SPECTROPHOTOMETRIC DETERMINATION OF HMX IN PBX 9404

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QUALITY DIVISION

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SUMMARY

An infrared spectrophotometric method was developed for determining HMX in PBX 9404. In this method a sample of explosive containing about 0.450 g HMX is dissolved in 100 ml of dimethylsulfoxide (DMSO). The mixture is then mechanically shaken for approximately 0.5 hour. An aliquot of the solution is transferred to a 0.5 mm NaCl cell and the IR spectrum at 1550 cm^{-1} measured. The percent HX is then calculated from the measured nitro peak. Approximately four samples in triplicate can be analyzed in an 8 hour day. The method is versatile, capable of measuring quantities of HMX of 1 to 1000 mg, depending upon the size of standard which is chosen. Comparison of analyses with previous assays shows recovery to be essentially 100 percent and without bias. The relative standard deviation for measuring 450 mg of HMX is $\pm 0.2\%$.

INTRODUCTION

The current method for determining HMX in PBX 9404 consists of determining the binder materials and assuming the difference to be HMX. This method is subject to HMX positive bias, as all impurities are counted as HMX. It is clear that a chemical method specific to the HMX is necessary for accurate, precise, and unbiased assays of PBX 9404 for HMX. Several diverse methods were attempted, and an IR spectrophotometric technique was chosen. Examination of the IR spectra of the HMX indicated that the plasticizer would not interfere.

In this method the PBX 9404 is dissolved in dimethylsulfoxide, and the solution is analyzed by IR spectroscopy. The absorbance of the nitro peak is directly proportional to the amount of HMX in the sample.

EXPERIMENTAL

APPARATUS

Spectrophotometric analyses are carried out with a Perkin-Elmer 521 Grating Infrared Spectrophotometer. Other instruments of equal competence may be used. Standards are prepared by dissolving HMX powder in DMSO.

PROCEDURE

A sample of explosive containing approximately 450 mg HMX is weighed into a 125 ml ground glass centrifuge bottle. One hundred ml DMSO is added and the mixture is mechanically shaken for 0.5 hour. After the PBX 9404 is dissolved the solution is then measured spectrophotometrically at a wavelength of 1550 cm^{-1} against a reference containing 350 mg of HMX in DMSO. The height of the nitro peak from the sample is compared with those peaks produced by standards and the composition of the explosive calculated from the measured HMX.

CALIBRATION

The calibration curve is prepared with HMX solutions in DMSO. The reference solution contains 350 mg HMX. Fig. 1 shows a typical calibration curve. Beers Law is obeyed in any small segment of the absorbance versus concentration curve (such as from 425 to 475 mg HMX). Sensitivity to different ranges is effected either by altering the amount of HMX in the reference sample or by changing instrument gain. Settings of the spectrophotometer are as follows:

Scan Drive	10
Scan Time	2
Suppression	0
Expansion	5X
Attenuator Speed	800
Slits	750, Manual
Gain	4.8
Slit Opening	3000
Scale Position	Variable, set most concentrated standards near A = 1.0
Cell Thickness	0.5 mm

ANALYSIS OF SAMPLE

Several analytical techniques were tested. The less successful approaches will be described only briefly. First, a titration of the $-\text{NO}_2$ groups by reduction by Cr^{+2} and back titration with Fe^{+3} was attempted. However, this also titrates the ONO_2 from nitrocellulose (NC). At the elevated temperatures required for complete titration of HMX erratic results are obtained on the NC. Therefore, further efforts along this path were suspended. Another process which was explored involved reaction(1) below.

Approximately 70% of the HMX was digested, and attempts were made to measure the NH_3 with the Orion Ammonia Electrode. However, formic acid and formaldehyde both interfere with the operation of the electrode. Ion exchange and extraction with CHCl_3 failed to separate the NH_4^+ from formaldehyde and formic acid. Since the digestion was incomplete and measurements of the product would be difficult, this effort was dropped in favor of a more promising path.

Fig. 1. Absorbance versus Concentration HMIX
Q-4

Examination of the IR spectrum of HMX indicated that a spectrophotometric method would give a method specific to HMX and that the other components of PBX 9404 would not interfere (Figs. 2 through 5). In this method the PBX 9404 is dissolved in dimethylsulfoxide and analyzed by IR spectroscopy. The absorbance of the nitro peak is directly proportional to the amount of HMX in the sample. Beers Law is obeyed over a wide range of absorbance values. However, in order to improve accuracy the portion of the absorbance curve from 425 to 450 mg HMX is chosen and measured against a reference containing 350 mg HMX in DMSO.

The method and apparatus were evaluated for inherent accuracy and precision by repeated analyses of a test PBX 9404. This particular material was chosen as a test specimen because a large body of data were already collected on it. Table I shows the results of these tests. As can be seen, the precision of the method is more than adequate. Table II compares the new assay method with data available from previous difference analyses. Agreement between the two methods is excellent. One point of note, however, is Sample 219-58. This material contains a sizable quantity of RDX which obviously was measured as HMX. Another technique for component analysis of PBX 9404 is high speed liquid chromatography. This method will separate HMX and RDX and measure each material separately.

CONCLUSIONS

A new method for determining macro amounts of HMX in PBX 9404 has been developed. It is rapid, quantitative, and precise. Nitrocellulose, CEF, and DPA do not interfere in the analysis, but RDX impurities will be measured as HMX. This latter interference is not important in analyses of recent batches of PBX 9404 (materials made after 1964), but could be significant in the analysis of older preparations.

Fig. 2. IR Spectrum of HMX in DMSO

Fig. 3. IR Spectrum of CEF in DMSO

Fig. 4. IR Spectrum of NC in DMSO

Fig. 5. IR Spectrum of DPA in DMSO

Table I. IR Spectrophotometric Analysis of HMX in PBX 9404

<u>Sample</u>	<u>Absorbance</u>	<u>HMX (mg)</u>	<u>Sample (mg)</u>	<u>HMX (%)</u>
93-140	0.460	446.7	479.0	93.26
	0.502	449.1		93.76
	0.463	447.0		93.32
	0.477	447.9		93.51
	0.462	446.9		93.30
	0.455	446.5		93.22
	0.460	446.7		93.26
	0.454	446.4		93.19
	0.454	446.4		93.19
	0.460	446.7		93.26
				93.29 ± 0.10

Table II. Comparison of Spectrophotometric Determination of HMX with Physical Methods

<u>Sample</u>	<u>% HMX (spectro)</u>	<u>% HMX (physical)</u>
219-58	92.59	92.33
37-62	93.79	93.95
93-90	93.87	93.68
93-110	94.02	-
93-140	93.29	93.26
620-4	93.80	93.75