

A Study upon the Possibility of the Chromatographic Investigation of the Nitrogen Rich Energetic Compounds Prepared By Picryl Chloride and Heterocyclic Amines

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Abstract

Nitrogen rich energetic compounds were prepared by the reaction of heterocyclic amines such as 3-aminopirazol, 3-amino-1,2,4-triazol, 3,5-diamin-1,2,4-triazol, 5-aminotetrazol, guanidine and semicarbazite with 1-chloro-2,4,6-trinitrobenzene (picryl chloride) in alcohol media. The resulting energetic compounds were characterized by elemental analysis, IR spectroscopy, mass spectroscopy, ¹HNMR, ¹³CNMR methods. The behavior of these compounds in ODS columns have also been investigated, using various MeCN, H₂O and MeOH mobile phase compositions and the most suitable mobile phase for the HPLC investigation of these compounds was found to be %60-%40 MeCN/H₂O. There was a slight quantity of hydrolysis observed in the water bearing media but it was concluded that this does not affect the HPLC analysis.

Keywords: Picryl chloride, picryl substituted energetic materials, nitrogen rich energetic materials, HPLC, chromatographic separation.

1. Introduction

1-Chloro-2,4,6-trinitro benzene or commonly known as picryl chloride readily reacts with amines. This is due to the fact that 2,4,6-trinitro benzene is a highly nucleophilic group [1,2]. Although many of the aromatic compounds give electrophilic substitution upon the aromatic ring, the aromatic ring in picryl group is much more suitable for the nucleophilic substitution due to the effects of three nitro groups. That is why picryl chloride readily gives substitution reaction with primary and secondary amines (Fig.1).

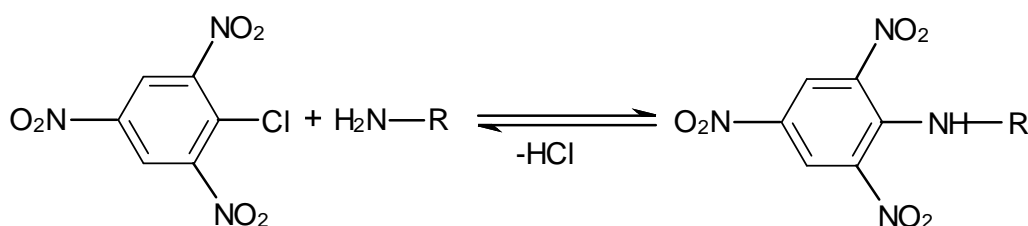


Figure 1. The reaction between picryl chlorides and amines

This feature of picryl chloride makes it very popular in the research related to the new energetic materials [3-5]. However a part of all the picryl compounds converts into picric acid as a result partial hydrolysis in aqueous media (Figure 2) Picric acid is stronger than most of the acids with a K_a value of 0.419 [6] and can form very strong hydrogen bonds and is very suitable for the ionization. That is the picryl compounds have the tendency to convert into picric acid due to its high stability.

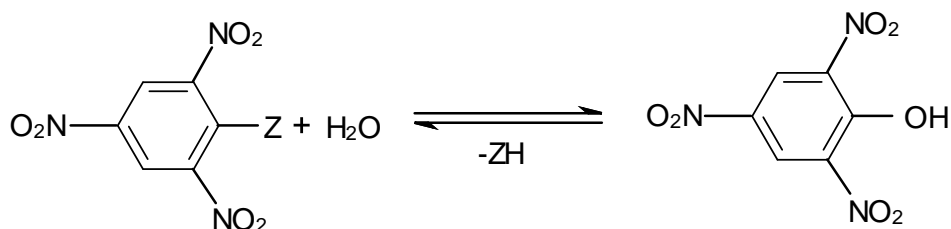
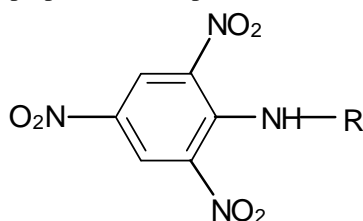


Figure 2. Hydrolysis of picryl compounds

The hydrolysis reaction is in competition with the aminolysis reaction based upon the nucleophilic power of the substituents attached to picryl group [7-8]. It is a long known fact that amine groups are much stronger nucleophiles than the hydroxyl group [9]. In spite of this there formation of small amount of picric acid reported even if the picryl moiety includes amine group [10]. The picryl compounds are reported to form a significant amount of picric acid which would cause problems in HPLC analysis. This study is carried out for the investigation of this situation.

There are six energetic compounds prepared based upon the following general formula



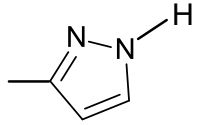
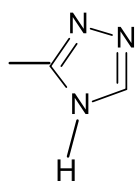
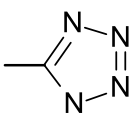
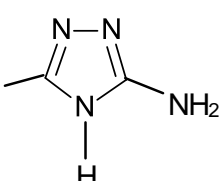
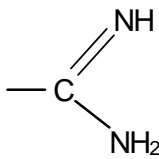
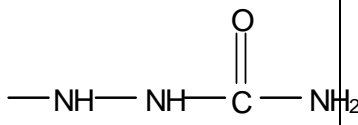
R=	 N(2,4,6-trinitrophenyl)-3-aminopyrazol (I)	 N(2,4,6-trinitrophenyl)-3-amino-1,2,4-triazol (II)	 N(2,4,6-trinitrophenyl)-5-aminotetrazol (III)
	 N(2,4,6-trinitrophenyl)-3,5-diamino-1,2,4-triazol (IV)	 N(2,4,6-trinitrophenyl) guanidine (V)	 N(2,4,6-trinitrophenyl) semicarbazide (VI)

Figure 3. The open structures of the energetic compounds prepared.

After the characterization of all the energetic compounds prepared they were passed through the ODS colon by the use of mobile phase mixtures of MeCN- H₂O, MeOH – H₂O and MeCN-MeOH-H₂O to determine whether the analysis of these compounds are possible by the use of this technique. The best results were obtained in MeCN-H₂O (%60-%40,V/V) mobile phase because MeCN is aprotic solvent and the probability of hydrolysis it can reduce. Consequently, possibility of the analysis of the energetic materials containing picryl group were proven by using HPLC systems.

Experimental

The configuration employed in the HPLC studies was Shimadzu LC-20AT Shimadzu LC-20AT gradient pumping system, Shimadzu SPD-20A the column oven Shimadzu CTO-2A model. The column temperature was kept constant at 40 °C. The flow rate was chosen as 0.75-1.0 cm³/minute and there was no gradient study and the detection was carried out at $\lambda = 280$ nm. The energetic compounds were injected to HPLC. After being diluted by the use of 50 ppm stock solution the FTIR spectra of the compounds synthesized were taken by the use of a Shimadzu infinity model FTIR connected to the 3 reflective ATR devices. The range of the measurement was 600-4000 cm⁻¹. The resolution of the apparatus was kept at 4 cm⁻¹ taking the average value of 20 scans. The mass spectra were taken by the Shimadzu 2010 plus GCMS however the compounds were injected into the system through direct inlet of the apparatus (since the energetic compounds dissociate in the GC column the use of gas chromatography was meaningless). ¹H-NMR and ¹³C-NMR spectra were taken in d₆-DMSO using Varian Mercury model 400 MHz NMR equipment and the elemental analyses were recorded using Eurovector 3018 CHNS analyzer apparatus.

The synthesis of picryl chloride: Picryl chloride was prepared by the reaction of picric acid with POCl₃ using N, N'-dimethylaniline as a proton scavenger following the procedures described in the literature [11]. 15 g picric acid was dissolved in 100 mL phosphorus oxychloride in a double necked round flask at room temperature. While stirring rapidly, N-N'-dimethylaniline was added to it in drop wise manner. The mixture was stirred for 30 minutes keeping the temperature around 80 °C. Following this process the flask was placed into an ice bath to cool the solution down to 10 °C. The cooled solution was poured on 800 mL salt-ice mixture stirring with a mechanical stirrer. Temperature was carefully kept under 40 °C by adding ice when needed. After all the excess phosphorus oxychloride was hydrolyzed, solid picryl chloride was filtered off and dried at 50 °C. The product was recrystallized in MeOH. The melting point and the yield were found to be 84-87 °C and 80%. The characterization results of the final product are as follows:

Elemental Analysis: Calculated (%), C: 29.11, H: 0.81, N: 16.96; Experimental (%), C: 28.77, H: 1.07, N: 17.24

IR absorption bands (cm⁻¹): $\nu_{C-H(Ar)}$: 3097,56 cm⁻¹, $\nu_{C=C}$: 1611,5 and 1591.59, $\nu_{C=C}$: 1564.83 cm⁻¹, $\nu_{N=O}$: 1334,74 cm⁻¹, $\delta_{C-H(ar)}$: 721,63

m/z: 247 (molecular peak), 212, 167 109, 120, 74 (base peak)

¹H-NMR peaks (δ , ppm, in d₆-DMSO): 8.91 s

¹³C-NMR peaks (δ , ppm, in d₆-DMSO): 148.52 s, 142.76 s, 125.82 s, 123.96 d.

The preparation of the explosive compounds

General preparation: 2.47 g (0.01 mole) 2,4,5-trinitrochlorobenzene (picrylchloride) was dissolved by heating in 50 mL MeOH in two necked flask and it was heated up to the boiling temperature in a reflux condenser. Then a solution of 0.01 mol aminoheterocyclic compound in 20 mL hot MeOH was added to it and the resulting mixture was boiled under reflux for 4 hours until half of the solution was evaporated. The yellow precipitate was filtered off and dried in air.

N-2,4,6-trinitrophenyl-3-aminopyrazol, (I) was prepared by the reaction of 2.47 g picrylchloride and 0.73 g 3-aminopyrazole. The yield was %80-82.

Elemental Analysis: Expected %, C: 36.75; H:2.06 ; N:28.56, Found % , C: 37.09 ; H:2.13 ; N: 29.86
IR data (cm⁻¹): ν_{N-H} : 3288.63, $\nu_{C-H(Ar)}$: 3091.89, $\nu_{C=N}$: 1612.49, $\nu_{C=C(Ar)}$: 1595.13-1543.05-1514.12, $\nu_{N=O}$:1323.17, $\delta_{C-H(Ar)}$:767.67

m/z: 294(molecular peak), 248 (base peak), 202, 156, 129, 102, 74

¹H-NMR data (δ , ppm, in d₆-DMSO): 12.51, 10.30, 8.91, 7.66, 6.16

¹³C-NMR data (δ , ppm, in d₆-DMSO): 147.28, 138.67, 137.39, 135.40, 130.39, 126.50, 97.69

N-2,4,6-trinitrophenyl-3-amino-1,2,4-triazol, (II) was prepared by the reaction of 2.47 g picrylchloride and 0.83 g 3-amino-1,2,4-triazol. Yield: %77-80.

Elemental Analysis: Expected %, C: 32.56 ; H:1.70; N:33.20, Found % , C: 31.87 ; H:1.21 ; N: 35.03
IR data (cm^{-1}) : $\nu_{\text{N-H}}$:3300.20-3248.13, $\nu_{\text{C-H(Ar)}}$:3088.03, $\nu_{\text{C=N}}$:1616.35, $\nu_{\text{C=C (Ar)}}$:1593.20-1512.19,
 $\nu_{\text{N=O}}$:1342.46, $\delta_{\text{C-H(Ar)}}$:713.66

m/z:295 (molecular peak), 249 (base peak), 203, 157,129,102,74

$^1\text{HNMR}$ data (δ , ppm), in d_6 -DMSO: 10.82, 10.38, 9.29, 8.98,

$^{13}\text{CNMR}$ data (δ , ppm), in d_6 -DMSO: 147.54, 145.68, 141.62, 140.28, 125.72, 124.90

N-2,4,6-trinitrophenyl-5-aminotetrazol, (III) was prepared by the reaction of 2.47 g picrylchloride and 0.85 g 5-aminotetrazol according to the method given in the literature[12]. Since 5-Aminotetrazol is sparingly soluble in MeOH so it was first dissolved in 10 mL DMF by heating and this solution was diluted with 40 mL MeOH before adding the solid. Yield: %35.

Elemental Analysis: Expected %, C: 28.39; H:1.36 ; N:37.83, Found % , C: 27.65 ; H:0.41; N: 38.68
IR data (cm^{-1}) : $\nu_{\text{N-H}}$:3319.49, $\nu_{\text{C-H(Ar)}}$:3084.18, $\nu_{\text{C=N}}$:1625.99, $\nu_{\text{C=C (Ar)}}$:1604.77-1558.46, $\nu_{\text{N=O}}$:1327.03,
 $\delta_{\text{C-H(Ar)}}$:702.09

m/z: 296 (molecular peak), 270, 228, 226, 213, 198, 178, 167, 132, 116, 62, 43 (base peak)

$^1\text{HNMR}$ data (δ , ppm), in d_6 -DMSO:

$^{13}\text{CNMR}$ data (δ , ppm), in d_6 -DMSO:

N-2,4,6-trinitrophenyl-3,5-diamino-1,2,4-triazol, (IV) was prepared from 2.47 g picrylchloride and 0.5 g 3,5-diamino-1,2,4-triazole . Although it was initially planned to attach picryl groups symmetrically on two amino groups the elemental analysis, IR spectroscopy, mass spectroscopy and NMR results revealed that there was only one picryl group attached to it .The yield was %48.

Elemental Analysis: Expected %, C: 30.98 ; H:1.95; N:36.11 , Found % , C: 29.51 ; H:1.46 ; N: 37.27
IR data (cm^{-1}): $\nu_{\text{N-H}}$: 3386.08-3246.01, $\nu_{\text{C-H(Ar)}}$:3088.03, $\nu_{\text{C=N}}$: 1618.28, $\nu_{\text{C=C (Ar)}}$:1602.02-1574.10,
 $\nu_{\text{N=O}}$:1323.17, $\delta_{\text{C-H(Ar)}}$:732.95

m/z: 310(molecular peak), 264 (base peak), 218, 172, 130, 103, 74

$^1\text{HNMR}$ data (δ , ppm), in d_6 -DMSO: 11.79, 10.15, 8.92, 6.19

$^{13}\text{CNMR}$ data (δ , ppm), in d_6 -DMSO: 148.11, 147.26, 137.90, 136.26, 126.10, 109.82

N-2,4,6-Trinitrophenylguanidin, (V) was prepared by 2.47 g picrylchloride and 0.9 g guanidiniumcarbonate. 0.9 g Guanidinium carbonate [$(\text{CH}_6\text{N}_3)_2\text{CO}_3$] was suspended in 40 mL MeOH and 1.12 g KOH solution in 50 mL MeOH was added to it .The resulting mixture was stirred for approximately ten minutes and then filtered off. There was 2.47 g solid picrylchloride was added to it and refluxed for 2 hours. At the end of this process the mixture was transferred to a beaker, evaporated to the half of its volume and left on the bench for a day. The resulting yellow product was filtered off and dried in air. The yield was % 45.

Elemental Analysis: Expected %, C: 31.12; H:2.24; N:31.09, Found % , C: 30.58 ; H:2.33 ; N: 32.86
IR data (cm^{-1}) : $\nu_{\text{N-H}}$:3473.80, $\nu_{\text{C-H(Ar)}}$:3082.25, $\nu_{\text{C=N}}$:1649.14, $\nu_{\text{C=C (Ar)}}$:1604.77-1556.55, $\nu_{\text{N=O}}$:1317.38,
 $\delta_{\text{C-H(Ar)}}$:711.73

m/z: 270 (molecular peak), 228 (base peak), 213, 198, 90, 75, 60, 43

$^1\text{HNMR}$ data (δ , ppm), in d_6 -DMSO:8.61, 6.95

$^{13}\text{CNMR}$ data (δ , ppm), in d_6 -DMSO:160.88, 157.93, 141.81, 125.28, 124.37

N(2,4,6-Trinitrophenyl)semicarbazite, (VI) was prepared with 2.47 g picrylchloride and 0.75 g semicarbazite .This compound gave a mono substitution process with only one hydrogen of the picryl group on amino group .

Elemental Analysis: Expected %, C: 31.12 ; H:2.24 ; N:31.09, Found % , C: 30.58; H:2.33; N: 32.86
IR data (cm^{-1}) : $\nu_{\text{N-H}}$:3473.80, $\nu_{\text{C-H(Ar)}}$:3082.25, $\nu_{\text{C=N}}$:1649.14, $\nu_{\text{C=C (Ar)}}$:1604.77-1556.55, $\nu_{\text{N=O}}$:1317.38,
 $\delta_{\text{C-H(Ar)}}$:711.73

m/z: 270 (molecular peak), 228 (base peak), 213, 198, 90, 75, 60, 43

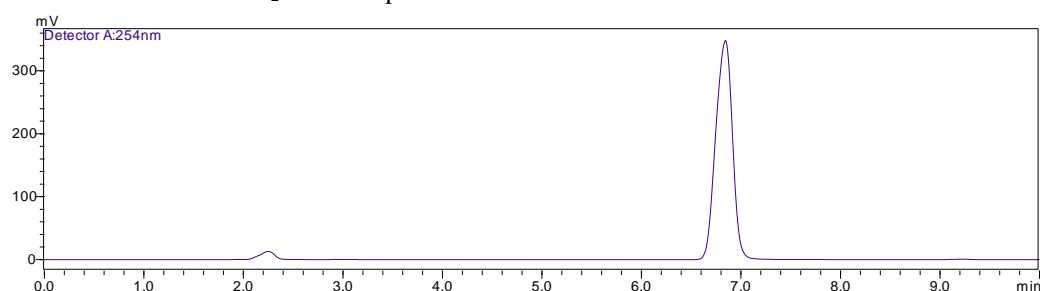
$^1\text{HNMR}$ data (δ , ppm), in d_6 -DMSO:

$^{13}\text{CNMR}$ data (δ , ppm), in d_6 -DMSO:

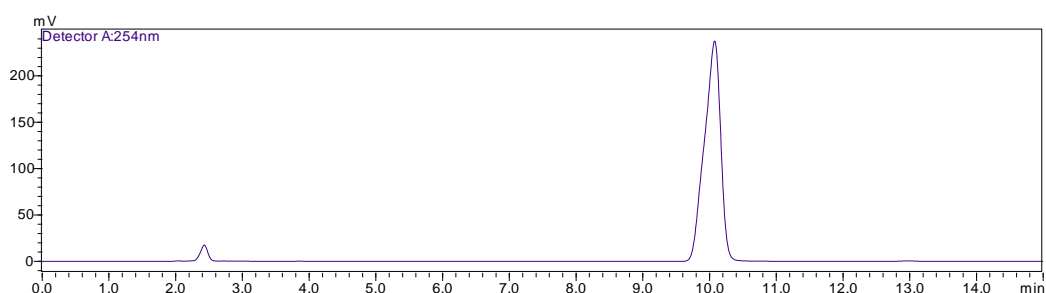
Results and Discussion

The mobile phases used in the study were MeOH-H₂O and MeCN-H₂O mixtures. Although there was not a significant difference between them the peaks obtained with MeCN mobile phase were much sharper than peaks obtained with the use MeOH which tends give broader peaks. That is why the mobile phase used throughout the study was MeCN-H₂O mixture. There was no difference observed between the capture times of %100 MeOH and %100 MeCN as mobile phases. There were no difference between of these mobile phases and they gave no separation. However the addition of certain amount of water made the separation possible. The optimal mobile phase composition was found to be between %60-%40 and %50-%50 MeCN/H₂O mixture. The increase in the amount of H₂O increase the risk of precipitation of the energetic compound so the H₂O ratio was increased up to %50 at the most. Since all the compound have been prepared by the use of picryl chloride one needs to know the behavior of picryl chloride in the carrier phases mentioned above. Figure 4 shows the recapture times (t_R) of picryl chloride in four different phase compositions. As expected the recapture time of picryl chloride in the colon is increased as the water content of the carrier phase is increased.

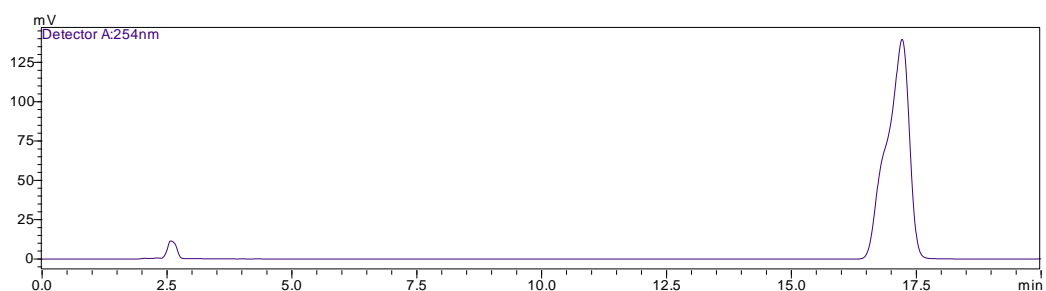
a. with %90-%10 MecN/H₂O mobile phase



b. with %70-%30 MecN/H₂O mobile phase



c. with %60-%40 MecN/H₂O mobile phase



d. %50-%50 MecN/H₂O mobile phase

Figure 4. The behavior of Picryl chloride in mixtures of MeCN/H₂O in ODS colon.

The striking point in the chromatograms depicted in Figure 4. Is that the signal occurred at is $t_R = 2.2-2.4$. This signal belongs to picric acid and intensifies as the amount of water is increased. Since picryl chloride gives a hydrolysis equilibrium in the aqueous media there is inevitably formation of some picric acid. It was reported in the literature that in the picric acid concentration was very high even in media which contain %30H₂O [10]. However the t_R value of the hydrolysis product or picric acid is observed to be unaffected by its concentration. On the other hand the t_R value of picryl chloride is seen to be highly dependent upon the composition of the mobile phase.

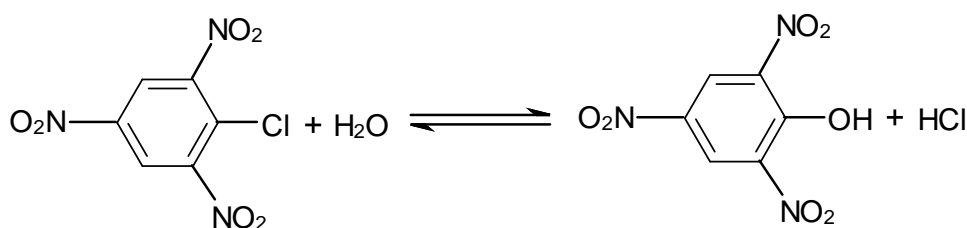
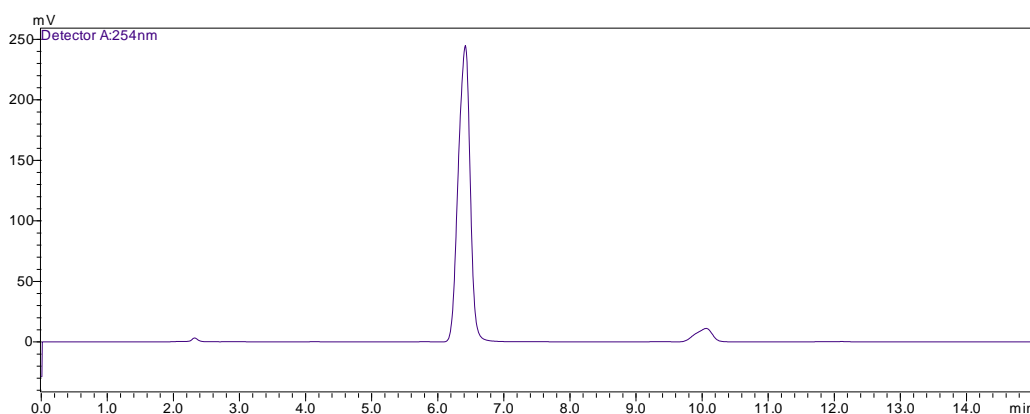
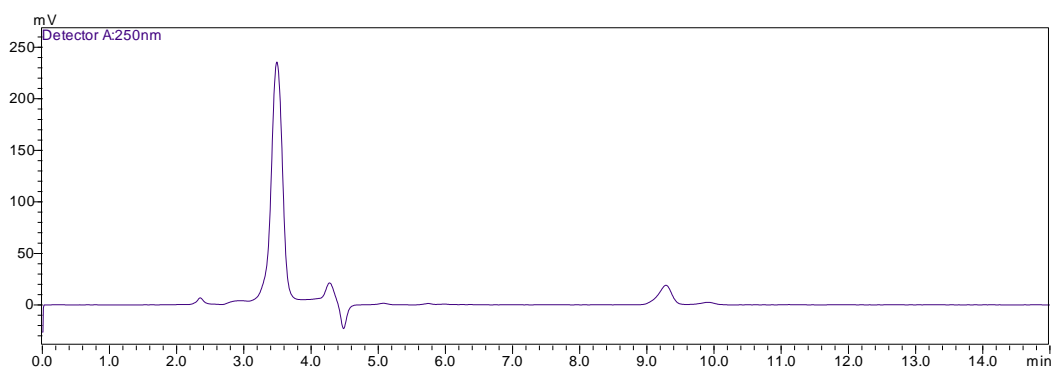


Figure 5. Picric acid formation in aqueous medium

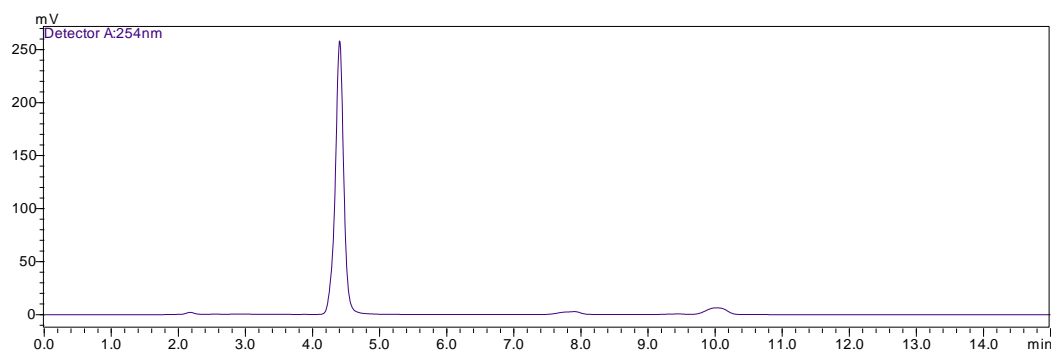
The behavior of other energetic compounds N- picryl -3-aminopyrazol; N- picryl -3-amino-1,2,4-triazol; n- picryl-3,5-diamino-1,2,4-triazol, and N-picrylguanide in %60-%40 MeCN/H₂O were given in Fig.6a-d .



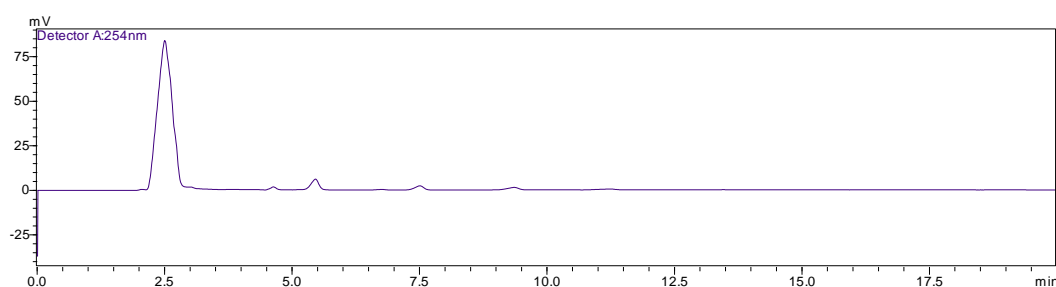
a. N- picryl -3-aminopyrazol, $t_R = 6.44$ minutes



b. N- picryl -3-amino-1,2,4-triazol, $t_R = 3.42$ minutes



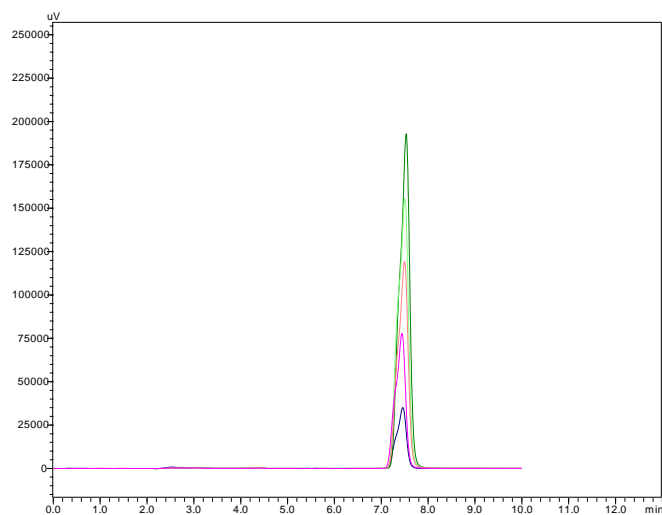
c. N- picryl -3,5-diamino-1,2,4-triazol, $t_R=4.41$ minutes



d. N- picryl guanidin, $t_R=2.59$ minutes

Figure 6. the recapture times of four energetic compounds in %60-%40 MeCN/H₂O

The t_R values of N- picryl -5-aminotetrazol and N- picryl semi carbazite not given in figure 6 were 2.81 and 2.88 minutes. The signal observed between $t_R = 2,2-2.4$ minutes belongs to picric acid formed as a result of hydrolysis and the signal which appears at $t_R = 9-10$ minutes is due to picryl chloride which could not be removed from the medium after the crystallisation process. In literature it was stated that these compounds rapidly convert into picric acid but this would not cause any problems in HPLC analyses [10]. As seen from the chromatograms depicted above there is some hydrolysis but it appears to be insignificant. The signals are very symmetrical and there were no tailing observed. So we need to know whether the intensity of these signals are directly related to concentration. The intensities of N- picryl -3-aminopyrazol and N- picryl -3-amino-1,2,4-triazol insolutions in 10,20,30,40 and 50 mg/L were found to change linearlywith concentrations (Figure 7).



Time (min.)

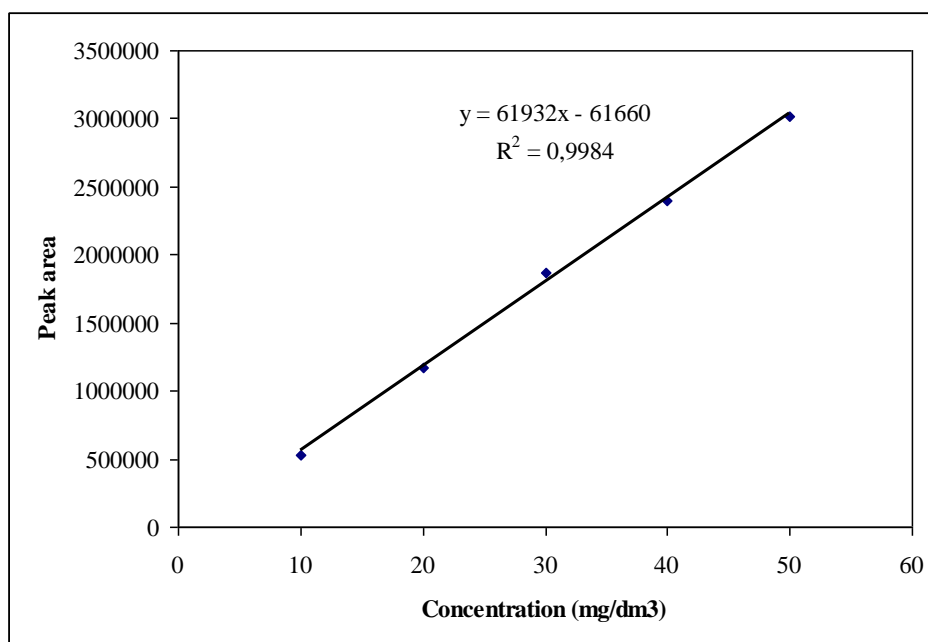


Figure 7. The change of signals of N- picryl -3-aminopyrazol with its concentration

In the studies carried out upon picryl compounds in the literature it was reported that there occurs an equilibrium hydrolysis reaction which results the formation of a significant amount of picric acid in aqueous media. That is why it was claimed that these compounds cannot be analyzed with HPLC[10]. However this study proved that it was not entirely true. The compounds have specific recapture values which were linearly correlated with their concentrations. It is clearly apparent that the energetic compounds prepared from picryl chloride can be analysed with HPCL . However some of the compound gave very close recapture values due to their very high polarity (picric acid, N-picryl-5-amino-tetrazol and N-picrylsemicarbazit) .This could be overcome by studying gradient studies or using different mobile phases . For instance if the purpose was the separation of N-picryl-5-aminotetrazole it can be separated from picric acid by solution gradient programming.

These compounds are at the research state at the moment .But they may be commercially utilised in the near future for the preparation of explosives. However the real explosives were not studied . The following figure shows the six compounds prepared in this study . The analyte were dissolved in 50 ppm in MeCN and injected in to colon belonged.

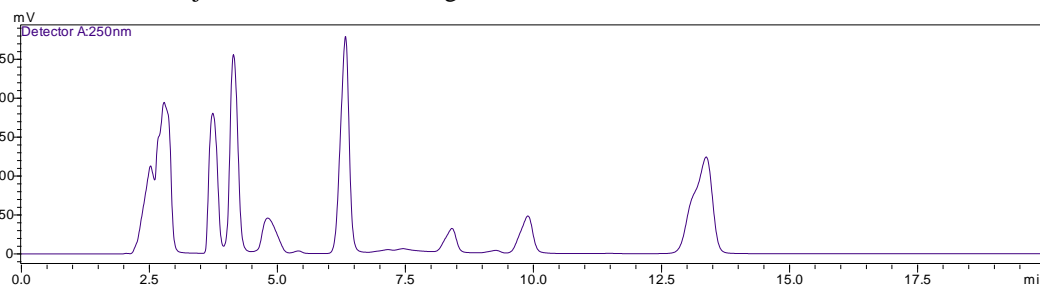


Figure 8. The chromatograms of 10 ppm picric acid, 50 ppm N-picryl-3-aminopyrazol (I), 52 ppm N-picryl-3-amino-1,2,4-triazol (II), 50 ppm N-picryl-3,5-diamino-1,2,4-triazol (IV), 50 ppm N-picryl guanidine (V) , 48 ppm N-picrylsemicarbazite (VI) and 50 ppm N-picryl-2,6-diaminopyridin mixtures . Left to right the first signal belong to picric acid , the asymmetric signal at $t_R=2.8$ minute belongs to N-picryl guanidin (V) and N-picrylsemikarbazite (VI) , the signal located at $t_R=3.6$ minutes belonged to N-picryl-3-amino-1,2,4-triazole (II) the signal at $t_R=4.8$ minutes belonged to N-picryl-2,6-diamino piridine, the peak at $t_R=4.2$ at belonged to N-picryl-3,5-diamino-1,2,4-triazole (IV), the peak appeared at $t_R=6.4$ minutes to N-picryl-3-aminopyrazole (I) and the signal at $t_R=13.$ minutes is due to picryl

chloride remained in the medium as a side product . The signals appeared at $t_R=8$ and 9.8 minutes are due to the side products .

One of the situations which cannot be explained is the asymmetry in the picryl chloride signal above the water content of % 40 in mobile phase. The reason for this phenomena is not clear. This asymmetry can be explained as the amount of water increases there is a hydrolysis equilibrium established giving a certain amount of picric acid and if the concentration of the compound increases it gives an intermediate structure between picric acid and energetic compound . However the same phenomenon exists for the pure picryl chloride. The ratio of H_2O could not be increased above %50 since the analyte precipitates above this ratio. This asymmetry might be due to the formation of a side product but there is not a net explanation of this phenomena.

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