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DETERMINATION OF BIS (2,2-DINITROPROPYL)
ACETAL/FORMAL IN PBX 9501

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QUALITY DIVISION

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*Process Development
Endeavor No. 105*

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INTRODUCTION

PBX 9501 is an explosive which will be utilized in future programs. As such, much interest has been expressed in the chemical assay of this material. The first step in any quality control testing program is a major components assay. The plasticizing component of this formulation (BDNPA/F) is potentially the most labile, and hence an accurate, precise method of measurement of this material is extremely important. Prior to this analysis, the BDNPA/F content was calculated as the difference between 100 and the sum of all other measured components. This practice incorporates any errors in other assays in the nitroplasticizer (NP) determination. Furthermore, any deterioration of the NP would not be detected by the difference technique. A direct determination of the NP is necessary for quality control assays and for determining the mechanisms of decomposition of the NP.

It was the purpose of this investigation to develop an accurate, precise determination of the two major components in the NP. In this technique a sample of PBX 9501 is extracted with methylethylketone (MEK). The residue from this extract is then

leached with hexane, evaporated to dryness and then taken up in MEK. An aliquot is injected into an LC system using a Partisil 5 column and an 85-15 Hexane/MEK carrier. The separated species are detected with an RI indicator and compared with a calibration curve. The method is unbiased and relative precisions of analysis are 2.5% and 3% for BDNPF and BDNPA, respectively.

EXPERIMENTAL

APPARATUS

All separations were performed using a Waters ALC-201 chromatograph. A 25 cm Partisil-5 column was employed, and the carrier was an 85/15 mixture of hexane and MEK at a 0.8 ml/min flow rate. A refractive index detector was used to detect the separated fractions.

PROCEDURE

A one gram sample of PBX 9501 is weighed into a 125 ml erlenmeyer flask. The sample is then extracted with 10 ml MEK for 1 hour. This extract is filtered through a medium porosity glass-fritted crucible and the filtrate (plus washings)

is evaporated to dryness at room temperature. To this residue are added 50 ml hexane. This mixture is mechanically agitated for 2 hours and then filtered and evaporated to dryness as before. This final residue is then taken up in 1 ml MEK. The sequence of extractions is important in separating the NP from HMX and estane. A 50 μ l aliquot is then injected onto the column, and peak heights of the separated species are recorded and compared against standards. From this comparison, the concentrations of BDNPA and BDNPF are calculated.

DISCUSSION

CONSTRUCTION OF CALIBRATION CURVE

For accurate quantization of this method for either species, it was necessary to demonstrate standard linear response throughout the concentration ranges studied. Fig. 1 shows typical calibration curves for the BDNPA and BDNPF^a. The coefficients of correlation of linearity are 0.999 and 0.997 for BDNPA and BDNPF, respectively, with 95% confidence limits of ± 10 and ± 16 at the 400 μ g quantities. As these data show, linearity was adequate for good quantitative work.

Fig. 1. Calibration Curves for BDNPA and BDNPF

^aThe 500 μ g standard was prepared by dissolving 200 mg standard in 20 ml MEK and injecting a 50 μ l aliquot, 500 μ g total injection.

ANALYSIS OF SYNTHETIC STANDARDS

In order to estimate the accuracy of the technique, a standard PBX 9501 was synthesized using WR grade components. An 8.550 g portion of HMX was weighed into a 1 l volumetric. To this were added 0.225 g estane, 0.1125 g BDNPA, and 0.1125 g BDNPF. Reagent grade acetone was added and the mixture put into solution. Nine 100 ml aliquots were then pipetted into 125 ml erlenmeyers. These samples were evaporated to dryness under air. This gave 9 synthetic PBX 9501 samples (with approximately WR formulation) which were extracted and assayed by the method described. The results are given in Table I. The results of a standard one way analysis of variance of these data are given in Table II. As shown, neither the BDNPA assay nor BDNPF assay is significantly biased. The known concentration for both components was 1.25%. The assay for BDNPA gave an average value of 1.28% with a standard deviation of measurement of ± 0.05 . The within-analysis (duplicates on one sample) standard deviation was ± 0.02 while the between-analysis standard deviation was ± 0.04 . The assay for BDNPF gave an average value of 1.24% with an overall standard deviation of measurement of ± 0.03 . The within-analysis and between-analysis standard deviations are ± 0.02 . These data suggest that the acetal is more sensitive to variation due to the extractions than is the formal.

ANALYSIS OF PBX 9501 AGING SAMPLES

This technique was then applied to a number of PBX 9501 samples which had been formulated and pressed (Table III). Samples 1 through 4 were freshly prepared granules of PBX 9501. It is to be noted that the LC assays for NP agree very well with the quantities of NP predicted by the difference technique. Samples 1A through 4A, however, have been through

a pressing cycle and have been machined. In each case, a slight amount of degradation is noted which would be detected by the difference technique.

SUMMARY

An accurate, precise technique has been developed for the direct assay of BDNPA and BDNPF in PBX 9501. The NP is extracted from the explosive and the extract separated on a Partisil-5 column with a 85/15 hexane-MEK carrier. The species are detected with an RI detector. Concentrations are calculated by comparison against standards. Approximately 4 samples can be analyzed in duplicate on an 8 hour shift.

Table I. Analysis of Synthetic PBX 9501 for BDNPA and BDNPF

Sample No.	BDNPA	BDNPF
1	1.28	1.22
	1.27	1.23
2	1.27	1.23
	1.32	1.26
3	1.31	1.24
	1.30	1.24
4	1.33	1.28
	1.32	1.28
5	LS	LS
6	1.23	1.24
	1.20	1.21
7	1.22	1.18
	1.24	1.24
8	1.32	1.26
	1.34	1.28
9	1.28	1.19
	1.31	1.22
Average	1.28	1.24

LS - Lost Sample

Table II. Analysis of Variance of Data from NP-Assays

	<u>SS</u>	<u>DF</u>	<u>MS</u>	<u>F</u>
	BDNPA			
SSB	0.02474375	7	0.00353482	12.568
SSE	0.00225	8	0.00028125	
SST	0.02699375	15		
Within Analysis	=	0.017		
Between Analysis	=	0.040		
Average Std. Dev.	=	1.284		
	=	0.042		
	BDNPF			
SSB (x)	0.009975	7	0.001425 (y)	2.714
SSE (y)	0.0042	8	0.000525 (x)	
SST	0.014175	15		
Within Analysis	=	0.023		
Between Analysis	=	1.236		
Average Std. Dev.	=	1.236		
	=	0.031		

Table III. Assay of PBX 9501 Formulations

<u>Sample No.</u>	<u>Total NP by Difference</u>	<u>LC Assay BDNPA (%)</u>	<u>LC Assay BDNPF (%)</u>	<u>Total NP LC Assay</u>
1	2.38	1.25 1.25	1.19 1.19	2.44 2.44
1A		1.09 1.12	1.02 1.08	2.11 2.20
2	2.35	1.19 1.21	1.15 1.15	2.34 2.36
2A		1.11 1.07	1.02 1.06	2.14 2.13
3	2.41	1.23 1.26	1.17 1.15	2.40 2.41
3A		1.08 1.08	1.03 1.07	2.11 2.15
4	2.28	1.20 1.17	1.10 1.10	2.30 2.27
4A		1.12 1.10	0.99 0.05	2.11 2.05