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A Hydroxyl Equivalent Weight Interlaboratory Study

December 1984

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FOREWORD

This is a report of a research and development study that was conducted under the Joint Army-Navy-NASA-Air Force (JANNAF) Propellant Characterization Subcommittee. The members of the Solid Propellant Ingredients Panel implemented the study. The data reduction and interpretation of the results were performed under in-house Air Force Rocket Propulsion Laboratory (AFRPL) project number 573005RE. The project manager was Roy Wurzbach, and the principle investigator was Lisa Emanuel. This report covers work on Task 1 of this project conducted at the AFRPL Physical Science Laboratory, Edwards Air Force Base, California 93523-5000, during August 1981-March 1983. Portions of this work were presented at the JANNAF Propellant Characterization Meeting held in Monterey, California, in April 1983.


The authors would like to thank Louis Dee of the AFRPL for providing the samples, and Ronald Law and Frank Bares of Morton-Thiokol, Wasatch Division, for supplying the methods and collecting the results.

This technical report has been reviewed and is approved for publication and distribution in accordance with the distribution statement on the cover and on the DD Form 1473.


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19 ABSTRACT (Continue on reverse if necessary and identify by block number) <p>An interlaboratory study was conducted to compare two new hydroxyl equivalent weight methods. The methods tested were a toluenesulfonyl isocyanate procedure and a N-methylimidazole catalyzed acetic anhydride procedure. The statistical analysis of the data, interpretation of the results are discussed, as well as the problems encountered in running this type of study and suggestions are made for conducting future studies.</p> <p style="text-align: right;"><i>2004/10/10</i></p>			
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11. STUDY (U)
18. ACETIC ANHYDRIDE/N-METHYLIMIDAZOLE METHOD,
STATISTICS.

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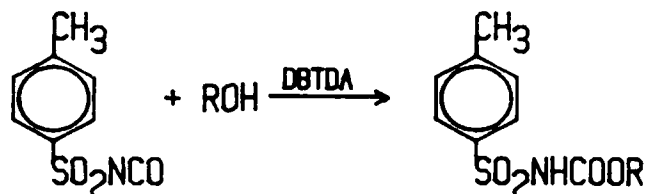
1. INTRODUCTION

The hydroxyl equivalent weight of a prepolymer is necessary for the calculation of a cure ratio for solid propellants. In recent years much work has focused on the development of accurate hydroxyl equivalent weight methods. In 1981, the Joint Army-Navy-NASA-Air Force (JANNAF) Propellant Characterization Subcommittee's Solid Propellant Ingredient Panel initiated a R-45M hydroxy terminated polybutadiene (HTPB) equivalent weight comparison study. The purpose of the study was to introduce and compare two new equivalent weight analysis techniques as possible replacement methods for the time consuming phthalic anhydride (PA/PY) method (ref. 1) and the pyridine catalyzed acetic anhydride (AA/PY) method (ref. 2).

The methods to be compared were an acetic anhydride/N-methyl-imidazole (AA/NMIM) catalyzed esterification method and a toluene-sulfonyl isocyanate (TSNCO) method. The AA/NMIM method was developed by L. A. Dee, et. al. (ref. 3) at the Air Force Rocket Propulsion Laboratory. The AA/NMIM reaction proceeds as follows:



The excess acetic anhydride is hydrolyzed and the acetic acid is titrated with methanolic potassium hydroxide to a visual endpoint. The TSNCO method was developed at Morton-Thiokol, Wasatch Division by F. Bares and S. Speak (ref. 4). The TSNCO reaction is catalyzed with dibutyl tin diacetate (DBTDA) resulting in the formation of a sulfonyl carbamate.



The hydrogen on the resulting sulfonyl carbamate is sufficiently acidic to be titrated with tetrabutylammonium hydroxide.

Both of these methods are improvements over the PA/PY and AA/PY methods. A four hour reaction time is required for the AA/PY method, which was shown by Dee (ref. 3) to cause degradation of unsaturated prepolymers. The TSNCO and AA/NMIM methods have reaction times of 15 minutes which should eliminate this problem. Neither method uses pyridine, eliminating an obnoxious chemical. In addition, the TSNCO method uses an isocyanate reaction which may more closely mimic the cure reaction in solid propellant, and thus could be a better measure of hydroxyl equivalent weight than an esterification reaction. The reagents used in the AA/NMIM method have a longer shelf life than the TSNCO reagents and hence may be a more cost effective analysis for laboratories that analyze hydroxyl equivalent weight infrequently.

The objective of this study was first, to compare the mean hydroxyl equivalent weight values of a sample of HTPB using the two methods to determine if the different reactions gave the same results, and second, to allow participants to comment on the methods. This paper will discuss the statistical analysis of the data (refs. 5 and 6) and interpretation of the results, as well as the problems encountered in conducting this type of study.

2. EXPERIMENTAL

Samples: Approximately 50 grams of R-45M HTPB (lot number unknown) were sent to interested laboratories. The samples were blanketed with nitrogen prior to mailing.

Methods: The analytical methods used are given in the Appendix. No data sheets for reporting the results were sent, and the participants had approximately one year to evaluate the analyses.

3. RESULTS AND DISCUSSION

Sixteen laboratories expressed an interest in the study. Eight laboratories reported their results. The participants are listed in Table 1.

Table 1- Equivalent Weight Study Participants

<u>Laboratory ID Code</u>	<u>Participants</u>
1	Hercules (Bacchus), John Keifer
2	United Technologies, W. Anderson
6	Naval Weapons Center, I. Katzenstein
7	Aerojet, Dave Knight
11	Jet Propulsion Lab, Lois Taylor
14	Larwence Livermore Lab, Walt Selig
15	Thiokol (Wasatch), Frank Bares
16	AF Rocket Propulsion Lab, L.Emanuel

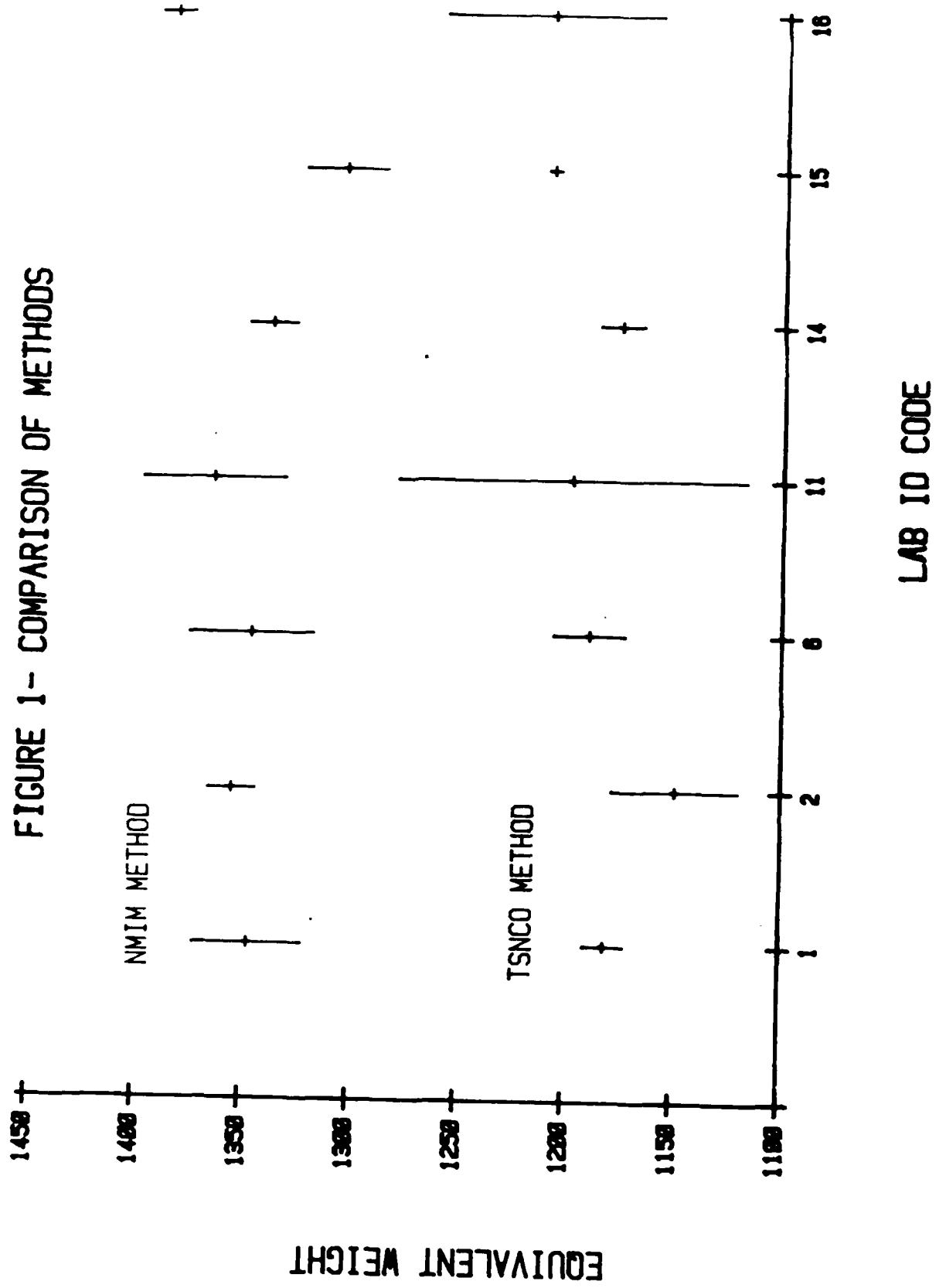
Some participants analyzed the samples using the PA/PY and the AA/PY methods as well as using the two new methods. Because not all of the laboratories used these methods, this paper will focus only on the AA/NMIM and the TSNCO results. Table 2 lists the mean (\bar{y}), standard deviation (s), range (r), and number of runs (n) for each laboratory and method.

Table 2- Results

<u>Lab ID/Method</u>	<u>TSNCO</u>		<u>AA/NMIM</u>	
1	y=1181.4 s=9.4499	n=5 r=25	y=1347.2 s=25.2032	n=5 r=63
2	y=1149 s=29.3802	n=6 r=80	y=1355.2 s=10.8950	n=5 r=30
6	y=1189.4 s=16.8008	n=8 r=48	y=1346.7 s=28.8629	n=6 r=79
7	N/A		y=1364.4 s=33.23285	n=5 r=83
11	y=1197.8 s=80.9789	n=4 r=198	y=1364.4 s=33.2385	n=5 r=83
14	y=1175.5 s=10.3441	n=4 r=23	y=1338 s=11.0454	n=4 r=25
15	y=1208.2 s=2.8723	n=4 r=6	y=1384.6 s=19.0000	n=5 r=37
16	y=1186.4 s=50.4477	n=6 r=140	y=1384.6 s=7.4364	n=5 r=18
OVERALL	y=1186.35 s=38.6941	n=37 r=115	y=1350.78 s=28.4295	n=36 r=108

Figure 1 is a graphic representation of this data, showing the mean value obtained by each lab and an error bar of one standard deviation about the mean. The most striking feature is that the methods vary by 200 g/eq from each other. Laboratory 15 has the smallest standard deviation for the TSNCO method and, similarly, Laboratory 16 has the lowest standard deviation for the AA/NMIM method. This is not surprising since these laboratories originated the methods. This suggests that perhaps the large standard deviations obtained by some of the laboratories may be a result of their inexperience with the methods and not a result of large random or systematic errors inherent in the methods. Laboratory 14, which obtained a

FIGURE 1- COMPARISON OF METHODS



consistent standard deviation using both methods has the best overall titration technique. The ranking of the laboratories' performance for each method is shown in Table 3. The ranking is based on the precision shown by the computed standard deviation.

Table 3- Ranking of Laboratories

<u>Lab ID/Method</u>	<u>TSNCO</u>	<u>AA/NMIM</u>
1	2	6
2	5	2
6	4	7
7	N/A	5
11	7	8
14	3	3
15	1	4
16	6	1

Figures 2 and 3 are histogram plots of the results obtained using each method. Both methods show unimodal distributions but the TSNCO method very closely follows a normal distribution. The AA/NMIM method has a skewed distribution which may indicate an incomplete reaction. Note that Laboratory 7 was not included in any of these figures since they did not report results for both methods.

Analysis of variance (ANOVA) calculations assume that the variance between laboratories is the same. Many researchers neglect to test this hypothesis. The Bartlett's Test (ref. 7) was performed to test the equality of variances within the methods. The variation in precision among the laboratories was found to be significant at the 5 percent level regardless of which method they used. As mentioned above the lack of precision may be due to inexperience. Some of the participants modified the methods which may also explain some of the variation.

FIGURE 2- TSNCO HISTOGRAM

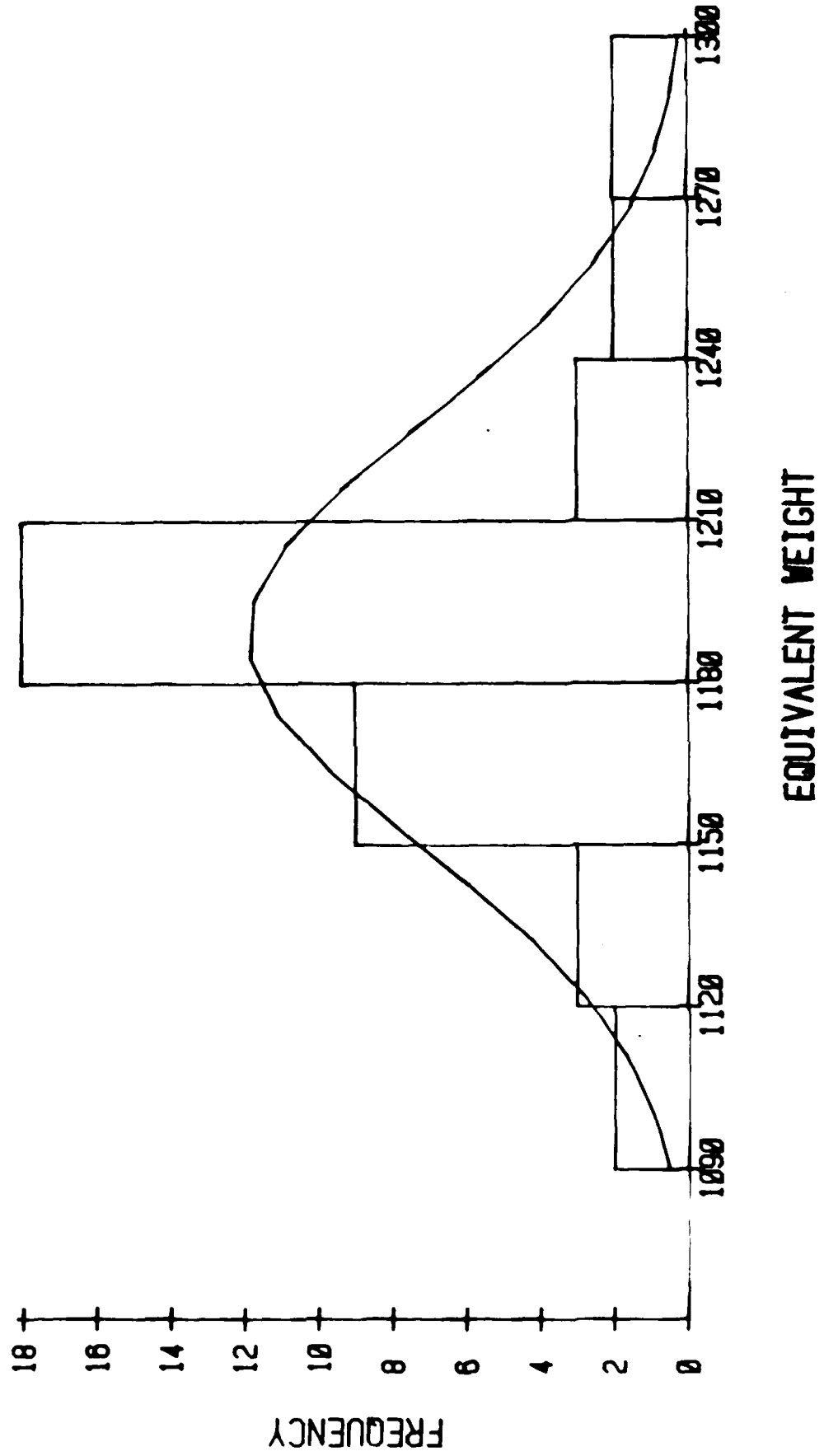
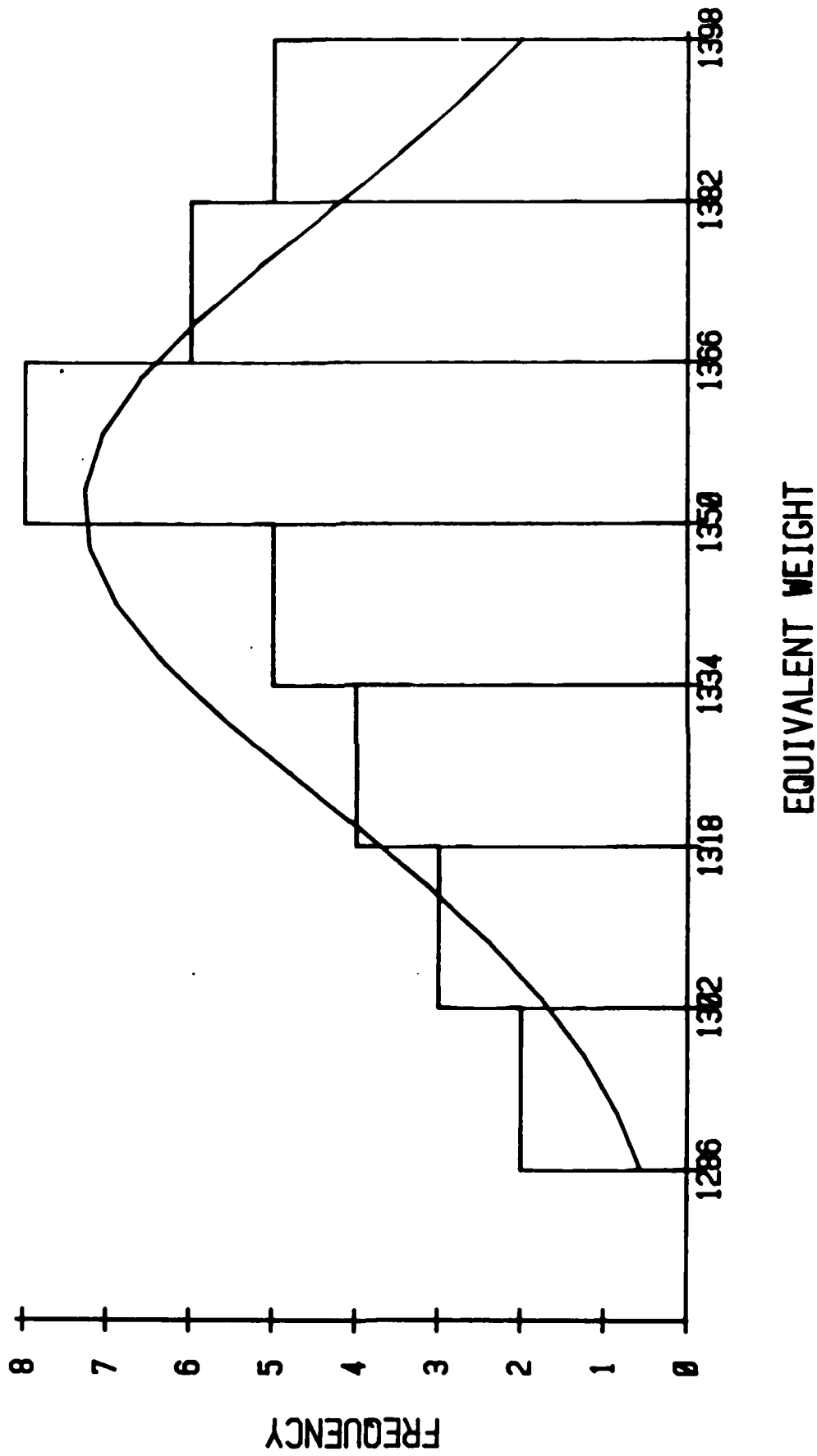


FIGURE 3- AA/NMIM HISTOGRAM



An ANOVA table was calculated for each method, but the means could not be compared statistically, in light of what was learned using the Bartlett's test. The analysis of variance is shown in Tables 4 and 5.

Table 4- ANOVA Table for the TSNCO Method

<u>Variation</u>	<u>Sum of Squares</u>	<u>D.F.</u>	<u>Mean Squares</u>
Between Labs	14508.014	6	2418.0025
Within Labs	39392.412	30	1313.0804
Total	53900.426	36	

Table 5- ANOVA Table for the AA/NMIM Method

<u>Variation</u>	<u>Sum of Squares</u>	<u>D.F.</u>	<u>Mean Squares</u>
Between Labs	14118.227	7	2016.8895
Within Labs	14170.008	28	506.0717
Total	28288.235	35	

The F test was used to compare the means between laboratories for each method. The F-ratio for the TSNCO method was found to be 1.34. The critical value for F at the 5 percent significance level and 6 and 30 degrees of freedom was 2.42. Therefore, there is no significant difference in means. The F-ratio for the AA/NMIM method was 3.9858. The critical value at the 5 percent significance level with 7 and 28 degrees of freedom was 2.3595, indicating that there are significant differences in the means. Based on this limited study the TSNCO method can be considered superior to the AA/NMIM method in measuring the mean hydroxyl equivalent weight value. However, it must be kept in mind, that the comparison of the mean results of these methods cannot be made with certainty because of the large lack of reproducibility between the laboratories.

Many of the participants made comments or modified the procedures. The

following suggestions were made for the AA/NMIM method:

1. Use a more dilute titrant to minimize buret error.
2. Dilute the acetic anhydride reagent to minimize pipette error.
3. Decrease the volume of solvent used.
4. Perform the titration under a nitrogen purge for a sharper endpoint.
5. Prepare the indicator daily, again for a sharper endpoint.

The following comments were made about the TSNCO method:

1. Inflection points were not sharp; hence, it was difficult to reduce the data.
2. Decrease the volume of solvent used.
3. Reagents decayed after three days.
4. No reaction occurred at room temperature.
5. A cloudy precipitate formed in the titrant.

The lack of reaction at room temperature was caused by an old lot of catalyst which had decomposed. Similarly, the precipitate which formed in the titrant was due to a bad lot of tetrabutylammonium hydroxide reagent.

4. CONCLUSION

Although, the objectives of this study were not fully met, valuable information was gained. The comments made by the participants will be useful if the originating laboratories want to conduct further method development work.

According to Youdon (ref. 8), the lack of reproducibility between laboratories is not uncommon and is the leading cause of failures in

interlaboratory studies. This lack of precision can be attributed to inexperience with the analysis procedure, small, seemingly insignificant changes from laboratory to laboratory, and large variability inherent in the test method. Both of the methods tested were new to the propellant community, and lack of experience most certainly contributed to the differences in precision. This may be avoided in the future by using presamples to allow the laboratories to gain proficiency with new methods.

The small changes made by each laboratory may also cause differences in precision. The originating laboratory performs the method the same way, under the same conditions, with the same equipment every time. The participating laboratories may intentionally or unintentionally substitute equipment, reagent vendors and operate under different environmental conditions which may cause significant differences. Youden (ref. 8) suggests that the originating laboratory conduct a Ruggedness Test prior to initiating an interlaboratory study to evaluate how sensitive a method is to small changes. Some of the laboratories in this study made major modifications to the methods. In future studies the participants must be made aware that the method, not the modifications, are being studied. Again, a presample would be useful, as it would give the laboratories a chance to perform the analysis as written.

The influence of environmental factors, temperature, humidity, and even different analysts on the variability and results can be assessed by using a data sheet. The results of replicate trials can be reported on this sheet, and time factors can be ascertained (i.e., do the results increase or decrease with time?). Also, the number of replicates can be specified to facilitate data reduction.

Determining if a method has a large variance is one of the purposes of conducting an interlaboratory study. Testing the means of several methods

to see if there are any statistically significant differences and evaluating variance of the methods can only be accomplished if the testing is rigorously controlled. Assuring that the laboratories are experienced in performing the test methods, that the methods themselves are insensitive to small changes between laboratory and the use of data sheets for reporting results may eliminate many of the problems encountered in this study.

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6. APPENDIX

Acetic Anhydride/N-Methyl Imidazole Hydroxyl Equivalent Weight Method

1.0 Test Description

Acetylation of the hydroxyl groups is catalyzed with N-methylimidazole. The excess hydrolyzed acetic anhydride is titrated with alcoholic potassium hydroxide.

2.0 Reagents

1. 1,2-Dichloroethane, ACS
2. Methyl Alcohol, anhydrous, ACS
3. Chloroform, ACS
4. N-Methylimidazole (Aldrich)
5. Acetic Anhydride Reagent (7mL acetic anhydride diluted to 50 mL with 1,2-dichloroethane)
6. Thymol Blue, 0.3% in methanol
7. Potassium Hydroxide, ACS , 0.5N in Methyl Alcohol
8. Benzoic Acid, primary standard grade

3.0 Standardization of 0.5N Alcoholic KOH

Weigh 1.5 grams of benzoic acid to 0.0001 grams. Dissolve the acid in 20 mL of methanol and then add 25 mL chloroform, 1 mL distilled water, 1mL

N-methylimidazole, and 4 drops of thymol blue indicator. Titrate the solution to the disappearance of yellow with the alcoholic KOH. A precipitate will form part way through the titration but will redissolve near the end point.

4.0 Polymer Analysis

Weigh 2.5 to 3.5 meq (3 to 4 grams HTPB) of polymer to 0.0010 grams in a 500 mL iodine flask. Add 20 mL of 1,2-dichloroethane and dissolve the polymer. Next add 4 mL N-methylimidazole, 4.00 mL of acetic anhydride reagent, mix, purge the flask briefly with gaseous nitrogen, and stopper the flask. Use polytetrafluoroethylene thread sealing tape on the stopper to provide a gas-tight seal. Prepare reagent blanks as above but without the polymer sample. Heat the sample and blank flasks on a steam bath for 15 minutes with occasional swirling. After heating, allow the flasks to cool for 5 minutes then add 200 mL chloroform, 25 to 35 mL methanol and 10 drops of thymol blue indicator. Titrate each with the standard alcoholic KOH to the absence of yellow. A precipitate will form during the titration but will dissolve prior to the end point.

5.0 Calculations

$$\text{Eq. Wt.} = \frac{\text{Polymer Weight} \times 1000}{(\text{Vol. Blank} - \text{Vol. Sample}) \times N}$$

Where: Polymer weight = weight in grams

Vol. Blank, Vol. Sample = Volume (mL) of KOH used for titration of blank and sample respectively.

N = Normality of standard KOH

Determination of Hydroxyl Content in HTPB Polymers Using the Toluenesulfonyl Isocyanate Method

1.0 Test Description

A sample of polymer is dissolved in tetrahydrofuran. The hydroxyl is reacted with an excess of toluenesulfonyl isocyanate (TSNCO) to form a sulfonyl carbamate. In a nonaqueous system, this sulfonyl carbamate is acidic and can be titrated directly with tetrabutylammonium hydroxide, after any unreacted TSNCO has been destroyed with water. The endpoint is determined potentiometrically.

2.0 Reagents and Apparatus

1. Tetrahydrofuran, stabilized, reagent grade
2. Isopropanol, reagent grade
3. Toluene sulfonyl isocyanate solution. Prepare by diluting 10 mL of TSNCO (commercially available from Aldrich or Eastman Chemical Co.) to 250 mL with stabilized tetrahydrofuran. Protect the solution from atmospheric moisture.
4. Tetrabutylammonium hydroxide (TBAH) solution, 0.1N. Dilute 20 mLs of TBAH (25% in methanol, commercially available) to 200 mLs with isopropanol.
5. Automatic titrator, Fisher Titrimeter II AEP or equivalent, equipped with a standard glass combination electrode, or a glass-platinum internal titrant reference electrode

combination. In the latter combination, the reference electrode, in the form of a platinum wire insert, is maintained in contact with the titrant through the delivery tip of the titrator.

3.0 Standardization of 0.1N Tetrabutylammonium Hydroxide

3.1 Weigh, to the nearest 0.1 mg, a 0.2 gram sample of benzoic acid into a beaker.

3.2 Add 60 to 80 mLs tetrahydrofuran and stir to dissolve.

3.3 Titrate potentiometrically as in paragraph 4.4. Calculate the normality of the tetrabutylammonium hydroxide as follows:

$$N = \frac{W}{V \times 0.12212}$$

Where: W = Weight of benzoic acid

V = Volume of TBAH solution (mL)

4.0 Procedure

4.1 Weigh, to the nearest 0.1 mg, approximately 1 gram of polymer into a 150 mL beaker. Add 10 mLs of tetrahydrofuran and stir to dissolve.

4.2 Add 10 mLs of the TSNCO solution, cover the beaker with a watch glass, and let stand for 3-5 minutes.

4.3 After the allotted reaction time, add 0.2 mLs of distilled water and mix well. Dilute to approximately 100 mLs with THF.

4.4 Titrate the sample with 0.1N tetrabutylammonium hydroxide in isopropanol using an automatic titrator equipped with a glass combination electrode or a glass-platinum internal titrant reference electrode

combination.

4.5 Run two or more blank determinations as above, eliminating only the sample.

NOTE

The titration curve for samples and blanks will have two breaks.

5.0 Calculations

$$\text{Hydroxyl Content (eq./100 g)} = \frac{(S_2 - S_1) - (B_1 - B_2) \times N}{10 \times W}$$

Where: S₂ = mL TBAH to titrate to second sample break

S₁ = mL TBAH to titrate to first sample break

B₂ = mL TBAH to titrate to second blank break

B₁ = mL TBAH to titrate to first blank break

N = normality of TBAH

W = Weight of sample

END

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