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FAST GC AND GC-MS ANALYSIS OF EXPLOSIVES

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Abstract

In this paper fast GC-ECD and GC-MS utilizing short narrow-bore capillary columns was evaluated for separation and detection of selected explosives. For injection splitless and on-column inlets were tested. In the case of MS detection different energies of electrons were tested in order to improve detectability of analyzed compounds. To eliminate strong adsorption of difficult explosives analyte protectants, formerly developed for GC analysis of pesticide residues, were tested. Significant improvements of peak shapes, linearity of responses and LODs were reached.

Keywords: explosives, fast gas chromatography, fast GC-MS, analyte protectants, matrix effects

1. Introduction

High explosives encountered in the forensic laboratory may be either pure or nearly pure compounds: nitroaromatics, nitrate esters, nitramines, or mixtures of these with or without other ingredients [1]. Gas chromatography (GC) methods with the advantage of a high resolving power are important to the trace analysis of explosives [2]. The highly efficient GC separation with the capillary columns permits the analysis of explosive oils, isomers of nitroaromatics and the high explosive pentaerythritol tetranitrate (PETN) and hexogen (RDX) in one run [3].

The importance of GC and also the distinct advantage over capillary electrophoresis and high-performance liquid chromatography is based on its compatibility with different detectors, rewieved by Yinon and Zitrin [4] and also by D.S. Moore [5]. GC can be interfaced the flame-ionization detector (FID), mass spectrometer (MS), nitrogen-phosphorus detector (NPD), electron capture detector (ECD) and thermal energy analyzer (TEA). The most selective detector for explosives is the TEA, which detects only compounds that produce NO and NO_2. The NPD is less selective than the TEA, but insensitive to nitrate esters. The ECD is less selective, but is more sensitive for nitroaromatics than the TEA or NPD [6,7,8].

Mass spectroscopic techniques have received perhaps the most extensive study for the detection of explosives. A mass spectrometer separates materials according to the mass to charge ratio of the parent ion and its fragments [5]. GC-MS with temperature-programmed injector was used by Yinon also for some thermally labile explosives [9]. Detailed study of injector conditions and extraction solvents on the detectability of nitroaromatic compounds was realised by Emmrich [10]. It was demonstrated that the packing material of the liner strongly influences the detectability of trinitrotoluene isomers.

As HMX and tetryl is difficult to analyze due to the thermal decomposition or the MS fragmentation is not sufficient for positive identification, the gas chromatography- tandem mass spectrometry (GC-MS/MS) can improve the selectivity and sensitivity by improving the differentiation of the target compounds from interfering and co-eluting compounds and reducing the background noise within an explosive debris sample [11,12].

Utilization of fast gas chromatography (fast GC) with narrow-bore capillary columns is advantageous for the use in routine laboratories due to the higher sample throughput, the same and even higher separation efficiency than conventional capillary GC, higher sensitivity and/or precision and simultaneous reduction of operating costs of a GC analysis [13,14].

The aim of this work was to study possibilities to reduce thermal decomposition and/or elimination of adsorption of selected explosives in order to improve quantitative data utilizing fast GC with narrow-bore capillary columns.

2. Experimental

All measurements were performed on narrow-bore capillary column CP-Sil 8 CB/Low Bleed – MS, 5 m long, I.D. 0.15 mm, film thickness 0.15 µm (Varian, Middelburg, The Netherlands) with 5 % diphenyl 95 % dimethylsiloxane stationary phase. Column was coupled to 1 m long retention gap, I.D. 0.32 mm with non-polar deactivation (Supelco, Bellefonte, USA) via press fit connector and sealed with polyimide resin (Supelco, Bellefonte, USA).

GC–MS measurements were performed on an Agilent 6890N GC coupled to 5973 MSD (Agilent Technologies, Avondale, PA, USA) equipped with PTV and autoinjector Agilent 7683. MS with electron impact ionization (EI) mode (70 eV) was operated in Full Scan and SIM mode; for each explosive two specific ions were selected (table I) and sorted into groups; the used dwell time was 10 ms. PTV was operated in splitless mode. The injection volume was 2 µl. Helium with purity 5.0 (Linde Technoplyn, Bratislava, Slovak Republic) was used as the carrier gas. Separations were performed at constant flow carrier gas conditions 1.2 ml/min and temperature program, 50°C (0.5 min), 90°C/min, 280°C. PTV inlet conditions: 175°C, split vent open time 0.5 min; flow rate 100 ml/min.

GC-MS measurements with analyte protectants were performed with PTV in solvent vent mode at following conditions: initial temperature 40°C (0.1 min), vent flow 50 ml/min (0.1 min), temperature ramp 300°C/min to 175°C, purge time 1.13 min, purge flow 100 ml/min. Oven temperature program: 50°C (1.13 min), ramp 90°C/min to 220°C.

GC-ECD measurements were performed on a HP 6890 gas chromatograph (Hewlett-Packard, Avondale, PA, USA) equipped with an on-column inlet operated in the oven-track mode. As a carrier gas, hydrogen (purity 99.99 %) was used (Linde, Technoplyn, Bratislava, Slovak Republic) with constant flow 1.5 ml/min. Temperature of ECD was 320°C, auxiliary gas flow rate was 60 ml/min and anode gas flow rate was 6 ml/min, nitrogen was used as auxiliary gas (99.999, Linde, Technolplyn, Bratislava, Slovak Republic). Data acquisition rate was 50 Hz.

Standards of explosives were obtained from different sources; standards mixture solution was prepared at the concentration 1 mg/ml in acetonitrile. For further work diluted standard solutions were prepared in acetone. All solvents used were suprasolv grade (Suprasolv, Merck, Darmstad, Germany).

As analyte protectants 3 compounds were used: 3-ethoxy-1,2-propanediol (98%), D-sorbitol (99%), L-gulonic acid χ-lactone (97%) (Aldrich, Germany); protectants solution at approximate concentration 40, 4, 4 mg/ml, respectively was prepared in the acetonitrile and water mixture (7:3). To 1 ml of explosives solution to be analyzed 20 µl of analyte protectants solution were added.

Table I. List of coumpounds under study, ions measured in SIM mode, SIM groups starts time for the methods for PTV in splitess mode and PTV in solvent vent mode. Ions in bold were used for quantitation.

Compound	SIM ions [m/z]	PTV splitless *SIM groups start times* [min]	PTV solvent vent *SIM groups start times* [min]
Nitrobenzene (NB)	**77**, 123	1	-
2-nitrotoluene (2-NT)	92, **120**	1.18	-
3-nitrotoluene (3-NT)	**91**, 137	1.25	-
4-nitrotoluene (4-NT)	91, **137**		-
2,6-dinitrotoluene (2,6-DNT)	148, **165**	1.50	2
2,4-dinitrotoluene (2,4-DNT)	89, **165**		
Trinitrotoluene (TNT)	180, **210**	1.90	2.50
Pentrite	**46**, 760		
RDX	**120**, 128	2.13	2.75

- not monitored

3. Results and Discussion

3. 1. Fast GC method development
3. 1.1 Set-up with splitless injection and MS detection

In fast GC with narrow-bore capillary columns when splitless injection is applied, retention gap or pre-column must be utilized. To obtain the narrow input-band width (to preserve the column efficiency) and to increase the transfer rate of solutes from the inlet to the column, solvent recondensation in the retention gap is required [15,16]. Moreover, volatile explosive analytes, such as nitrobenzene and nitrotoluenes also require solvent effect for proper peak focusation. Therefore, 1 m long 0.32 mm I.D. retention gap with non-polar deactivation was connected to the analytical column. The oven initial temperature was set to 50°C in order to achieve conditions for solvent (acetone) recondensation. This temperature is 37°C below the pressure corrected boiling point of acetone.

The base for fast GC and GC-MS method development was the use of Speed Optimized Flow (SOF) of carrier gas for which a simple formula was derived by Blumberg [17]:
$SOF=SOF_{100\mu m}$ x 0.01 x I.D. (µm),where $SOF_{100\mu m}$ is 1.0 ml/min for hydrogen and 0.8 ml/min is for helium.

The used PTV inlet in splitless mode has an advantage of significantly smaller internal volume of 150 µl instead of conventional splitless inlet with internal volume in the ranges of 250 – 980 µl. Smaller internal volume is advantageous for the analysis of thermolabile compounds due to the shorter residence time of sample vapors in a hot vaporizing chamber and thus decreased thermal decomposition is expected. However, other important parameter preventing thermal decomposition is the temperature of GC inlet. In figure 1, average relative responses (calculated to 2,6-DNT, n=3) of thermolabile compounds under study are presented for different inlet temperatures. The highest relative responses for TNT, pentrite and RDX were obtained for 150 and 175°C, respectively. The increase of relative responses of RDX is visible increasing the temperature from 125°C to 150, 175°C due to the better vaporization process. At these temperatures a slight degradation of pentrite starts. At the higher inlet temperatures (>175°C) a decrease of relative responses is caused by the thermal degradation of all tested compounds. In figure 2, the relative standard deviations (RSD, n=3) of relative responses are presented. RSDs generally increase with increasing temperatures; the lowest values were found at temperatures 150 and 175°C. For further work temperature 175°C was chosen.

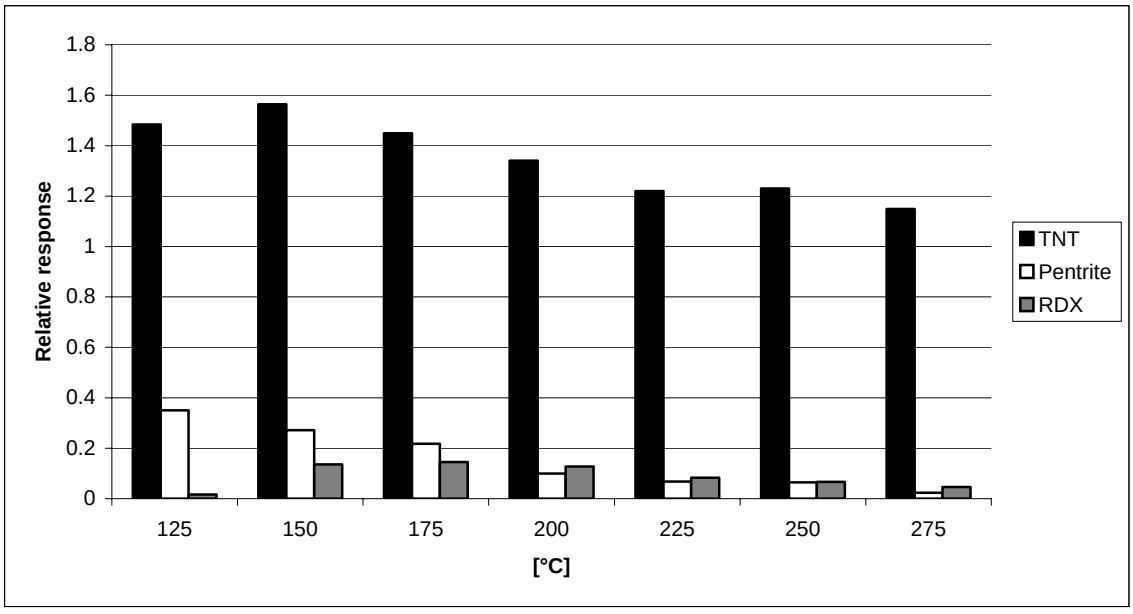

Fig. 1. Average relative response (n=3), calculated to 2,6 DNT, for problematic compounds in the dependence on temperatures of PTV in splitless mode, concentration 10 ng/µl, injected volume 0.5 µl.

As the PTV has small internal volume, the hot splitless injection can suffer from overloading the vaporizing chamber by the sample vapor resulting in the loss of a sample via septum purge vent. Therefore, also capacity of PTV multibaffled liner was checked by the injection of different volumes: 0.2, 1 and 2 µl of solution of explosives at the concentration 1 ng/µl in acetone. Average responses (n=3) were linear over the interval tested, what means that no losses of sample occurred.

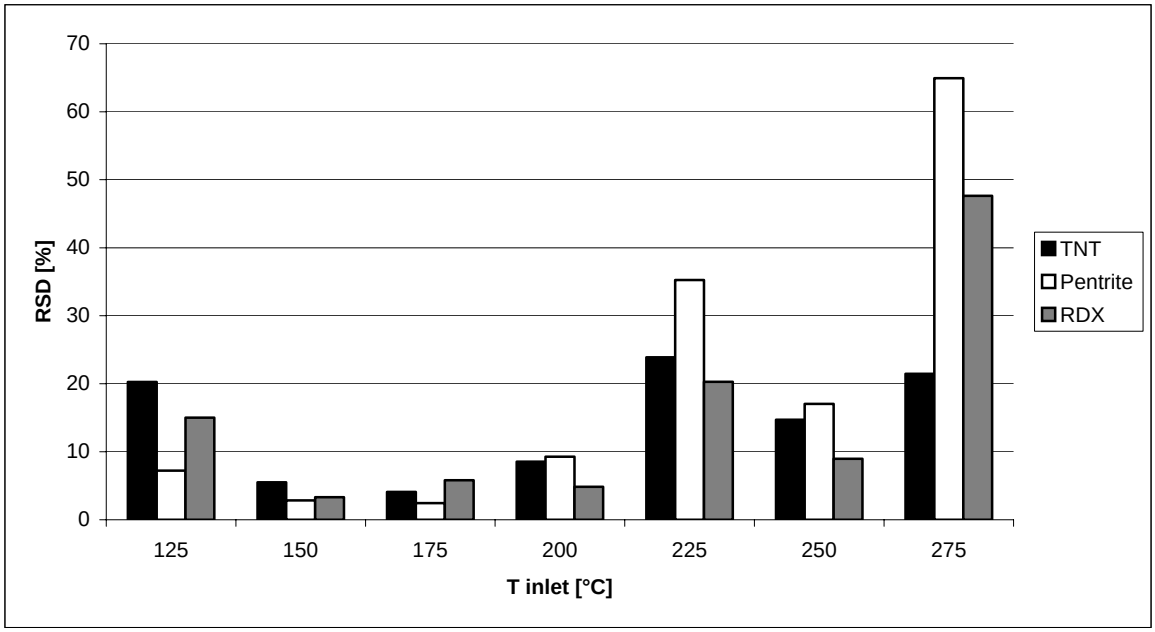

Fig. 2. Dependence of relative standard deviations of relative responses (n=3) of problematic compounds on temperatures of PTV inlet in splitless mode.

An optimal temperature ramp rate for GC is that which renders the best separation in the least time. Blumberg and Klee recommend such a ramp rate: 10 °C per void time (t_M) [18]. At SOF conditions (1.2 ml/min) and the used column, the void time is 5.1 s and the temperature ramp required is 117°C/min. The maximal temperature ramp provided by GC Agilent 6890 over wide temperature range is 90 °C/min. The influence of oven temperature ramp on the detectability of compounds under study expressed as signal to noise ratio was compared at two different temperature ramps, 30 and 90°C/min, respectively. The use of lower temperature ramp resulted in significantly decreased S/N ratios (table II) what is supposed to be caused by the increased peak widths obtained when compared to the higher ramp (table II). The analysis time was 4 and 2.2 min for 30 and 90°C/min, respectively. Therefore, for further work 90°C/min temperature ramp was used.

Table II. Comparison of signal to noise ratios and peak widths of explosives at different oven temperature ramps.

Compound (m/z)	30°C/min		90°C/min	
	S/N	$W_{1/2}$ [min]	S/N	$W_{1/2}$ [min]
NB (123)	310	0,008	390	0,008
2-NT (120)	287	0,009	2450	0,008
3-NT (137)	536	0,015	816	0,005
4-NT (137)	213	0,017	379	0,009
2,6-DNT (165)	221	0,021	259	0,009
2,4-DNT (165)	54	0,022	91	0,011
TNT (210)	203	0,021	498	0,014

The last tested parameter that could influence the detectability of explosives under study was the electron energy used for electron impact ionization (EI). The conventional energy of electrons used is 70 eV; in the range of electron energies around 70 eV the influence on the fragmentation process of most of the organic compounds molecules is not significant. Therefore, the checked electron energies for explosives were 70, 50, 30, 10 and 5 eV. The significant change of mass spectra occurred only at 5 eV. The significant decrease of absolute ion abundances was observed with the decreasing electron energies. However, also noise level was decreasing and resulted in compounds dependent S/N ratios (figure 3) measured for quantification ions, which were either almost constant, or changed. The

decrease of ion abundances is probably caused by the decreased ionization efficiency at lower potentials.

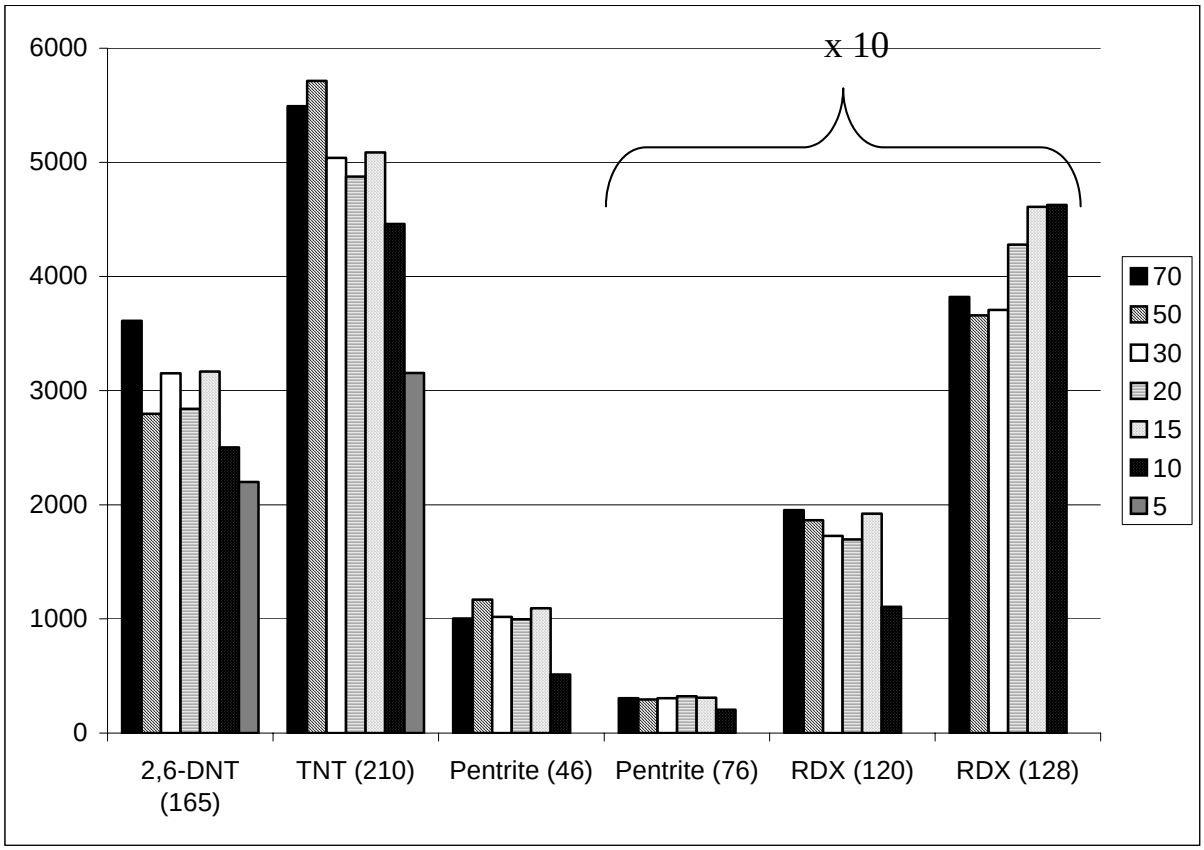

Fig. 3. Dependence of signal to noise ratios of explosives for EI electron energies, injected volume 1 µl, concentration 10 ng/µl.

3.1.2 Set up - on-column injection with ECD

The other experimental set-up tested was fast GC with on-column inlet, hydrogen as carrier gas and electron capture detection (ECD). In the case of on-column inlet, an initial oven temperature is critical for compounds focusation. The initial oven temperature has to be below the pressure corrected boiling point of the used solvent. At excessively low temperatures and/or insufficient lengths of retention gap for the given injection volume the injected liquid can be transported by the stream of carrier gas to the analytical column and subsequently peak shape distortion occurs [19,20]. The optimum initial temperature for injection of 2 µl was found to be 60°C utilizing 1 m long retention gap.

The other investigated parameter was the flow of an auxiliary gas for ECD – nitrogen tested in order to decrease the peak widths and peak tailing, but even at the maximal flow (200 ml/min and 12 ml/min anode) no improvement of peak shape was observed.

3.1.3 Utilisation of analyte protectants

Polar organic compound to be analyzed by GC suffer from their adsorption on active sites on the surface of inlet liner, retention gap and/or analytical column. Typical example widely studied in literature are pesticides residues [21,22,23]. Their responses are strongly dependent on the presence of co-extracted matrix components. In the real sample analysis ever present matrix co-extractives are retained by active sites of the separation system used more strongly than the analytes and thus higher amount of pesticide residues is transported to the detector, what increase their response. This effect is in the analysis of pesticide residues practice called chromatographic matrix induced response enhancement, or shortly matrix effect. To reduce the matrix effect and thus eliminate arising errors in quantitation, novel approach has been adopted by Anastassiades and Lehotay et al. [24,25]. In this concept special compounds called analyte protectants are added to the sample and to the standards solution in a neat solvent. The role of these compounds is to adsorb on the active sites and thus decrease their number in the separation system, predominantly on the injector site. Subsequently

lower amount of polar analytes are adsorbed and the higher response is obtained on the detector site. Except the improvement of response, also significant peak tailing elimination has been observed with the application of analyte protectants [25]. As effective combination of analyte protectants 3-ethoxy-1,2-propanediol, D-sorbitol, L-gulonic acid χ-lactone were proposed. A mixture solution of these three compounds is prepared in the acetonitrile and water mixture (7:3). A small portion of analyte protectants is added to the sample. Water present in the solution can adversely influence the stationary phase in the column. Therefore, we decided to use PTV inlet in solvent vent mode to eliminate the solvent and water and MS detection.

In table III average peak tailing for the searched explosives is presented; as can be seen, significant improvement of peak tailing is observed for all compounds.

Table III. Improvement of peak tailing with application of analyte protectants in GC-MS measurement at concentration level 0.1 ng/µl.

	Peak tailing	
	Without AP	With AP
2,6-DNT	2.57	0.81
2,4-DNT	3.30	1.00
TNT	2.00	0.93
Pentrite	3.20	1.35
RDX	3.37	1.60

AP – analyte protectants

During the optimization of PTV inlet in solvent vent mode no conditions were found suitable for the proper solvent elimination without a loss of volatile explosives (NB, 2-NT, 3-NT and 4-NT). Therefore, only DNTs, TNT, pentrite and RDX were evaluated. In figure 4, chromatograms measured in SIM mode at the concentration level 0.1 ng/µl is presented.

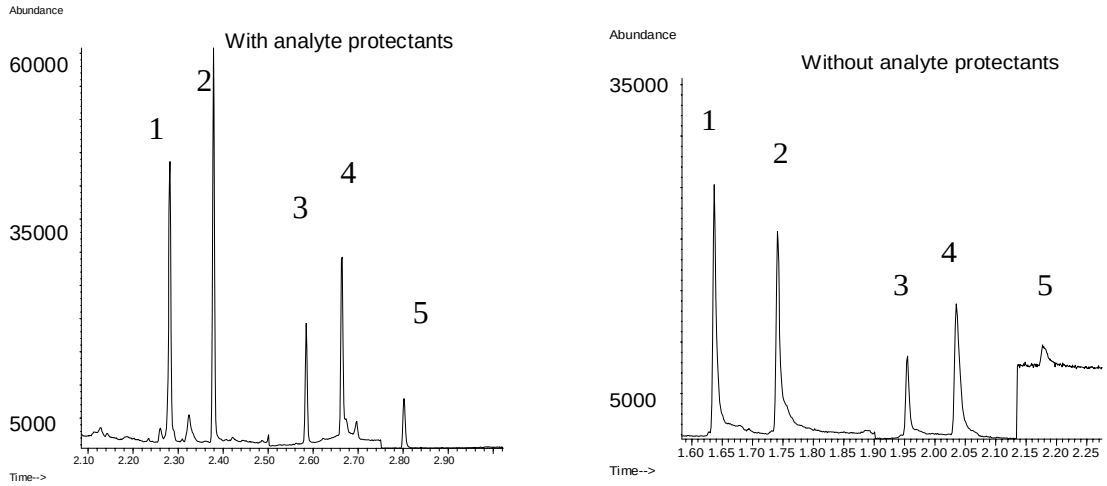

Fig. 4. SIM chromatograms of explosives with and without analyte protectants, concentration 0.1 ng/µl, injection volume 2 µl; other experimental conditions - in experimental part; 1 – 2,6 DNT, 2 – 2,4 DNT, 3 – TNT, 4 – pentrite, 5 – RDX.

3.2. Calibration

Calibration of GC-MS with solutions of explosives in a neat acetone and with addition of analyte protectants and GC-ECD was performed at the following concentration levels: 0.001, 0.005, 0.01, 0.05, 0.1, 0.5, 1 and 5 ng/µl. For GC-MS linear calibration model was used, while for GC-ECD polynomial line of 2nd order was chosen. In table IV coefficients of determination, limits of detection (LOD) and limits of quantification (LOQ) are presented.

Table IV. Coefficients of determination (R^2), LODs, LOQs for GC-MS calibration experiments: with and without application of analyte protectants and GC-ECD set-up.

	GC-MS R^2	GC-MS +AP R^2	ECD R^2	GC-MS LOD S/N pg/µl	GC-MS +AP LOD S/N pg/µl	ECD LOD pg/µl	GC-MS LOQ S/N pg/µl	GC-MS +AP LOQ S/N pg/µl	ECD LOQ pg/µl
NB	0.9999	-	0.9995	0.071	-	0.32	0.24	-	1.1
2-NT	0.9998	-	0.9996	0.28	-	0.22	0.95	-	0.72
3-NT	0.9996	-	0.9997	0.17	-	0.55	0.57	-	1.8
4-NT	0.9993	-	0.9997	0.065	-	1.1	0.22	-	3.6
2,6-DNT	0.9994	0.9998	0.9993	0.088	0.028	0.18	0.29	0.093	0.61
2,4-DNT	0.9987	0.9996	0.9989	0.063	0.035	0.41	0.21	0.12	1.4
TNT	0.9966	0.9976	0.9997	0.029	0.042	0.41	0.096	0.14	1.4
Pentrite	0.9989	0.9991	0.9984	0.13	0.15	33	0.44	0.51	110
RDX	0.9996	0.9997	0.9996	27	0.19	0.60	89	0.63	2.0

Coefficients of determination are slightly higher for the calibration with the addition of analyte protectans except of TNT. LODs and LOQs were calculated from signal to noise ratios, for LOD three times the noise and for LOQ ten times the noise level was taken. LODs and LOQs are better for GC-MS set-up than GC-ECD set-up for all compounds except of 2-NT. The use of analyte protectants has the highest positive impact on RDX for which LOD increased from 0.027 ng/µl to 0.00019 ng/µl. Improvement of the searched parameters with analyte protectants has been observed also for DNTs.

4. Conclusions

For separation and detection of explosives fast GC with ECD and fast GC with quadrupole MS detector were employed. In order to improve detectability of tested explosives, several parameters of experimental set-up were optimized. In the case of splitless injection great effect of inlet temperature on the decomposition of problematic compounds was observed. Small internal volume of the PTV inlet in the splitless mode provided very fast transport of solutes to the column and enabled injection of 2 ul of acetone solution of explosives. Energy of electrons for EI ionization was found to have no significant influence on the detectability of the searched explosives. In the case of ECD utilized for detection, significant band broadening was observed in the cell of the detector and increase of auxiliary gas flow rate had no positive effect on the peak shapes. GC separation of polar explosives suffers from their adsorption in the chromatographic system resulting in decreased response and peak tailing. Application of analyte protectants has significantly lowered the degree of explosives adsorption in the system resulting in improved peak shapes, linearity of response and LODs and LOQs, mainly for dinitrotoluenes and RDX.

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