LIQUID CHROMATOGRAPHIC DETERMINATION
OF
NITROCELLULOSE AND CEF IN PBX 9404

C. S. MacDougall
Assisted By
G. E. McGaugh

QUALITY DIVISION

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MASTER

Mason & Hanger-Silas Mason Co., Inc.
Pantex Plant
P. O. BOX 647
AMARILLO, TEXAS 79177
806-335-1581

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SUMMARY

A high speed liquid chromatographic method for determination of NC and CEF in PBX 9404 has been developed. A 1 g sample of explosive is extracted with 10 ml THF for 1 hour after which the mixture is centrifuged. A 40 μ l aliquot of the supernatant is then injected into an LC system using a 5 m Corasil II column and a THF carrier at ~ 0.6 ml/min flow rate. The separated NC and CEF components are measured with a differential UV-detector and RI detector, respectively. The amounts of NC and CEF are then calculated from measured peak heights. Analyses of standards show recovery of NC to be 99.2 ± 0.7 percent, while CEF is 97.3 ± 0.9 percent recovered. Approximately six samples in duplicate can be analyzed in an 8-hour day. Neither HMX nor RDX interferes in the analysis.

INTRODUCTION

As PBX 9404 is utilized in several weapons systems, a simple, accurate, and precise assay for binder-plasticizer components is critical for production and stockpile laboratory evaluations (SLT). At present the nitrocellulose (NC) binder is determined by a chemically obscure reaction, the exact stoichiometry of which is not clearly delineated. A critical feature of this spectrophotometric method is that the original nitrogen content of the NC used in the PBX preparation must be known. The tris-(beta-chloroethyl)phosphate (CEF) is determined by a spectrophotometric method specific for the phosphate group. A sample of the explosive is digested with $H_2SO_4-HNO_3$. The phosphate thus liberated is treated with ammonium molybdate to form the heteropolymolybdate, whose absorbance is measured at 428 m μ . Both of these analyses are tedious and time-consuming. The NC determination is chemically unsound, due to the uncertainty of the actual reaction. Although the method for CEF is specific for phosphate, it assumes that all phosphate is present as CEF, which is not necessarily true.

Therefore, a high speed liquid chromatographic technique was developed for the rapid and simultaneous determination of NC and CEF. This method is specific for both NC and CEF, and does not depend upon other analyses for calculations of data. In this technique a sample of PBX 9404 is extracted with tetrahydrofuran (THF). An aliquot of extract is injected into a THF carrier. A 5 m Corasil II column separates the CEF and NC. Nitrocellulose is detected with a differential UV detector while CEF is measured with a refractive index detector. Peak heights are directly proportional to quantities of the respective components.

EXPERIMENTAL

APPARATUS

All separations were performed using a Waters Associates Model ALC 202 Liquid Chromatograph. The column was fabricated from 0.3175 OD x 458 cm stainless steel tubing and was packed with Corasil II. The carrier was THF stabilized with BHT and flow rate was maintained at 0.6 ml/min. A differential UV detector at 254 nanometers was used to detect the separated components.

PROCEDURE

A 1 g sample of PBX 9404 is weighed into a 10 dram vial. The sample is then extracted with 10 ml THF for one hour and centrifuged. A 40 μ l aliquot is injected into the liquid chromatograph and the NC and CEF are separated, detected and quantitatively measured from their peak heights.

DISCUSSION

CALIBRATION OF EQUIPMENT

Identification of the species separated by the liquid chromatograph necessitated calibration of retention times. Accordingly, the major components of PBX 9404 were chromatographed in the same manner as samples. Retention times are recorded in Fig. 1. The UV detector is more sensitive and reproducible for nitrocellulose measurements while RI measurements optimized CEF assay. The RDX and HMX peaks are superimposed, and neither material interfered with CEF or NC determinations. Calibration curves were prepared with solutions of purified NC and CEF in THF. Fig. 2 shows typical calibration curves for each material. Beers Law is obeyed over the concentration ranges chosen.

INHERENT ACCURACY OF ANALYSIS

A synthetic standard was prepared to contain 5 μ g/ μ l each of CEF and NC. The mixture was saturated with HMX. This standard was analyzed repeatedly for NC and CEF, and results are given in Table I. Nitrocellulose recovery is 99.2 ± 0.7 percent and CEF recovery is 97.3 ± 0.9 percent. Analysis of this synthetic standard gives the maximum accuracy and precision which may be attained by use of this method. Sample heterogeneity would, of course, decrease precision, but should not affect accuracy of measurement.

ANALYSIS OF SAMPLE

In order to establish the accuracy of the LC method as compared with the older spectrophotometric methods, several library samples were assayed for CEF and NC. The results are shown in Table II. The values obtained by the new LC method agree extremely well with the older techniques and precision is excellent.

CONCLUSIONS

A new method for determining CEF and NC in PBX 9404 has been developed. It is rapid, quantitative and precise. In addition, this technique is theoretically sound and does not involve empirical data or outside analyses.

Fig. 1. PBX 9404 Chromatogram

Fig. 2. Calibration Curves for NC and CEF

Table I. Reproducibility of Measuring NC and CEF

<u>Sample</u>	<u>CEF Added (μg)</u>	<u>CEF Found (μg)</u>	<u>Recovery (%)</u>	<u>NC Added (μg)</u>	<u>NC Found (μg)</u>	<u>Recovery (%)</u>
Std	200	192	96	200	196	98.0
		192	96		198	99.0
		192	96		196	98.0
		194	97		197	98.5
		196	98		199	99.5
		196	98		199	99.5
		194	97		199	99.5
		196	98		199	99.5
		196	98		199	99.5
		196	98		200	100.0
		196	<u>98</u>		200	<u>100.0</u>
			Avg = 97.3 $\pm$ 0.9		99.2 $\pm$ 0.7	

Table II. Analysis of Archive Samples

<u>Sample</u>	<u>NC (LC)</u> <u>(%)</u>	<u>NC (Spec)</u> <u>(%)</u>	<u>CEF (LC)</u> <u>(%)</u>	<u>CEF (Spec)</u> <u>(%)</u>
219-58	3.66	3.80	4.06	4.0
37-62	2.83	2.86	3.00	2.96
93-90	3.04	2.98	3.00	2.96
93-110	2.87	2.90	2.85	2.90
93-140	2.95	2.88	3.00	2.91
620-4	3.07	2.94	3.05	3.06