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**INVESTIGATION OF ANALYTICAL TECHNIQUES FOR  
THE RAPID DETERMINATION OF THE MOISTURE CONTENT OF  
NOL 130 PRIMER MIX AND LEAD AZIDE**

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An investigation of the vacuum oven, Karl Fisher (KF) and nuclear magnetic resonance spectrometric (NMR) techniques for the rapid determination of moisture in NOL 130 primer mix and lead azide was carried out. In comparison to the currently specified ambient pressure oven methods (ARL-D-14978A), the KF method reduces the time for the determination of moisture in lead azide by 88%. The vacuum oven method was found to reduce the time for determination		

(continued)

## 20. ABSTRACT (CONTINUED)

of moisture in NOL 130 by 50%. The precision and accuracy of both methods were found to be comparable with the currently used ambient pressure oven methods. The KF and NMR techniques were found inapplicable for the determination of moisture in NOL 130 because of matrix interference.

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## CONTENTS

	Page
Introduction	1
Results and Discussion	1
Vacuum Oven Method	1
Karl Fisher (KF) Method	2
Nuclear Magnetic Resonance Spectrometric Technique	3
Experimental Procedure	4
Synthetics Simulating Samples Containing Moisture	4
Vacuum Oven Method for Determination of Moisture in NOL 130	5
Ambient Pressure Method for Determination of Moisture in NOL 130 and Lead Azide	5
Karl Fisher Method for Determination of Moisture in Lead Azide	5
Conclusions	7
Recommendations	7
References	21
Distribution List	23

## TABLES

	Page
1 The determination of added moisture in NOL 130 primer mix by the vacuum oven and ambient pressure oven methods	9
2 Karl Fisher direct titration of dried tetracene with diluted hydranol composite 2	10
3 Karl Fisher method, extraction mode, using methanol as solvent for reducing interference by tetracene in NOL 130	11
4 Karl Fisher method, extraction mode, 80/20 dried methanol/methylene chloride solvent mixture for reducing interference by tetracene in NOL 130	12
5 Karl Fisher, method extraction mode, recovery of water added to 80/20 methanol/methylene chloride mixture in the presence of NOL 130	13
6 Determination of moisture content of dextrinated lead azide containing known amounts of water, by the Karl Fisher method, extraction mode	14
7 Determination of moisture content of special purpose lead azide containing known amounts of water by the Karl Fisher method, extraction mode	15
8 Determination of moisture content of special purpose and dextrinated lead azide, containing known amounts of water by the ambient pressure oven method	16
9 Adsorption of moisture by aluminum, polyethylene, and glass containers on exposure to 95% RH at 30°C for 16 hours	17

## FIGURE

1 NMR spectrum showing the proton absorption curve for water (liquid) on a solid	19
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## INTRODUCTION

Military specification MIL-D-14978A, covering the loading, assembly, and packaging of the M55 stab detonator, requires the moisture content of NOL 130 primer mix in the M55 detonator shall not be greater than 0.3%. It also specifies the lead azide, a component of NOL 130, shall not have a moisture content greater than 0.5%. The determination of the moisture content in both materials is currently carried out using ambient pressure oven methods, described in MIL-D-14978A.

Over the years the ambient pressure oven method has been considered time consuming and cost ineffective in the production of the M55 detonator. As a consequence, Mr. P. Monteleone, Energetics System Process Division, initiated an MMT effort, Project No. 5844523, to investigate the practicability of replacing the current method with rapid, cost-effective, state-of-the-art techniques. This Division was therefore requested to carry out an investigation of the vacuum oven, Karl Fisher (KF), and nuclear magnetic resonance (NMR) spectrometric techniques for the rapid determination of moisture in NOL 130 and lead azide. This report covers the results of the investigation and makes recommendations for the replacement of the current oven methods with methods found suitable for the rapid determination of moisture in the primer mixture and lead azide.

## RESULTS AND DISCUSSION

### Vacuum Oven Method

The analysis time for determining the moisture content of NOL 130 primer mix has been effectively reduced from 2 hours for the specification ambient pressure oven method to 45 minutes with the vacuum oven method described in the Experimental Section of this report. The weighing and cooling times are not included since they are common to both methods. A comparison of the two methods, using the data obtained with NOL 130 containing known amounts of moisture, is shown in table 1. The vacuum oven method is superior with respect to analysis time and comparable to the military specification MIL-D-1978A method with respect to accuracy and precision.

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## Karl Fisher (KF) Method

### NOL 130 Primer Mixture

The KF method<sup>1</sup> was found unsuitable for the determination of moisture in NOL 130. The tetracene component of NOL 130 primer mix reacted with the KF reagent to the extent that it interfered with the usual KF reaction with water. The extent of the interference is shown in table 2. In the direct titration mode 50 mg of tetracene, the nominal amount found in 1 g of NOL 130 sample, consumed 8.61 mL of KF reagent. That volume is equivalent to 4.6 mg of water or 0.46% moisture in a NOL 130 sample. Since the level of moisture requirement in NOL 130 is 0.3% or lower, a blank of 0.46% is not acceptable.

The extraction mode, using methanol as the solvent, was investigated as a procedure for reducing the tetracene interference to an acceptable level. A comparison of volume of blanks, in milliliter of reagent, obtained with the methanol solvent alone, tetracene/methanol and dried NOL 130/methanol is shown by table 3. As expected, the methanol extraction step drastically reduced the interference due to the matrix. The blanks, however, were still too large to be considered acceptable. Values of 0.3 mL or less are generally desired. Moreover, the spread in the blank values, as shown by the standard deviations of the methanol extracts, was too large in comparison to that exhibited by the methanol solvent.

Consideration was given to further reducing the solubility of the interfering matrix by mixing methanol with a less polar solvent. Of several chlorinated solvents investigated, methylene chloride was found most promising for suppressing matrix interference. The results obtained using an 80/20 methanol/methylene chloride mixture is shown in table 4. The blank of 0.69 mL for the 2 g of dried NOL 130 compared favorably with 0.43 mL for the solvent. However, when known amounts of water were added to the NOL 130/solvent mixture, the resulting recovery values were considered unacceptable in comparison to those obtained for the solvent mixture (see table 5). It appears that the addition of small amounts of water increased the solubility of the interfering matrix in the extraction solvent causing the resulting high recovery values.

Since the KF technique was found to be unsuitable for determining moisture in NOL 130, further investigation of the technique was discontinued. Based on the accumulated data, it is concluded that the KF technique is not applicable for the determination of the moisture content of NOL 130 primer mix due to interference from tetracene.

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<sup>1</sup> For a discussion of the nature of the KF reaction, see reference 1a.

## Lead Azide

On investigating the KF technique in the direct titration mode for the determination of moisture in lead azide, it was discovered that the azide also reacted with the KF reagent. However, in the extraction mode, the technique was found to be applicable. When known amounts of water in special purpose and dextrinated lead azides were determined by the method described in the experimental section of this report, data shown by tables 6 and 7 were obtained. Comparison of that data to that obtained with the referee method, table 8, shows the KF method to be comparable to the ambient pressure oven method with respect to precision and accuracy. However, the KF method was found to be superior with respect to the analysis time. A reduction of 1 hour and 45 minutes can be realized when the KF method is used instead of the current method for the determination of moisture in lead azide.

## Nuclear Magnetic Resonance Spectrometric Technique

Since the application of proton NMR spectrometry to the determination of moisture in liquids, gases, and solids is quite well known (refs 1b, 2, and 3), the details of the technique will not be discussed in this report. The technique is known to be rapid, nondestructive, and capable of carrying out a moisture determination, under optimum conditions, in a matter of minutes. The wide line spectrometer is usually utilized for the determination of moisture in solids.

A wide line spectrometer was not available for the investigation of the NMR technique nor was it possible to acquire one within the time allotted for the technical effort. To gain an insight of the applicability of the technique to NOL 130, NMR instrument manufacturers were contacted and the problem discussed with their technical people. It was learned that wide line NMR instruments were available for the determination of moisture in solids with acceptable accuracy and precision. However, it was pointed out that the sample matrices affected the properties of the water signal. In the case of the NOL 130, the surface moisture would be seen as a sharp NMR band. Since the composition of NOL 130 mix contains proton rich lead styphnate and tetracene, an NMR spectrum such as shown by figure 1, would most likely be obtained. The sharp signal due to the liquid water protons, is superimposed on the broad signal caused by the NOL 130. Because of the requirement for low moisture content (0.3% or less) in NOL 130, the peak height would not be significant enough, sensitivity-wise, to afford a precise and accurate quantitative measure of moisture value. It was indicated, however, that high cost and more sensitive NMR instruments, used for research purposes, could achieve the required accuracy and precision. Such instruments would require highly trained personnel to operate and interpret the data. Since one of the objectives of this study was to obtain a rapid method for the determination of moisture in NOL 130 using inexpensive, simple-to-operate instrument applicable to routine analysis the more expensive and sophisticated NMR spectrometer was not considered. It was, therefore, decided to discontinue the investigation of the technique and, based on the available information, consider the NMR technique to be inapplicable for the determination of moisture in NOL 130.

## EXPERIMENTAL PROCEDURE

### Synthetics Simulating Samples Containing Moisture

#### Vacuum and Ambient Pressure Oven Techniques

Prior to adding known amounts of moisture to samples, several types of sample containers were tested for moisture uptake. Empty aluminum, glass, and plastic containers were stored in a 95% relative humidity (RH) at 30°C chamber, and the weight gain recorded after 16 hours. The chamber was prepared by placing 500 mL of sulfuric acid/water solution, containing 75 mL conc., sulfuric acid, in an empty dessicator of adequate size. Of the three, aluminum was the only one to undergo an insignificant weight gain. See table 9 for adsorption data.

Using aluminum containers, dried NOL 130 and lead azide samples were stored in several RH chambers to obtain the optimum exposure time for achieving the desired moisture uptake.

Synthetics were prepared by drying the NOL 130 and lead azide plant sample to constant weight in an ambient pressure oven maintained at 60°C. Accurately weighed dried samples in tared aluminum dishes were placed in 95% RH at 30°C for one hour for a moisture uptake of approximately 0.3% and 1.5 hour for approximately 0.6%.

#### Karl Fisher Technique

Preparation of synthetic samples for use in the investigation of the KF technique was carried out by drying a 1 or 2-g sample, contained in an 8 mL vial to constant weight at 60°C. Five mL of dried methanol<sup>2</sup> and an accurate volume of water were added to the dried lead azide by means of a hypodermic syringe and capped with a septum cap. The volume of water at a given temperature was converted to weight of water and to percent of moisture in lead azide.

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<sup>2</sup> The procedure used for drying methanol is described in the "Karl Fisher Method for the Determination of Moisture in Lead Azide" portion of this report under "Reagents."

## Vacuum Oven Method for Determination of Moisture in NOL 130

### Apparatus

1. Vacuum oven with vacuum gage.
2. Weighing dish - aluminum, 50 mm diameter O.D. by 20 mm depth, with cover
3. Dessicator containing an indicating dessicant

### Procedure

Place an accurately weighed 1-g sample into a tared weighing dish and cover. Heat the dish and contents with the cover removed for 45 minutes in a vacuum oven maintained at  $60^{\circ} \pm 5^{\circ}$  and a pressure of  $80 \text{ mm} \pm 10 \text{ mm}$  mercury. Cover the dish and cool the sample for 1/2 hour to room temperature in the dessicator. Determine the loss in weight and calculate the percentage of moisture in the sample as follows:

$$\text{Percent moisture} = \frac{100A}{B}$$

where

A = loss in weight, g.

B = weight of sample, g.

## Ambient Pressure Method for Determination of Moisture in NOL 130 and Lead Azide

The determination of moisture in synthetic samples was carried out in accordance with the procedure described in reference 4.

## Karl Fisher Method for Determination of Moisture in Lead Azide

### Apparatus

The Brinkmann Metrohm KF Titration System containing Automatic Unit Model 633 and Dosimeter Model 655 or equivalent.

A 10  $\mu\text{L}$  and a 1,000  $\mu\text{L}$  hypodermic syringe capable of delivering exactly 1  $\mu\text{L}$  and 1  $\text{mL}$  respectively, of solvent. Calibrate syringes by delivering the appropriate volume of water to a tared 5  $\text{mL}$  beaker. Using a microbalance quickly weigh the beaker and water. Take the increase in weight of the beaker as the

weight of water. Using the density of water at the temperature of the water used for the calibration, convert the weight to volume of water.

Vials, 15 mm x 60 mm, 8 mL capacity, fitted with septum screw caps.

Pipette, 5 mL capacity.

### Reagents

Hydranal-Composite 2 Eugen Scholz reagent, 1 mL = 2 mg H<sub>2</sub>O.

Hydranal solvent: methanol anhydrous, 0.04 percent water or less. Store over coarse anhydrous calcium sulfate. Use calcium sulfate, retained on a No. 14 U.S. Standard Sieve, dried at 500°C for 1 hour. After the addition of the calcium sulfate to the methanol allow desiccant to settle before using.

KF reagent: 1:1 Hydranal Composite 2 and Hydranal solvent, 1 mg H<sub>2</sub>O = 1.5 mL titrant.

### Standardization of the KF Reagent

Add approximately 15 mL of methanol into the reaction vessel, enough to cover the electrode. Titrate with the KF reagent to a preliminary end point. Reset the volume to 0.00, weigh the 10 µL syringe containing 1 µL of H<sub>2</sub>O, and inject the water into the reaction vessel. Again titrate to the end point. Note the volume of titrant. Weigh the empty syringe to determine the weight of water titrated. Calculate the mL of KF reagent per 1 mg of water. Standardize the reagent daily.

### Blank Determination

Methanol. The methanol blank shall be checked daily, or more often if necessary, to determine if its moisture content is maintained below 0.04%.

Methanol Plus Dried Lead Azide. This blank shall be determined initially and shall be used for the calculation of the lead azide moisture content. To determine the blank, place a 2-g sample of lead azide in each of six vials. Dry vials containing the lead azide to constant weight in oven maintained at 60 ± 5°C. Add 5 mL of dried methanol to each of the cooled samples. Cap the vials and shake contents briefly. Allow the lead azide to settle for 5 minutes. Withdraw a 1 mL aliquot with the syringe and inject into the reaction vessel containing the methanol which had been titrated to a preliminary end point. The average of six volumes of titrant is the blank value.

## Procedure

**Sample.** Accurately weigh 2 g of lead azide into a vial which had been previously dried to constant weight at 100°C. Add 5.0 mL of dried methanol, cap, and shake briefly. Allow the sample to settle 5 minutes before taking a 1.00 mL aliquot. Titrate the mixture and record the volume.

**Calculation.** The moisture content of the sample may be calculated as follows:

$$\% \text{ moisture} = \frac{(V-v)/f}{W}$$

Where:

f = mL of KF reagent equivalent to 1 mg H<sub>2</sub>O, as shown above.

V = mL of KF reagent used for sample.

v = mL of KF reagent used for blank.

W = weight of sample.

## CONCLUSIONS

1. The vacuum oven method rapidly, with excellent precision and accuracy, determines the moisture content of NOL 130.
2. The KF method, in the extraction mode, rapidly, with acceptable precision and accuracy, determines the moisture content of lead azide.
3. The KF and the NMR techniques were found inapplicable for the determination of moisture in NOL 130.

## RECOMMENDATIONS

1. Replace the current ambient pressure oven method (MIL-D-14978A) with the vacuum oven method for the determination of moisture in NOL 130.
2. Replace the current oven method (MIL-D-14978A) with the KF method, extraction mode, for the determination of moisture in lead azide.

Table 1. The determination of added moisture in NOL 130 primer mix by the vacuum oven and ambient pressure oven methods

Sample no.	Vacuum oven method			Ambient pressure oven method		
	Moisture added (%)	Moisture found (%)	Recovery (%)	Moisture added (%)	Moisture found (%)	Recovery (%)
1	0.33	0.33	100.0	0.35	0.35	100.0
2	0.31	0.31	100.0	0.31	0.31	100.0
3	0.28	0.28	100.0	0.31	0.31	100.0
4	0.24	0.24	100.0	0.29	0.29	100.0
5	0.26	0.26	100.0	0.22	0.22	100.0
6	0.24	0.24	100.0	0.22	0.22	100.0
		Average	100.0		Average	100.0
		S.D.	0.0		S.D.	0.0
1A	0.75	0.75	100.0			
2A	0.66	0.66	100.0			
3a	0.69	0.69	100.0			
4A	0.61	0.61	100.0			
5A	0.59	0.59	100.0			
6A	0.52	0.52	100.0			
		Average	100.0			
		S.D.	0.0			
Drying time, hrs		0.75			2.0	

Table 2. Karl Fisher direct titration of dried tetracene with diluted hydranal composite 2<sup>a</sup>

<u>Tetracene (mg)<sup>b</sup></u>		<u>Hydranal (mL)</u>	<u>Tetracene (mg)/ hydranal (mL)</u>
56.9	8.67	6.56	
55.4	8.72	6.35	
52.6	8.76	6.01	
45.8	8.28	5.53	
48.4	8.94	5.41	
54.9	8.44	6.50	
50.4	8.47	<u>5.99</u>	
		Average	6.05

<sup>a</sup>1.88 mg = 1 mL H<sub>2</sub>O.

<sup>b</sup>Nominal amount of tetracene present in 1-gram sample of NOL 130 is 50 mg.

Table 3. Karl Fisher method, extraction mode, using methanol as solvent for reducing interference by tetracene in NOL 130

Aliquot no.	Blank, mL								
	10 mL Methanol			500 mg Dried tetracene in 10 mL methanol			1 g of Dried NOL 130 in 10 mL of methanol		
	Vial 1	Vial 2	Vial 3	Vial 1	Vial 2	Vial 3	Vial 1	Vial 2	Vial 3
1	0.30	0.27	0.30	0.60	0.92	0.76	0.85	0.74	0.77
2	0.29	0.28	0.20	0.62	0.97	0.87	0.75	0.70	0.73
3	<u>0.30</u>	<u>0.28</u>	<u>0.29</u>	<u>0.80</u>	<u>0.90</u>	<u>0.82</u>	<u>0.82</u>	<u>0.79</u>	<u>0.80</u>
Average	0.30	0.28	0.29	0.67	0.93	0.82	0.81	0.74	0.77
S.D.	0.01	0.01	0.01	0.11	0.04	0.06	0.05	0.05	0.04
Average of 1, 2, and 3		0.29			0.81			0.77	
S.D. of 1, 2, and 3		0.01			0.13			0.04	

Table 4. Karl Fisher method, extraction mode, 80/20 dried methanol/methylene chloride solvent mixture for reducing interference by tetracene in NOL 130

<u>Aliquot</u>	<u>Blank, mL</u>	
	<u>Solvent</u>	<u>2 g NOL 130/solvent mixture</u>
1	0.46	0.71
2	0.40	0.67
3	0.46	0.67
4	<u>0.40</u>	<u>0.67</u>
Average	0.43	0.69

Table 5. Karl Fisher method extraction mode, recovery of water added to 80/20 methanol/methylene chloride mixture in the presence of NOL 130

<u>Solvent mixture</u>			<u>2 g of dried NOL 130 solvent mixture</u>		
<u>Added</u> <u>%</u>	<u>Found</u> <u>%</u>	<u>Recovery</u> <u>%</u>	<u>Added</u> <u>%</u>	<u>Found</u> <u>%</u>	<u>Recovery</u> <u>%</u>
0.05	0.05	100.00	0.05	0.13	260.00
0.15	0.13	86.67	0.15	0.23	155.33
0.30	0.34	<u>113.33</u>	0.30	0.37	<u>123.33</u>
Average		100.00			180.00
S.D.		13.33			71.48

Table 6. Determination of moisture content of dextrinated lead azide containing known amounts of water, by the Karl Fisher method, extraction mode

Determination No.	Moisture, %									
	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found
1	0.10	0.10	0.20	0.18	0.30	0.28	0.40	0.37	0.50	0.51
2	0.10	0.09	0.20	0.19	0.30	0.28	0.40	0.38	0.50	0.51
3	0.10	0.08	0.20	0.16	0.30	0.28	0.40	0.37	0.50	0.50
4	0.10	0.08	0.20	0.17	0.30	0.28	0.40	0.37	0.30	0.51
5	0.10	0.08	0.20	0.18	0.30	0.28	0.40	0.37	0.50	0.49
	<u>0.10</u>	<u>0.10</u>	<u>0.20</u>	<u>0.19</u>	<u>0.30</u>	<u>0.28</u>	<u>0.40</u>	<u>0.38</u>	<u>0.50</u>	<u>0.51</u>
Average	0.10	0.09	0.20	0.18	0.30	0.28	0.40	0.37	0.50	0.51
S.D.		0.01		0.01		0.00		0.01		0.01
Accuracy, % H <sub>2</sub> O Absolute		-0.01		-0.02		-0.02		-0.03		0.01

Analysis time, 15 minutes for each determination

Table 7. Determination of moisture content of special purpose lead azide containing known amounts of water by the Karl Fisher method, extraction mode

Determination No.	Moisture, %									
	Added	Found	Added	Found	Added	Found	Added	Found	Added	Found
1	0.10	0.13	0.20	0.21	0.30	0.30	0.40	0.39	0.50	0.50
2	0.10	0.13	0.20	0.20	0.30	0.32	0.40	0.39	0.50	0.51
3	0.10	0.13	0.20	0.21	0.30	0.32	0.40	0.37	0.50	0.52
4	0.10	0.13	0.20	0.21	0.30	0.31	0.40	0.40	0.30	0.50
5	0.10	0.12	0.20	0.19	0.30	0.33	0.40	0.39	0.50	0.51
6	<u>0.10</u>	<u>0.12</u>	<u>0.20</u>	<u>0.19</u>	<u>0.30</u>	<u>0.32</u>	<u>0.40</u>	<u>0.39</u>	<u>0.50</u>	<u>0.51</u>
Average	0.10	0.13	0.20	0.20	0.30	0.32	0.40	0.39	0.50	0.51
S.D.		0.01		0.01		0.00		0.01		0.01
Accuracy, H <sub>2</sub> O%, Absolute		0.03		0.00		0.02		0.01		0.01

Table 8. Determination of moisture content of special purpose and dextrinated lead azide, containing known amounts of water by the ambient pressure oven method

DETN no.	Lead Azide					
	Special Purpose			Dextrinated		
	Added (%)	Found (%)	Recovery (%)	Added (%)	Found (%)	Recovery (%)
1	0.00	0.00	100.00	0.28	0.28	100.00
2	0.07	0.07	100.00	0.42	0.42	100.00
3	0.20	0.20	100.00	0.31	0.31	100.00
4	0.12	0.12	100.00	0.29	0.29	100.00
5	0.14	0.14	100.00	0.31	0.31	100.00
6	0.09	0.09	100.00	0.48	0.48	100.00
	Average		100.0	Average		100.0
	Standard		0.0	Standard		0.0

Analysis time, 2 hrs for each determination.

Table 9. Adsorption of moisture by aluminum, polyethylene, and glass containers on exposure to 95% RH at 30°C for 16 hours

<u>Material</u>	<u>Weight gain,</u>
Aluminum*	0.0000
Polyethylene	0.0004
Glass	0.0005

\*The physical dimensions of the tested container were the same as those used in the study.

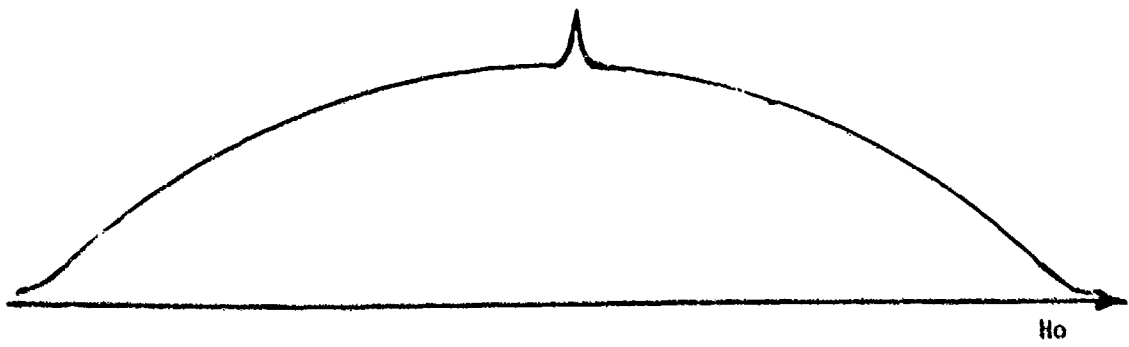


Figure 1. NMR spectrum showing the proton absorption curve for water (liquid) on a solid

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**INFORMATION**

AD-A168415

ERRATA

TECHNICAL REPORT ARAED-TR-86015

INVESTIGATION OF ANALYTICAL TECHNIQUES FOR THE RAPID  
DETERMINATION OF THE MOISTURE CONTENT OF NOL 130 PRIMER MIX  
AND LEAD AZIDE

CHARLES RIBAUDO  
JOSEPH WINGLER

MAY 1986

The attached papers should be added to the original report stated above. They include test results and a discussion of the revised conclusions and recommendations of tests conducted by Lone Star Army Ammunition Plant to determine the applicability of the developed methods to plant samples.

June 1988

## INTRODUCTION

In the course of implementing methods of analysis for the rapid determination of moisture in special purpose lead azide and NOL 130, the Lone Star Army Ammunition Plant (LSAAP) in Texarkana, Texas conducted tests to determine the applicability of the developed methods to plant samples.

## DISCUSSION OF LSAAP RESULTS

The LSAAP data on the accuracy of the vacuum-oven method (table 1) are practically identical to data reported. The test data confirm the accuracy of the vacuum-oven method for the determination of the moisture content of NOL 130\* primer mixture. Based on the agreement of the two sets of accuracy data, the vacuum-oven method is found applicable for the rapid determination of moisture in NOL 130.

The results obtained by LSAAP using the Karl Fisher (KF), vacuum-oven, and specification-oven methods for the determination of known amount of moisture in special purpose (SP) lead azide are shown in table 2. The moisture was added by means of a humidity chamber after the lead azide had been dried to constant weight at  $95 \pm 5^\circ\text{C}$ . Since the LSAAP data agree with what was previously reported, the KF and vacuum-oven methods are comparable, with respect to accuracy, to the specification method for the determination of moisture in SP lead azide. As with NOL 130, the agreement indicates the applicability of the two methods for the moisture determination in SP lead azide samples. However, additional test carried out by LSAAP with plant SP lead azide proved otherwise.

In the drying of wet SP lead azide, LSAAP dries the azide for 120 minutes in cubicles kept at temperatures between 95 and 115°F. The moisture content of the lead azide after a 2-hour drying period was tested using the ambient pressure-oven method as specified in MIL-D-14978A.

To further check the applicability of the KF and vacuum-oven methods, LSAAP ran a comparison of the two methods with the specification method using wet SP lead azide from the plant stock. The results of the comparison using samples taken out of a drying cubicle at the drying time indicated are shown in table 3. The data show that the two methods do not agree with the specification method with respect to moisture content for the plant SP lead azide. The

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\* C. Ribaldo and J. Wingler, "Investigation of Analytical Techniques for Rapid Determination of the Moisture Content of NOL 130 Primer Mix and Lead Azide," Technical Report ARAED-TR-86015, ARDEC, Picatinny Arsenal, NJ 07806

KF and vacuum oven data, in agreeing with each other, indicate a lower moisture content than obtained by the specification method. This didn't make sense since the KF method is specific for moisture. It was, therefore, concluded that the plant SP lead azide contained a component or components, at approximately the 0.1% level, which boil off (high boilers) at  $95 \pm 5^\circ\text{C}$ . This indicated that the specification method did not measure the true moisture content of plant SP lead azide.

The specification-oven method determines moisture by measuring the loss in weight of SP lead azide by heating a sample at  $95 \pm 5^\circ\text{C}$  for two hours at ambient pressures. The vacuum-oven method is also a loss in weight method but uses a temperature setting of  $60 \pm 2^\circ\text{C}$  and a pressure of  $80 \pm 10$  mm. The difference in moisture values between the two methods is due to the temperature settings. This is shown by the LSAAP test data in table 4. The data indicate that the components that remain in lead azide after the 120 minute drying are driven off at  $95 \pm 5^\circ\text{C}$  but not at  $60 \pm 2^\circ\text{C}$  and reduced pressure. The data were obtained by taking two samples from a batch of lead azide dried for 120 minutes and determining the moisture content of one by the specification-oven method and the other by the vacuum-oven method (test A). After test A, the tested samples were crossed (test B) by placing the specification-oven sample in the vacuum oven and vacuum-oven sample in the specification oven. The sample that had originally been in the vacuum oven lost an additional 0.09% indicating the  $60 \pm 2^\circ\text{C}$  temperature and reduced pressure was insufficient for driving off the high boiler.

Prior to drying the ethyl alcohol wet SP lead azide, buggies are used to transfer the wet SP lead azide from storage containers to drying cubicles. LSAAP conducted tests to determine if the high boiler was residual ethyl alcohol or an alcoholic extract of SP lead azide or its packing material. The results of the test are shown in table 5. Test A used ethyl alcohol from the transfer buggy and pure ethyl alcohol was used for test B. The data show that the high boiler is a component of the ethyl alcohol from the transfer buggy and indicate that the component is part of lead azide or the storage containers holding the azide.

As a consequence of the LSAAP test results, the vacuum-oven method was modified by raising the temperature setting to  $95 \pm 5^\circ\text{C}$  from  $60 \pm 5^\circ\text{C}$ . A comparison of results obtained with the specification-oven method and the modified vacuum-oven method is shown in table 6. The data indicate the modified vacuum-oven method exhibits an accuracy that is comparable to the specification method. The vacuum-oven method is, therefore, considered applicable for the determination of "moisture" (moisture and high boilers) in SP lead azide.

Since high boilers appear to be characteristic of the SP lead azide used at LSAAP, an investigation should be initiated to determine its identity and its effect, if any, on the properties of lead azide. If no effect is found, the moisture requirement for SP lead azide in MIL-D-14978A should be changed to read "Total Volatiles at  $95 \pm 5^\circ\text{C}$ ." If an effect is found, then steps should be taken to eliminate the high boiler from the SP lead azide and rapid moisture methods specification for moisture, e.g., KF, should replace the present specification method.

## CONCLUSIONS

1. The vacuum-oven method set at  $95 \pm 5^\circ\text{C}$  and  $80 \pm 10$  mm has been found applicable for the determination of the "moisture" content of special purpose (SP) lead azide.
2. The Karl Fisher method is applicable to the determination of the SP lead azide content provided moisture is the only volatile component in the sample.

## RECOMMENDATIONS

1. Replace the current ambient pressure-oven method currently specified in MIL-D-14978A with the rapid vacuum-oven method with settings at  $95 \pm 5^\circ\text{C}$ ,  $80 \pm 10$  mm pressure, and 45 minutes drying time for the determination of SP lead azide.
2. Specify the current moisture method in MIL-D-14978A as an alternate to the vacuum-oven method for the determination of the moisture content of SP lead azide.
3. Replace the current ambient pressure-oven method, specified in MIL-D-14978A, with the rapid vacuum-oven method with settings at  $60 \pm 5^\circ\text{C}$ ,  $80 \pm 10$  mm pressure, and 45 minutes drying time for the determination of the moisture content of NOL 130.
4. Initiates an investigation to identify the high boiler in lead azide and determine if its presence has a significant effect on the properties of SP lead azide. If the high boiler has an effect on lead azide, determine its origin and find ways of eliminating it.
5. If the high boiler compound is eliminated from lead azide, specify the Karl Fisher method as an alternate to the vacuum-oven method for the determination of moisture in SP lead azide.

Table 1. Moisture content of NOL 130 containing known amounts of moisture as determined by LSAAP using the specification-oven and the vacuum-oven methods

<u>Vacuum oven (%)</u>		<u>Specification oven (%)</u>	
<u>Added</u>	<u>Found</u>	<u>Added</u>	<u>Found</u>
0.12	0.12	0.10	0.10
0.10	0.10	0.09	0.10
0.12	0.11	0.12	0.11
0.29	0.28	0.29	0.29
0.28	0.29	0.25	0.24
0.25	0.25	0.23	0.23
0.40	0.40	0.37	0.35
0.43	0.42	0.36	0.36
0.34	0.33	0.37	0.37

Table 2. Moisture content of special purpose lead azide containing known amounts of moisture as determined by LSAAP using three analytical techniques

<u>Karl Fisher (%)</u>		<u>Vacuum oven (%)</u>		<u>Specification oven (%)</u>	
<u>Added</u>	<u>Found</u>	<u>Added</u>	<u>Found</u>	<u>Added</u>	<u>Found</u>
0.15	0.14	0.15	0.15	0.14	0.14
0.16	0.16	0.15	0.15	0.14	0.15
0.16	0.15	0.16	0.16	0.14	0.14
0.35	0.31	0.33	0.33	0.32	0.32
0.35	0.29	0.32	0.31	0.34	0.35
0.33	0.29	0.30	0.30	0.31	0.30
0.48	0.47	0.50	0.50	0.47	0.46
0.45	0.45	0.50	0.49	0.49	0.48
0.46	0.46	0.52	0.52	0.46	0.47

Table 3. Comparison of moisture content of wet special purpose lead azide from various stages of the drying process as determined by LSAAP using three analytical methods

<u>Drying time (min.)</u>	<u>Karl Fisher (%)</u>	<u>Vacuum oven (%)</u>	<u>Specification oven (%)</u>
15	3.94	4.73	4.76
	4.02	4.78	4.36
	3.92	3.58	4.44
30	2.77	4.00	4.59
	2.21	4.39	4.19
	1.93	4.08	3.58
60	0.13	0.21	0.24
	0.12	0.25	0.27
	0.11	0.16	0.22
120	0.06	0.08	0.14
	0.07	0.07	0.15
	0.07	0.08	0.17

Table 4. Comparison of moisture methods by crossing a two-hour dried sample of special purpose tested by the specification method to the vacuum-oven method and vice versa at LSAAP

<u>Specification method</u>		<u>Vacuum-oven method</u>	
<u>Sample no.</u>	<u>Moisture (%)</u>	<u>Sample no.</u>	<u>Moisture (%)</u>
<b>Test A</b>			
2-1-S	0.15	2-1-V	0.07
2-2-S	0.16	2-2-V	0.07
2-3-S	0.16	2-3-V	0.07
<b>Test B</b>			
2-1-V	0.09	2-1-S	0.00
2-2-V	0.09	2-2-S	0.00
2-3-V	0.10	2-3-S	0.00

Table 5. LSAAP test runs to determine the effect of ethyl alcohol type on the determination of the moisture content of special purpose lead azide

Test A -- Ethyl alcohol from transfer buggy

	<u>Sample 1 (%)</u>	<u>Sample 2 (%)</u>	<u>Sample 3 (%)</u>
Alcohol added to lead azide dried to constant weight at $95 \pm 2^\circ\text{C}$	5.57	6.20	4.41
After 15 min. drying at $98 \pm 2^\circ\text{C}$	0.26	0.26	0.12
30 min.	0.11	0.14	0.08
60 min.	0.11	0.12	0.07
120 min.	0.11	0.12	0.07
After 45 min. in vacuum oven at $60 \pm 5^\circ\text{C}$	0.03	0.03	0.00
After 2 hr in $95^\circ\text{C}$ oven	0.00	0.00	0.00

Test B -- Same test as A except pure ethyl alcohol

Alcohol added	5.49	4.21	4.78
After 15 min.	0.09	0.06	0.04
After 30 min.	0.00	0.00	0.00

Table 6. Comparison of the modified vacuum-oven method (45 min. at  $95 \pm 5^\circ\text{C}$  and  $80 \pm 10$  mm Hg) and specification-oven method using special purpose samples from two drying cubicles at LSAAP

<u>Cubicle</u>	<u>Sample after drying, min.</u>	<u>Modified vacuum-oven method</u>	<u>Specification oven method</u>
1	15	0.25	0.26
		0.26	0.26
		0.25	0.26
	30	0.26	0.26
		0.25	0.25
		0.24	0.23
	60	0.23	0.24
		0.25	0.25
		0.24	0.23
	120	0.21	0.21
		0.21	0.21
		0.20	0.21
2	15	3.13	2.91
		2.99	3.12
		2.87	2.63
	30	0.26	0.25
		0.24	0.24
		0.22	0.24
	60	0.24	0.25
		0.25	0.24
		0.25	0.25
	120	0.23	0.24
		0.23	0.24
		0.22	0.23