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Identification and determination of trinitrotoluenes and their degradation products using liquid chromatography–electrospray ionization mass spectrometry

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ABSTRACT

In the environs of ammunition plants and former military area, contaminations caused by explosives and their degradation products are of great environmental relevance. During the production of worldwide mostly used explosive compound – 2,4,6-trinitrotoluene its isomers were distributed into the environment. Therefore determination of 14 selected nitroaromatic compounds (trinitrotoluenes, amino dinitrotoluenes and diamino nitrotoluenes) by means of LC–MS–MS coupling utilizing electrospray ionization was developed. Therewith, these compounds were identified and quantified on the basis of specific precursor/product ion traces using the high selectivity and sensitivity of multiple reaction monitoring mode (MRM) of a triple quadrupole mass spectrometer. A new stationary phase designed especially for separation of EPA explosive mixture was used for separation of specific mixture of nitroaromatics compounds. Modification of HPLC properties enables base-line separation of all analytes and therefore improving of their MS identification and quantification. Limits of detection obtained using highly specific mass spectrometric detection MRM mode were in range 4–114 pg/μL. MS–MS qualification and quantification of explosives and their biodegradation products is feasible also in case of samples with complex matrix and high amount of co-eluting compounds.

1. Introduction

The worldwide mostly used highly energetic compounds like 2,4,6-trinitrotoluene (2,4,6-TNT) and other polynitro organic compounds have been discharged into the environment since the WWI [1]. Contamination of soil and water by these compounds is caused by various military activities (manufacturing, testing, training, demilitarization, open burning/open detonation) and as a result of local military conflicts [2]. TNT and its constitutional isomers (2,4,5-trinitrotoluene and 2,3,4-trinitrotoluene) were distributed into the environment by wastewaters as a result of 2,4,6-TNT production (commonly known as the "red water") [3]. Asymmetric trinitrotoluenes have almost similar properties as 2,4,6-TNT. Higher hygroscopicity and lower thermal stability were only determined [4]. Due to these properties are studied compounds and other nitroaromatic compounds relatively widespread.

2,4,6-TNT is often biologically stepwise reduced to amino dinitrotoluenes (Am-DNTs), diamino nitrotoluenes (Dam-NTs) and triaminotoluenes (Tam-Ts). However, only limited data about their toxicity and mutagenicity are available. TNTs and products of their degradation have been found to be cytotoxic presumably due to induced oxidative stress and demonstrated mutagenic capability. 2,4,6-TNT is classified as possible human carcinogen. The evidence for human carcinogenicity is inadequate, and the animal carcinogenicity data are limited [5]. 2,4,6-TNT and several of its reduced metabolites isolated from human and rat urine showed mutagenic activity without metabolic activation in Salmonella mutagenicity assay [6,7].

TNTs and products of their biotransformation may be strongly adsorbed by soils even covalently bonded to soil organic matter [1]. For that reasons their transport in the environment may be very slow. Therefore the precise identification and quantification of the TNTs and their degradation products in soils and ground waters at the level of low environmental concentration is essential. To be able to provide insight into the environmental fate of explosives and the risk associated with their presence, analytical tools capable to analyse such chemicals and their transformation products in various environmental media has to be available. Gas chromatography [8–11], capillary electrophoresis [12,13] and thin layer chromatography [14] have been used in special cases. High performance liquid chromatography (HPLC) has remained to be the best analytical tool

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for the detection and quantification of nitroaromatic compounds [15–19].

The most commonly used method for the analysis of explosives recommended by U.S. Environmental Protection Agency (EPA) is HPLC with UV detection [20] due to its widespread availability, while HPLC combined with MS and electrochemical detection (ED) are also viable but less frequently available methods of detection and determination of explosives [21]. There is no information about use of LC/MS for determination of a large group of TNTs aminoderivatives than included in EPA explosives mixture. Previously published methods of explosives determination were focused on the use of C18 RP-HPLC and acetonitrile or methanol as the organic modifier of mobile phase [15]. Acetonitrile is of significantly greater health and environmental concern than methanol and therefore methods avoiding the use of acetonitrile are desirable [22].

In contrast to EPA recommended mixture we have used in our study a mixture of isomers of TNT and their amino metabolites. These compounds are presumably present in contaminated sites, because of significant amount of asymmetric trinitrotoluenes in industrial production wastewater [3]. Using of HPLC/UV method for determination of whole mixture was published in previously work [23], however HPLC–MS–MS analytical methods have not been used for separation of TNTs and their amino metabolites.

The present paper is focused on developing of HPLC analytical method coupled with MS–MS detection for a group of 14 nitroaromatic compounds (2,4,6-TNT, 2,4,5-TNT, 2,3,4-TNT, Am-DNTs and Dam-NTs). The ionization technique often utilized for nitroaromatic compounds is atmospheric pressure chemical ionization (APCI) [24–26]. The HPLC–MS, with electrospray ionization (ESI) was found to provide best sensitivity and selectivity for determination of standard EPA explosive mixture [27,28] or polar nitroaromatics compound in contaminated waters as well [19]. The detection limits (LODs) for HPLC/UV method of 2,4,6-TNT and its amino metabolites ranged between 25 and 50 ng/mL, while LODs for ESI-MS are about 3 ng/mL [19]. Set of amino and diamino derivatives are not available in the literature, unfortunately. Therefore coupling of HPLC-ESI–MS–MS with positive and/or negative ionization of nitroaromatic compounds was studied. A new HPLC column designed specially for separation of EPA explosives mixture was tested for more effective resolution of amino derivatives used in this study.

2. Methods

2.1. Chemicals

Standard solutions of 2-amino-4,6-dinitrotoluene (2-Am-4,6-DNT), 4-amino-2,6-dinitrotoluene (4-Am-2,6-DNT), 2,6-diamino-4-nitrotoluene (2,6-Dam-4-NT), 2,3,4-trinitrotoluene (2,3,4-TNT), 2,4,5-trinitrotoluene (2,4,5-TNT), 2,4-diamino-5-nitrotoluene (2,4-Dam-5-NT), 2,5-diamino-4-nitrotoluene (2,5-Dam-4-NT), 2-amino-3,4-dinitrotoluene (2-Am-3,4-DNT), 2-amino-4,5-dinitrotoluene (2-Am-4,5-DNT), 3-amino-2,4-dinitrotoluene (3-Am-2,4-DNT), 4-amino-2,5-dinitrotoluene (4-Am-2,5-DNT), 4-amino-2,3-dinitrotoluene (4-Am-2,3-DNT), 5-amino-2,4-dinitrotoluene (5-Am-2,4-DNT) and 2,4,6-trinitrotoluene (2,4,6-TNT) were synthesized according to procedures optimized for preparation of clean substances (purity > 97%) [29]. Standard stock solutions (0.1–10 μg/mL) were prepared by dissolution of each compound in methanol (Riedel de Haën, Germany). Ammonium acetate (Fluka, Switzerland) was used for buffer mobile phase preparation. The water used for HPLC analysis was prepared using Simplicity 185 equipment (Milipore, Molsheim, France).

2.2. HPLC

Agilent 1200 Series (Agilent Technologies, Inc., Palo Alto, CA, USA) was used for HPLC separation. The detection of analytes was realized by measuring the UV absorption with diode array detector at two wave length (230 and 254 nm) and by mass detector. Chromatographic separation was achieved with an Acclaim Explosives E1 column (4.6 mm × 250 mm, 5 μm; Dionex, Sunnyvale, CA, USA) Methanol:water (43:57) mobile phase at the column temperature 32 °C and a flow rate 1 mL/min were used for isocratic elution. Mobile phase containing methanol and ammoniumacetate buffer in a same ratio was used in the case of MS detection because of better ionization of studied compounds. Temperature was adjusted to 25 °C. Injected sample volume was 1 μL.

2.3. MS condition

The mass spectrometer (Agilent 6410, Triple Quad, Agilent Technologies, USA) was mass-calibrated against a HPLC–MS Tuning mix (Agilent Technologies, USA). Full scan analyses of TNTs and their transformation products were acquired in the MS-scanning mode (first quadrupole) in the mass range of 100–600 Da. Selected precursor ions were used for SIM mode (selected-ion monitoring) quantifying of studied compounds or fragmented in the collision cell using nitrogen gas. Subsequently in the second quadrupole the product ion spectra were registered, and intensive characteristic product ions were chosen for detection in the MRM mode (multiple reaction monitoring). The flow and temperature of the drying gas (nitrogen) in ion spray source were set to 11 mL/min and 450 °C, respectively according to technical properties of the MS instrument used. The suitable value of capillary voltage was optimized. Fragmentor energy and collision energy were adjusted individually depending on the substance.

3. Results and discussions

3.1. HPLC-UV

Separation of 14 studied nitroaromatic compounds is generally difficult due to coelution of the structural isomers. Using of column special developed for separation of standard EPA explosives mixture [20] facilitated separation of TNTs and theirs degradation products. With the small changes in mobile phase content and mobile phase temperature satisfactory separation with good resolution were attained (Fig. 1).

3.2. HPLC-ESI–MS–MS

3.2.1. Ionization properties, precursor ions formation

An HPLC–MS method for the qualitative and quantitative determination of TNTs and their metabolites was developed and optimized using triple quadrupole system Agilent 6410 with electrospray ionization (ESI), which is especially suited for the ionization of polar analytes. Positive or negative ESI mode was used for ionization of investigated compounds. Protonated $[M+H]^+$ or deprotonated $[M-H]^-$ ions were used for determination of compounds in SIM mode or as precursor ions in MRM mode. In general, m/z 168 ion (ESI+) was chosen for diamino nitrotoluenes, m/z 196 ion (ESI−) for amino dinitrotoluenes and m/z 226 ion for TNTs (ESI−), respectively.

A pH value of buffered mobile phase is important parameter affecting ESI ionization. Several volatile buffers, including ammonium nitrate, ammonium acetate, ammonium formate, formic acid and acetic acid, respectively, were tested for ability to reproducibly promote ion formation in electrospray ion source [26]. In order to support dissociation and therewith ionization of nitroaromatic

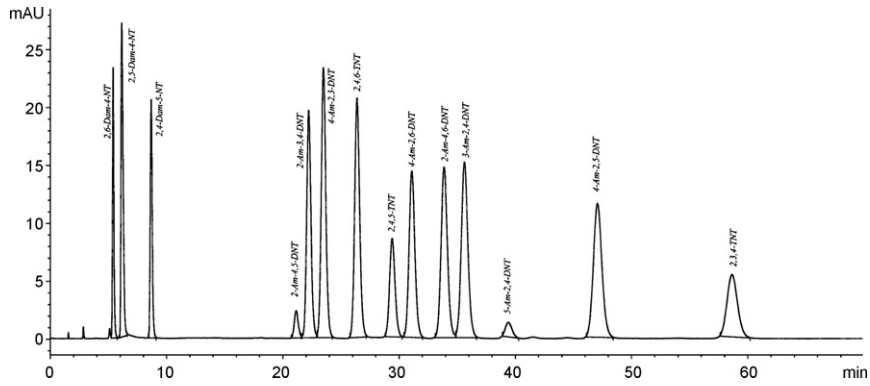

Fig. 1. HPLC separation of tested compounds. Column: Acclaim Explosives E1, 250 mm × 4.6 mm I.D., 5 μm; mobile phase: methanol:water (43:57), flow rate = 1 mL/min and mobile phase temperature = 32 °C, UV detection 254 nm.

compounds changes of pH using ammonium acetate is well suited [27,30,31]. In the current work, an effect of pH in the range of 4–7 using 5 mmol/L ammonium acetate was studied. Generally stated the best ionization of investigated group of analytes was achieved under pH 7 (Fig. 2). The ionization of diamino nitrotoluenes in positive mode are strongly dependent on pH value and are minimally ionized in the case of lower pH value (pH 4–6). All of amino dinitrotoluenes are well ionized in mobile phase with pH 6 in negative mode. Using mobile phase pH 7 only two from seven amino dinitrotoluenes were worse ionized comparing to pH 6. The effect of pH mobile phase on ionization of trinitrotoluenes is not significant.

ESI source parameters (drying gas temperature and capillary voltage) have significant effect on ionization of nitroaromatic compounds [19,27,28,32]. Changes of capillary voltage in the range of 1000–4500 V in negative or positive mode (Fig. 3) demonstrate significant effect especially for 2,4-Dam-5-NT. Reducing of the capillary voltage to 1500 V, intensity of selected precursor ions increased. After reducing the capillary voltage to the value 1000 V the intensity of ions with generally low response decreased. Therefore 1500 V was set as a compromise capillary voltage.

Effect of value of fragmentor voltage on the signal of $[M+H]^+$ or $[M-H]^-$ ions had been investtigated in the range of 50–200 V in SIM mode using selected precursor ion masses of individual compounds. The highest responses were obtained for fragmentor voltage in the range of 90–120 V (Fig. 4). The fragmentor voltage used for MS analyses was set as 110 V.

The ESI(+) spectra of diamino nitrotoluenes are presented in Fig. 5A. The *m*/*z* 190 and 206 ions would be $[M+Na]^+$ and $[M+K]^+$ adducts, respectively. The *m*/*z* 151 and 150 ions correspond to fragment $[M+H-OH]^+$ and $[M+H-H_2O]^+$, respectively. The *m*/*z* 133 ion is ion created by loss of OH group from *m*/*z* 150 ion.

Simple and almost identical ESI(−) spectra were obtained for six from seven used amino dinitrotoluenes with dominant *m*/*z* 196 ion corresponding to $[M-H]^-$. Spectrum of 2-Am-4,6-DNT selected as an example is in Fig. 5B. However ionization of 3-Am-2,4-DNT was very weak both in negative and positive mode within the range of ionization parameters applicable by used mass spectrometer. The MS spectra obtained in ESI(−) mode for TNT isomers differs slightly (Fig. 5C). Dominant $[M-H]^-$ ion with *m*/*z* 226 was attained. The *m*/*z* 180 ion corresponding to $[M-H-NO_2]^-$ fragment was significantly observed only in the case of 2,3,4-TNT and 2,4,5-TNT.

3.2.2. MS–MS properties, product ions formation

Capillary voltage 1500 V and fragmentor voltage 110 V were used in the study of effect of collision energy on creation of suitable product ions from selected precursor ions (protonated or deprotonated molecules). The effect of collision energy on intensity of fragment ions available for multiple reaction monitoring analytical mode (MRM) was studied in the range of 5–15 V (Fig. 6).

The precursor and product ion masses selected for SIM and MRM detection of individual compounds and identification are summarized in Table 1. The product spectra of studied compounds

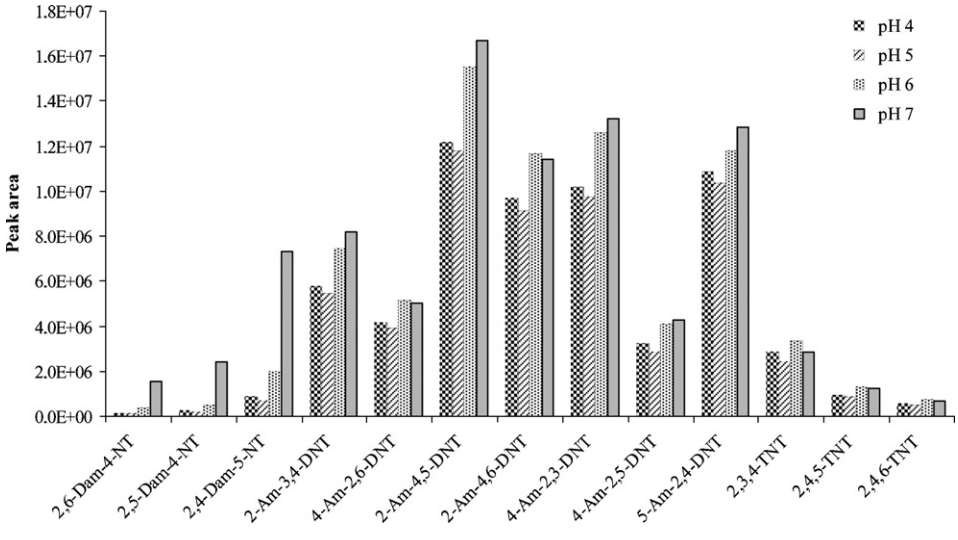

Fig. 2. Effect of mobile phase pH on ionization of studied compounds. Mobile phase: methanol:ammonium acetate buffer (43:57), flow rate = 1 mL/min, drying gas temperature 450 °C, capillary voltage 4500 V.

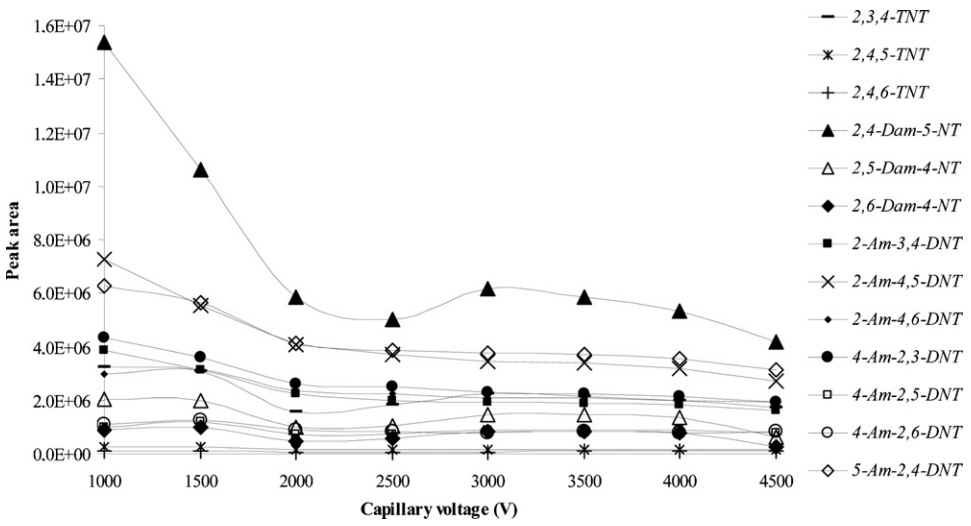

Fig. 3. Effect of the capillary voltage on ionization of studied compounds. Mobile phase: methanol:ammonium acetate buffer pH 7 (43:57), flow rate 1 mL/min, drying gas temperature 450 °C.

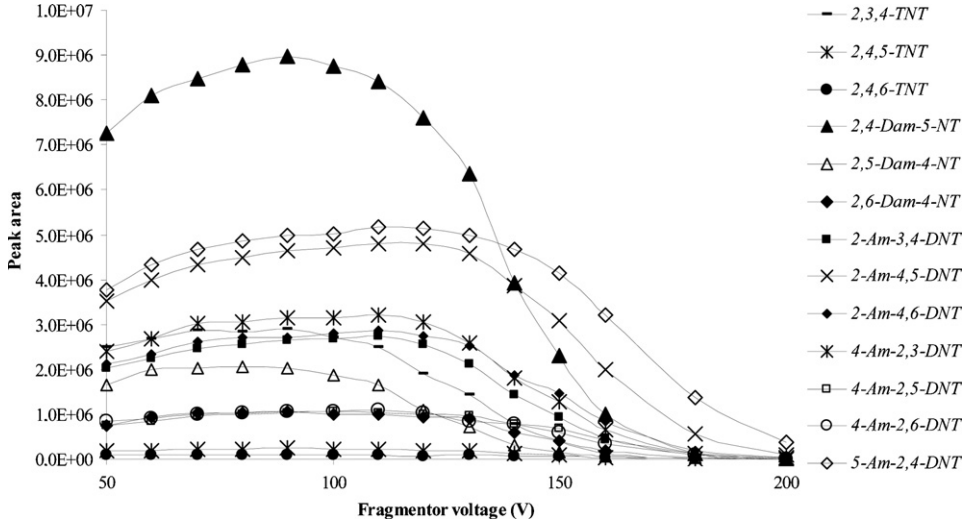

Fig. 4. Effect of fragmentor voltage. Mobile phase: methanol:ammonium acetate buffer pH 7 (43:57), flow rate = 1 mL/min, drying gas temperature 450 °C, capillary voltage 1500 V.

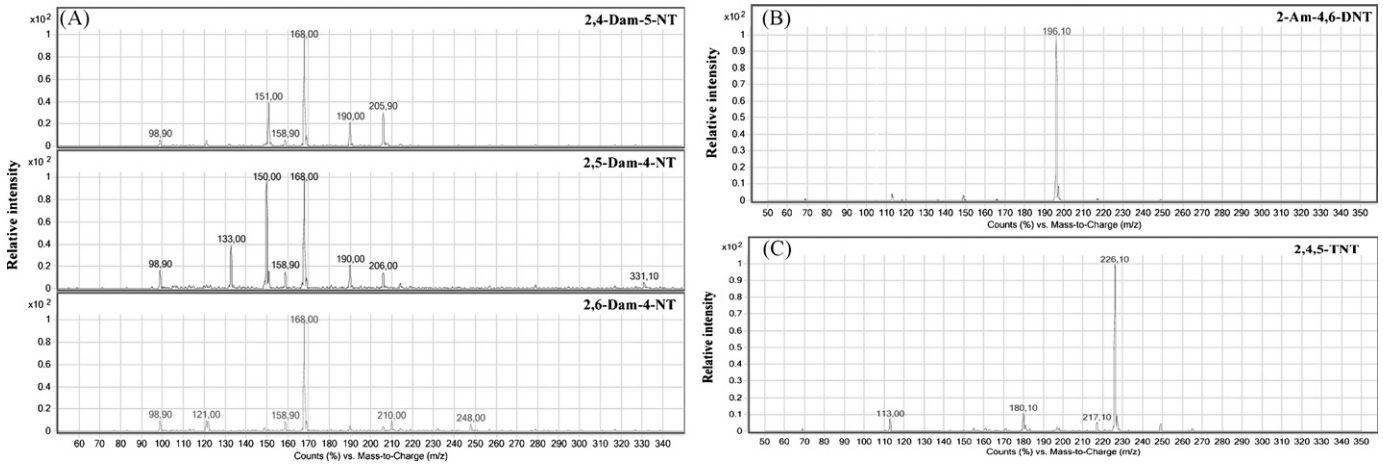

Fig. 5. MS spectra of (A) 2,4-diamino-5-nitrotoluene, 2,5-diamino-4-nitrotoluene and 2,6-diamino-4-nitroitoluene; (B) 2-amino-4,6-dinitrotoluene; and (C) 2,4,5-trinitrotoluene in SCAN mode.

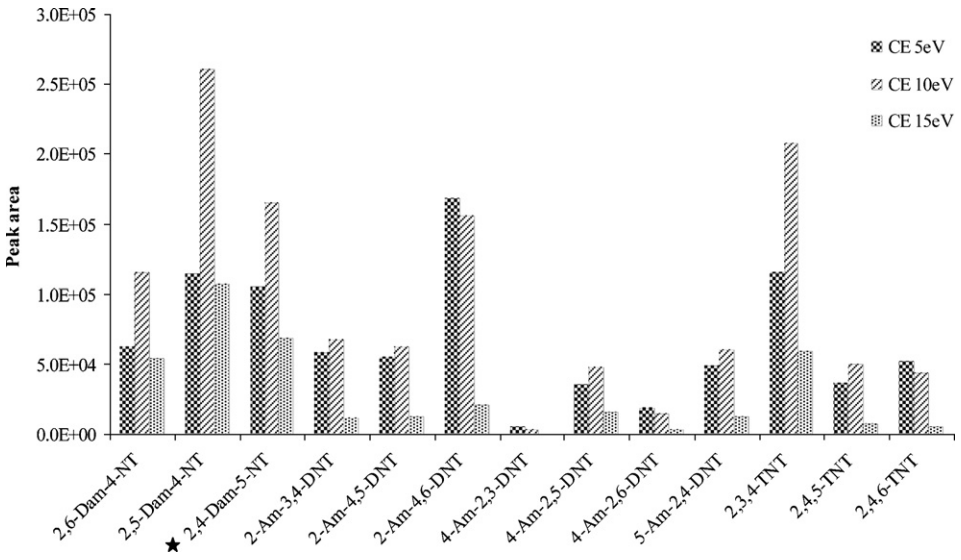

Fig. 6. Effect of collision energy on intensity of fragment ions. Mobile phase: methanol:ammonium acetate buffer pH 7 (43:57), flow rate = 1 mL/min drying gas temperature 450 °C, capillary voltage 1500 V. (★) Intensity of 2,4-diamino-5-nitrotoluene was tenfold decreased because of better lucidity.

used for interpretation of collision induced dissociation and selection of suitable identification and quantification ions are in the Fig. 7A–D.

3.2.2.1. Diamino nitrotoluenes. As to product ions created from *m*/*z* 168 ions of diamino nitrotoluenes (Fig. 7A) quite different results were obtained. The most abundance fragment created from 2,4-Dam-5-NT precursor ion suitable for MRM quantification is *m*/*z* 151 ion $[M–OH]^+$. The second significant fragment is *m*/*z* 121 $[M–OH–NO]^+$ ion. The *m*/*z* 105 ion would be created by the loss of NO_2 group from *m*/*z* 151 ion.

The most abundant ion created from 2,5-Dam-4-NT precursor ion is *m*/*z* 133 ion. It creates by the loss of OH group from *m*/*z* 150 ion $[M–H_2O]^+$. Similar as to 2,4-Dam-5-NT a loss of NO group resulted in *m*/*z* 120 ion. Fragmentation of 2,6-Dam-4-NT precursor ion resulted in two most abundant *m*/*z* 122 ion $[M+H–NO_2]^+$ and *m*/*z* 121 ion $[M+H–HNO_2]^+$. The *m*/*z* 105 ion can be created by a loss of HNO_3 group $[M+H–HNO_3]^+$.

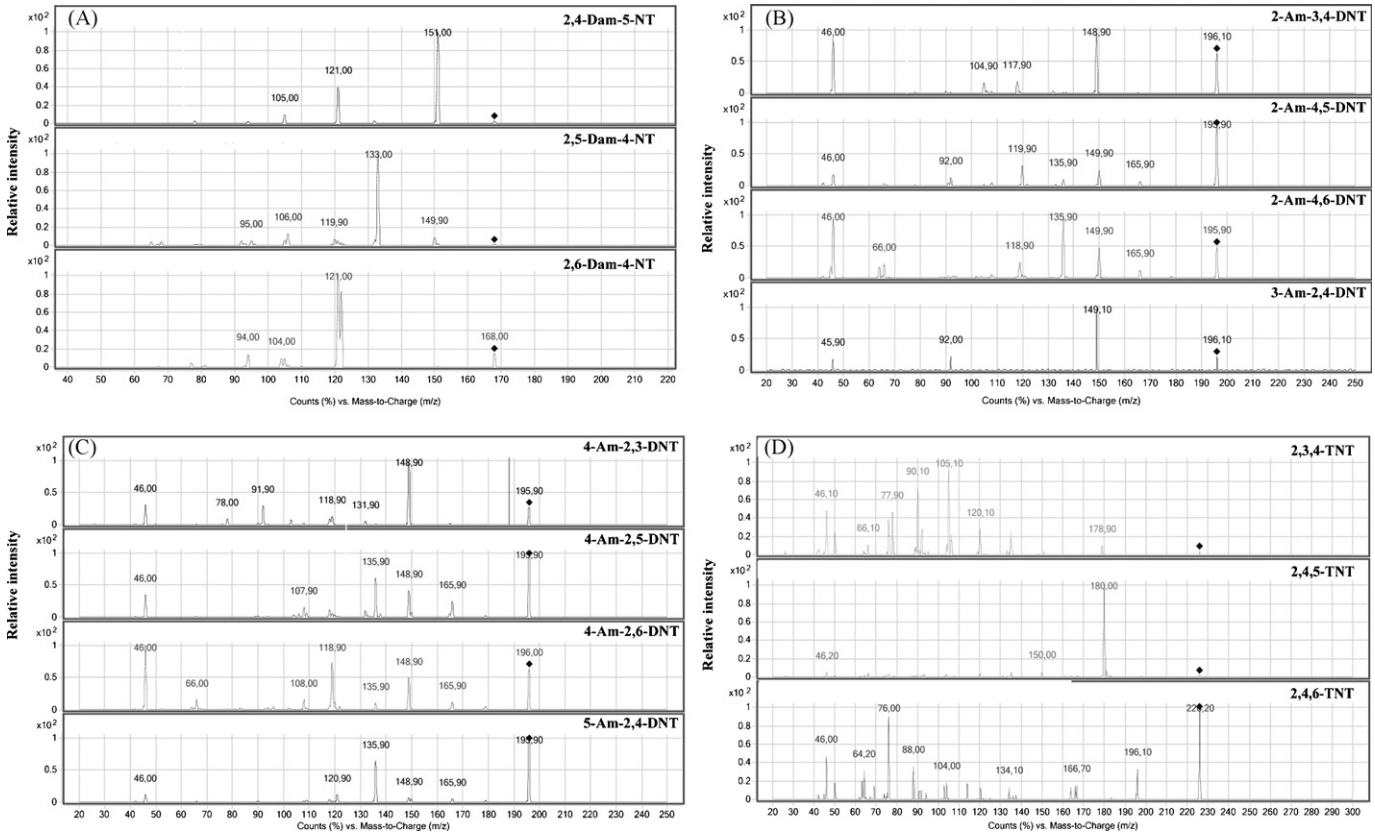

Fig. 7. MS product spectra of (A) diamino nitrotoluenes, (B and C) amino dinitrotoluenes and (D) trinitrotoluenes.

Table 1
Properties of HPLC–MS–MS identification and determination of TNTs and their amino derivatives in elution orders. Capillary voltage 1500 V, fragmentor voltage 110 V and collision energy 10 eV.

Peak	Compound	R_T (min)	Quantifier MRM	Qualifier MRM
1	2,6-Dam-4-NT	5.88	168/121	168/122
2	2,5-Dam-4-NT	6.27	168/133	168/133
3	2,4-Dam-5-NT	9.27	168/151	168/121
4	2-Am-4,5-DNT	21.96	196/120	196/150
5	2-Am-3,4-DNT	23.07	196/148	196/118
6	4-Am-2,3-DNT	24.38	196/150	196/119
7	2,4,6-TNT	27.22	226/76	226/196
8	2,4,5-TNT	30.33	226/180	226/150
9	4-Am-2,6-DNT	31.95	196/119	196/149
10	2-Am-4,6-DNT	34.72	196/136	196/150
11	5-Am-2,4-DNT	40.12	196/136	196/121
12	4-Am-2,5-DNT	45.93	196/136	196/149
13	2,3,4-TNT	48.52	226/105	226/90

3.2.2.2. Amino dinitrotoluenes. MS product ion spectra created from amino dinitrotoluenes precursor m/z 196 ions include the same fragment ion $[M–H–HNO_2]^-$ (m/z 149) and a ion 46 $[NO_2]^-$ (Fig. 7B).

In the case of 4-Am-2,5-DNT, 2-Am-4,5-DNT, 2-Am-4,6-DNT and 5-Am-2,4-DNT significant fraction of m/z 166 ion $[M–H–NO_2]^-$ and m/z 136 ion $[M–H–2NO]^-$ is created. Presence of m/z 119 ion created by the loss of NO group from the m/z 149 ion $[M–H–HNO_2]^-$ can be found in product spectra of amino dinitrotoluenes (Fig. 7B and C).

3.2.2.3. Trinitrotoluenes. Fragmentation of TNT isomers offers quite different main product ions created by subsequent loss of groups containing nitrogen and oxygen (Fig. 7D). The most simple spectrum was obtained in the case of 2,4,5-TNT with dominant m/z 180 ion $[M–H–NO_2]^-$.

Fragmentation of symmetric 2,4,6-TNT and related polynitro arenes with a hydrogen atom in the γ-position towards the nitro group is not quantitative due to formation of 4,6-dinitro-2,1-benzoisoxazole and other decomposition products. Therefore most abundant ion in the spectrum is precursor m/z 226 ion $[M–H]^-$. Comparable abundance can be observed for m/z 76 ion of 5-methylidenecyclopenta-1,3-diene fragmentation intermediate. The most abundant product ion resulted from fractionation of 2,3,4-TNT is m/z 105 ion $[M–H–2NO_2–NO]^-$.

3.2.3. Limits of detection

Under optimized conditions seven equidistantly prepared calibration samples in the range of 0.1–1 μg/mL were measured and calibration curves analyzed by the linear regression analysis. Relative standard deviations calculate as an absolute value of the coefficient variation of three repetitions was up to 8%. The instrumental limits of detection X_D^α and X_D^β were calculated according to Graham method [33] from the calibration plots. Comparison of SIM and MRM modes limits of detection are presented in Table 2.

Results demonstrate comparable values for SIM and MRM mode. The use of MRM enables to improve identification of studied compound especially in the case of co-eluting compounds.

Table 2
Limits of detection of nitroaromatic compounds using HPLC–MS or HPLC–MS–MS.

Compound	SIM		MRM	
	X_D^α (pg/μL)	X_D^β (pg/μL)	X_D^α (pg/μL)	X_D^β (pg/μL)
2,3,4-TNT	2.9	48.4	35.1	79.8
2,4,5-TNT	50.0	103.9	44.8	112.3
2,4,6-TNT	39.6	79.1	40.2	113.7
2,4-Dam-5-NT	21.6	62.7	26.7	76.8
2,5-Dam-4-NT	23.3	67.6	11.2	75.6
2,6-Dam-4-NT	15.4	45.0	26.0	83.6
2-Am-3,4-DNT	8.5	55.3	37.3	111.9
2-Am-4,5-DNT	14.3	75.7	26.9	84.2
2-Am-4,6-DNT	23.4	67.6	13.1	53.7
4-Am-2,3-DNT	25.2	72.7	58.0	135.7
4-Am-2,5-DNT	6.7	44.8	54.2	143.0
4-Am-2,6-DNT	29.4	86.7	4.0	55.6
5-Am-2,4-DNT	23.3	67.7	39.2	104.2

4. Conclusions

Optimized properties of analytical method based on RP-HPLC coupled with electrospray ionization tandem mass spectrometry were used for the separation and quantification of trinitrotoluenes and their degradation products. A new stationary phase designed especially for separation of EPA explosive mixture was used for separation of specific mixture of TNT isomers and their degradation products aminodinitro and diaminonitro derivatives. Modification of HPLC properties enables base-line separation of all analytes and therefore improving of their UV and MS identification and quantification. The use of on-line UV and MS–MS detection make possible to improve likelihood of identification, combining information obtained from UV and MS spectra. Using MS product spectra of collision induced dissociation fragmentation pathways can be described. Differences between dissociation of selected biodegradation products were showed and explained. Relations between products ions forming in case of multiple reaction monitoring analytical mode (MRM) and precursor ion structure were broadly clarified.

MS–MS qualification and quantification of explosives and their biodegradation products is feasible also in case of samples with complex matrix and high amount of co-eluting compounds. These advantages will be utilizing in the determination of polar explosives biotransformation products in environmental contaminated sites.

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