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QUALITY DIVISION

MASTER

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ANALYSIS OF NITROCELLULOSE AND TRIS-BETA-CHLOROETHYL PHOSPHATE IN PBX 9404 BY HIGH PERFORMANCE LIQUID CHROMATOGRAPHY

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ABSTRACT

A procedure for determining the nitrocellulose and tris-beta-chloroethyl phosphate content in PBX 9404 by high performance liquid chromatography is discussed. For a sample which contained 2.88% NC, 2.87% was found with a standard deviation of 0.02%. The same sample, known to contain 2.72% CEF, was found to be composed of 2.69% CEF with a standard deviation of 0.04%.

INTRODUCTION

The high explosive PBX 9404 is a composite material normally consisting of 94% 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX), 3% nitrocellulose (NC), and 3% tris-beta-chloroethyl phosphate (CEF). It also contains 0.1% diphenylamine (DPA) as a stabilizer for the NC binder. In order to characterize this explosive as to physical strength and detonability, a compositional analysis was considered essential. When NC decomposes, the very labile nitro groups of the nitrate ester, in leaving the polymer, cause a decrease in the physical strength of PBX 9404. Therefore, a procedure has been developed which analyzes the NC and CEF content of the explosive(*1*). However, the purpose of this paper is to report on improvements in the above procedure. These involve different sample and standard sizes, a different column and solvent delivery system, and a new calibration method. Chromatograms and a discussion of results are included.

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1. *C. S. MacDougall, "Liquid Chromatographic Determination of Nitrocellulose and CEF in PBX 9404," MHSMP-75-24P (April - June 1975).*

EXPERIMENTAL

The method developed for NC and CEF analysis utilized a Waters ALC-202 Liquid Chromatograph equipped with a refractive index detector. This equipment had been modified for use at higher column back pressures (up to 6000 psi) with an Altex Model 110A pump. A fixed-loop of 50 μl was installed onto a Rheodyne 7010 injection valve. The column used was a 25-cm x 4.6-mm Zorbax SIL (6 μm particle size). The solvent used was non-UV grade tetrahydrofuran (THF) from J. T. Baker. The THF was filtered and degassed prior to use. A helium blanket was placed over the solvent in order to maintain it in a degassed condition. The flow rate of the solvent was adjusted to 1.4 ml/minute. The 1/16-inch tubing between the column and RI detector was minimized in order to obtain maximum sensitivity; this provided less room for band broadening within the tubing.

As with type procedures which require a calibration, this analysis utilized a standard material. However, the only NC available was either not WR grade or impure. Another material was suggested for this use. The standard was a sample of PBX 9404, Lot Number 620-12, which had been analyzed to contain 2.88% NC and 2.72% CEF. The NC analysis for this relatively new lot of PBX was derived from Holston data; the CEF analysis was performed in the Quality Chemistry Laboratory at Pantex. An approximately 4-g sample of the PBX was weighed and placed into a 60-ml flint glass bottle equipped with a Teflon-lined screw-type cap. Into the bottle was pipetted 10 ml of THF. This mix was capped and allowed to shake on a platform shaker for approximately one hour. The samples were prepared by weighing approximately 2 g of the samples of the PBX 9404 to be tested and placing this portion into a 25-ml flint glass vial equipped with a Teflon-lined screw-type cap. A 5-ml portion of THF was pipetted into the vial, then it too was shaken on the platform shaker for one hour. Both samples and standards were allowed to settle before analysis. The number of samples which could be run per day was determined and that many were prepared daily; a new standard was also prepared daily.

The method of calibration and sample analysis consisted of injecting a 50-μl aliquot of the standard onto the column, followed by duplicate injections of each sample. After each set of duplicates, another standard run was made. From the two standard runs, an average sensitivity for the NC and CEF over the entire sample analysis time could be calculated. These sensitivities took the form of:

$$S = \frac{\text{peak height of NC or CEF peak in mm or counts}}{\left(\frac{\text{(wt. fraction of NC or CEF) (standard wt., g)}}{\text{10 ml final volume of standard}}\right)\left(\frac{1000\ \text{mg}}{1\ \text{g}}\right)\left(\frac{1000\ \mu\text{g}}{1\ \text{mg}}\right)\left(\frac{1\ \text{ml}}{1000\ \mu\text{l}}\right)\left(50\ \mu\text{l loop size}\right)}$$

The weight fraction of NC was 0.0288, and for CEF 0.0272. The peak height measurements could be made by either the computer (in counts) or by a manual method (mm). After the average sensitivity for each compound was determined, the peak heights of the sample runs were found (in counts or mm, depending on the method of the standard's peak height measurements). The percentage of NC or CEF was then determined in the following manner:

$$\%\ \text{NC or CEF} = \frac{\left[\dfrac{\left(\dfrac{\text{peak height of NC or CEF peak in sample run in mm or counts}}{\text{average NC or CEF sensitivity in mm/µg or counts/µg}}\right)}{50\ \mu\text{l loop size}}\right]\left(\dfrac{1\ \text{mg}}{1000\ \mu\text{g}}\right)\left(\dfrac{1\ \text{g}}{1000\ \text{mg}}\right)\left(\dfrac{1000\ \mu\text{l}}{1\ \text{ml}}\right)\left(5\ \text{ml}\right)}{\text{sample weight, g}}\ \text{X}\ 100$$

RESULTS AND DISCUSSION

A typical chromatogram displaying both standard runs and duplicate runs of a sample are shown in Fig. 1. The NC peak elutes first, followed by the CEF peak. The analysis of several samples of Lot #620-12, based upon a standard made from Lot 620-12, yielded the following data precision and accuracy (Table I).

Table I. Analysis of Lot #620-12

Sample Number	% NC	% CEF
1	2.87	2.66
2	2.88	2.64
3	2.89	2.71
4	2.83	2.73
5	2.89	2.71
6	2.89	2.73
7	2.83	2.68
8	2.90	2.69
9	2.88	2.73
10	2.87	2.61
Avg. Std. Dev.	2.87 ± 0.02	2.69 ± 0.04

These data show that the procedure is very accurate and precise. The coefficient of variation of the NC analysis was 0.70% and for CEF, 1.49%.

This method is now being implemented in the routine testing of samples for PBX 9404 for determining the effects of the stockpile environments on the high explosive.

Column: 25 cm x 2.4 mm
Zorbax SIL (6 μm)

Mobile Phase: Non-UV Grade,
Unstabilized THF

Flow Rate: 1.4 ml/minute

Temperature: 24°C

Detector: Refractive Index

Sample: 50 μl of Extract

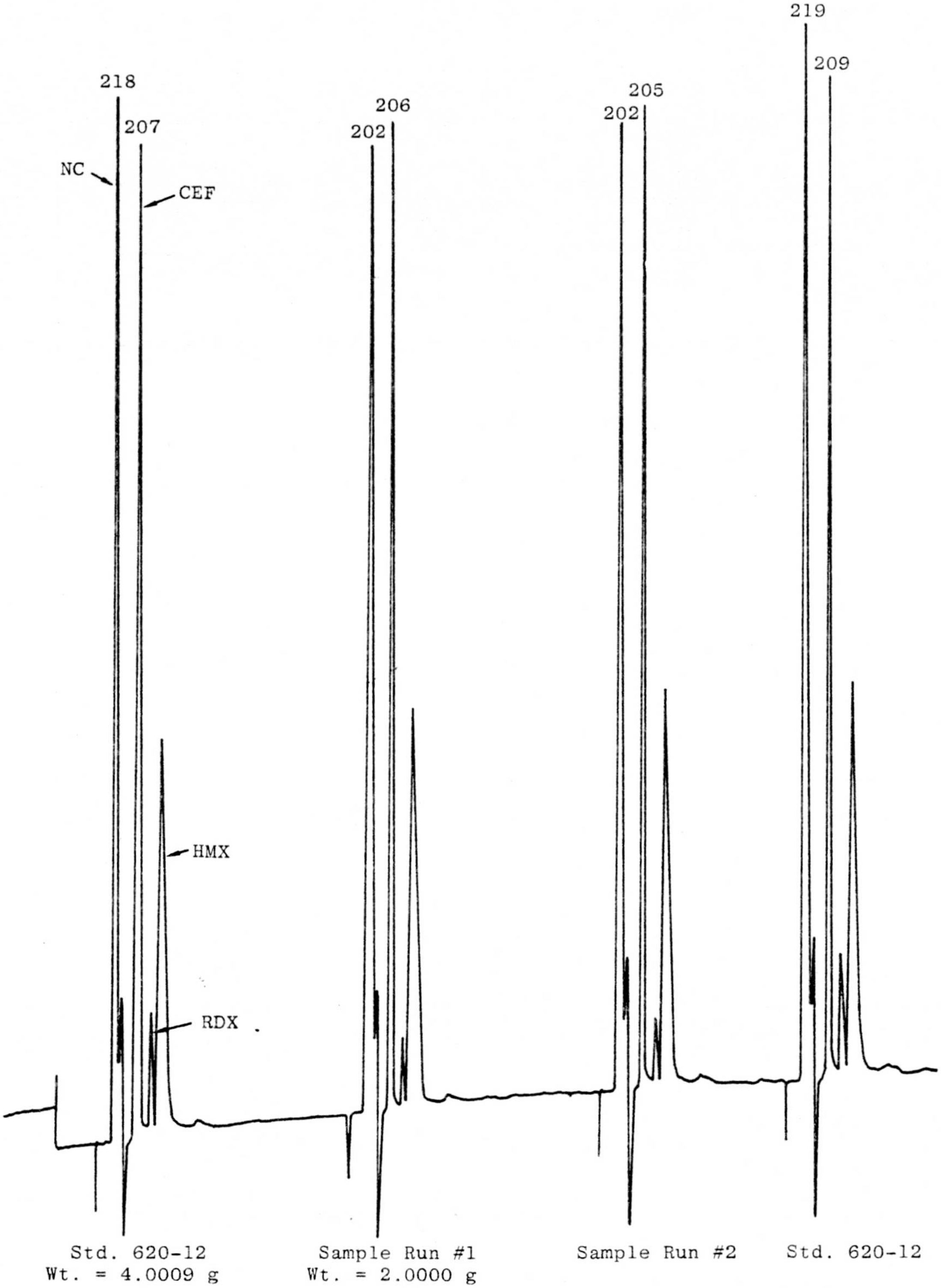

Fig. 1. Separation of NC and CEF

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