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SURVEILLANCE OF THE ARMY'S PROPELLANT STOCKPILE: ANALYSIS OF STABILIZER CONTENT BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

Dudley Robertson
Lewis Kansas

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Armament Engineering Directorate

Picatinny Arsenal, New Jersey

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The Surveillance Team at ARDEC acts as technical advisor to the Single Stock Pile Manager for Propellants at Rock Island, IL. As the lead laboratory for propellant safe storage life issues, the Surveillance Team establishes the procedures to be used to determine the safe storage life of the Army's propellant assets. For some years this laboratory has used high performance liquid chromatography to monitor the level of stabilizer and its daughter products in propellant. Three of those methods are presented along with statistics and some comments about their application.

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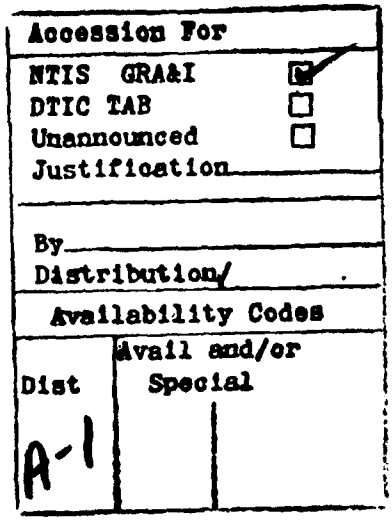

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INTRODUCTION

Nitrocellulose-based propellants degrade with time. If unchecked a state is reached where the nitrocellulose autoignites. To prevent this from occurring propellant formulations include stabilizers. These compounds react easily with nitrogen oxides and prevent autoignition from occurring. The reaction of these compounds is complex with the formation of many daughter products. Some of these products act as stabilizer and others do not.

These reactions have been known and studied for many years, but the advent of high performance liquid chromatography has provided a way to observe them quantitatively and rapidly. Current efforts, based on this technology, are being made to understand the underlying chemistry and kinetics involved with the stability of propellants. These techniques are also being used to routinely monitor the levels of stabilizer in the Army's propellant stockpile to assure that aging propellant remains safe for continued storage. The Army is unique in terms of the volume of samples processed and in terms of the number of propellant formulations analyzed. In excess of 12,000 samples are tested each year by this laboratory in its capacity as technical advisor to the the Single Stock Pile Manager, Rock Island, IL. About 18 different propellant formulations are analyzed routinely for stabilizer content. The quantity and diversity of the samples tested directly influences the choices made in establishing these procedures.

This report presents methods for the analysis of two stabilizers, diphenylamine (DPA) and 2-nitrodiphenylamine (2NDPA) and their daughter products. Three methods currently used to observe the stabilizer content of the Army's propellant assets are presented. Two of the methods have been in use for some years and are well established in terms of performance and reliability. Statistics are presented for the DPA method. These are considered typical for all the methods presented. The third method, developed to replace the 2NDPA method, provides marked improvements over its predecessor. It uses a ternary solvent system. The analysis time is reduced from 65 minutes to 25 minutes. The complexity of the method is reduced by replacing three columns with one. It is anticipated that the use of a larger proportion of organic mobile phase and the use of isopropyl alcohol will increase the solubility of nitrocellulose present and lengthen the life of the column used in this method. For all the methods, those compounds known to coelute are identified. The success of any analytical methods depends upon extracting the required compounds from the sample matrix. Near total dissolution using methanol is used for these procedures. This approach eliminates the environmental hazards of methylene chloride called for by the standard soxlet extraction method. The nearly complete dissolution of the sample with methanol assures that the less soluble higher nitrate daughters are fully extracted.

PROCEDURE

Laboratory Equipment and Material

High Performance Liquid Chromatography Equipment

Waters 840 chromatography systems
510 solvent pumps
490 programmable multiwavelength spectrophotometer
712 WISP autosampler
Digital 380 computer with Waters Expert Software
Fiatron CH-30 column oven

Columns

Brownlee cartridge column system
RP-18 22X.46 CM analytical column (end capped)
RP-18 10X.46 CM analytical column (end capped)
RP-8 CM analytical column (end capped)
C18 or C8 guard column
Waters in-line filter

Macherey - Nagel column
ET 250/8/4 NUCLEOSIL 120-3C18
(A 3 micron, 4 x 250 mm C18 column)

Reagents

Acetonitrile, HPLC grade
Isopropyl alcohol, HPLC grade
Methanol, HPLC grade
Methanol, reagent grade
Water, treated with a MiliQ reagent water system

The specification of a particular vendor is not an endorsement of that equipment, but rather a reflection of the equipment used in this study. Equivalent equipment would be suitable. It should be noted that the columns specified were chosen after a considerable survey of commercially available products and that those specified provided the best performance for the conditions given in this report.

Sample Preparation

Propellant samples are reduced in size, if necessary, by slicing the grains to roughly 2 to 3 mm squares. This process may be aided by using an analytical mill. Samples are accurately weighed, about 0.4 to 0.5g +/- 0.2 mg, into a 100 mL volumetric flask and 80 mL of reagent grade methanol is added. This solution is allowed to stand over night, then sonicated if necessary until most of the material is dissolved. The dissolved sample is diluted to the mark with reagent grade methanol. The solution is then filtered through a membrane filter (0.45 microns, nylon 66) directly into autosampler vials for injection into the chromatograph. Filtration can be difficult due to the presence of gelled or suspended nitrocellulose. The practice in this laboratory has been to allow the solution to stand overnight. This works well with the large sample load processed by this laboratory. Centrifugation is effective as a filter aid, but requires additional operator time. A simpler method might be a coarse filtration followed by the 0.45 micron filter required by the HPLC analysis.

Chromatographic Conditions

2NDPA

Injection	20 microliters
Flow	1.2 mL/min
Temperature	35°C
Mobile phase	58/42% water/acetonitrile
Columns	RP-8 5 micron 3 cm RP 18 5 micron 10 cm RP 18 5 micron 22 cm Waters guard column
Detector	245, 258, 264 nm (when using Maxplot)
Analytes	2-nitrodiphenylamine N-nitroso-2-nitrodiphenylamine 2,2′-dinitrodiphenylamine 2,4-dinitrodiphenylamine 2,4′-dinitrodiphenylamine 2,2′,4-trinitrodiphenylamine 2,4,6-trinitrodiphenylamine

	2,4,4´-trinitrodiphenylamine 2,3´,4,6-tetranitrodiphenylamine 2,2´,4,4´-tetranitrodiphenylamine

DPA

Injection	15 microliters
Flow	1.5 mL/min
Temperature	50°C
Mobile phase	48/52% acetonitrile/water
Columns	RP-18 5 micron 22X.46 CM Brownlee guard column
Detector	245, 258, 265 nm (Maxplot)
Analytes	Diphenylamine 2-Nitrodiphenylamine 4-nitrodiphenylamine 2,2´-dinitrodiphenylamine 2,4-dinitrodiphenylamine 2,4´-dinitrodiphenylamine 4,4´-dinitrodiphenylamine N-nitrosodiphenylamine

2NDPA, New Method

Injection	10 microliters
Flow	0.6 mL/min
Temperature	35°C
Mobile phase	54% (30/70 IPA/AN)/46% water
Column	Macherey - Nagel column ET 250/8/4 NUCLEOSIL 120-3C18 (A 3 micron, 4 x 250 mm C18 column)
Detector	245, 258, 265 nm

Analytes	2-nitrodiphenylamine
	N-nitroso-2-nitrodiphenylamine
	2,2′-dinitrodiphenylamine
	2,4-dinitrodiphenylamine
	2,4′-dinitrodiphenylamine
	2,2′,4-trinitrodiphenylamine
	2,4,6-trinitrodiphenylamine
	2,4,4′-trinitrodiphenylamine
	2,3′,4,6-tetranitrodiphenylamine
	2,2′,4,4′-tetranitrodiphenylamine

Standards

Standards are produced by diluting a stock solution as needed. The stock solution is kept in the cold and in the dark. The quantities added to the stock solution reflect the level of concentration expected in the samples. Typical concentrations for the more common daughters are listed below:

Compound	250 mL, mg Stock A	100 mL, mg Stock B	mg/100 mL 1/10 of B
Diphenylamine	50	20	2.0
N-nitrosodiphenylamine	20	8	0.8
2-nitrodiphenylamine	10	4	0.4
4-nitrodiphenylamine	10	4	0.4
2,4-dinitrodiphenylamine	10	4	0.4
2,4′-dinitrodiphenylamine	10	4	0.4
2,2′-dinitrodiphenylamine	10	4	0.4
4,4′-dinitrodiphenylamine	10	4	0.4

DISCUSSION

Typical chromatograms for the standards used for each method are presented in figures 1, 2, and 3. The closest peaks have a resolution of about 1.25 or better. The one exception is the elution of 2,3′,4,6-tetranitrodiphenylamine (2,3′,4,6TNDPA) and N-nitroso-2-nitrodiphenylamine by the new method (fig. 3). The two compounds do not occur together during the life of the propellant and their overlap does not pose a serious problem. The effect of column temperature was studied extensively. The temperatures chosen were based on the maximum resolution produced. There is the added benefit of reduced column pressure with increased temperature due to an increase in the solubility of nitrocellulose and to the decrease in mobile phase viscosity. Peak areas observed at ambient and elevated temperatures were comparable, indicating no presence of degradation resulting from the higher temperatures.

To increase sensitivity the Maxplot function of the detector is used. Wavelengths are chosen near the maxima for several of the standards. The detector compares the slope for each wavelength near the start of each peak and the most sensitive wavelength is automatically chosen to record the peak area or peak height. Daughter products reported are calculated as weight percent of virgin stabilizer. The total of the mono-, and di- substituted compounds are used in reporting total stabilizer present. N-nitroso compounds are not included.

The analytical approach attempts to dissolve as much of the sample as possible. This assures complete extraction of the degradation products. The one difficulty with this approach is that some NC is dissolved or suspended in solution. This may cause problems with column performance and with back pressure. To minimize these problems frequent washes are required. It is recommended that a 10 to 15 column volume wash using 100% organic phase be performed after every third or fourth set of samples (three or four injections) and standards (two injections).

STATISTICS

The precision and accuracy for the DPA method was established in detail. The other methods presented produce similar statistics. All the methods use a bracketing technique for standardization. A standard is injected followed by three samples and another standard. The peak areas for the two standards are averaged and compared to the samples to obtain the weight of daughter product present. These cycles are run overnight as required. For the DPA method, there is about an hour and a half separating standard injections. Between some cycles there is a purge, wash, and equilibration. This requires another hour and a half. Statistics were produced for the paired standards, and also for the standards over the entire run (tables 1, 2, and 3) for the DPA method. The tables contain the peak areas (times 1000) for seven pairs of standards, or about 21 hours of continuous operation with three samples being analyzed between each set of standards. Table 1 is probably atypical in that the precision for the entire day is 1% or less except for DPA. The autoinjector (WISP) is guaranteed for a precision of 2%. In every case the bracketing (statistics for the paired standards) is 1% or less despite higher daily variations of up to 7%. These values are typical for well controlled determinations using fresh columns. The calculation for the duplicate statistics is as follows:

$$\text{Standard deviation} = \text{SQRT}\left((1/2N)\,(\text{SUM } D^{\wedge}2)\right)$$

where

N is the number of duplicates
D is the differences between duplicates

A standard was injected as a sample to establish the accuracy of the method. Three sets of three injections were performed. The bracket technique was used to standardize the procedure. The following recoveries were obtained:

4NDPA	100.2% ± 0.5%
NNODPA	99.9% ± 0.7%
2,4'DNDPA	100.1% ± 0.6%
DPA	99.9% ± 1.0%
2,2'DNDPA	100.1% ± 0.5%
2,4DNDPA	100.0% ± 0.6%
2NDPA	100.2% ± 0.4%

The precision and accuracy of the method is excellent. It is the practice of this laboratory to monitor the standard deviation of the paired injections of the virgin stabilizer standard. The method is considered in control if that standard deviation is less than three percent. Typically it runs less than two percent.

APPLICATION

Ring substituted nitroso compounds present in aged propellant are not quantified by this method. Picric acid in propellant that has or is about to fume has been observed. This polar compound is not well retained by these methods. The companion nitro-analines have not been observed, nor has hexanitrodiphenylamine.

A peak has been observed late in the life of the propellant that interferes with 2,4'-dinitrodiphenylamine in the DPA method. It is well separated in the 2NDPA method and by the new method. This compound has been collected and submitted to UV, IR, and NMR analysis. The UV scans are similar to a di-substituted DPA. The NMR however shows no phenyl groups present. The IR scan matches a scan of 13.6% nitrocellulose.

The application of these methods to routine samples, and the interpretation of the results produced is vital to maintaining safe propellant in the Army's stockpile. Practical problems exist in interpreting these results. Homogeneity being one example. A typical DPA stabilized propellant was tested for total stabilizer present based on nine separate weighings. The results are presented:

Test	Total as % DPA
1	0.43
2	0.40
3	0.38
4	0.33
5	0.36
6	0.34
7	0.35
8	0.35
9	0.32

The average for the total stabilizer is 0.36% with a standard deviation of 0.035% (9.74% relative standard deviation). The deviation observed is due to the inhomogeniety of the propellant. The total stabilizer, using a three sigma rule, falls between 0.105% and 0.465%. The range for stability category B is 0.30% to 0.49%. A single test result for this propellant could fall in category B, C, or D. The 0.4 g sample size is sensitive to variations in stabilizer content grain to grain, and within individual grains. It is the practice in this laboratory to retest a propellant in triplicate if a single test result moves the propellant to a critical stability category (D).

As stated, the total stabilizer is reported based on the sum of the mono- and di-substituted daughter products excluding the nitroso compounds calculated as weight percent virgin stabilizer. This approach is not without controversy. It is argued that the nitroso compounds are indeed stabilizers. There is indication in more recent literature that N-nitrosodiphenylamine should not be counted as an efficient stabilizer. This compound in fact may act as an inhibitor to the stabilization process by consuming significant quantities of DPA that remain unavailable for further reaction for much of the life of the propellant. The reaction can go backward forming DPA or forward to form 4-nitrosodiphenylamine that oxidizes to form 4-NDPA. The DPA and 4-NDPA thus produced are counted over the life of the propellant even though the N-nitrosodiphenylamine is not measured. Excessively high levels of N-nitrosodiphenylamine have been observed in relatively new small arms propellant. NNO 2,4DNDPA degrades rapidly in the solid state (total disappearance within hours). This material immediately begins to darken. Overnight an orange brown material is obtained along with brown fumes filling the container. The compound is stabilized in water, but degradation is accelerated by drying. (Synthesis of this compound can be found in the appendix.) The N-nitroso- compounds release NO at accelerated aging temperatures and may in fact decrease the time to fume for propellants where the N nitroso- is high.

Propellants containing dibutylphthalate (DBP) present a problem in that the DBP has a long retention time (about 45 minutes). Careful adjustment of injection times will cause that peak to elute near the beginning of the chromatogram for the next sample. This reduces the time for each chromatogram from 45 minutes to about 20 minutes (fig. 4).

CONCLUSIONS

Three chromatographic methods have been presented that allow testing of a broad range of propellants over their life span. The methods are accurate and precise. That precision is maintained in day-to-day use establishing its ruggedness.

Table 1. Precision based on the injection of a standard (day 1)

	4NDPA	NNO	2,4′	DPA	2,2′	2,4	2N
1	769.7	331.3	668.0	798.5	744.8	644.6	1289.3
	779.7	338.0	697.2	807.1	755.1	657.8	1311.4
2	794.0	341.1	704.9	864.3	763.2	664.2	1328.2
	783.1	338.2	697.8	860.0	756.2	654.2	1311.4
3	787.1	340.8	700.8	881.6	755.7	654.5	1317.2
	792.2	337.4	700.6	891.0	758.2	656.4	1325.3
4	789.7	338.6	702.6	891.0	758.7	657.1	1317.5
	793.4	337.0	699.7	887.5	758.9	656.6	1326.3
5	786.5	338.6	701.3	901.0	756.1	656.9	1312.4
	795.1	341.5	707.1	911.5	766.7	663.8	1327.6
6	795.3	334.3	699.1	935.6	759.8	656.4	1331.4
	793.6	340.2	706.7	957.7	765.1	663.4	1323.8
7	782.4	338.6	700.3	912.3	756.8	654.9	1311.0
	787.1	338.5	701.1	912.9	756.4	659.1	1313.7
Avg	787.8	338.0	700.4	886.6	758.0	657.1	1317.6
Std dev	7.2	2.7	5.1	43.8	5.2	4.9	10.9
% RSD	0.92	0.80	0.73	4.95	0.69	0.75	0.83
Effect of bracketing							
Std dev	5.1	2.3	3.9	4.7	4.4	4.8	9.1
% RSD	0.64	0.69	0.56	0.53	0.58	0.73	0.69

Table 2. Precision based on the injection of a standard (day 2)

	4NDPA	NNO	2,4´	DPA	2,2´	2,4	2N
1	1200.0	525.0	1167.0	1186.0	1200.0	1144.0	2099.0
	1182.0	538.0	1185.0	1151.0	1194.0	1174.0	2112.0
2	1219.0	554.0	1238.0	1194.0	1259.0	1228.0	2200.0
	1201.0	551.0	1212.0	1164.0	1221.0	1229.0	2154.0
3	1205.0	558.0	1242.0	1173.0	1252.0	1242.0	2206.0
	1224.0	552.0	1224.0	1152.0	1229.0	1225.0	2191.0
4	1271.0	565.0	1274.0	1176.0	1268.0	1275.0	2236.0
	1252.0	562.0	1242.0	1157.0	1231.0	1266.0	2210.0
5	1292.0	579.0	1268.0	1198.0	1262.0	1306.0	2283.0
	1289.0	576.0	1261.0	1181.0	1246.0	1291.0	2247.0
6	1284.0	574.0	1261.0	1170.0	1246.0	1301.0	2252.0
	1302.0	578.0	1256.0	1189.0	1241.0	1292.0	2242.0
7	1284.0	584.0	1249.0	1197.0	1228.0	1297.0	2244.0
	1313.0	594.0	1263.0	1209.0	1245.0	1308.0	2262.0
Avg	1251.0	563.6	1238.7	1178.4	1237.3	1255.6	2209.9
Std dev	44.6	18.8	31.7	18.2	21.8	51.01	55.2
% RSD	3.57	3.34	2.56	1.54	1.76	4.06	2.50
Effect of bracketing							
Std dev	13.5	4.1	13.1	15.2	16.1	10.3	17.9
% RSD	1.08	0.72	1.06	1.29	1.30	0.82	0.81

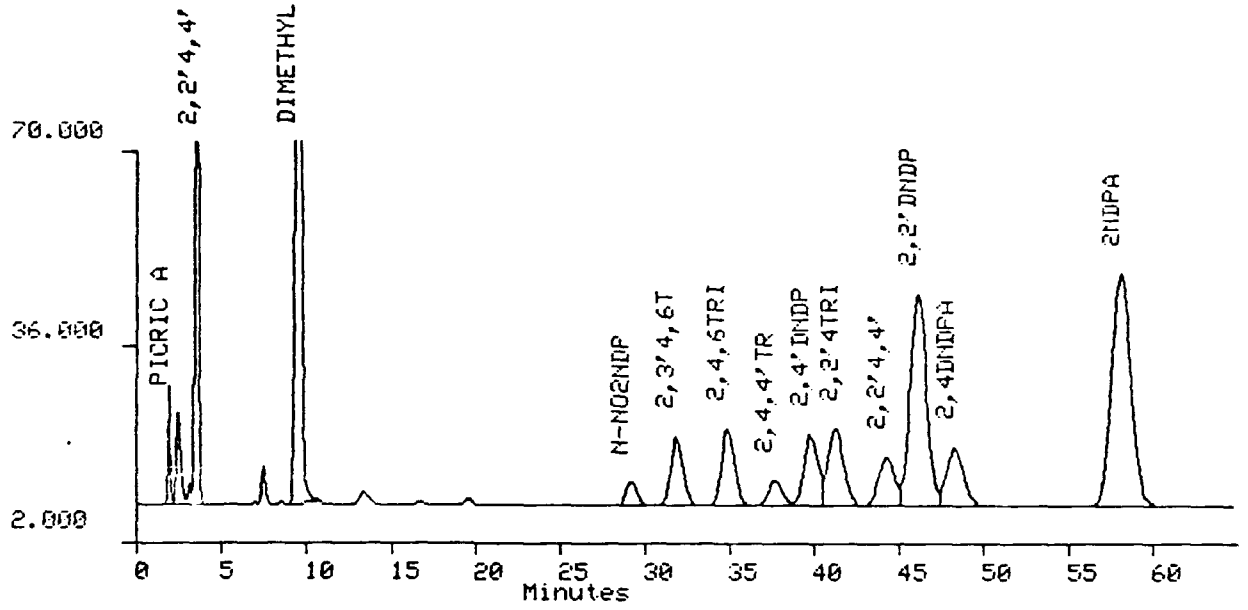
Table 3. Precision based on the injection of a standard (day 3)

	4NDPA	NNO	2,4´	DPA	2,2´	2,4	2N
1	862.0	399.0	810.0	800.0	773.0	832.0	1501.0
	842.0	392.0	798.0	772.0	765.0	824.0	1481.0
2	938.0	413.0	855.0	925.0	837.0	874.0	1618.0
	955.0	429.0	880.0	934.0	857.0	898.0	1644.0
3	980.0	441.0	904.0	961.0	877.0	921.0	1694.0
	968.4	439.0	898.0	964.0	866.0	918.0	1675.0
4	969.0	438.0	897.0	954.0	873.0	916.0	1686.0
	955.0	435.0	890.0	953.0	862.0	915.0	1663.0
5	975.0	443.0	905.0	960.0	876.0	923.0	1693.0
	975.0	443.0	905.0	960.0	876.0	923.0	1693.0
6	957.0	441.0	893.0	957.0	865.0	919.0	1675.0
	955.0	441.0	892.0	951.0	869.0	910.0	1667.0
7	962.0	441.0	896.0	964.0	871.0	918.0	1675.0
	958.0	432.0	891.0	948.0	863.0	910.0	1665.0
Avg	946.4	430.4	879.1	929.1	851.0	899.9	1643.9
Std dev	41.6	16.8	34.2	61.9	36.5	33.0	67.8
% RSD	4,40	3.90	3.89	6.66	4.28	3.67	4.12
Effect of bracketing							
Std dev	9.0	5.1	8.6	8.5	7.3	7.1	13.1
% RSD	0.96	1.20	0.98	0.92	0.86	0.79	0.79

TESTMIX 1/27/89 14:30:04

Acquisition method	2ndpa	Quantitation method	2ndpa
Units		System number	1
Channel	1	Vial	10
Injection	1	Total injections	1
Run time	65.00 min	Sample rate	5 per sec
Injection volume	25 uL	Sample amount	
Internal standard amt		Scale factor	0.00
Mode	Analysis	Response factors	Average
Version	REV 4.0	Channel to calibrate	1

Description
METHOD FOR 2NDPA AND ITS DERIVATIVES. 58/42% H2O/ACETONITRILE@1.2ML/MIN COL.TEMP.= 35C. 1 BROWNLEE RP-8(3CM) PLUS 2 RP-18(10+22CM) CARTRIDGES IN SERIES. ALL 2NDPA DERIVATIVES REPORTED AS 2NDPA MOL.WT. EQUIVALENTS. WATERS 490 DETECTOR-MAXPLOT MODE: 258,264,245 nm.



Peak Name	Ret time	Area	Height	Type	Amount	RF
PICRIC ACID	2.01	212372	20614	BV	0.004	4.9300e+07
2,2'4,4'6,6'HEXA	3.62	1954702	157975	VB	-1.000	0.0000e+00
DIMETHYLPHTHALAT	9.49	4555186	262788	BB	0.202	2.2569e+07
N-NO2NDPA	29.23	192580	4239	BB	1.117	1.7237e+05
2,3'4,6TETRA	31.89	604637	11837	BB	0.764	7.9148e+05
2,4,6TRINDPA	34.93	717884	13301	BV	0.901	7.9697e+05
2,4,4'TRINDPA	37.77	248397	4449	VV	1.068	2.3260e+05
2,4'DNDPA	39.85	703703	12184	VV	0.773	9.1063e+05
2,2'4TRINDPA	41.33	855313	13161	VV	1.582	5.4079e+05
2,2'4,4'TETRA	44.32	541192	8293	VV	-1.000	0.0000e+00
2,2'DNDPA	46.18	2489139	36835	VV	2.832	8.7879e+05
2,4DNDPA	48.38	703321	9867	VB	1.222	5.7534e+05
2NDPA	58.12	3224186	40239	BB	4.302	7.4952e+05

Figure 1. 2-nitrodiphenylamine three column method

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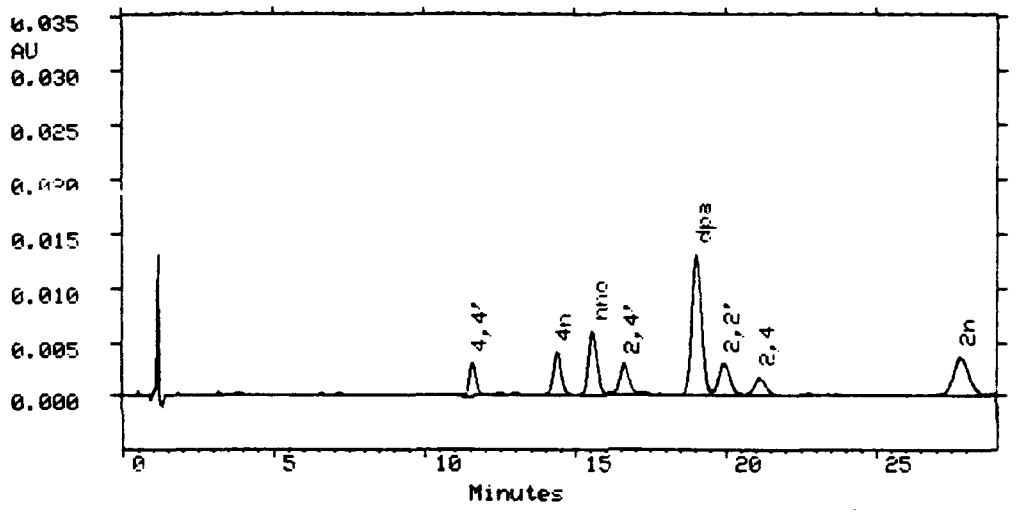
Acquisition method	dpa	Quantitation method	dpa
Units		System number	1
Channel	1	Vial	48
Injection	1	Total injections	1
Run time	29.00 min	Sample rate	2.00 per sec
Injection volume	15 uL	Mode	Calibration
Version	5.1		

MP

LC3. Method for DPA and its deriv.s. reported as DPA equiv.s.
Brnlee ODS 22 cm x 4.6mm 5µm col. T = 55°C
41/59 AN/H2O @ 2.0 ml/min. UV at 258/264/245nm

Chromatogram of std29



Conditions

Run time	29.00 min	Sample rate	2.00 per sec
Injection volume	15 uL	Sample amount	0.00
Internal standard amt		Scale factor	0.00
Mode	Calibration	Response factors	Replace

Keyboards of Remote Devices Locked

Single Point Calibration — Quantitation by Area
Force Through Zero is Enabled — Peak Detection Threshold 1

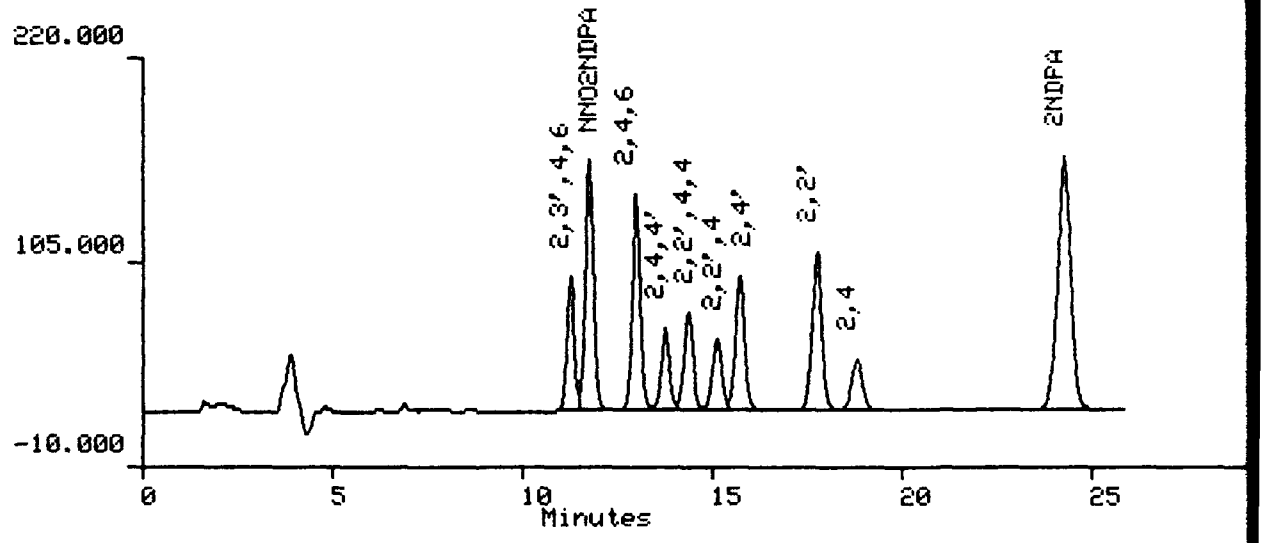
Peak Name	Ret time	Area	Height	Type	Response	Deviation	Intercept	Slope
4,4'	11.59	47200	3028	BB	4.72000e+04		0	1.7226e+05
4n	14.40	77620	3975	BB	7.76200e+04		0	2.0534e+05
nno	15.58	118589	5994	BV	1.18589e+05		0	9.5252e+04
2,4'	16.64	64229	2848	VB	6.42290e+04		0	3.0732e+05
dpa	19.04	294361	12969	BV	2.94361e+05		0	1.4718e+05
2,2'	19.96	79737	3002	VV	7.97370e+04		0	3.0434e+05
2,4	21.15	46484	1633	VB	4.64840e+04		0	2.0036e+05
2n	27.82	130715	3545	BB	1.30715e+05		0	2.6677e+05

Figure 2. Diphenylamine

S2 9/13/90 17:42:51

Acquisition method	2n	Quantitation method	2n
Units		System number	1
Channel	1	Vial	48
Injection	1	Total injections	1
Run time	26.00 min	Sample rate	1 per sec
Injection volume	10 uL	Sample amount	
Internal standard amt		Scale factor	
Mode	Calibration	Response factors	Average
Version	REV 4.0	Channel to calibrate	1

Description
LC4. Method for 2NDPA and its deriv.s. Temp = 35°C.
Mach-Nag C18 3µm 25cm col. 54(30/70 IPA/ACN)/46H20 @ 0.55mL/min.
UV Maxplot @ 258, 264, and 245nm.



Peak Name	Ret time	Area	Height	Type	RF
2,3′,4,6	11.29	1072296	76471	BV	1.0585e+06
NNO2NDPA	11.79	1990984	141725	VB	5.5468e+05
2,4,6	13.02	1884667	123852	BV	8.9197e+05
2,4,4′	13.79	740832	46599	VV	7.2617e+05
2,2′,4,4′	14.40	917007	55051	VV	1.2364e+06
2,2′,4	15.16	670317	40329	VV	7.9485e+05
2,4′	15.77	1212694	76147	VB	6.9315e+05
2,2′	17.81	1674876	89798	BV	5.7035e+05
2,4	18.87	550987	28228	VB	5.406/e+05
2NDPA	24.34	3516083	142196	BB	5.5611e+05

Figure 3. 2-nitrodiphenylamine new method

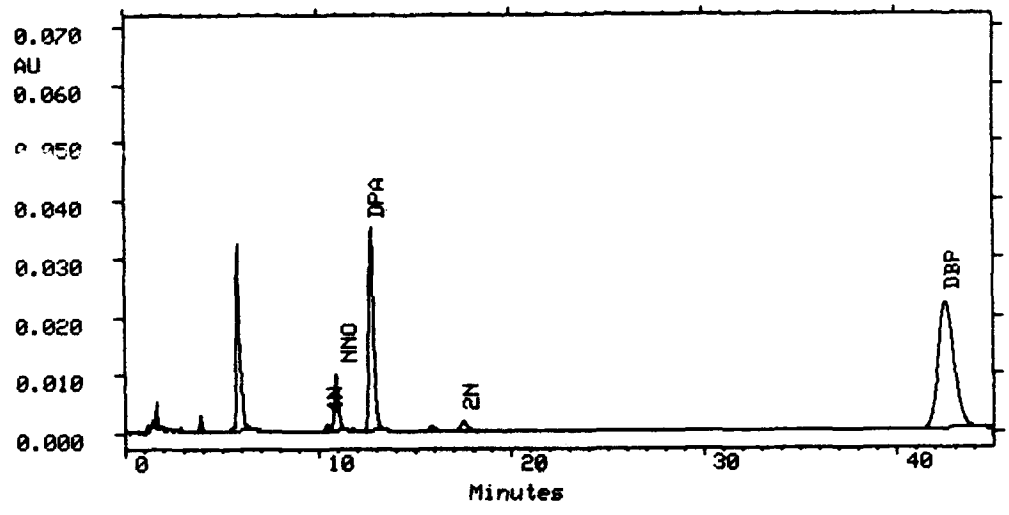
49429WC 14-Feb-90 17:27:03

Acquisition method	dpa	Quantitation method	dpa
Units		System number	1
Channel	1	Vial	1
Injection	1	Total injections	1
Run time	45.00 min	Sample rate	2.00 per sec
Injection volume	15 uL	Mode	Analysis
Version	5.1		

MAX

LC2. Method for DPA and its deriv.s.
Brnlee C18 22cm X 4.6mm 5µm col. T = 45°C
46/54 AN/H20 @ 1.5mL/min. UV at 258/264/245nm

Chromatogram of 49429WC



Conditions

Run time	45.00 min	Sample rate	2.00 per sec
Injection volume	15 uL	Sample amount	
Internal standard amt		Scale factor	
Mode	Analysis		

Keyboards of Remote Devices Locked

Single Point Calibration — Quantitation by Area
Force Through Zero is Enabled — Peak Detection Threshold 10
Errors Reported From Integration/Quantitation
Error 7 response or amount missing for all levels

Peak Name	Ret time	Area	Height	Type	Amount	Intercept	Slope	Response
4N	10.46	14603	1112	BV	0.047	0	3.1307e+05	1.46030e+04
NNO	10.90	149736	9782	VB	0.956	0	1.5662e+05	1.49736e+05
DPA	12.73	576596	34967	BB	2.447	0	2.3567e+05	5.76596e+05
2N	17.50	32142	1474	BB	0.074	0	4.3304e+05	3.21420e+04
DBP	42.55	1234646	21714	BB		0	0.0000e+00	0.00000e+00

Figure 4. Chromatogram showing presence of dibutylphthalate

APPENDIX

SYNTHESIS OF N-NITROSO-2,4-DINITRODIPHENYLAMINE

2,4-dinitrodiphenylamine (0.5 g) was dissolved in a mixture of 100 mL of trifluoroacetic acid and 100 mL glacial acetic acid. The mixture was warmed to 45°C to accelerate the dissolution process. The orange solution was then cooled to 5°C in an ice bath and sodium nitrite (0.1 g) added all at once with vigorous stirring. As soon as the orange color of the solution faded to a pale greeninsh yellow (approx. 1 minute), the mixture was poured into a mixture of 800 mL water and 200 g ice. A yellow precipitate soo formed and this was filtered off, washed thoroughly with water and dried under vacuum in a desiccator containing some solid potassium hydroxide pellets. During this work up, the material was observed to darken. Upon storage in a vial overnight an orange brown material was obtained and brown fumes filled the vial. The yield of decomposed material was 0.26 g.

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