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Investigation of Moisture in Titanium Metal Powder by Pulsed NMR

Albert Attalla, Robert C. Bowman, Jr., Bartlett D. Craft, Calvin M. Love and Ralph L. Yauger

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ABSTRACT

A sample of titanium metal powder QC 1779 was subjected to five different treatments of drying and moisture exposure to estimate the effectiveness of normal drying and handling procedures used in the pyrotechnics processing. The treatments were drying in air, drying in two different vacuum furnaces, exposure to normal humidity and exposure to 100% humidity. Statistical evaluation of the NMR results indicate that there is a significant difference between the moisture content of each treatment. Although the combined effects of temperature, pressure, humidity, and treatment time were not studied in a designed manner to determine their significance on the effectiveness of the drying techniques and moisture uptake by sample QC 1779, the experimental evidence does indicate that all four variables do affect the results of the treatments.

INTRODUCTION

A long-range study is under way to evaluate the effect of moisture on the firing performance of titanium hydride/potassium perchlorate pyrotechnics. It is believed that during long-term storage (20 yr) the effect of low-grade chemical reaction of moisture in the pyrotechnic may cause detrimental effects on the function of the pyrotechnic device. Since the greatest source of moisture in pyrotechnic materials is the atmosphere, knowledge of the moisture content of pyrotechnic materials subjected to various treatments of drying and atmospheric moisture exposure would be valuable in evaluating the behavior of pyrotechnic mixtures.

EXPERIMENTAL

The purpose of this NMR study was the evaluation of several drying techniques and of several treatments for the desorption and adsorption of water by titanium metal powder. From each of the five treatments, three aliquots of approximately 0.7 g were sealed in 9 mm o.d. pyrex glass tubes for NMR study. Tubes from treatments I, IV, and V were sealed in air; the others were sealed under vacuum.

Six 1/2 -ml H_2O standard samples were used to calibrate the response of the NMR spectrometer to hydrogen. The concentration

TREATMENTS

I. Damp, softly caked, titanium metal powder identified as sample QC 1779 was allowed to dry at room temperature in the laboratory over the weekend.

II. 8.36 g of the air-dried material was subjected to a vacuum of 10^{-5} torr at 195°C for 88 hr.

III. The remainder of the air-dried material, from treatment I, was heated for 24 hr in a vacuum furnace at 105°C and 50 μm pressure.

IV. The remainder of the material from the third treatment was exposed to air for 1 hr.

V. The remainder of the material from the fourth treatment was exposed to 100% humidity in a sealed desiccator for 45 hr at room temperature.

of the standards were 11.0, 9.0, 7.2, 5.0, 3.0, and 1.0 in units of 10^{20} nuclear spins per 1/2 ml. The weakest water standard was used to correct for hydrogen background. The NMR proton signal from the background sample was subtracted electronically from that of the others. The NMR standards data were plotted as a function of corrected concentration to obtain a straight-line function. The titanium metal powder samples were run under the same conditions as the standards. The free induction decay (FID) amplitude at zero time was measured from the straight-line extrapolation of the FID signal to zero time (Figure 1). An empty glass tube was used to correct for the hydrogen background in the titanium samples. The proton spin-count of each titanium sample was determined from a linear regression analysis of the standards' data. The hydrogen content of each sample was calculated in terms of wt % hydrogen and wt % water for data interpretation.

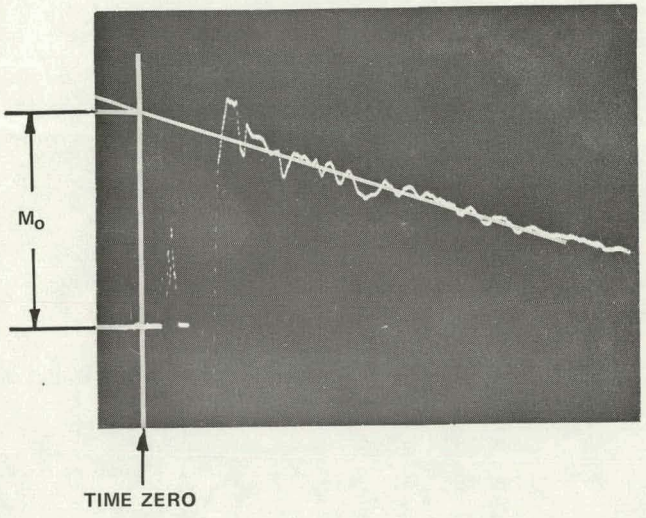

FIGURE 1 - Pulsed NMR proton free induction decay signal extrapolated to zero time in titanium metal powder sample QC 1779.

STATISTIC EVALUATION

Table 1 lists the results of the NMR hydrogen determinations in weight percent water and hydrogen. The latter results are added for later comparison with total hydrogen determinations by other methods. Statistical evaluation of these results was performed only on the weight percent water data, since the difference between the two sets of data is a factor of nine (the ratio of the molecular weights of water and hydrogen). The mean moisture content for each treatment is listed in Table 2. Equality of the means of each set of three aliquots in Table 1 was tested to eliminate nonrepresentative titanium samples. The results of an F-test [1]for comparison of the equality of sample means for each set of aliquots are given in Table 3. The experimental F-value is the ratio of the variance of the among-aliquot means and the variance of the within-aliquot observations. Since there are three aliquots and five observations for each aliquot, there are 2 and 12 degrees of freedom for each treatment. The theoretical F-value for 2 and 12 degrees of freedom at the 5% significance level is 3.8853 [2]. As evident from Table 3 only the aliquots of treatment V differ in the means of their observations. The conclusion reached in this statistical evaluation is that aliquots within treatments I, II, III, and IV do not differ significantly at the 5% level. The level of significance [3] is the probability of committing a type I error which is the rejection of a hypothesis that is true. The hypothesis in evaluating the aliquots of each treatment is that the means of the observations of the three aliquots for each treatment are equal. Thus there is a 0.05 chance that the observations of the three aliquots of treatment V belong to the same population. This chance is even more unlikely because at the 0.5% significance level for 2 and 12 degrees of freedom, F = 8.5096, and the aliquots of treatment V still show a difference in their means.

To locate the nonrepresentative aliquot in treatment V, a t-test [4] was applied to their observations. The results in Table 4 indicate that the mean of the observations of aliquot S_1 of treatment V differs significantly from the other two at the 5% significance level for 8 degrees of freedom (t - 1.860 [5]). There is still a significant difference at the 0.5% level (t = 3.355). The results of this aliquot were dropped in the final comparison between the means of the five treatments.

To establish that a difference exists among the means of the observations of the five treatments, an F-test was applied to the entire set of data. Table 5 lists the pertinent statistics. It is highly obvious that a significant difference exists in the treatments.

The final statistical evaluation (Table 6) compares all the treatments, one pair at a time, to establish that all treatments are significantly different from one another. The degrees of freedom for those pairs containing treatment V are five less than the others because the five observations of

Table 1

NMR RESULTS FOR TREATMENTS OF TITANIUM METAL POWDER SAMPLE QC 1779

Weight Percent Water

Treatment	I Air-Dried Over Weekend			II High-Vac Furnace 10^{-5} torr, 195°C, 88 Hr			III Low-Vac Furnace 50 μm, 105°C, 24 Hr			IV Treatment III Plus 1 Hr Air Exposure			V Treatment III Plus 45 Hr 100% Humidity in Sealed Dessicator		
Aliquot	S_1	S_2	S_3	S_1	S_2	S_3	S_1	S_2	S_3	S_1	S_2	S_3	S_1	S_2	S_3
Date															
11-30-76	1.17	1.17	1.17	0.54	0.49	0.49	0.65	0.69	0.64	0.83	0.80	0.85	2.32	1.74	1.74
11-30-76	1.16	1.10	1.17	0.50	0.50	0.50	0.78	0.78	0.70	0.99	0.89	0.93	1.90	1.50	1.48
12-01-76	1.14	1.20	1.14	0.48	0.47	0.46	0.79	0.79	0.74	0.95	0.86	0.86	1.88	1.49	1.42
12-01-76	1.17	1.18	1.17	0.41	0.37	0.38	0.80	0.78	0.75	0.90	0.86	0.86	1.92	1.52	1.45
1-202-76	1.20	1.16	1.06	0.45	0.42	0.47	0.77	0.77	0.74	-	-	-	1.99	1.57	1.57
12-03-76	-	-	-	-	-	-	-	-	-	0.93	0.93	0.91	-	-	-

Weight Percent Hydrogen

11-30-76	0.127	0.127	0.127	0.060	0.054	0.054	0.072	0.077	0.071	0.092	0.089	0.094	0.258	0.193	0.193
11-30-76	0.129	0.122	0.127	0.056	0.056	0.056	0.087	0.087	0.078	0.110	0.099	0.103	0.211	0.167	0.164
12-01-76	0.127	0.133	0.127	0.053	0.052	0.051	0.088	0.088	0.082	0.106	0.096	0.095	0.213	0.169	0.161
12-01-76	0.130	0.131	0.130	0.045	0.041	0.042	0.089	0.087	0.083	0.100	0.096	0.095	0.213	0.169	0.161
12-02-76	0.133	0.129	0.129	0.050	0.047	0.052	0.086	0.086	0.082	-	-	-	0.221	0.174	0.074
12-03-76	-	-	-	-	-	-	-	-	-	0.103	0.103	0.101	-	-	-

Table 2

AVERAGE MOISTURE CONTENT OF VARIOUS TREATMENTS OF TITANIUM METAL POWDER SAMPLE QC 1779

Treatment	Description	Mean Moisture Content (wt %)
I	Air-dried 72 hr Loaded in air	1.164
II	High-vac furnace 10^{-5} torr, 195°C, 88 hr Loaded in vacuum	0.462
III	Low-vac furnace 50 μm, 105°C, 24 hr Loaded in vacuum	0.745
IV	Low-vac furnace Exposed to air 1 hr Loaded in air	0.890
V	Low-vac furnace Exposed to 100% humidity 45 hr Loaded in air	1.548

Table 3

F-TEST ANALYSIS OF VARIANCE FOR TESTING EQUALITY OF ALIQUOT SAMPLES

Treatment No.	Identification	Experimental "F" Ratio
I	Air dried 72 hr Loaded in air	0.0874
II	High-vac fur 88 hr Loaded under vac	0.3381
III	Vac fur dried 24 hr Loaded under vac	1.4149
IV	Vac fur dried 24 hr Exposed 1 hr air Loaded in air	1.5210
V	Vac fur dried 24 hr exposed 100% humidity 45 hr Loaded in air	17.064

Significance level : 5%
Degrees of Freedom : 2 and 12
Critical Region : $F > 3.8853$

Table 4

T-TEST FOR COMPARISON OF OBSERVATIONS FOR ALIQUOTS OF TREATMENT V

Aliquot Comparison	Experimental t
S_1 and S_2	4.671
S_1 and S_3	4.700
S_2 and S_3	0.433

Significance Level : 5%
Degrees of Freedom : 8
Critical Region : $t > 1.860$

Table 5

F-TEST ANALYSIS OF VARIANCE FOR EQUALITY OF TREATMENT OBSERVATIONS

Significance Level : 5%
Degrees of Freedom : 4 and 70
Critical Region : $F > 2.5252$
Experimental "F" Ratio : 221.51

Table 6

t-TEST FOR COMPARISON OF TREATMENT OBSERVATIONS

Treatment Comparison	Pooled Degrees of Freedom	Experimental t
I and II	28	50.48
I and III	28	28.47
I and IV	28	18.89
I and V	23	13.28
II and III	28	15.54
II and IV	28	23.91
II and V	28	34.19
III and IV	28	7.796
III and V	23	24.85
IV and V	23	20.45

Significance Level : 5%
Degrees of Freedom : 23 28
Critical Region : t > 1.714 5 > 1.701

aliquot S_1 were dropped. The pooled degrees of freedom is the sum of the degrees of freedom of the treatments being compared.

RESULTS AND DISCUSSION

The purpose for these NMR experiments on high-surface-area titanium metal powder was the following:

1. Demonstrate whether the proton NMR spin-counting technique is sensitive enough to quantitatively determine the amount of "motionally narrowed" hydrogen, that is, adsorbed H_2O or OH, in high-surface-area titanium metal powder.
2. Estimate the effectiveness of "normal" drying procedures, that is, 24 hr at 105°C in "vacuum" of approximately 50 torr, used in pyrotechnics processing.
3. Determine the effect of "normal" atmospheric exposure on "hydrogen/H_2O" content of the titanium powder.
4. Determine maximum amount of moisture removable by drying under reasonable production conditions.

The pulsed NMR investigation provided positive results for all the goals sought in this study. The spin-counting technique is sensitive enough to detect "adsorbed" moisture. Under the conditions of this experiment the sensitivity of detection of H_2O is estimated to be 0.03 wt % from the results of Figure 2. The limit of detection is defined here as a signal having a 2:1 signal-to-noise ratio. This signal would be distinguishable from noise and would be observable on the oscilloscope screen. Greater sensitivity can be achieved simply by increasing the number of scans. The signal-to-noise ratio increases in proportion to the square root of the number of scans. Normal drying (treatment III) did prove effective in drying titanium metal powder sample QC 1779 (0.42 wt % H_2O lost, the difference between treatments I and III). Normal atmospheric exposure (treatment IV) of sample QC 1779 does result in adsorption of moisture (0.15 wt % increase in a 1-hr exposure the difference between treatments III and IV). Reasonable drying conditions (treatment III) desorbs 60% of the removal moisture (the ratio of the differences between treatments I and III and treatments I and II).

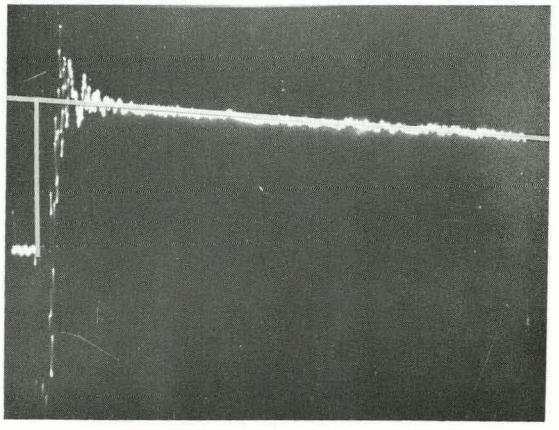

FIGURE 2 - Proton pulsed NMR free induction decay signal to illustrate the sensitivity of detection of hydrogen in a 0.6 g sample of deuterium oxide containing 1.25×10^{20} hydrogen nuclei (<0.2 wt % H_2O).

The interpretation of the NMR results can be seen more clearly if the treatments are divided into two groups. One group consisting of treatments I, II, and III provides information on the most effective

drying method (treatment II). The other group consisting of treatments II, III, and V establishes that moisture is readily adsorbed by titanium metal powder sample QC 1779.

The titanium powder used in this investigation is essentially a moist sample taken from a larger batch of material shipped to Mound Laboratory from Sandia, Albuquerque, in a very wet condition. The moist sample was kept in a closed black container for approximately five months prior to the weekend exposure to air (treatment I). During the five-month storage period the material gradually lost moisture and appeared nearly dry (in a caked condition) at the start of the experimental treatments.

In treatment I the moisture in the sample was allowed to equilibrate with the moisture in the atmosphere (humidity unknown, but much less than 100%) at room temperature over the weekend (72 hr). In treatments II and III progressively more moisture was removed from the samples because of a combination of decreased pressure (5.0×10^{-2} torr to 10^{-5} torr), increased temperature (105 to 195°C), and increased time of treatment (24 to 88 hr).

No experiments were designed to determine the effect of temperature, pressure, and time in reducing the moisture content of the samples. The design of this experiment would require eight treatments (2 x 2 x 2 factorial experiment) of a sample in a high vacuum furnace. The factorial experiment would have to be repeated at least twice to obtain the experimental error.

The results of treatments III, IV, and V indicate that uptake of moisture by titanium metal powder sample QC 1779 depends on relative humidity. Again no experiments were designed to determine the combined effect of temperature, relative humidity, and time on the uptake of moisture by these samples. This design would also be a 2 x 2 x 2 factorial experiment.

The apparent residual moisture found in the samples of treatment II indicates that some water is chemically bound in the titanium or that hydrogen exists in some other form, such as $Ti(OH)_x$. All physically adsorbed water should have been expelled under the extreme conditions of treatment II. Hydrogen atoms in the hydride phase of $TiH_{0.15}$ (QC 1779) are "rigid lattice" protons that do not contribute to the slow decaying signal which is assumed to be adsorbed water or other form of OH. The results of this study and the CEC (Consolidated Electrodynamics Corp.) moisture data for the $TiH_{0.15}$ material support the validity of this assumption. The results of a chemical analysis of sample QC 1779 are given in Table 7. The sample submitted for this chemical analysis was heated for 24 hr in a vacuum furnace at 105°C and 50 μm pressure. After cooling to room temperature and exposed to air, the sample was stored in a sealed black Velostat conductive container for an undetermined time before the moisture analysis. This sample is comparable to our treatment number IV Sample, which approximates the normal pyrotechnics process treatment described above. Oxygen was obtained from neutron activation analysis, hydrogen from decomposition of the material at 1000°C, and moisture from a Consolidated Electrodynamics Corporation moisture analyzer. Assuming that only water is driven from the samples during mild heat treatment (100-200°C), the difference (0.428 wt % H_2O) in water content between treatments II and IV agrees very closely with the CEC analysis (0.42 wt % H_2O). The NMR technique for determining hydrogen includes all forms of mobile hydrogen, resulting in a value larger than the CEC analysis. The sample of treatment II serves as a background sample which corrects for all hydrogen not removed as water. The chemical analysis and the statistical evaluation strongly indicate that the NMR method does give a representative measure of the moisture gained or lost during the various treatments. This was the main purpose of this investigation.

REFERENCES

1. Jerome C. R. Li, "Stastical Inference I," Edwards Brothers, Inc., Ann Arbor, Michigan, Chapter 12, 1969.

2. Ibid., table 7a, p. 603.

3. Ibid., p. 54.

4. Ibid., Chapter 10.

5. Ibid., table 6, p. 602.

Table 7

DATA SUMMARY

Sample QC # 1779 ET

Elemental Analysis	(wt %)
Oxygen	5.19 ±0.11
Hydrogen	0.31
Nitrogen	0.4 ±0.2
Carbon	0.10
Sulfur	0.016

Trace Impurities - Emission Spectroscopy (wt %)

Silicon	0.15	Aluminum	0.02
Iron	0.1	Zinc	0.008
Zirconium	0.08	Copper	0.007
Phosphorus	0.06	Boron	$\leq$0.005
Magnesium	$\geq$0.3	Chromium	$\leq$0.005

Assay (wt %)	94.48% Ti
Moisture (wt %)	0.42% H_2O
Sodium	25 ppm
Particle Size-Coulter Counter (µm/50%)	1.1
Apparent Stoichiometry	$TiH_{0.15}$

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