MASTER

ASSAY OF NITROPLASTICIZER FOR PBX 9501

C. S. MacDougall

QUALITY DIVISION

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Normal Process Development
Endeavor No. 105

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SUMMARY

A series of standard procedures for component and contaminant analysis of the nitroplasticizer in PBX 9501 was checked for accuracy and precision. Acid number was determined by a titration with methanolic KOH. Water was assayed by a Karl Fisher titration. The refractive index was measured at 25 C by a refractometer, and density was determined by a pycnometer. The BDNPA/BDNPF was assayed by a liquid chromatographic technique. A gas chromatographic method was developed for determination of ethanol. The antioxidant was measured by a spectrophotometric method.

INTRODUCTION

The utilization of a 50-to-50 mixture of PDNPA-PDNPF [bis (2,2-dinitro-propyl) acetal/formal] as the nitroplasticizer in PBX 9501 necessitated development of assay capabilities for the major components and contaminants in the plasticizer, as Pantex will perform the qualification of all such material. The tests to be performed are (1) acid number, (2) water, (3) refractive index, (4) density, (5) BDNPA/F, (6) ethanol, and (7) antioxidant. This paper concerns the transfer of technology to the Quality Chemical Laboratory and describes the accuracy and precision of the methods.

APPARATUS

The spectrophotometric analyses are performed using a Perkin-Elmer 356 spectrophotometer. Liquid chromatographic analyses utilize a Waters ALC 202 chromatograph. The acid number is performed using a Beckman automatic titrator. Refractive indices are measured with a Bausch and Lomb refractometer. Water determinations were made on a photovolt Karl Fisher coulometric titrator. For any analysis, an instrument of equal competence could be substituted.

DISCUSSION

ACID NUMBER

A 10 g sample of nitroplasticizer is weighed into a 400 ml beaker and dissolved in 75 ml CHCl_3 . The sample is then titrated with methanolic KOH (0.10 N). The potentiometric endpoint is monitored with a glass-calomel electrode system buffered to a pH of 10. The sample is purged with N_2 during titration. To test the accuracy of the titration, a synthetic standard of 50 to 50 PDNPA/F was spiked with known quantities of acetic acid (Table I). As can be seen, both accuracy and precision of the analysis are more than adequate. Next, a test sample of the nitroplasticizer was analyzed for acid number. Results of these analyses are included in Table II, and are well within specifications of the nitroplasticizer.

WATER

A 1 g sample of nitroplasticizer is weighed in a syringe and injected into 150 ml Karl Fisher vessel solution. The sample is then titrated coulometrically. Standards containing known quantities of water were titrated using this method and the results are shown in Table III. Accuracy and precision are adequate. A test sample of nitroplasticizer was then analyzed for water (Table II). The water value on the test sample met specifications.

REFRACTIVE INDEX

The refractive index of the test sample of nitroplasticizer was read on a Baush and Lomb refractometer (Table II).

DENSITY

The density of the test sample of nitroplasticizer was measured by the pycnometer technique (Table II). The relative standard deviation of measurement is 0.12%.

BDNPA/F

A high speed liquid chromatographic method for simultaneous determination of BDNPA/F was developed by Swartz et al at LASL. The technology was transmitted to Pantex via personal correspondence and employed for the BDNPA/F assay. In this method, a 1 g sample of nitroplasticizer is dissolved in methylethylketone (MEK). Two hundred mg of 2,4-dinitrotoluene internal standard are added and the mixture is made up to 50 ml with the solvent. A 5 m Corasil II column with the 85/15 Hexane/MEK carrier at 2 ml/min separates the DNT, BDNPA, AND BDNPF. All components are measured with a refractive index detector. The ratios of the component peak height to the internal standard peak height are directly proportional to the quantities of the respective components. A synthetic standard was prepared containing 200 mg 2,4-DNT, 500 mg recrystallized BDNPA, and 500 mg recrystallized BDNPF. This standard was repeatedly chromatographed in the manner described for the samples (Fig. 1). Results are given in Table IV. This shows that at the 500 mg level BDNPA is measured with $\pm 1.43\%$ variation and BDNPF is measured with a 2.78% variation. This precision is more than adequate for the analyses at hand. The test sample of nitroplasticizer was then analyzed for BDNPA/F and the results are recorded in Table II. This ratio of BDNPA/BDNPF (0.972) is within specifications, but the sample exhibits some deterioration, as both components are considerably less than 50%.

ETHANOL

A 1 g sample is extracted for 1 hour with 1 ml hexane. A 10 μ l aliquot is then injected into a gas chromatograph with a helium flow rate of 30 ml/min. The ethanol is separated on a 4 ft Porapak Q column at 170 C and detected with a flame-ionization device. The peak heights are directly proportional to the quantity of ethanol present. A standard curve for ethanol was prepared from GC runs on ethanol solutions in hexane; results are given in Fig. 2. Sensitivity is more than adequate, the relationship between peak height and concentration is linear over the range of interest, and results are reproducible within 2% at the 100 ppm level. This technique was used in analysis of the nitroplasticizer for ethanol (Table II), and ethanol content was within specifications.

ANTIOXIDANT

The determination of the antioxidant or phenyl-beta-naphthylamine is based upon the coupling reaction of the diazo group to an aromatic amine. The subsequent color formation is utilized in a spectrophotometric determination. The chemical reaction is given by equation (1).

A 5 g sample of nitroplasticizer is weighed into a 100 ml volumetric flask and diluted to volume with methyl alcohol. A 5 ml aliquot is then pipetted into another 100 ml volumetric, 1 ml of diazotized sulfanilic acid is added, and the mixture is diluted to volume with methyl alcohol. Color development proceeds for 20 min in a dark place, after which the absorbance at 500 $\text{m}\mu$ is measured. The blank is 5 ml of sample diluted to 100 ml with methyl alcohol (no addition of diazotized sulfanilic acid). The total PBNA is then read from a standard curve prepared by plotting absorbance versus mg PBNA. A typical standards curve is given in Fig. 3. The test sample of nitroplasticizer was repeatedly analyzed for PBNA (Table V), and precision is 2.15 relative percent. Approximately half of the original stabilizer has been depleted or has decomposed.

Table I. Calibration for Acid Number

<u>Run No.</u>	<u>meq Acetic Acid Added</u>	<u>meq HOAC Found</u>	<u>Recovery (%)</u>
1	0.005	0.0049	98.0
2	0.005	0.0050	100.0
3	0.005	0.0045	90.0
4	0.005	0.0047	94.0
5	0.005	0.0046	92.0
6	0.005	0.0042	84.0
7	0.005	0.0051	102.0
8	0.005	0.0048	96.0
9	0.005	0.0049	98.0
10	0.005	0.0044	88.0
			94.2 $\pm$ 5.6

Table II. Total Assay of Nitroplasticizer

<u>Component</u>	<u>Specification</u>		<u>Measured</u>
	<u>Minimum</u>	<u>Maximum</u>	
Acid No. (meq KOH/g)	-	0.50	0.02
Water (wt %)	-	0.05	0.04
Refractive Index at 25 C	1.462	1.464	1.4632
Density at 25 C (g/ml)	1.383	1.397	1.3894
BDNPA (wt %)	45	55	46.51
BDNPF (wt %)	45	55	47.87
Ethanol (wt %)	-	0.04	< 0.005
PBNA (wt %)	0.08	0.18	0.092

Table III. Determination of H₂O in Sodium Tartrate

Run No.	Theoretical (g H ₂ O)	Observed (g H ₂ O)	Recovery (%)
1	0.000197	0.000237	120.3
2	0.000381	0.000379	99.5
3	0.000221	0.000261	118.1
4	0.000205	0.000156	76.1
5	0.000305	0.000247	81.0
6	0.000261	0.000230	88.1
7	0.000396	0.000384	97.0
8	0.002741	0.002747	100.2
			97.5 ± 15.9

Table IV. Calibration for Bis (2,2-Dinitropropyl) Acetal/Formal

Run No.	Calibration Factor (Acetal)	Calibration Factor (Formal)
1	0.708	0.563
2	0.706	0.534
3	0.717	0.555
4	0.705	0.533
5	0.692	0.527
6	0.689	0.539
7	0.691	0.516
8	0.690	0.542
		0.539 ± 0.015
Relative Std. Dev.	0.700 ± 0.010 1.43%	2.78%

Table V. PBNA Analysis in Nitroplasticizer

<u>Run No.</u>	<u>PBNA (mg)</u>	<u>PBNA (%)</u>
1	0.226	0.090
2	0.225	0.090
3	0.246	0.098
4	0.230	0.092
5	0.233	0.093
6	0.230	0.092
7	0.238	0.095
8	0.238	0.095
9	0.238	0.095
10	0.233	0.093
11	0.230	0.092

0.093 ± 0.002

Fig. 1. Chromatogram of BDNPA/F

Ethanol in Hexane, UV Grade (ppm) (10 μ l samples, F10 Detector, 4-ft Porapack Q Columns @ 170 C)

Fig. 2. Standard Curve for Ethanol in Hexane

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Fig. 3. PBNA in Nitroplasticizer

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