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THIN-LAYER CHROMATOGRAPHIC/SPECTROPHOTOMETRIC ANALYSIS OF CERTAIN COMPONENTS IN AGED DOUBLE-BASE PROPELLANT

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SUMMARY

A combination of thin-layer chromatography and spectrophotometry provides a reliable means for measuring typical plasticizers and stabilizers in aged double-base propellants. The use of a thin-layer chromatographic separation eliminates analysis errors encountered in other methods. Both nitrated stabilizers and nitroglycerin breakdown products are removed before measurement of the unused stabilizers and nitroglycerin. Satisfactory thin-layer separations and recoveries were demonstrated even with an application sample size of up to 40 mg. The analysis time was not significantly longer than with other methods and acceptable accuracy and precision were shown in a reliability study.

INTRODUCTION

The determination of nitroglycerin and stabilizers in the presence of degradation products such as lower nitrate esters of nitroglycerin and nitrated stabilizers in aged double-base propellant and in micro propellant samples has been a problem for some time. GRINDLEY AND JEACOCKE[1] and SCHROEDER *et al.*[2], have shown the presence of considerable amounts of nitration products of the stabilizers, resorcinol and 2-nitrodiphenylamine, in aged composite modified double-base propellant. In unpublished work, samples of aged propellant (stored at ambient for five years) were examined for stabilizer breakdown. The main breakdown products observed were resorufin and resazurin. These seemed to be the primary stabilizer nitration products formed. In some samples, very small quantities of 2,4- and 2,4'-dinitrodiphenylamine were observed. Denitration of nitroglycerin in propellant samples appeared to result in the formation of 1,2- and 1,3-dinitroglycerin and the 1- and 2-mononitroglycerin.

Most of these degradation products, if not removed, interfere in the determination of the original components from which they were derived. All procedures currently used for the determination of 2-nitrodiphenylamine[3,4], resorcinol[3,5,6] and nitroglycerin[6-8] in composite modified double-base propellant fail to distinguish between the compound of interest and many of the nitrated/denitrated derivatives. Furthermore, these procedures require samples varying in weight from 0.5 to 5 g. An analytical scheme based on spectrophotometric measurement of double-base propellant

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components following a Soxhlet extraction was reported recently[6], and was shown to reduce analysis time by 70% as compared to wet methods. Although the spectrophotometric scheme is very rapid and reliable when used in connection with relatively fresh propellant, it does not provide for the removal of analytically interfering species in aged propellant. A rapid, yet reliable method for the quantitative determination of nitroglycerin and stabilizers in the presence of degradation products was needed.

Several methods for the removal and separation of degradation products from the original components before analysis have been reported[9,10]. Most of these include separations employing column or thin-layer chromatography (TLC) and were at most semi-quantitative. Quantitative TLC analysis involves either on-plate measurement or removal of the support followed by elution and measurement. However, according to BOBBITT[11], TLC methods involving off-plate U.V. and visible spectrophotometric measurements gave 2–3% accuracy and seemed appropriate for our requirements.

HARTOG AND SHAFER[12] recently succeeded in separating a mixture of nitroglycerin, dinitrotoluene, and diethylene glycol dinitrate by TLC using toluene–chloroform (90 : 10). Following the separation, the three components were eluted from the support and assayed spectrophotometrically, which resulted in 90% recovery. This recovery, although considered excellent in TLC analysis, did not seem sufficient for our purposes since precision of instrumental methods was far superior. Furthermore, the above separation did not provide for the removal of breakdown products.

This investigation reports a technique for rapidly separating a complex mixture while using plate overloading to obtain sufficient sample from a TLC plate for spectrophotometric measurements of nitroglycerin, triacetin, 2-nitrodiphenylamine, and resorcinol utilizing the U.V., visible, and I.R. regions of the spectrum. Only the stabilizers (2-nitrodiphenylamine and resorcinol) were U.V.-visible active while the other two components of interest (nitroglycerin and triacetin) were U.V.-visible inactive and to be determined quantitatively would require either some relatively time consuming color development method[13,14] or collection of sufficient material from the plate for I.R. analysis. To develop a suitably rapid method it was necessary to separate sufficient material on one plate for direct I.R. measurements of all components of interest.

For over a year this technique has been successfully used by this laboratory for the determination of the above components in composite modified double-base propellant containing decomposition products such as mono- and dinitroglycerins and nitrated and nitrosated diphenylamines and resorcinols. However, it is not within the scope of this report to actually measure these breakdown products.

EXPERIMENTAL

Apparatus and reagents

Precoated silica gel TLC plates (E. Merck, A. G., Catalog No. 5715) containing the sample were eluted in a developing tank (Kensington Scientific Corp., Catalog No. K-4097). For U.V. and visible measurements, solutions were read in a 1 cm silica cell against a matched reference on a Beckman DK-2A spectrophotometer. I.R. measurements were performed on a Beckman IR-7 spectrophotometer in a 0.2 mm calcium fluoride liquid cell against a matched reference. All reagents used were reagent grade.

Procedure

Standard solutions were prepared in concentration ranges shown in Table I and scanned against a solvent reference using conditions as indicated in Table II. The absorptivity for each component was determined by plotting net absorbance against concentration and determining the slope of the calibration curve.

Using diethyl ether, enough propellant was Soxhlet extracted such that 40 mg of extract was obtained. After a 24-hour extraction, the ether was allowed to evaporate from the extract and the residue redissolved in about 5 ml of ethyl acetate.

TABLE I

STANDARD SOLUTIONS

Component	*Concentration range (mg/ml)*	*Solvent*
Nitroglycerin	1–5	1,2-Dichloroethane
Triacetin	2–10	1,2-Dichloroethane
2-Nitrodiphenylamine	0.004–0.020	Ethyl acetate
Resorcinol	0.004–0.020	Ethyl acetate

The ethyl acetate solution containing the propellantextract was applied with a syringe evenly across a TLC plate and a chromatogram developed by the ascending method using benzene–ethyl acetate (85 : 15). Following the development the strip of support containing the separated components of interest was removed from the plate and the components eluted from the support with ethyl acetate. The ethyl acetate was evaporated and the individual components quantitatively dissolved in the appropriate solvent. Nitroglycerin and triacetin were measured in the I.R., resorcinol

TABLE II

OPERATING CONDITIONS

Component	*Scanning range*	*Base line*	*Peak*	*Cells*	*Reference*
Nitroglycerin	1600–1950 cm^{-1}	1900 cm^{-1}	1659 cm^{-1}	0.2 mm calcium fluoride	8
Triacetin	1700–1950 cm^{-1}	1900 cm^{-1}	1745 cm^{-1}	0.2 mm calcium fluoride	8
2-Nitrodiphenylamine	400–750 mμ	700 mμ	420 mμ	1 cm silica	4
Resorcinol	250–350 mμ	300 mμ	272 mμ	1 cm silica	6

in the U.V., and 2-nitrodiphenylamine colorimetrically. The absorbance of the solutions was determined as outlined in Table II and corresponding percentages of each were obtained.

DISCUSSION

In developing a satisfactory chromatographic procedure for the separation of nitroglycerin, triacetin, 2-nitrodiphenylamine and resorcinol, it was necessary to (1)

completely separate from each other and from interferences all components to be spectrophotometrically measured on one plate, (2) confine each separated component to a narrow range of R_F values, *i.e.*, to avoid "streaking" in the chromatogram, and (3) separate enough material for quantitative measurement. Incomplete separation of components on the plate may cause interference when measured spectrophotometrically depending on the components involved and their analytical wavelengths. Streaking of a component complicates the recovery operation due to the large amount of support material that must be eluted.

To optimize the developer to be used for the desired separation a test solution containing purified nitroglycerin, triacetin, resorcinol, and 2-nitrodiphenylamine was applied to a TLC plate and developed using a variety of solvents. Benzene alone was found to provide an excellent separation of nitroglycerin and 2-nitrodiphenylamine but failed to move the triacetin and resorcinol out of the origin. Incremental additions of ethyl acetate to the benzene increased the R_F values of all components. A benzene–ethyl acetate (85 : 15) mixture allowed for satisfactory separation of the above components. Further increase of ethyl acetate caused resorcinol and nitroglycerin to approach the R_F values of triacetin and 2-nitrodiphenylamine, respectively.

To determine the optimum range of sample sizes that could be handled by the TLC plate, six synthetic mixtures containing nitroglycerin, triacetin, resorcinol, and 2-nitrodiphenylamine were prepared by combining aliquots from standard solutions containing the above components. Aliquots of the combined standard solution were then chromatographed, and each component determined spectrophotometrically. The results are shown in Table III. Although the recoveries of triacetin and 2-nitrodiphenylamine were relatively independent of the amounts in the sample, nitroglycerin

TABLE III

PLATE LOADING AND RECOVERY DATA

Mix No.	*Nitroglycerin, TLC/I.R.*			*Triacetin, TLC/I.R.*		
	Nominal (mg/ml)	*Determined (mg/ml)*	*Recovery (%)*	*Nominal (mg/ml)*	*Determined (mg/ml)*	*Recovery (%)*
1	36.02	34.65	96.2	3.21	3.17	98.8
2	32.30	31.53	97.6	6.44	6.48	100.6
3	29.02	28.15	97.0	9.70	9.77	100.7
4	26.92	26.40	98.1	12.85	12.86	100.1
5	22.81	22.62	99.2	16.04	16.12	100.5
6	20.15	20.12	99.9	19.31	19.44	100.7
	Resorcinol, TLC/U.V.			*2-Nitrodiphenylamine, TLC/Visible*		
	Nominal (mg/ml)	*Determined (mg/ml)*	*Recovery (%)*	*Nominal (mg/ml)*	*Determined (mg/ml)*	*Recovery (%)*
1	0.404	0.385	95.3	0.400	0.398	99.5
2	0.808	0.734	90.8	0.400	0.997	99.5
3	0.404	0.381	94.4	0.800	0.792	99.0
4	1.212	0.991	81.8	0.400	0.400	100.0
5	0.404	0.396	98.1	1.200	1.174	97.8
6	0.404	0.402	99.5	0.400	0.398	99.5

and resorcinol recoveries were severely affected by the amount contained in the chromatographed aliquot. Aliquots containing up to 40 mg of components were satisfactorily separated; however, further increase in sample size resulted in streaking and low recoveries of nitroglycerin and resorcinol. Samples containing less than 20 mg did not yield sufficient material for reliable I.R. analysis of nitroglycerin and triacetin.

Precision data for the methods were obtained from an ethyl acetate solution containing nitroglycerin, triacetin, 2-nitrodiphenylamine, and resorcinol. Six 1 ml aliquots, each containing about 40 mg of sample were developed and the separated components spectrophotometrically measured using the described procedure. Relative standard deviations found were 0.59%, 1.91%, 0.76%, and 1.13% for nitroglycerin, triacetin, 2-nitrodiphenylamine, and resorcinol, respectively (Table IV).

TABLE IV

PRECISION DATA FOR THE METHODS

Run	*Nitroglycerin (mg)*	*Triacetin (mg)*	*2-Nitrodiphenyl-amine (mg)*	*Resorcinol (mg)*
1	36.1	2.77	0.391	0.406
2	36.1	2.91	0.395	0.400
3	36.4	2.80	0.396	0.414
4	36.5	2.84	0.391	0.404
5	36.4	2.77	0.390	0.407
6	36.6	2.84	0.395	0.406
Average	36.4	2.82	0.393	0.406
S. D.	0.21	0.05	0.003	0.005
Rel. S.D. (%)	0.59	1.91	0.76	1.13

Emphasis had to be placed on the careful application of the sample to the plate. The success or failure in obtaining a satisfactory chromatogram from a sample of this magnitude lies primarily in the application. The sample solution was applied in a thin uniform band about 5 mm wide across the plate, about 2 cm from the bottom.

Of the components to be analyzed, only 2-nitrodiphenylamine and some nitration products were visually detected. To locate the remaining components, several spray reagents were investigated. Although specific spray reagents were available for the detection of the components of interest, visualization of the non-colored components could be affected by spraying with phosphomolybdic acid[11]. Since the components separated on the plate were to be spectrophotometrically measured, spraying the plate containing the sample with phosphomolybdic acid was not feasible. Instead a test strip was spotted and developed along with the sample plate. After development, the test strip was sprayed and the separated components located. The precoated plates used were of sufficient uniformity that changes in R_F values of the components from plate to plate were negligible.

Removal of the support containing the separated components and elution of the components from the support was a simple task. The efficiency of the described

separation was insured by qualitatively and quantitatively determining each recovered component. I.R. spectra were obtained of each separated component and found to be identical to the I.R. spectra of nitroglycerin, triacetin, the stabilizers. In addition, the U.V. spectra obtained from the separated stabilizers were identical to those of the pure components.

A recent study performed on aged propellant samples showed that resorcinol was the major stabilizer in ammonium perchlorate containing propellant. The first nitration product was 4-nitroresorcinol which then appeared to react rapidly with more resorcinol to form resorufin and resazurin. Finally, the 2,4-dinitroresorcinol began to appear and was the dominating species just prior to auto-ignition. No 2-nitroresorcinol was found in any of the aged propellants.

The 2-nitrodiphenylamine nitrated more slowly than resorcinol in propellant. Nitration of 2-nitrodiphenylamine did not occur until most of the resorcinol was reacted. In resorcinol-depleted samples, 2-nitrodiphenylamine yielded on nitration 2,4-, 2,4'- and 2,2'-dinitrodiphenylamine.

From the results of this study, the conclusion can be made that as long as a sufficient level of resorcinol exists in the propellant, nitrated derivatives of 2-nitrodiphenylamine need not be expected. In this case only resorufin and resazurin appear to be the major stabilizer nitration products. After exhaustion of resorcinol, however, 2-nitrodiphenylamine undergoes nitration to form the previously mentioned products.

TABLE V

R_F VALUES OF COMPOUNDS TO BE ANALYZED AND LIKELY DECOMPOSITION PRODUCTS

Adsorbent: Silica gel (precoated TLC plates, E. Merck, A.G., Cat. No. 5715). Developer: benzene–ethyl acetate (85:15).

Compound	*R_F value*
Nitroglycerin	0.74
Triacetin	0.52
2-Nitrodiphenylamine	0.82
Resorcinol	0.26
1,2-Dinitroglycerin	0.30
1,3-Dinitroglycerin	0.47
1-Mononitroglycerin	0.02
2-Mononitroglycerin	0.05
2,4-Dinitrodiphenylamine	0.79
2,4'-Dinitrodiphenylamine	0.69
2-Nitroresorcinol	0.84
2,4-Dinitroresorcinol	0.00
2,4-Dinitrosoresorcinol	0.00
Styphnic acid	0.00
Resorufin	0.00
Resazurin	0.00

Table V lists the R_F values of several common products obtained from the breakdown of composite modified double-base propellant which, if not removed, interfere in the determination of the primary stabilizers and nitroglycerin. The separation using benzene–ethyl acetate (85 : 15) was excellent for samples containing no nitration products of 2-nitrodiphenylamine. If the latter are present, a change of

solvents from benzene–ethyl acetate (85 : 15) to benzene has been shown to separate the nitrated diphenylamines satisfactorily. However, using benzene as the developer, resorcinol and triacetin remain in the origin and an additional separation employing benzene–ethyl acetate (85 : 15) is necessary to move these components.

We have shown that although some overlapping occurs, particularly with 1,3-dinitroglycerin and triacetin, and 1,2-dinitroglycerin and resorcinol, the R_F interferences caused by these lower nitrates do not affect the absorbances of the compounds to be determined.

The methods were considered accurate for the determination of nitroglycerin, triacetin, 2-nitrodiphenylamine, and resorcinol in double-base propellant without sacrificing precision and accuracy. The TLC separation described above provided the analyst with a method of removing undesirable decomposition products which usually interfere with the determination of nitroglycerin and stabilizers.

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