic signal three times higher than background noise and ranged between 0.02–0.24 and 0.02–0.22 $\mu\text{g mL}^{-1}$ for mobile phase with NH_3 and TFA, respectively. The LOQ was defined as the three times LOD and ranged between 0.07–0.72 and 0.07–0.65 $\mu\text{g mL}^{-1}$ for mobile phase with NH_3 and TFA, respectively.

The calibration curve, was obtained by plotting peak height versus concentration of DADNE over the range from 4.45 to 53.34 $\mu\text{g mL}^{-1}$. The straight line corresponded to the typical linear equation of $y = 9.6633x - 3.9624$ and is presented in Fig. 9. Excellent linearity was obtained, with the correlation coefficient of $R^2 = 0.9998$.

Table 2
Limits of detection and quantification of investigated compounds.

Compound	Additives of mobile phase			
	NH ₃		TFA	
	LOD ($\mu\text{g mL}^{-1}$)	LOQ ($\mu\text{g mL}^{-1}$)	LOD ($\mu\text{g mL}^{-1}$)	LOQ ($\mu\text{g mL}^{-1}$)
FOX-7 (H ₂ O)	0.12	0.35	0.09	0.26
FOX-7 (DMF)	0.14	0.41	0.12	0.37
FOX-7 (acetone)	0.24	0.72	0.14	0.41
DADNE	0.19	0.56	0.22	0.65
MPD	0.02	0.07	0.02	0.07
MNPD	0.16	0.47	0.11	0.34
NMNPd	0.18	0.54	0.12	0.35

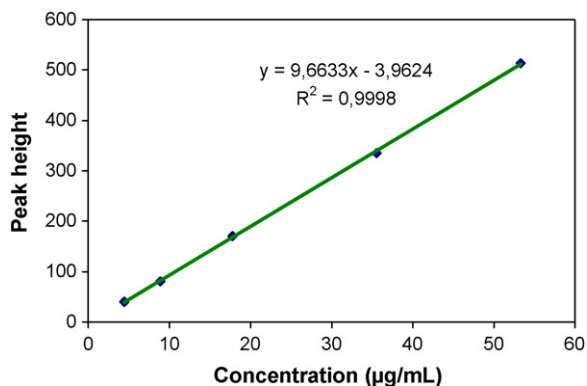


Fig. 9. Calibration of DADNE.

Table 3
Data for sample analysis.

Compound	t_R (min)		% of contamination above LOQ and its t_R	
	NH ₃	TFA	NH ₃	TFA
FOX-7 (H ₂ O)	8.88	9.29	ND ^a	ND
FOX-7 (DMF)	8.95	9.34	ND	$t_R = 7.56, 14.7\%$
FOX-7 (acetone)	9.14	9.50	ND	$t_R = 7.73, 5.3\%$
DADNE	8.54	9.94	ND	ND
MPD	6.27	7.50	ND	ND
MNPD	7.76	8.32	$t_R = 6.77, 5.8\%$ $t_R = 6.38, 86.1\%$	$t_R = 7.65, 5.8\%$ $t_R = 7.48, 3.6\%$
NMNPd	8.94	9.69	$t_R = 6.62, 21.0\%$ $t_R = 7.22, 5.0\%$	$t_R = 7.98, 7.0\%$ $t_R = 9.02, 4.7\%$

^a ND, not detected.

3.6. Application of the method to real samples

The applicability of the overall method was demonstrated by the analysis of the samples purity of DADNE in different recrystallization conditions and some intermediate products of its synthesis. Data from the analysis are collected in Table 3. It can be seen that for DADNE crystallized from dimethylformamide and acetone some contaminations are appeared. Also in the case of MPD and NMNPd, as intermediate products, we detected small amount of unknown contaminations.

4. Conclusion

The analytical methodology developed in this study demonstrates the efficiency of PGC in analyzing DADNE and some intermediate products to control its synthesis. 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 HPLC–UV in combination with PGC represents an improved

alternative to existing analytical methods based on derivatized silica reversed-phase columns. The use of ion-pairing additives such as TFA and NH₃ in the mobile phase allows the elution of the most strongly retained compounds from the PGC surface and improves UV detection. The LOD, LOQ, linearity and sensitivity have all been tested and found to give excellent results.

References

- [1] H. Östmark, H. Bergman, U. Bemm, P. Goede, E. Holmgren, M. Johansson, A. Langlet, N.V. Latypov, A. Pettersson, M.-L. Petterson, N. Wingborg, C. Vörde, H. Stenmark, L. Karlsson, M. Hohkiö, 2,2-Dinitro-ethene-1,1-diamine (FOX-7)—properties, analysis, and scale-up, in: Proceedings of the 32nd International Annual Conference of ICT, Karlsruhe, Germany, 2001.
- [2] S. Cudziło, W. Kiciński, Otrzymywanie i właściwości 1,1-diamino-2,2-dinitroetenu (Synthesis and properties of 1,1-diamino-2,2-dinitroethene), Biul. WAT 53 (2004) 183–200 (in Polish).
- [3] B. Janzon, H. Bergman, C. Eldsäter, C. Lamnevik, H. Östmark, Östmark, FOX-7—a novel, high performance, low vulnerability high explosive for warhead applications, in: Proceedings of the 20th International Symposium on Ballistics, Orlando, FL, USA, 23–27 September, 2002.
- [4] N.V. Latypov, J. Bergman, Synthesis and reactions of 1,1-diamino-2,2-dinitroethylene, Tetrahedron 54 (1998) 11525–11536.
- [5] G. Herve, G. Jacob, N. Latypov, The reactivity of 1,1-diamino-2,2-dinitroethene (FOX-7), Tetrahedron 61 (2005) 6743–6748.
- [6] G. Herve, G. Jacob, Novel illustrations of the specific reactivity of 1,1-diamino-2,2-dinitroethene (DADNE) leading to new unexpected compounds, Tetrahedron 63 (2007) 953–959.
- [7] Z. Chyłek, S. Cudziło, J. Błądek, S. Pietrzyk, Optimization of 1,1-diamino-2,2-dinitroethene synthesis, Biul. WAT 53 (2005) 633 (in Polish).
- [8] D.S. Moore, Instrumentation for trace detection of high explosives, Rev. Sci. Instrum. 75 (2004) 2499–2512.
- [9] M.E. Walsh, T. Ranney, Determination of nitroaromatic, nitramine, and nitrate ester explosives in water using solid-phase extraction and gas chromatography-electron capture detection: comparison with high-performance liquid chromatography, J. Chromatogr. Sci. 36 (1998) 406–416.
- [10] V.K. Balakrishnan, A. Halasz, J. Hawari, Alkaline hydrolysis of the cyclic nitramine explosives RDX, HMX, and CL-20: new insights into degradation pathways obtained by the observation of novel intermediates, Environ. Sci. Technol. 37 (2003) 1838–1843.
- [11] E. Holmgren, H. Carlsson, P. Goede, C. Crescenzi, Determination and characterization of organic explosives using porous graphitic carbon and liquid chromatography-atmospheric pressure chemical ionization mass spectrometry, J. Chromatogr. A 1099 (2005) 127–135.
- [12] T. Hanai, Separation of polar compounds using carbon columns, J. Chromatogr. A 989 (2003) 183–196.
- [13] R. Kaliszán, K. Ośmiałowski, B.J. Bassler, R.A. Hartwick, Mechanism of retention in high-performance liquid chromatography on porous graphitic carbon as revealed by principal component analysis of structural descriptors of solutes, J. Chromatogr. 499 (1990) 333–344.
- [14] Y. Polyakova, K.H. Row, HPLC of some polar compounds on a porous graphitized carbon Hypercarb column, J. Liq. Chromatogr. Relat. Technol. 28 (2005) 3157–3168.
- [15] T. Hanai, Analysis of the mechanism of retention on graphitic carbon by a computational chemical method, J. Chromatogr. A 1030 (2004) 13–16.
- [16] B. Buszewski, M.J. Kulpa, J. Liq. Chromatogr. Rel. Technol. 16 (1993) 75.
- [17] J.H. Knox, P. Ross, in: P.R. Brown, E. Grushka (Eds.), Advances in Chromatography, vol. 37, M. Dekker, New York, USA, 1997, p. 73.
- [18] P. Ross, J.H. Knox, in: P.R. Brown, E. Grushka (Eds.), Advances in Chromatography, vol. 37, M. Dekker, New York, USA, 1997, p. 122.
- [19] C.K. Lim, in: J.C. Giddings, R.A. Keller (Eds.), PGC in biomedical applications, Advances in Chromatography, vol. 32, M. Dekker, New York, USA, 1992, pp. 1–19.
- [20] G. Machtalere, V. Pichon, M.-C. Hennion, Relationships between retention factors and analyte hydrophobicity on cyanopropyl and *n*-octadecyl bonded silicas, cross-linked polymers and porous graphitic carbon stationary phases. Consequences for the trace analysis of highly polar organic compounds, J. High Resolut. Chromatogr. 23 (2000) 437–444.
- [21] J. Kriz, E. Adamcova, J.H. Knox, J. Hora, Characterization of adsorbents by HPLC using aromatic hydrocarbons. PG and its comparison with silica gel, alumina, C18 and phenylsilica, J. Chromatogr. A 663 (1994) 151–161.
- [22] X.H. Ju, H.M. Xiao, Q.Y. Xia, A density functional theory investigation of 1,1-diamino-2,2-dinitroethylene dimers and crystal, J. Chem. Phys. 119 (2003) 10247–10255.
- [23] H. Östmark, A. Langlet, H. Bergman, N. Wingborg, U. Wellmar, U. Bemm, FOX-7—a new explosive with low sensitivity and high performance, Proc. Eleventh (Int.) Det. Symp. Preprints, 1998.
- [24] U. Bemm, H. Östmark, 1,1-Diamino-2,2-dinitroethylene: a novel energetic material with infinite layers in two dimensions, Acta Crystallogr. C54 (1998) 1997–1999.
- [25] P. Politzer, M. Concha, M. Grice, J. Murray, P. Lane, D. Habibollahzadeh, Computational investigation of the structures and relative stabilities of

- amino/nitro derivatives of ethylene, *J. Mol. Struct. (THEOCHEM)* 452 (1998) 75–83.
- [26] J.W. Dolan, Reader questions: mobile phase, *LC–GC N. Am.* 7 (2005).
- [27] G. Thevenon-Emeric, A. Tchaplal, M. Martin, *J. Chromatogr.* 550 (1991) 267.
- [28] M. Yang, S. Fazio, D. Munch, P. Drumm, Impact of methanol and acetonitrile on separations based on π – π interactions with a reversed-phase phenyl column, *J. Chromatogr. A* 1097 (2005) 124–129.
- [29] R. Brindle, K. Albert, Stationary phases with chemically bonded fluorene ligands: a new approach for environmental analysis of π -electron containing solutes, *J. Chromatogr. A* 757 (1997) 3–20.
- [30] B. Buszewski, M. Michel, Porous graphitized carbon as stationary phase for separation technologies, in: A.P. Terzyk, P.A. Gauden, P. Kowalczyk (Eds.), *Carbon Materials Theory and Practice*, Research Signpost, Kerala, India, 2007.