



UV-VIS and FTIR Investigations of Long-Term Aged Explosives Part 1

Petar SHISHKOV, Milena NEDKOVA, Petia ATANASOVA
and Ivan GLAVCHEV*

*University of Chemical Technology and Metallurgy,
8 Kl. Ohtidski St., 1756 Sofia, Bulgaria*

**E-mail : ivgl@uctm.edu*

Abstract: An investigation of TD-50 and tetryl samples obtained by dismantling of weapons, made in 1961 in Bulgaria, was carried out. The weapons were stored in non-heated military stores and the explosives were aged in this time (50 years). The results from UV-VIS and FTIR spectroscopy showed the formation of H-bonds in the solutions and in the investigated materials. The most available properties for determination of H-bond formation from UV-VIS spectra were: the shift, ($\Delta\lambda$); ratio shift/dilution, ($\Delta\lambda / C_1/C_n$, nm, and $\Delta\lambda/\Delta C$, nm.ml/mg) in acetone solutions and only the shift, ($\Delta\lambda$) in toluene solutions. The results from FTIR spectroscopy showed that the most available for determination of H-bond formation were: absorbances of some maxima for $-\text{NO}_2$ groups, divided from maxima for $-\text{CH}_2$ at 917 and 715 cm^{-1} like internal standards and some values of $\Delta h^*_{1/2}$.

Keywords: UV-VIS, FTIR, TD-50, tetryl, H-bond

Introduction

H-bond formation was one of the reasons for obtaining “liquid crystal” – temporary formations of several polar molecules, bonded with H-bonds. Usually, with temperature increase the number of the molecules in “liquid crystal” decreases. For example, this number in “liquid crystal” of water decreases from 7 in 4 °C to 1 in 100 °C. In [1, 2] this phenomenon was analyzed by UV-VIS spectroscopy – with temperature increase as the maxima shifted to red. The shift was obtained also with changing of the concentration [3]. Usually, the

shift ($\Delta\lambda$) was measured from the main maximum in UV-VIS spectrum and with some maxima in IR spectra. In the diluted solutions the number of molecules in “liquid crystal” decreased. The decrease of the concentration of the solutions was equal to the values of the dilution, given with ratio between the investigated concentrations – C_1/C_n and with the difference between these concentrations, given with $C_1 - C_n = \Delta C$. The application of UV-VIS spectroscopy for investigation of explosives was described in many works [4-7]. The last two articles are on investigation of tetryl and dinitronaphtalene. It is known that TD-50 consists of trinitrotoluene and dinitronaphtalene 50:50 [8]. Dinitronaphtalene has 9 isomers [9]. In [10] the authors determined the shift of all maxima in the FTIR spectrum of treated nitrocellulose. The same method was applied in [11] for products of interaction of beech wood and its derivates (lignine, hemicellulose and cellulose) with phenol-formaldehyde resin. The goal of our investigation was to determine the available properties for characterization of “liquid crystal” in acetone or toluene solutions of TD-50 and tetryl and in the solid samples of the investigated long-term aged explosives. These properties were connected with H-bond formation and with ageing of investigated materials.

Experimental

Samples of TD-50 and tetryl were weighted with an accuracy of 0.0001 g and were dissolved in acetone or toluene, p.a. (Merck products) to clear solutions. Diluted solutions were made with addition of different quantity of acetone or toluene and their UV-VIS spectra were obtained with apparatus Cary 100 Scan UV-VIS spectrophotometer (Varian, Germany). From all maxima in UV-VIS spectra, the average values of the shift, ($\Delta\lambda$), $\Delta\lambda / C_1/C_n$, nm, and $\Delta\lambda/\Delta C$ (where $\Delta C = C_1 - C_n$ nm.ml/mg) were calculated. The spectra of thin layers of the investigated samples, dissolved in acetone or toluene, were made with FTIR spectrophotometer (Varian, Germany) – small amounts of the solutions were placed on plates from alkali salts and after evaporation of the solvents the spectra were made. From all the spectra by equation 1:

$$A = \log (100-i)/ I \quad (1)$$

where: i is the distance between 100% A and cross point of the basic line of the investigated maximum and perpendicular line, passed from the peak; I is the distance from the end of this peak to 0 of absorbance, the absorbances of the peaks A were obtained and the values of reduced absorbances $A_1, A_2, A_3 - A_n = A/A_{i.s.}$

(i.s. was the absorbance for the peaks of $-\text{CH}_2$ groups) were calculated. The values of A^* were calculated from the complicated large maxima around 3500 cm^{-1} from equation 2:

$$A^* = A / A_{\text{max}} \quad (2)$$

The distances $\Delta h_{1/2}$ of maxima for $-\text{NO}_2$ or for $-\text{CH}_2$ were measured from FTIR spectra and the values of reduced peak width at half height $\Delta h^*_{1/2}$ were calculated from equation 3:

$$\Delta h^*_{1/2} = \Delta h_{1/2} / \Delta h_{1/2 \text{ i.s.}} \quad (3)$$

where $\Delta h_{1/2}$ is peak width at half height for absorption bands of $-\text{NO}_2$ and $\Delta h_{1/2 \text{ i.s.}}$ are for internal standards, measured from peaks of $-\text{CH}_2$ groups.

Results and Discussion

Samples of TD-50 (No. 1) and tetryl (No. 2) obtained by dismantling of weapons, made in 1961 in Bulgaria, were investigated. The weapons were stored in non-heated military stores and the explosives were aged in this time (50 years). The theoretical content of elements in the investigated materials is given in Table 1.

Table 1. Theoretical content of elements in samples Nos. 1 and 2

No.	Material	C,%	H,%	N,%	O,%
1	TD-50	46.02	2.48	15.67	35.83
2	Tetryl	29.27	1.74	24.39	44.6
3	Ratio 1/2	1.572	1.425	0.6425	0.8034

The ratios of oxygen (O_1/O_2), nitrogen (N_1/N_2) and hydrogen (H_1/H_2) contents were: 0.8034, 0.6425 and 1.425. It was known that these three elements take part in the formation of H-bonds. Actually, during the ageing process, the contents of oxygen and nitrogen in the molecules of explosives decreased. It was the same with H-bonds formation.

From the obtained UV-VIS spectra it is evident that after dilution there are maxima with constant and with changeable wavelengths. The values of all properties were calculated from maxima in UV-VIS spectra with changeable wavelength with decrease of the concentration of the investigated compounds. The obtained values for the investigated properties of the acetone or toluene

solutions are shown in Tables 2 and 3.

Table 2. The results from acetone solutions

No.	Material	Shift, ($\Delta\lambda$)nm	$\Delta\lambda / C_1/C_n$, nm,	$\Delta\lambda/\Delta C$, nm.ml/mg
1	TD-50	3.063	0.3828	0.1211
2	Tetryl	5	2.5	0.513
3	Ratio1/2	0.6126	0.1531	0.2361

Table 3. The results from toluene solutions

No.	Material	Shift, ($\Delta\lambda$)nm	$\Delta\lambda / C_1/C_n$, nm,	$\Delta\lambda/\Delta C$, nm.ml/mg
1	TD-50	2	0.2857	2.2349
2	Tetryl	2.1815	0.159	1.223
3	Ratio1/2	0.9168	1.7969	1.8264

It was evident that the values of some of the investigated properties were the highest for solutions in polar acetone and for solutions of tetryl. It is known that the higher contents of oxygen and of nitrogen in the molecule of tetryl determine the higher possibility of H-bond formation.

From the results in Tables 2 and 3 it is evident that the shift, ($\Delta\lambda$); $\Delta\lambda / C_1/C_n$, nm, and $\Delta\lambda/\Delta C$, nm.ml/mg in acetone solutions and only the shift ($\Delta\lambda$) in toluene solutions are available for characterization of obtaining H-bonds in solutions of TD-50 and tetryl.

From many articles in the literature on application of IR spectroscopy for investigation of H-bond formation, only several of our works [12-14] were quoted. In these articles it was determined that it is possible to measure H-bond formation with several properties: shift ($\Delta\nu$, cm^{-1}), absorbances of some maxima $A = A/A_{i.s.}$ and $\Delta h^*_{1/2}$. In [13, 14] were given the values of A^* for measurement of H-bond formation in nitrocellulose in single-based propellants. It was established that during ageing of these compounds a part of $-\text{NO}_2$ was transformed into $-\text{OH}$ groups and the presence of the maximum around 3500 cm^{-1} was the measure of this process. It was difficult to explain the presence of this maximum for TD-50 and tetryl. From the results of these investigations it is evident that the kind of compounds changes the values of the maxima according to equation 2.

The results from FTIR analysis of TD-50 dissolved in acetone were:

$$A^* = A_{3534} / A_{3411} = 0.7549$$

Because in the literature there are no values of IR spectra of investigated materials, aged 50 years and for determination of the shift of bands, in this work

were given the values of the bands of TD-50:

Maxima, cm^{-1} : 3534.157,m; 3411.769,m; 3100.119,m; 2918.290,m; 1833.237,f; 1611.140,s; 1563.891,s; 1546.322,s; 1539.14,s; 1537.231,s; 1505.345,m; 1347.549,s; 1201.096,f; 1165.914,f; 1083.591,m; 909.636,m; 834.268,m; 796.471,m; 723.946,m.

Table 4. Values of the investigated properties of FTIR spectrum made from acetone solutions of TD-50

N	ν, cm^{-1}	A_1	A_2	A_3	$\Delta h^{*1}_{1/2}$	$\Delta h^{*2}_{1/2}$	$\Delta h^{*3}_{1/2}$
1	3534.157	4.2353	0.7483	2.2535	10.63	16.06	21.41
2	3411.769	3.1975	0.5805	1.7013	12.04	11.8	18.89
3	3100.119	1.6177	0.2937	0.8607	0.98	0.97	1.74
4	1611.140	2.6437	1.4794	1.4070	1.08	1.06	1.93
5	1563.891	1.3468	0.9264	0.7166	-	-	-
6	1546.322	4.9385	3.3370	2.6277	1.28	2.37	2.28
7	1539.14	5.4139	3.7240	2.8806	1.17	2.14	2.08
	1537.231	5.7276	1.0400	3.0472	1.17	1.14	2.07
9	1504.345	1.2039	0.8281	0.6406	-	-	-
10	1347.549	5.7269	3.1406	3.0472	1.02	1.36	2.04
11	1073.591	1.4533	0.2638	0.7733	0.54	0.46	0.96
12	834.268	1.7392	0.9537	0.9254	0.54	0.72	1.06

Internal standard ν, cm^{-1} : 1 – 2918.290, 2 – 909.636, 3 – 723.946

The bands at 1563.891, 1546.322 and 1539.14 cm^{-1} were obtained with different scanning of the maximum at 1537.231 cm^{-1} .

The results from FTIR analysis of TD-50 dissolved in toluene were:

$$A^* = A_{3532} / A_{3413} = 0.4581$$

Maxima, cm^{-1} : 3532.403,m.; 3413.341,m; 3099.611,m; 2880,547,f; 1610.177,s; 1538.504,s; 1348.215,s; 1200.253,f; 1082.403,m; 909.636,m; 835.835,m; 798.126,m; 750.748,m; 725.375,m.

It is evident that not only the kind of the investigated compounds, but also the applied solvent changes the value of A^* and the characteristics of the maxima. On the other hand, the value of A^* from acetone solution of TD-50 is bigger, compared with the same characteristic, obtained from toluene solution. In this way, the polarity of the solvents may change the values of A^* .

Table 5. Values of the investigated properties of FTIR spectra, made from toluene solutions of TD-50

N	ν , cm^{-1}	A_1	A_2	A_3	$\Delta h^1_{1/2}$	$\Delta h^2_{1/2}$	$\Delta h^3_{1/2}$
1	3532.403	2.7312	0.4727	0.2664	8.57	13.33	14.12
2	3413.341	5.9611	1.0317	0.5813	7.86	12.22	12.94
3	3099.611	5.5144	0.9579	0.5397	0.79	1.22	1.29
4	1610.177	8.2486	1.4277	0.8044	0.61	0.94	1
5	1538.504	26.9693	4.6685	2.6306	1.14	1.78	1.88
6	1348.215	25.5556	4.4231	2.4923	0.82	1.28	1.35
7	1082.403	3.9436	0.6832	0.3846	0.32	0.5	0.53
8	835.835	5.2288	0.9048	0.5099	0.64	0.78	1.06

Internal standard ν , cm^{-1} : 1 – 2880,547; 2 – 909.636; 3 – 725.375

The band at 1538.504 cm^{-1} was complicated similarly to the band at 1537.231 cm^{-1} in FTIR spectrum, obtained from acetone solution of TD-50.

It is possible to explain the changes in FTIR spectra and in the values of the obtained properties by presence of a small amount of moisture or of solvent in the investigated thin layers of the materials. The data in [15] confirmed the supposition of presence of solvent. In this way, it was necessary to compare only the results obtained from the samples made from one and the same solvent.

In the next calculations and conclusions, only the comparison between spectra of samples made from acetone solutions of TD-50 and tetryl was made.

The results from FTIR analysis of tetryl dissolved in acetone are:

$$A^* = A_{3382.434} / A_{3415.437} = 0.9647$$

Maxima, cm^{-1} : 3415.437,s; 3098,876,s; 3025.87,f; 2920.711,m; 2889.095,m; 2682.594,f; 2529.283,f; 1863.997,m; 1834.624,m; 1610.852,s; 1564.12,s; 1557.48,s; 1537.231,s; 1504.475,s; 1456.341,m; 1424.204,m; 1341.382,s; 1281.107,s; 1190.674,m; 1111.757,m; 1072.558,s; 956.076,s; 917.577,s; 822.838,m; 797.23,s; 750.025,m; 715.634,s.

Table 6. Values of the investigated properties of the samples made from acetone solutions of tetryl.

No.	ν , cm^{-1}	A_1	A_2	A_3	$\Delta h^1_{1/2}$	$\Delta h^2_{1/2}$	$\Delta h^3_{1/2}$
1	3415.437	0.7968	0.4725	0.2664	1.56	6.49	7.27
2	34382.434	0.7683	0.1069	0.5813	1.82	7.57	8.49
3	3098.876	1.3496	0.8623	0.8448	0.42	1.73	1.94
4	2682.594	0.6463	0.413	0.4046	0.56	2.32	2.61
5	2529.283	0.5595	0.3584	0.3512	0.26	1.08	1.21
6	1834.624	0.69756	0.4446	0.4366	0.23	0.92	1.03
7	1707.348	0.9050	0.5792	0.5674	0.24	0.97	1.09
8	1610.852	2.0558	1.3143	1.2875	0.25	1.05	1.18
9	1564.12,	3.1775	2.0303	1.989			
10	1557.48	3.9803	2.4977	2.4915			
11	1548.64	3.9958	2.5532	2.5012			
12	1537.231	4.0155	2.5658	2.5135	0.52	2.16	2.42
13	1504.475	0.5954	0.3736	0.3660			
14	1341.382	2.1717	1.3871	1.3588	0.51	2.15	2.41
15	1281.107	1.9455	1.2442	1.2188	0.36	1.51	1.69
16	1072.558	1.4619	0.9351	0.9160	0.22	0.92	1.03
17	797.231	1.1283	0.721	0.7063	0.21	0.27	0.3

Internal standard ν , cm^{-1} : 1 – 2920.711; 2 – 917.577; 3 – 715.634

From the results in Tables 4 and 6 were made the values in Table 7.

Table 7. Comparison between some properties of the samples of TD-50 and tetryl, made from their acetone solutions

N	Samples	A^*	A_23100	A_21611	A_21539	A_21073	A_31073
1	TD-50 ₁	0.7829	0.2937	0.4794	1.0400	0.2638	0.7733
2	Tetryl ₂	0.9647	0.8623	1.3143	1.9481	0.9160	0.9160
3	Ratio 1/2	0.8116	0.3406	0.3648	0.5339	0.288	0.8442

N	Samples	$\Delta h^2_{1/2}$ 1539	$\Delta h^2_{1/2}$ 1347	$\Delta h^2_{1/2}$ 1073	$\Delta h^3_{1/2}$ 1073	$\Delta h^3_{1/2}$ 1539	$\Delta h^3_{1/2}$ 1347
1	TD-50 ₁	1.17	1.36	0.46	0.96	2.07	2.04
2	Tetryl ₂	2.16	2.15	0.92	1.03	2.42	2.41
3	Ratio 1/2	0.5417	0.6326	0.5	0.932	0.8554	0.8465

From the obtained results in Table 7, the maxima available for internal standards and for determination of H-bond formation in the investigated long-term aged explosives could be found.

Conclusion

The properties of acetone or toluene solutions of TD-50 and tetryl available for characterization of H-bond formation, determined by UV-VIS and FTIR spectroscopy are shown in the paper, as well as the connections of these characteristics with processes in long-term aged tetryl and TD-50 explosives.

References

- [1] Pominov S., Navlova A.A., Effect of Temperature and Salts on the UV Absorption Spectra of Acetone and Methyl ethyl ketone, *J. Appl. Spectrosc.*, **1967**, 9(1), 700-702.
- [2] Thöny A., Rossi M. J., Gas-phase UV Spectroscopy of Anthracene, Xanthone, Pyrene, 1-bromopyrene and 1,2,4-trichlorobenzene at Elevated Temperatures *J. Photochem. Photobiol. A*, **1997**, 104(1-3), 25-33.
- [3] Tsunekawa S., Fukuda T., Kasuya A., Blue Shift in Ultraviolet Absorption Spectra of Monodisperse CeO_{2-x} Nanoparticles, *J. Appl. Phys.*, **2000**, 87(3), 1318.
- [4] Burks R.M., Hage D.S., Current Trends in the Detection of Peroxide-Based Explosives, *Anal. Bioanal. Chem.*, **2010**, 395(2), 301-313.
- [5] Comanescu G., Manka Ch. K., Grun J., Nikitin S., Zabetakis D., Identification of Explosives with Two-Dimensional Ultraviolet Resonance Raman Spectroscopy, *Appl. Spectrosc.*, **2008**, 62(8), 833-839.
- [6] Myers St.R., Spinato J.A., Tissue Distribution and Elimination of *N*-methyl-*N*-2,4,6-Tetranitroaniline (Tetryl) in Rats, **2007**, *Arch. Toxicol.*, 81(12), 841-848.
- [7] Neisen St.F., Weaver M.N., Konradsson A.E., Telo J.P., Clark T., Electron Transfer within 2,7-Dinitronaphthalene Radical Anion, *J. Am. Chem. Soc.*, **2004**, 126(47), 15431-15438.
- [8] Grozev V.I., Valchev V.P., Lazov N.K., Kazakov I.T., *Vzrivni veshtestva I baruti*, Izdatelstvo na MO "Sveti Georgi Pobedonosec", Sofia, **1997**, p. 192 (in Bulgarian).
- [9] Talukder M., Kates K.R., Naphthalene Derivatives, *Kirk-Othmer Encycl. Chem. Technol.*, John Wiley & Sons, Ltd., published online, **2000**.
- [10] Oh S.Y., Yoo D.I., Shin J., Kim H.C., Kim H.Y., Chung Y.S., Park W.H., Youk J.H., Crystalline Structure Analysis of Cellulose Treated with Sodium Hydroxide and Carbon Dioxide by Means of X-ray Diffraction and FTIR Spectroscopy, *Carbohydr. Res.*, **2005**, 340(15), 2376-2391.
- [11] Genov I., *Izsledvane vlianieto na svarzvashtite veshtestva varhu kachestvoto na darvesni kompoziti*, LTU, **2011**, p. 95 (in Bulgarian).
- [12] Glavcheva Z., Kolev T., Glavchev I., Investigation of Squaric Acid Derivates, *Polym. Test.*, **2001**, 20(2), 205-208.
- [13] Ganev R., Glavchev I., Tzvetkoff T., Ivanova M., Totev T., Investigation of Long-Term Ageing of Single Base Propellants by IR Spectroscopy, *Journal of Explosives and Propellants*, R.O.C., **2004**, 20(1), p. 7.

-
- [14] Ganev R., Glavchev I., IR Spectroscopy Characterization of Single-Base Propellants during Their Natural Ageing, *J. Tech. Phys.*, **2004**, 45(4), 301-308.
- [15] Glavchev I, Petrova K., Devedjiev I., Investigation of Solvent Interaction in Epoxy Coatings, *Polym. Test.*, **2000**, 19(1), 111-114.

