



## Chromatographic Determination of Stabilizer in Nitrocellulose Based Propellants

(A new extraction based chromatographic method for the determination  
of stabilizers in propellants)

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**Abstract:** Regarding the chromatographic analysis of the stabilizers in the double based propellants, nitrocellulose causes an interference problem with diphenylamine and its derivatives. In this study, specific extraction of the stabilizer was planned before the chromatographic analysis and the stabilizer was extracted into  $\text{CHCl}_3$  by means of a Soxhlet extraction in order to eliminate this problem. Then, most of the  $\text{CHCl}_3$  was evaporated under hydrothermal conditions and the residue was analyzed with HPLC after being dissolved in MeCN. By means of an isocratic work, the stabilizer 2-nitro diphenylamine (2NDPA) was clearly detected with 85% MeCN and 15%  $\text{H}_2\text{O}$  carrier phase in C18 column. The effect of the matrix that could be found in the ambient was examined and the recovery was found between  $95.06 \pm 3.09 - 99.88 \pm 3.34\%$ . No matrix effect was determined in the ambient.

**Keywords:** HPLC, propellants, nitrocellulose based propellants, energetic materials, explosives

## Introduction

As it is known, the propellants used as propelling charges in conventional weapons are produced in three types as mono, double and triple based [1-3]. The common ingredients in double and triple based propellants are trinitrocellulose and trinitroglycerine. As trinitrocellulose and trinitroglycerine mixtures can easily disintegrate with light and heat, a stabilizer of 1.8-2.0% by weight is added to the mixture during production. These stabilizers are generally diphenylamine derivatives and mostly 2-nitro diphenylamine [2-5]. The stabilizer amount is an important parameter regarding the transportation and storage of propellants. Propellants containing less than 1.8% stabilizer bear risk in transportation. The diphenylamine content in the propellants can be determined with bromometry which is a classical volumetric method. However, nitro diphenylamine derivatives cannot be determined with this method as the electron attractive effect of the nitro group deactivates the diphenylamine molecule and bromine electrophiles do not undergo addition reaction with the aromatic rings. Therefore, the most appropriate method to determine the stabilizers, particularly the nitro diphenylamines in propellants is by HPLC [4, 6]. There are formerly published studies on this issue conducted in military laboratories [7, 10]. In these studies, the stabilizer in the propellants was extracted within 20%  $\text{CH}_2\text{Cl}_2$  and 80% cyclohexane and was delivered to the HPLC column. The analyses were done with 60-40%; MeCN- $\text{H}_2\text{O}$  carrier phase [7] or the propellant was processed with MeOH-MeCN-THF and the extract was analyzed with the same carrier phase. Another method is that the propellant was dissolved in acetone and the nitro cellulose content was precipitated by adding about 25% water by volume. After this precipitate was filtered, the residue was analyzed with 60-40%; MeCN- $\text{H}_2\text{O}$  carrier phase in C18 column [8]. There is no data in the literature about the validation of these methods.

More recently, there are several articles in the literature related to the analysis of the stabilizers in the propellants. In these studies, the analysis of stabilizers within mono based propellants by HPLC [6], monitoring stabilizers within nitrocellulose by means of UV-Vis spectroscopy [11] and the analysis of stabilizers in the propellants by means of LCMS/MS [12], GC-MS [13] and polarographic methods [14] have been reported.

This study was designed with the idea where only non-polymeric organic nitro components are extracted without extracting the nitrocellulose in the propellant and where the obtained extract is analyzed with HPLC.

In the widely used method, the propellant dissolves in  $\text{CH}_3\text{COCH}_3$  where inorganic components and high molecular weight nitro celluloses remain undissolved and are separated through filtering where some nitrocellulose remains

in the acetone solution. The remaining nitrocellulose content is precipitated with H<sub>2</sub>O addition and the solution is transferred to the column after being filtered. However, according to our thoughts, nitro celluloses can absorb some amount of stabilizer during precipitation or some stabilizer can precipitate by itself. With this in mind, propellant samples were extracted for a long time with CHCl<sub>3</sub> which is thought to dissolve only nitro components with small molecules and not nitrocellulose. The solvent was largely evaporated from the extract and the residue was dissolved in MeCN and was analyzed in C18 column with 60-40%; MeCN-H<sub>2</sub>O carrier phase. The results were observed as much more simple and explainable in comparison to previous studies.

A former study in the literature gave this idea [15]. This study is about to treat propellant with CH<sub>2</sub>Cl<sub>2</sub> and taking the small organic compounds into CH<sub>2</sub>Cl<sub>2</sub> phase. And then 2-nitro diphenylamine is defined with a normal HPLC phase study. This study is designed as a reverse phase study.

## Experimental

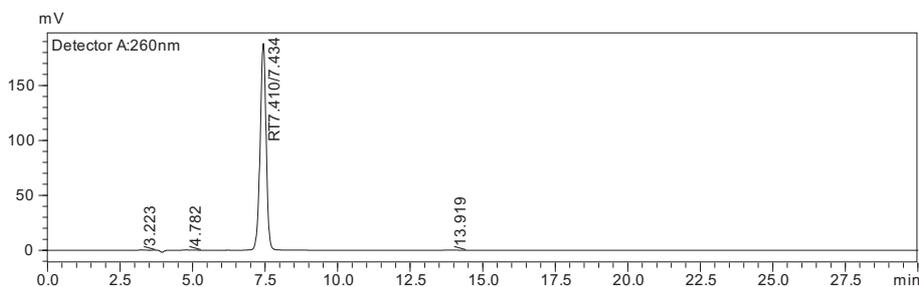
**General:** In the study, a 4.6x150 mm ODS-3 column inside a Shimadzu CTD column furnace and a Shimadzu LC-20AT pump system were used and the analytes were detected by a Shimadzu SPD-20A UV-Vis detector. 2NDPA (Merck) was used, recrystallized two times in MeOH and was used as standard. In order to determine optimum operating conditions and resolution, different compositions of MeCN, MeOH and H<sub>2</sub>O mixture were employed as the carrier phase. It was observed that MeOH had no effect on separation as the highest absorbent and retention time was found in the MeCN-H<sub>2</sub>O; 85-15% composition.

## Procedure

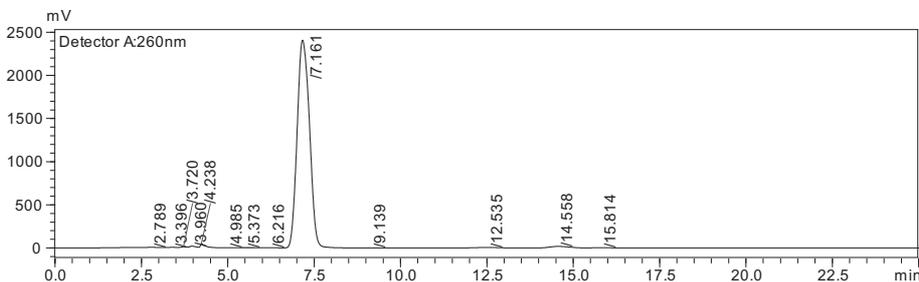
1 g samples of 5 different propellants were weighed. The samples were dissolved in approximately 50 mL THF and 50 mL acetone constantly stirred for a few hours. To each mixture prepared from different gun powders, H<sub>2</sub>O was added up to 9.1%, 16.67%, 23.50%, 28.57%, 33.33% (V/V) ratios in order to precipitate nitro celluloses. The achieved mixtures were filtered through black band filter papers and the filter papers were washed with 10-15 mL solvent and the solvent was evaporated almost to dryness in beakers. The final residue was dissolved in 15-20 mL MeCN. The solution was transferred to a volumetric flask and was diluted with MeCN up to the final volume of 100 mL. In parallel,

1.00 gram samples of the same gun powders were weighed. Soxhlet cartridges of them were prepared with black band filter paper. They were cycled 10 times in about 2 hours within a soxhlet system with 50-60 mL  $\text{CHCl}_3$ . In the last two cycles the solutions were almost colourless.  $\text{CHCl}_3$  was evaporated in a beaker and the residue was dissolved in 15-20 mL MeCN. The solution was transferred into a volumetric flask and was diluted with MeCN up to the final volume of 100 mL. Each application was repeated three times at least.

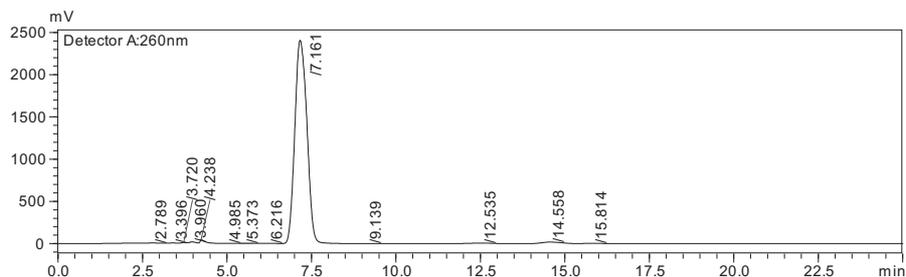
By drawing simple calibration graphs, 2NDPA amounts in the three group of solutions were determined. In order to interpret the accuracy of the analysis being carried out, standard addition was performed afterwards. In Figure 1, the chromatogram of 15 mg/L standard 2NDPA in the optimum mobile phase with 0.5 mL/min flow rate; in Figure 2, the chromatogram of the solution dissolved in THF which was prepared by adding 33.33%  $\text{H}_2\text{O}$ ; in Figure 3, the chromatogram of the solution achieved as a result of the soxhlet extraction with  $\text{CHCl}_3$  are shown. The calibration curve obtained from the readings of the standards is given in Figure 4.



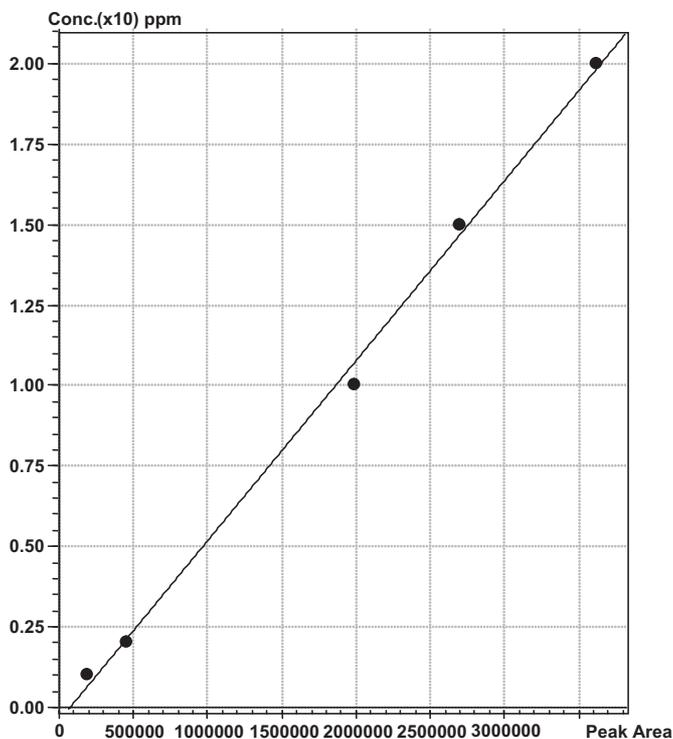
**Figure 1.** The chromatogram of 15 mg/L standard 2NDPA in the optimum mobile phase with 0.5 mL/min flow rate.



**Figure 2.** The chromatogram of the solution dissolved in THF which was prepared by adding 33.33%  $\text{H}_2\text{O}$ .



**Figure 3.** The chromatogram of the solution achieved as a result of the soxhlet extraction with  $\text{CHCl}_3$ .



**Figure 4.** The calibration curve obtained from the readings of the standards.

## Results and Discussion

The analysis of the results obtained from five different double-based propellant samples are given in Table 1, 2 and 3, respectively. In Table 1, the

solutions obtained from the propellant dissolved in acetone and the results obtained by making standard additions to these solutions can be seen. 9.1%, 16.67%, 23.50%, 28.57% and 33.33% (V/V) H<sub>2</sub>O was added to the acetone solutions and nitro celluloses were precipitated. The filtered solution was evaporated almost to dryness and the residue was dissolved in MeCN to a final volume of 100 mL. The solutions which contain 9.1%, 16.67% and 23.50% water, it was observed that the nitro celluloses had not completely precipitated where this case was not observed in solutions containing 28.57%, 33.33% of water. For this reason, 9.1%, 16.67% and 23.50% water added solutions were not injected as they bear a risk of plugging the column. After the 2NDPA amount in 100 mL MeCN solutions was calculated from the calibration curve, additions were made from the stock standard solution to these solutions and the recovery was found between  $96.18 \pm 2.25$  -  $100.75 \pm 1.42\%$ .

A similar procedure was also applied to the propellant samples dissolved in THF. In Table 2, the results, where propellants dissolved in THF and standards were added to these solutions are shown.

On the other hand, the soxhlet extracts obtained with CHCl<sub>3</sub> were directly evaporated and the residues were dissolved in 100 mL MeCN. The 2NDPA amount in these solutions was determined from the calibration curve and then standard addition was applied to these solutions and the recovery was found between  $97.24 \pm 3.34$  -  $101.24 \pm 4.08\%$ . The results are shown in Table 3.

The propellants which are used in this study are made of fabric and the manufacturer declared that between 1.8-2% 2NDPA were added during production process. The values that are recorded was obtained by dissolving with acetone and THF then sedimenting with adding water, differs between 1.02-1.36% which also can be seen in Table 1 and Table 2. The standard addition to these solutions were made to test accuracy of the HPLC results and to define the matrix effect which could be possibly found in the ambient. Finding the average recovery 98.51%, proves the accuracy of the HPLC analysis and nonexistence of the matrix. But the values are found in the analysis between 1.02-1.36% which means, they are above the half of the expected values or little more. On the other hand, the analysis which is performed with CHCl<sub>3</sub> extraction has more expected results like between 1.80-1.99%. Finding 96.88% recovery when the standard added to the solutions which obtained CHCl<sub>3</sub> extraction is to prove that there is no problem with this analysis.

Consequently, in the analysis of small molecular weight organic substance in double or triple based propellants, the nitrocellulose polymers should not extract as much as can be. And treating with the polar aprotic solutions like CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub> seems to be more safe.

**Table 1.** The solutions obtained from the propellant dissolved in acetone and the results obtained by making standard additions to these solutions

Propellant No.	Added H <sub>2</sub> O % (V/V)	Obtained 2NDPA(ppm) from calibration curve	Standard additions								% Recovery
			Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	
1	33.33	99.11	309.99	309.01	351.99	351.88	379.99	371.34	399.98	398.60	99.26 ± 1.04
	28.57	102.08	311.04	318.75	357.56	352.83	380.69	379.53	400.59	398.58	100.75 ± 1.42
2	33.33	94.42	317.21	314.72	345.78	361.77	391.47	375.06	412.69	408.54	97.46 ± 1.91
	28.57	95.05	316.23	309.06	362.03	362.02	391.68	379.05	412.87	412.74	98.52 ± 1.71
3	33.33	122.46	322.80	312.19	351.80	354.98	380.82	358.63	399.27	375.38	96.50 ± 2.78
	28.57	135.59	316.35	320.08	353.01	360.24	385.20	378.45	403.03	402.70	98.83 ± 0.88
4	33.33	122.69	310.35	326.04	351.38	355.08	380.90	370.48	399.34	379.58	98.58 ± 3.39
	28.57	110.52	304.23	304.23	334.58	350.21	376.84	351.47	395.86	387.38	96.18 ± 2.25
5	33.33	101.19	300.38	300.96	324.93	340.48	367.06	345.63	386.05	386.87	97.53 ± 3.19
	28.57	113.97	306.98	292.61	334.08	345.59	371.32	369.86	389.70	383.43	97.50 ± 1.89
Average (%)											98.11

**Table 2.** The solutions obtained from the propellant dissolved in THF and the results obtained by making standard additions to these solutions

Propellant No.	Added H <sub>2</sub> O % (V/V)	Obtained 2NDPA(ppm) from calibration curve	Standard additions								% Recovery
			Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	
1	33.33	102.52	321.26	315.78	365.01	355.96	394.17	385.17	415.01	413.28	98.28±0.93
	28.57	112.66	326.33	326.85	369.06	366.64	397.55	385.60	417.90	402.53	99.00±1.80
2	33.33	110.11	330.06	328.51	374.04	372.52	403.37	403.16	424.32	424.10	99.76±0.23
	28.57	115.45	332.72	338.63	376.18	371.49	405.15	384.10	425.84	418.33	98.39±2.86
3	33.33	129.92	334.96	331.83	375.97	348.31	403.30	404.28	422.83	410.27	97.24±3.34
	28.57	135.71	322.85	345.76	360.28	352.24	385.24	383.02	403.06	405.70	101.24±4.08
4	33.33	132.72	326.36	314.03	365.09	383.94	390.91	370.60	409.35	422.68	99.86±5.12
	28.57	136.64	328.32	317.92	366.66	364.82	392.22	376.81	410.47	406.36	97.85±1.66
5	33.33	121.11	315.56	334.15	354.44	349.08	380.37	373.98	398.89	368.44	98.77±5.54
	28.57	128.72	319.36	318.89	357.49	352.62	382.91	364.50	401.06	406.54	98.76±2.63
Average (%)											98.92

**Table 3.** The results of the soxhlet extracts obtained with  $\text{CHCl}_3$  were directly evaporated and the residues were dissolved in 100 mL MeCN

Propellant No.	Obtained from calibration curve 2NDPA(ppm)	Standard additions								% Recovery
		Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	Calculated	Experimental	
1	180.56	340.28	341.91	420.14	403.38	287.04	280.37	388.20	383.64	98.25±1.88
2	194.39	347.19	345.73	423.60	418.10	296.26	309.70	393.04	388.24	99.88±3.34
3	178.05	339.02	328.21	419.51	381.15	285.37	283.46	387.32	374.36	95.91±3.58
4	196.14	348.07	330.79	424.04	395.77	297.43	281.55	393.65	386.46	95.30±2.05
5	199.76	349.88	333.28	424.94	387.43	299.84	296.00	394.92	375.50	95.06±3.09
Average (%)										
96.88										

## References

- [1] O'Keefe M.P., *Modern Applications of Chemistry*, 2nd ed., McGraw Hill Inc., **1995**, pp. 336-338.
- [2] Akhavan J., *The Chemistry of Explosives*, The Royal Society of Chemistry, **1998**, pp. 146-147.
- [3] Klapötke T.M., *Chemistry of High Energy Materials*, Walter de Gruyter, Berlin/ New York, **2011**, pp. 3, 38-40.
- [4] Oehrle S.A., Analysis of Stabilizer Degradation Products in Propellants Using HPLC and Photodiode Array (PDA) Dedection, *Propellants, Explos., Pyrotech.*, **1998**, 23(1), 56-60.
- [5] Vyazovkin S., Dranca I., Lang A.J., *Mechano Chemical Effect in Degradation of Nitrocellulose and Nitrocellulose-Diphenylamine Mixture*, *Thermochim. Acta*, **2005**, 437, 75-81.
- [6] Jelisavac L.J., Filipovic M., Determination of Diphenylamine and Its Monoderivatives in Single Base Gun Propellants During Aging HPLC, *Chromatographia*, **2002**, 55, 239-241.
- [7] Dooll J.O., Juhasz A.A., The Quantitative Determination of 2-Nitrodiphenylamine in a Composite Modified Double-Base Propellants Using HPLC, *BRL Memorandum Report 2478*, **1975**.
- [8] Groupe SNPE, SNPE Propulsions, *Standard test method*, PF 202 D4, last updating **1995**.
- [9] Carver J.G., Propulsion Directorate, Research Development and Engineering Center, Technical Report. RK-85-7, AD-A159282 US, *Army Missile Command*, Redstone Arsenal Alabama, www.dtic.mil/cgi.bin/ **1985**, Erişim tarihi (Access date) 26/07/2010.
- [10] Olah George A., David R. Squire, *Chemistry of energetic materials*, Academic Press Inc., **1991**.
- [11] Moniruzzaman M., Bellerby J.M., Use of UV-VIS Spectroscopy to Monitor Nitrocellulose Degradation in Thin Films, *Polymer Degradation and Stability*, **2008**, 93, 1067-1072.
- [12] Laza D., Bart N., Kinder J.D., Mesmaker A.K., Moucheron C., Development of a Quantitative LC-MS/MS Method for the Analysis of Common Propellant Powder Stabilizers in Gunshot Residues, *J. Forensic Sci.*, **2007**, 52, 4.
- [13] Dalby O., Birkett J.W., The Evaluation of Solid Phase Micro Extraction Fibre Types for the Analysis of Organic Components in Unburned Propellant Powders, *J. Chromatography*, **2010**, 1217(46), 7183-7188.
- [14] Perez A. de Diego Martinez, Tascon M.L., Vazquez M.D., Batanero P.S., Polarographic Study on the Evolution of the Diphenylamine as Stabiliser of the Solid Propellants, *Talanta*, **2004**, 62(1), 165-173.
- [15] Doall O.J., Juhasz A.A., Determination of 2-Nitrodiphenylamine in a Composite Modified Double Based Propellant by High Performance Liquid Chromatography, *Anal. Chem.*, **1976**, 48, 1859-1860.