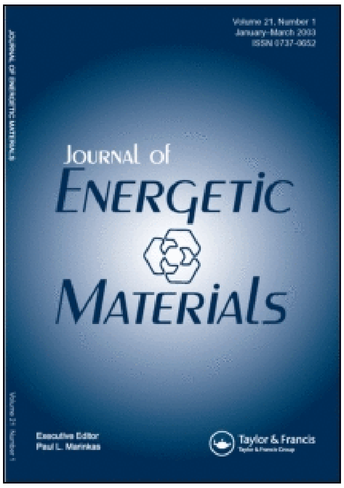

Journal of Energetic Materials
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713770432

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To cite this Article Pesce-Rodriguez, R. , Sagear, P. and Leffers, R.(1999) 'Moisture absorption by JA2 gun propellant under extreme conditions', Journal of Energetic Materials, 17: 2, 215 — 232
To link to this Article: DOI: 10.1080/07370659908216105
URL: http://dx.doi.org/10.1080/07370659908216105

MOISTURE ABSORPTION BY JA2 GUN PROPELLANT UNDER EXTREME CONDITIONS

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ABSTRACT

JA2 propellant downloaded from a 120-mm tank round that had been subjected to conditioning at high temperature and humidity was observed to be discolored and covered with an unknown liquid. Analysis of the propellant indicated a decrease in the nominal diethylene glycol dinitrate (DEGDN) plasticizer content. The nitroglycerine (NG) content was not observed to deviate significantly from its nominal level. The cause of the discoloration of the propellant was traced to its high moisture content. The liquid covering the material was determined to be a mixture of water and DEGDN. In follow-up experiments it was

Journal of Energetic Materials Vol. 17, 215-232 (1999)
Published in 1999 by Dowden, Brodman & Devine, Inc.

determined that JA2 propellant can absorb in excess of 13 wt-% moisture. It was also learned that graphite glaze can reduce the tendency of a grain to absorb moisture for grains immersed in water. When conditioned in a high humidity environment, graphite glaze appeared to have no effect on the level of moisture absorbance. It is suspected that graphite serves to plug pores on the surface of the propellant and thereby inhibit, but not prevent, moisture absorption.

INTRODUCTION

A solventless desorption-gas chromatography-mass spectroscopy (D-GC-MS) method for determination of moisture in solid gun propellants has been developed and was used for the analysis of JA2 gun propellant (a modified double base propellant). There are several traditional methods that might otherwise be used to determine moisture content of solid propellants, including gravimetric techniques that involve heating the propellant and monitoring weight loss, or methods which involve extracting water with dry solvents, and then analyzing the extract by liquid or gas chromatography. The D-GC-MS method was developed to meet the urgent request for analysis of JA2 samples suspected to have been exposed to excessive moisture. Conventional extraction methods could not be employed by the authors because there was neither time to dry the required solvents nor the local environmental conditions to keep the solvents dry (due to high ambient humidity and the absence of adequate air conditioning). To meet the deadline for the required analyses, it was decided that an alternate, solvent-free technique be developed. This was successfully accomplished, and yielded results in a relatively short period of time (instrument calibration plus approximately 30 sample runs in 10 hours). In addition, the method did not require the use of organic solvents and consumed only small amounts of propellant The main disadvantages of the method are that multiple analyses are required to assure representative results (since the test requires a very small sample size), and that the method requires specialized instrumentation (e.g., a device in which materials may be desorbed from the propellant and then transferred directly into a GC-MS).

JA2 propellant which had been downloaded from a tank round that had been subjected to extreme temperature cycling at high ambient humidity was analyzed by this method and found to be several weight-percent below specifications with respect to plasticizer content, and several weight-percent above specifications with respect to moisture content. The color of the samples was yellow-green, as opposed to the usual black-green color of "normal" JA2 propellant. When the yellow-green propellant was allowed to dry in a desiccator, it was observed to turn black-green. A sample of the dried, black-green propellant which was subsequently placed in a warm, high-moisture environment was observed to absorb moisture and revert to the previous yellow-green color. "Standard" samples of JA2 propellant placed in the same environment underwent the same color change on absorption of moisture.

While the information regarding plasticizer content was of interest, it was perhaps of greater interest that JA2 could absorb enough water to result in a color change. The level of moisture found in the samples was well above that previously thought possible for JA2 propellant (i.e. approximately 1 wt-%). Given the significant effect that moisture can have on gun performance, it was decided that the issue of moisture absorption under "extreme" conditions deserved further attention. This paper presents results of analyses of the downloaded propellant, as well as of propellants conditioned in our laboratory. The goal of analyzing the latter was to better understanding the upper limit of moisture absorption by JA2, as well as the effect of graphite glazing on moisture absorption.

EXPERIMENTAL

Samples:

Propellant samples downloaded from a tank round had previously been subjected to temperature cycling at high relative humidity (RH) for 28 days following the program outlined below:

Step 1 - Set parameters @41°C and 90 %-RH over 2 hour period.

Step 2 - Condition @ 41°C and 90 %-RH for 16 hours.

Step 3 - Set parameters @21°C and 95 %-RH over 2 hour period.

Step 4 - Condition @ 21°C and 95 %-RH for 4 hours.

Steps 1-4 were repeated for 28 cycles, for a total elapsed time 672 hours. The tank rounds were not in sealed canisters when tested; the only protection for the components within the round was its combustible case.

Samples conditioned in the lab were either hexagonal grains with 19-perforations and graphite glaze (1.1 cm diameter), or partially cut sticks with 19-perforations and no graphite glaze (1.7 mm diameter). Propellant conditioned at 38%-RH was stored in an auto-desiccator. Propellant conditioned at 92%-RH was stored over an 11% sulfuric acid solution. Measurements of relative humidity in both the auto-desiccator and 92%-RH chamber were made using a Abbeon certified hygrometer (Model AB167B).

Instrumentation:

Desorption was achieved via a CDS Model 122 Pyroprobe® (coil type) connected to a heated interface chamber to the splitless injector of a Hewlett Packard GC-FTIR-MS system (Model 5890 GC, Model 5970 mass spectrometric detector (MSD) and Model 5965 infrared detector (IRD)). The GC column used for plasticizer analysis and initial moisture analyses was a Quadrex capillary column (0.32 mm x 25 m; 3 μm OV-17 film). Analysis of JA2 samples conditioned in the lab were analyzed using a J&W Scientific capillary column (0.25mm x 15 m; 0.25 μm DB5 film). Choice of columns used was based solely on availability. Accurate results were obtained with both columns. The GC injector temperature was 200°C. The oven temperature program used was as follows: 50°C isothermal for 1 min; 70°C/min to 250°C; 250°C for 4 min (total run time 7.86 min). The pyroprobe interface chamber was maintained at 150°C.

Analysis of downloaded JA2 propellant by Fourier transform infrared (FTIR) microreflectance spectroscopy was performed using a Mattson Polaris FTIR spectrometer interfaced to a Spectra-Tech IR-Plan infrared microscope with a mercury-cadmium-telluride (MCT) detector. The microscope was operated in reflectance mode, and aluminum foil was used to obtain a background spectrum. For all spectra, 32 scans were collected with a resolution of 8 cm^{-1}.

Procedure:

Using a razor blade, small samples of the solid propellant were cut, weighed, and placed into quartz tubes containing a plug of glass wool. The glass wool was used to prevent propellant from coming out of the tube. The quartz tube was then placed within the coils of the pyroprobe heating element (see diagram in Figure 1), which was subsequently inserted into the pyroprobe interface and screwed into place. At the start of the GC run, a 150°C pulse (20 sec duration) was given to the sample via the pyroprobe. It was confirmed that these conditions are sufficient for desorption of all moisture by giving a second pulse to the sample, and observing no subsequent moisture desorption.

For preparation of a calibration curve, known masses of potassium sodium tartrate tetrahydrate ($KNaC_4H_4O_6 \cdot 4H_2O$), PSTT, were used. PSTT melts at 70-80°C, loses 3 H_2O at 100°C, and becomes anhydrous at 130-140°C. Desorption of the water of hydration of PSTT was achieved by pulsing at 150°C in a 150°C interface. The PSTT standards were analyzed in the same manner described above.

"Total ion chromatograms", TICs, (based on MS response), were collected for each analysis. "Selected ion chromatograms" (SIC's) were extracted from the TICs to distinguish between response due to desorbed water and plasticizer (the peaks partially overlap with one another). Integration of the selected ion chromatogram for $m/z = 18$ yielded the peak area for water. An example of a TIC and SIC are given in Figure 2.

RESULTS AND DISCUSSION

Plasticizer content:

Since the focus for this report is on the determination of moisture absorption by JA2 under extreme conditions, plasticizer analysis was performed only on propellant downloaded from the tank rounds. Samples conditioned in the lab were not analyzed for plasticizer content.

Downloaded propellant was found to contain the nominal level of nitroglycerine (NG). The diethylene glycol dinitrate (DEGDN) level was found to be between 2 and 6 wt-% less than the nominal value. Variation in the DEGDN levels are suspected to depend on the location in the tank round from which it had been sampled.

Nitrocellulose analysis:

Comparison of the infrared spectra of downloaded JA2 with that of a "standard" JA2 sample indicate that the downloaded samples had not undergone a detectable degree of denitration as evidenced by the absence of carbonyl peaks (which absorb near 1700 cm^{-1}) in its spectrum (see Fig. 3, top). The presence of carbonyl peaks would have been indicative of the loss of nitrate functional groups with the resultant formation of aldehyde functional groups. No measurements of the molecular weight of the NC were made.

Identity of unknown liquid:

Desorption GC-MS analysis of the liquid found on the surfaces of the downloaded propellant and other components of the round revealed that the liquid was a mixture of water and DEGDN. No NG was detected in the liquid.

It is suspected that DEGDN is responsible for most of the water absorption. DEGDN is more likely than NG to form hydrogen bonds with water. Nitrocellulose propellant containing only nitroglycerine are known to be quite water resistant (and was at one time advertized as being "waterproof")[1], whereas neat nitrocellulose is very water absorbent. DEGDN has a vapor pressure that is more than twice that of NG (0.48 Pa verses 0.20 Pa at 20°C for DEGDN and NG, respectively), and is known to exude from propellants stored at elevated temperatures.

As a note of interest,[2] there is a sample of 100-year old double-base flake propellant (40% NG) at the Hercules Plant in Kenvil, NJ which was made at the Laflin and Rand Haskell plant (also in NJ) that has been stored under water for most of its lifetime. After being dried in an oven overnight and fired in the small caliber gun that it was originally designed for, the ballistics have not changed since the day it was made.

Instrument calibration:

A typical moisture calibration curve obtained by analysis of known masses of PSTT is given in Figure 4.

Moisture content:

Appearance of "wet" propellant: The initial motivation for the chemical characterization of JA2 propellant conditioned under high humidity was concern by test personnel about the appearance of the propellant downloaded from the tank rounds; the propellant had changed from its initial black-green color to a yellow-green color. It was observed that downloaded propellant returned to its initial black-green color after storage under low humidity conditions. The propellant reverted to the yellow-green color after either soaking in a water bath or being exposed to a warm, moist environment.

D-GC-MS Data: The moisture content of the downloaded JA2 propellant was found to be on the order of 7 wt-%. Based on subsequent analyses of samples prepared in the laboratory, it is suspected that the moisture content of the sample might have been higher had the samples been analyzed *immediately* after the propellant was downloaded. Table 1 presents the results for moisture analysis of samples conditioned in our laboratory. Note that U.S. military specifications for JA2 propellant call for 0.5 ± 0.3 wt-% moisture.

Comparison of D-GC-MS data with Karl Fischer Data: Although the D-GC-MS measurements of moisture content reported in Table 1 were not compared with side-by-side measurements by a traditional method, the results from propellant conditioned at both 38 %-RH and 92%-RH are about what one would expect based on data obtained using a Karl Fischer method by a laboratory that routinely performs such analyses.[3] In Figure 5, moisture determinations made by the Meppen lab for two "typical" JA2 lots conditioned over the range of 10%-RH to 95%-RH are compared with results obtained at ARL for propellant conditioned at 38%-RH and 92%-RH .

Effect of graphite glaze on moisture absorption: As indicated in Table 1, unglazed JA2 propellant can absorb in excess of 13 wt-% moisture when stored under extreme conditions (i.e. in a water bath for 1 month). Under the same conditions, a glazed grain of JA2 propellant absorbs less than 4 wt-% moisture. It is suspected that the graphite serves to plug pores at the propellant surface and thereby inhibits moisture absorption. It was observed that the unglazed grain (which absorbed only 11.3 wt-% moisture) was much lighter than the glazed grain (which absorbed only 4 wt% moisture).

When stored at 92%-RH, both glazed and unglazed propellant absorbed on the order of 1.1 wt-% moisture. In this case, it is suspected that even with many pores plugged with graphite, there are still sufficient sites available for the moisture content to reach 1 wt-%. No color difference was observed between the glazed and unglazed samples stored at 92%-RH.

Estimation of drying rate of "wet" propellant: While no formal kinetic study of the drying rate of JA2 propellant was made, it was qualitatively observed (see data in the bottom block of Table 1) that the moisture content of a *thin* slice of propellant initially containing approximately 11 wt-% moisture drops to approximately 4 wt-% moisture when allowed to dry under ambient conditions (i.e. 43 %-RH, 22°C) for just one hour. After 20 hours, the moisture content droped to 0.30 wt-%, and was probably as low as it ever would be under those ambient conditions.

CONCLUSIONS

Conditioning of JA2 propellant (in a fully loaded tank round) under conditions of high humidity and temperatures for a period of 28 days resulted in a reduction of the nominal level of DEGDN plasticizer, but appeared to have no effect on the level of NG plasticizer. No analysis of stabilizer content or NC molecular weight were performed. Analysis of the propellant by microreflectance FTIR spectroscopy suggested that no gross chemical changes had occurred. Changes in coloration of the propellant were ascribed to moisture absorption.

While the "common knowledge" regarding moisture absorption by JA2 was that the propellant does not absorb more than ca. 1 wt-% water, it has been shown that moisture levels in excess of 13 wt-% are possible. Color changes (from black/green to yellow/green) are concomitant with absorption of large amounts moisture by JA2 propellant. A return to the original black/green color occurs when the propellant is allowed to dry. Graphite glaze was found to inhibit absorption of water when propellant is submerged in water, but appears to have little effect when propellant is exposed to high humidity (at room temperature).

ACKNOWLEDGMENTS

The authors are grateful to Mr. Ron Simmons of the Naval Surface Warfare Center/Indian Head Division for valuable discussions, and the German Federal Office of Defense Technology and Procurement for providing support for Ms. Leffers. This work was performed while Dr. Sagear was an NRC-ARL Postdoctoral Research Associate.

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2. Ibid.

3. The Gun and Rocket Propellant Lab of the Federal Armed Forces Technical Center for Weapons and Ammunition, Meppen, Germany. Unpublished results.

TABLE 1: Results for Moisture Analysis of JA2 Propellant

Sample Identification/Remarks (all samples conditioned for 1 month)	**Peak Area (arb. units)**	**Mass (mg)**	**Water (wt-%)**
38% RH, 22°C; no graphite glaze	17.1	7.900	0.35
38% RH, 22°C; no graphite glaze	11.1	5.756	0.26
92% RH, 22°C; no glaze; small piece	50.3	8.848	1.14
92% RH, 22°C; no glaze; small piece	32.4	5.340	1.15
92% RH, 22°C; glazed; full grain	36.5	5.923	1.19
92% RH, 22°C; glazed; full grain	44.1	7.452	1.17
water bath; 22°C; no glaze; small piece	318.4	5.020	13.71
water bath; 22°C; no glaze; small piece	376.9	6.325	12.91
water bath; 22°C; glazed; full grain	128.6	7.290	3.73
water bath; 22°C glazed; full grain	90.3	6.049	3.11
water bath ; no glaze; full grain (t=0.00 hr @ 45 %-RH)	416.4	7.991	11.3
"water bath"; no glaze; full grain (t=0.48 hr @ 45 %-RH)	151.3	7.749	4.16
"water bath"; no glaze; full grain (t=0.82 hr @ 45 %-RH)	130.7	6.531	4.24
"water bath"; no glaze; full grain (t=0.90 hr @ 45 %-RH)	174.3	9.926	3.87
"water bath"; no glaze; full grain (t=19.0 hr @ 45 %-RH)	25.1	11.796	0.38
"water bath"; no glaze; full grain (t=19.3 hr @ 45 %-RH)	19.1	10.870	0.30

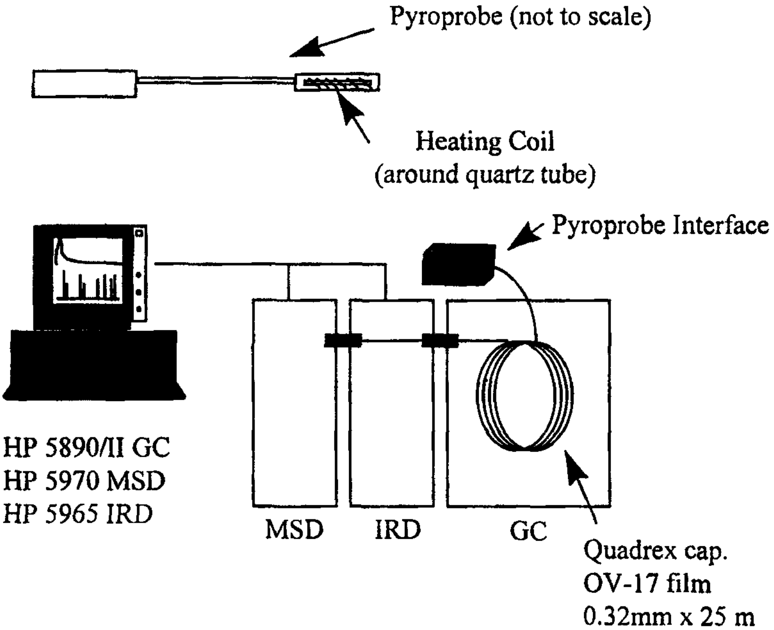

FIGURE 1

Schematic representation of experimental apparatus.

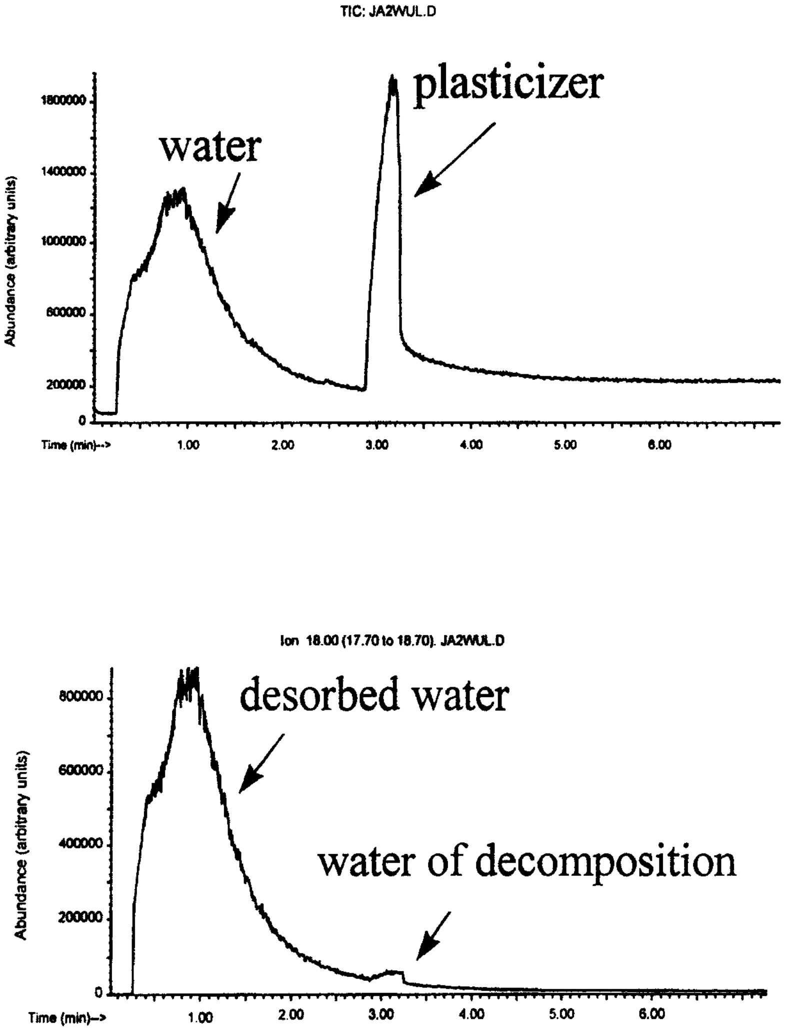

FIGURE 2

Gas chromatograms (Top: Total ion chromatogram. Bottom: Selected ion chromatogram, m/z = 18)

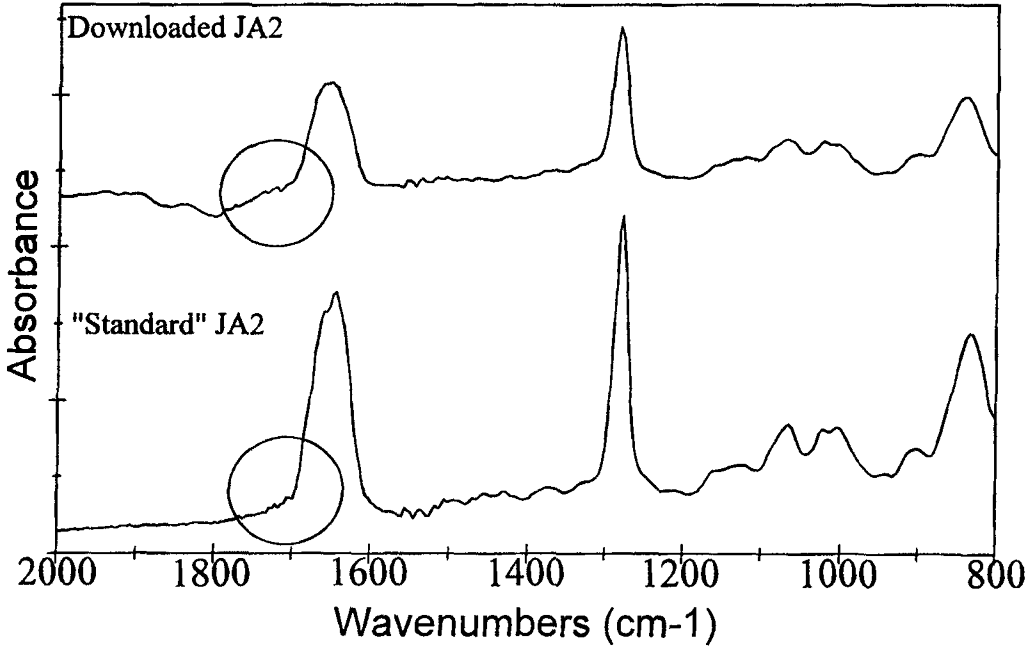

FIGURE 3

FTIR spectra of untreated JA2 propellant (Bottom) and downloaded JA2 Propellant (Top). Circles indicate the region of the spectrum in which carbonyl functional groups would absorb if they were present in the samples.

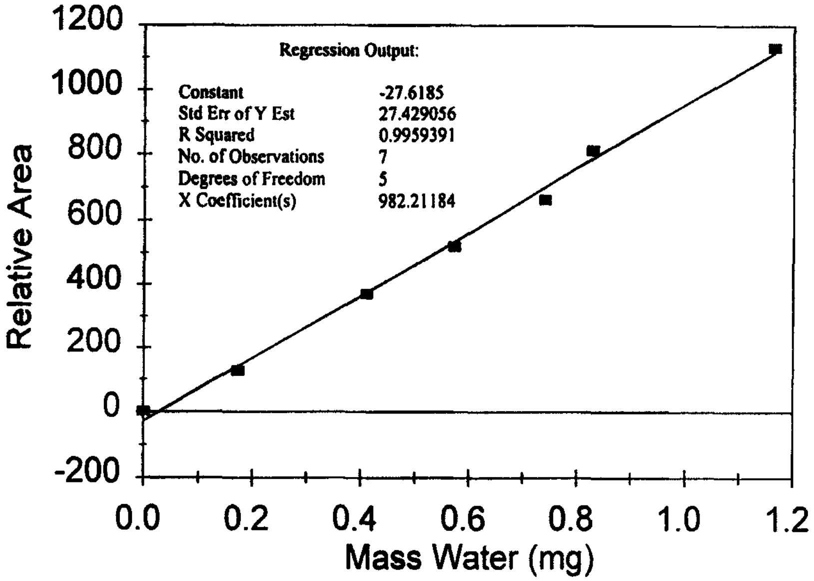

FIGURE 4

Calibration curve for moisture analysis generated by desorption of water from potassium sodium tartrate tetrahydrate

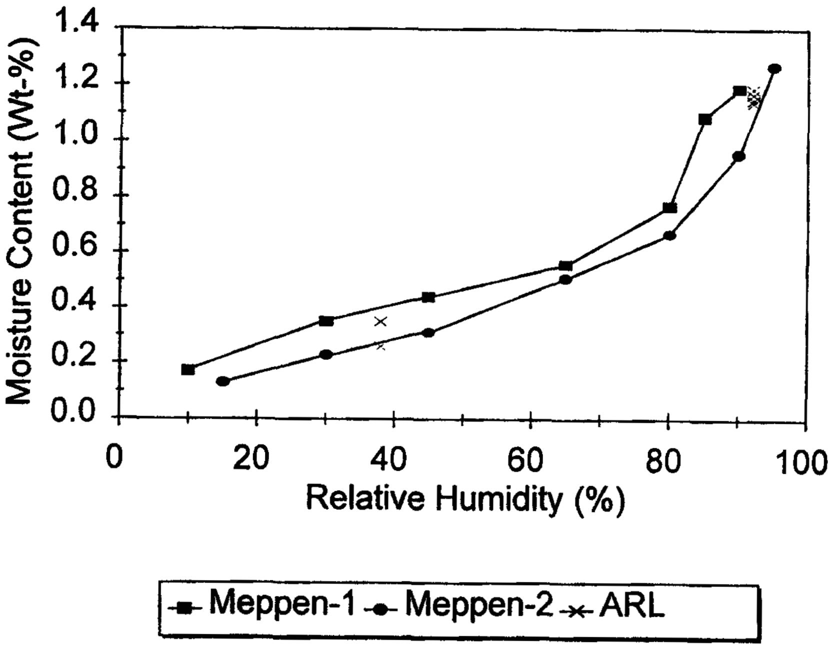

FIGURE 5

Moisture content of JA2 propellant measured in Meppen using a Karl Fischer method, and by ARL using the D-GC-MS method.