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MHSMP-75-58

Liquid Chromatographic Analysis of Nitration of
Diphenylamine Stabilizer in Explosives

By

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Quality Division

December, 1975

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LIQUID CHROMATOGRAPHIC ANALYSIS OF NITRATION OF
DIPHENYLAMINE STABILIZER IN EXPLOSIVES

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ABSTRACT

A high speed liquid chromatographic method was developed for the quantitative analysis of nitrated diphenylamines in PBX-9404. The procedure included extraction of the nitrated diphenylamines into methylene chloride, followed by chromatographic separation and examination of the various species. The method requires a 10 g sample of high explosive in order to provide a sample of nitro DPA suitably concentrated for chromatographic analysis.

INTRODUCTION

Diphenylamine (DPA) is used as a stabilizer in PBX-9404. In order to predict the effective life of the explosive, it is necessary to examine in detail the extent of nitration of the DPA. In addition, a careful examination of the types and amounts of each species of nitrated diphenylamine as a function of age and environmental conditions is paramount to understanding the chemistry of the decomposition process of the explosive.

As a stabilizer, it is believed that the DPA combines with the nitrogen products of decomposition of the nitrocellulose and thus prevents the acceleration of the decomposition caused by the autocatalytic effects of these decomposition products. Much work has been reported in the literature on the nature of the nitrated diphenylamines. Yasuda utilized a thin layer chromatographic method for separating and identifying some of these nitrated DPA's. Quinlin² used a TLC method for separation and a spectrophotometric method for quantitative analysis of the separated species of nitrated diphenylamines. Schroeder et.al.³ used a column chromatographic separation of the nitro species of DPA followed by collection and examination of the fractions by absorption spectrophotometry. These methods are all tedious and time-consuming and are not amenable to adaptation on a routine, production basis. High speed liquid chromatography appears to be an ideal method for quickly separating and quantitatively identifying the nitrated diphenylamines. In addition, this method does not enhance the structural transformations of the more labile species. Some work has been reported concerning the LC method for examining explosives components.^{4,5} Again, however, no attempts have been made to adapt these methods to a routine, production basis or to comprehensively study the decomposition of explosives as a function of age or environment.

It was the purpose of this investigation to develop a rapid, quantitative

method for analysis of the various species of nitrated diphenylamines. The new techniques were then applied to examination of library samples of aged PBX-9404.

EXPERIMENTAL

Apparatus: All separations were performed using a Perkin-Elmer Model 621 Liquid Chromatograph. The column was fabricated from 0.3175 OD X 200 cm stainless steel tubing and was packed with Corasil II. The carrier was a mixture of methylene chloride and hexane (proportions were varied in order to best separate particular species -- see discussion section), and flow rate was maintained at 1.5 ml/min. A differential UV detector at 254 nanometers was used to detect the separated fractions. Each fraction was collected and positively identified by its UV-visible absorption spectrum. These scans were done on a Perkin Elmer Model 356 Spectrophotometer.

Procedure: A 10 g sample of PBX-9404 is weighed into a 250 ml beaker. The sample is then extracted with 50 ml methylene chloride for 2 hours. The supernatant is filtered through a medium porosity glass frit crucible, transferred to a 100 ml beaker and allowed to concentrate by evaporation (until crystals start to form). The concentrate is transferred to a 1 ml volumetric flask, a 30 μ l aliquot is injected into the liquid chromatograph, and the nitrated diphenylamines are separated, detected, and quantitatively assayed.

DISCUSSION

Calibration of Equipment: Identification of the species separated by the liquid chromatograph necessitated calibration of the retention times and acquisition of the UV-visible spectra of the pure nitrated diphenylamines. Twenty nitro- and nitroso-diphenylamines were obtained as standards. The UV-visible spectra were run on a PE-356 spectrophotometer, and the absorption peaks are given in Table I. The standards were chromatographed in the same manner as samples, and the retention times and sensitivities of measurement are recorded in Table I. As has been previously reported³ the nitro group in the ortho position has a marked effect on the relative absorption affinities. The 2-nitro diphenylamines are less strongly absorbed than would be predicted on the basis of molecular polarity. This effect has been attributed to the chelation of the 2-nitro group + the amino group.

Qualitative Analysis of Library Samples of PBX-9404: Seven library samples of PBX-9404 representing a 17 year span, were qualitatively analyzed for nitrated diphenylamines. The chromatographic peak retention times were used to tentatively identify the nitrated products. Fractions were then collected and analyzed spectrophotometrically to positively identify each chromatographic peak. Aliquots of extract injected into the chromatograph were very highly concentrated in order to enhance detection of every species of nitrated DPA present. Later quantitative analyses of these same library samples do not show the presence of some of the less prevalent species. Table II shows the results of these analyses. We have shown that most products of nitration of diphenylamine can be easily and accurately identified using

this LC technique. The peaks which remain unidentified probably represent nitrated DPA's for which a standard was not available, oxidized products of NC degradation, or quinoidal compounds, as it is known that organic nitrates⁶ oxidize DPA to intensely blue quinoidal compounds. In any case, the unidentified peaks are only minute fractions of the sample. One generalization which may be made from examination of Table II is that the younger 9404 samples have a greater number of products of nitration. They also tend to have a greater preponderance of nitroso-DPA's. The N-nitrosodiphenylamine appears in every sample, indicating that the nitrosation of the DPA is a pivotal step in the stabilization of the nitrocellulose. Since the N-nitroso DPA is a labile compound, its presence in even the oldest materials lends credence to this supposition. Also present in nearly all the materials are 2-nitro diphenylamine and 4-nitro diphenylamine. This could indicate either a rearrangement of the N-nitroso diphenylamine or a direct nitration of these positions. And, as expected, the older samples are more highly nitrated.

Quantitative Analysis of Library Samples of PBX-9404: Quantitative analysis for the nitrated DPA species assumes reproducibility of chromatographic readings, as well as linearity of response. In order to facilitate reproducibility of results, a standard 30 μ l loop injection system was installed. Table III shows the response of a series of injections of 2-Nitro DPA. This material was chosen because of its easy availability. As can be seen, at the 30 μ g level, the relative standard deviation of measurement is approximately 4 percent. It is believed that this figure is representative of the other compounds of interest. The linearity of response with increasing quantities of sample was examined using DPA and

2-Nitro DPA as test compounds. Beers law is obeyed within the concentration ranges of interest, and the loop injection system provides adequate reproducibility of measurement. Accordingly, the seven 9404 library samples were quantitatively analyzed for nitrated DPA species. Total quantities of DPA species were calculated from chromatograph peak heights and the sensitivities recorded in Table I. The results are tabulated in Table IV. As shown by the qualitative analyses, the older samples contain a greater concentration of highly nitrated diphenylamines. And, as expected, newer samples exhibit greater concentration of unnitrated DPA. An exception is 37-62. Independent tests show that 1) 37-62 has a high value of nitrogen in the NC binder, 2) total nitration of the 37-62 stabilizer is abnormally low, and 3) the average molecular weight of this particular sample approaches that in a freshly prepared blend of 9404. Examination of records reveals that this blend contained gelatin. Calculations show that only about 50 percent of the DPA originally present in the formulations can be recovered as DPA or the derivatives.

In conclusion, a rapid quantitative method for analyzing explosives and propellants for nitrated diphenylamines has been developed. The method is amenable to routine production work, and requires about 1 hour of technician "hands-on" time per 8 hours.

ACKNOWLEDGMENT

The author wishes to thank L. M. Boyles, F. L. Rogers, and K. K. Bellamy, and other members of the Quality Chemistry Laboratory for the performance of the analytical tests.

REFERENCES

1. Yasuda, S. K., "Identification of N-Nitroso- and Nitrodiphenylamines by Two-Dimensional thin -Layer Chromatography," Journal of Chromatography, 14, p65-70 (1964).
2. Quinlin, W. T., "Thermal Analysis - Analysis for the Diphenylamines in PBX-9404," MHSMP Quarterly Report Oct-Dec. 1968.
3. Schroeder, W. A., Malmberg, E. W., Fong, L. L., Trueblood, K. N., Landerl, J. D., and Hoerger, E., "Chromatographic Investigation of Smokeless Powder", Industrial and Engineering Chemistry, 41 pp. 2818-2827 (1949).
4. Doali, J. O., and Juhasz, A. A., "Application of High Speed Liquid Chromatography to the Qualitative Analysis of Compounds of Propellant and Explosives Interest, " Journal of Chromatographic Science, 12, pp. 51-56, Jan (1974).
5. Quinlin, W. T., "Analytical Applications of Liquid Chromatography", MHSMP Quarterly Report Oct-Dec. 1970.
6. Feigl, F., "Spot Tests in Organic Analysis," Elsevier Publishing Company, p. 301.

TABLE I
SPECTROPHOTOMETRIC PROPERTIES AND LIQUID CHROMATOGRAPHIC
RETENTION TIMES OF NITRO AND NITROSO DIPHENYLAMINES

Derivative	(in methylene chloride, mμ) Spectrophotometric Maxima	Retention Volumes (ml) 10% MeCl ₂ - 90% Hexane	Retention Volumes (ml) 40% MeCl ₂ - 60% Hexane	Sensitivity (μg/div)
Diphenylamine	* 284	20	Eluted in one peak at Beginning of Chromatogram	1.25
2-Nitrodiphenylamine	* 430, 282, 269	22.4		0.58
4-Nitroso, 4-Nitrodiphenylamine	* 388, 321, 250	25.6		2.99
N-Nitrosodiphenylamine	* 292, 248	64.0		1.96
2, 2'-Dinitrodiphenylamine	* 267 429, 384, 289	88.8		2.37
N-Nitroso, 2-Nitrodiphenylamine	None	136.0		3.26
2, 4-Dinitrodiphenylamine	* 355, 264	169.6		3.70
2, 4'-Dinitrodiphenylamine	* 410, 353, 258	232.0		20.0
N-Nitroso, 4, 4'-Dinitrodiphenylamine	* 390, 311	190.0		31.2
4-Nitrodiphenylamine	* 385, 250	277.6		2.22
2, 4, 6-Trinitrodiphenylamine	361, 247	Retained on Column	49.6	2.28
N-Nitroso, 2, 2'-Dinitrodiphenylamine	320, 250		70.4	4.16
N-Nitroso, 2, 4'-Dinitrodiphenylamine	* 361, 315, 247		88.0	1.32
4, 4', 6-Tetranitrodiphenylamine	* 375, 225		121.6	4.18
4, 4'-Trinitrodiphenylamine	* 362, 249		144.0	3.70
2, 3', 4, 6-Tetranitrodiphenylamine	* 335, 230		190.4	0.89
4'-Dinitrodiphenylamine	* 395, 247		237.6	6.27
2, 4, 4'-Tetranitrodiphenylamine	* 404, 352, 300		252.0	7.38
2, 2', 4, 4', 6-Pentanitrodiphenylamine			329.6	5.73
2, 2', 4, 4', 6, 6'-Hexanitrodiphenylamine	* 358	Retained on Column - Eluted with 60% MeCl ₂ - 40% Hexane		10.71

TABLE II

QUALITATIVE ANALYSIS OF PBX-9404 FOR NITRATED DPA'S

SAMPLE PEAK RETENTION VOLUME (ml) 10% MeCl ₂ - 90% HEXANE	219-58 (1958)	37-62 (1962)	93-90 (1966)	93-110 (1966)	93-140 (1967)	620-4 (1971)	620-9 (1973)	NITRATED DPA
20	X	X	X	X	X	X	X	DPA
22.4	X	X	X	X	X	X	X	2 - Nitro DPA
25.6					X	X	X	N-Nitroso, 4-Nitro DPA
30			X	X	X		X	?
39		X	X	X	X	X		?
64	X	X	X	X	X	X	X	N-Nitroso DPA
88.8	X	X	X	X		X		2, 2' - Dinitro DPA
136	X				X		X	N-Nitroso, 2-Nitro DPA
169.6		X				X	X	2, 4 - Dinitro DPA
190				X	X	X		N-Nitroso, 4, 4'-Dinitro DPA
232		X			X	X		2, 4' - Dinitro DPA
277.6	X		X	X	X	X	X	4 - Nitro DPA

TABLE II (Continued)

QUALITATIVE ANALYSIS OF PBX-9404 FOR NITRATED DPA'S

<div>SAMPLE</div> <div> PEAK RETENTION VOLUME (ml) 40% MeCl₂ - 90% HEXANE </div>	219-58	37-62	93-90	93-110	93-140	620-4	620-9	NITRATED DPA
49.6	X		X	X		X		2, 4, 6 - Trinitro DPA
70.4		X	X		X	X	X	N-Nitroso, 2, 2' - Dinitro DPA
88.0		X		X	X			N-Nitroso, 2, 4' - Dinitro DPA
95		X	X					?
115	X							?
121.6					X		X	2, 4, 4', 6 - Tetranitro DPA
144.0	X	X	X	X				2, 4, 4' - Trinitro DPA
190.4	X	X				X	X	2, 3', 4, 6 - Tetranitro DPA
237.6	X	X	X			X	X	4, 4' - Dinitro DPA
252.0					X		X	2, 2', 4, 4' - Tetranitro DPA
329.6	X				X		X	2, 2', 4, 4', 6 - Pentanitro DPA

TABLE III
REPRODUCIBILITY OF CHROMATOGRAPHIC READINGS
(FOR 2-NITRODIPHENYLAMINE)

<u>Amt., μg</u>	<u>Response, chart divisions</u>	<u>Sensitivity, $\mu\text{g}/\text{div}$</u>
30 ↓	53.1	0.565
	51.6	0.581
	54.1	0.554
	54.0	0.556
	51.6	0.581
	50.7	0.592
	50.5	0.594
	49.2	0.610
	<u>49.1</u>	<u>0.611</u>
av =	51.5 $\pm$ 1.9	0.583 $\pm$.021

TABLE IV

QUANTITATIVE ANALYSIS OF LIBRARY SAMPLES OF PBX-9404

LIBRARY SPECIES OF DPA	219-58 (1958)	37-62 (1962)	93-90 (1966)	93-110 (1966)	93-140 (1967)	620-4 (1971)	620-9 (1973)
Diphenylamine	16	30	19	15	34	54	42
2 Nitrodiphenylamine	3	3	4	10	3	29	22
N-Nitroso, 4 - Nitrodiphenylamine					2	23	12
N-Nitrosodiphenylamine	6	5	19	12	8	44	38
2, 2' - Dinitrodiphenylamine		10	32	21			
N-Nitroso, 2-Nitrodiphenylamine					32		
2, 4 - Dinitrodiphenylamine							
N-Nitroso, 4, 4' - Dinitrodiphenylamine				41	10		
2, 4' - Dinitrodiphenylamine					15	10	
4 - Nitrodiphenylamine	13		13	12	34	2	12
2, 4, 6 - Trinitrodiphenylamine	15		15	15			
1 Nitroso, 2, 2' - Dinitrodiphenylamine		112	95		16	125	85
N Nitroso, 2, 4' - Dinitrodiphenylamine		5		16	24		
2, 4, 4', 6 - Tetranitrodiphenylamine					8		
4, 4' - Trinitrodiphenylamine	81			60			
2, 3', 4, 6 - Tetranitrodiphenylamine	50	1					
4' - Dinitrodiphenylamine	39	43	39				17
2, 2', 4, 4' - Tetranitrodiphenylamine							
2, 3', 4, 4', 6 - Pentanitrodiphenylamine	40						
Reaction of DPA Accounted For (Assuming 0.1% DPA in Original)	49.7	47.0	52.0	43.0	45.0	68.7	52.

Numbers on Chart Represent μg Nitro DPA in 30 μl aliquot

LINEARITY OF RESPONSE FOR DPA

FIGURE 2
LINEARITY OF RESPONSE (FOR 2 - NITRO DPA)