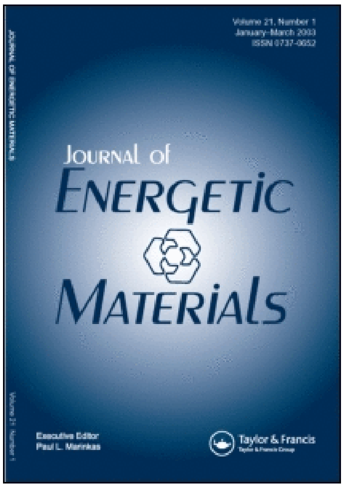

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MODIFIED VACUUM THERMAL STABILITY TEST APPARATUS FOR ENERGETIC MATERIALS

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ABSTRACT

An apparatus, hereinafter named the modified vacuum thermal stability (MVTS) test apparatus, that replaces the mercury manometric method used to determine the vacuum thermal stability of energetic materials is described. The volume calibrated MVTS system provides continuous pressure/time data for the duration of the test via a computerized data acquisition system. Total gas volume (reduced to STP) is computed from the pressure data. Subsequent gas chromatographic analysis of the evolved gaseous mixture further provides identification and individual volumes of the components. Water/solvent volume is obtained by difference ($V_P - V_{\text{Calibrated Gases GC}}$).

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INTRODUCTION

The standard vacuum thermal stability (VTS) test, developed in the early 1900s, measures the chemical stability of an explosive at an elevated temperature under vacuum for a specific time period. Generally, a weighed sample of explosive (5.00 ± 0.05 g) is sealed in an all-glass apparatus designed to measure gas pressure by the mercury manometric method. The system is evacuated and that portion containing the sample is heated at 100 °C for 48 hours. The pressure generated by the decomposition gases is measured after the entire system has equilibrated to ambient temperature[1]. Some of the problems associated with this simple system have been previously described[2]. Specifically, these problems include (1) the toxic characteristics of mercury, (2) the fragile characteristics of the all-glass system, (3) condensation of water due to the experimental technique and (4) potential inaccuracies associated with corrections used in the associated calculations. Plus factors for this method are simplicity and overall cheapness of the system.

Two alternate methods have also been described[1]. The first of these was developed for higher temperature evaluation of thermally stable explosives. Temperatures as high as 300 °C are normal and it is stated that temperatures as high as 400 °C should present no problem. The test can also be used for the standard test at 100 °C. The second alternate method was designed as a two hour test at 260 °C, but samples are often left in the heating block for longer periods of time to monitor further decomposition. It is further stated that this test can be carried out at any temperature appropriate to the explosive application. In other words, the technique may be substituted for a standard VTS test or carried out at a lower temperature, e.g. 90 °C for double-base propellants.

Another modified test procedure, Discontinuous Vacuum Thermal Stability (DVTS) test, has also been described[2]. The sample is heated in a calibrated, glass reaction tube equipped with a valve, a septum and a connector port. A pressure transducer equipped with a valve, connector and a connection to a vacuum pump is attached to the reaction tube only for pressure measurements at predetermined times. This technique provides only discontinuous pressure values, but has the advantage of requiring only one pressure transducer regardless of the number of reaction vessels. Other advantages are presented.

This paper describes the development of a Modified Vacuum Thermal Stability (MVTS) apparatus that provides continuous pressure/time data for the duration of the test. The energetic material is contained in a calibrated, stainless steel reaction vessel assembly that is connected to a pressure sensor. The entire system is heated in an oven and the real-time pressure/time data are recorded by a computerized data acquisition system.

Total gas volume is computed, reduced to STP and supported by gas chromatographic analysis.

EXPERIMENTAL

1. Modified Vacuum Thermal Stability Apparatus

a. Reaction Vessel Assembly

The reaction vessel assembly was manufactured to Cajon welding system standards by the Mobile Valve & Fitting Co., 7883 Airway Park Drive, Mobile, AL 36609, from 316 stainless steel. The Cajon Part Number for this assembly is SS-1-ASYV-04069. A schematic of the vessel is shown in Figure 1. The assembly is composed of a lower reaction vessel subassembly and an upper connector subassembly equipped with two NUPRO SS-4H TH1 Bellows Sealed valves. One valve is attached to a pressure sensor and the other to a vacuum pump/helium source. The lower and upper subassemblies are connected by means of a VCO O-ring face sealed fitting. The O-ring used in this fitting is a Parker 75 Viton, size 112. The upper subassembly is also connected to the helium and vacuum piping systems with the same type fittings. These are sealed with specially ordered Viton O-rings from DBR Industries, Inc., 18 Penns Trail, Newtown, PA 18940, Part Number 5-686 VO747-75. The reaction vessel volume referred to in a later section is that volume below valves A and B in Figure 1.

b. Pressure Sensor/Heater Assembly

The pressure sensor/heater assembly is composed of an MKS Instruments, Inc., Type 615A sensor (absolute) with a calibrated pressure range of 0 to 100 mm of Hg (full scale) and an upper temperature limit of 200 °C. Each sensor is supplied with a calibration curve traceable to the National Institute of Standards and Technology. On the average, the error is ≤ 0.06 mm at 100 mm and ≤ 0.04 mm at 50 mm. Calibrations were carried out at 100 °C with a CEC Air Dead-Weight Tester. Each sensor is housed in its own oven which is located external to the main oven where the actual samples are heat treated. The temperature of the sensor heater is controlled by an MKS Type 272 temperature controller. The power and signal conditioning for each sensor is provided by an MKS Model 270C-5 Signal Conditioner. The temperature of each pressure sensor is maintained at the same temperature as that programmed for the experiment, almost always 100 °C. During the setup for each experiment, which includes at least three evacuation and two helium refill sequences, the oven and pressure sensor temperatures may drop to around 50 and 90-95 °C, respectively. After the setup operation is completed, the temperatures equilibrate to 100 °C in approximately 30 minutes. The initial pressure reading (P_i) is always taken at time zero to ensure that all evolved gases are considered in the final volume calculation.

c. Primary MVTS Oven

The primary oven used to heat soak the MVTS samples is a mechanical convection oven, Model 625, manufactured by Precision Scientific. The upper temperature limit of the oven is 325 °C, however, all MVTS experiments involving main charge or booster explosives are carried out at 100 °C. The maximum temperature variation over the 48-hour time period should not exceed ±0.1 °C. Any deviation from these experimental conditions must be specified in detail.

d. Volume Calibration Procedure

The reaction tube and dead volumes were determined by the expanding gas method. The dead volume is that volume between valve B and the pressure sensor. The average standard deviation of the mean for nine reaction tube and three dead volumes was ±0.01 cm^3. The reaction tube and dead volumes used in experiments described in this paper are (1) 18.81, (2) 18.84, (4) 18.94, (5) 19.02, (6) 19.05 and (1) 3.64, (2) 3.66 and (3) 3.67 cm^3, respectively.

2. Pre-test Conditioning

Non-volatile powders are dried under vacuum in the temperature range 40 to 60 °C for at least two hours. Volatile powders and PBX-type formulations are dried at atmospheric pressure for the same time in the same temperature range. Reaction vessels and glass inserts are dried at 100 °C prior to use. Post-drying exposure of samples/metal parts/glass inserts to laboratory atmosphere is kept to a minimum. Non-melting powders are sieved to the range 300 to 341 microns, whereas those that melt are not sieved. PBX formulations are cut into approximately 3 mm cubes.

3. MVTS Test Procedure

Three samples, either powdered or pieces (PBX formulations), are weighed into glass sample tubes that are then inserted into the stainless steel reaction vessels and connected to the three pressure transducers and the vacuum system. They are then evacuated to a pressure less than 10 microns and refilled to atmospheric pressure with helium a minimum of two times. During this procedure the reaction vessels with volatile samples are cooled with an ice and water bath. In addition, the power to the primary oven is in the off position, while the modules for the pressure transducer heaters remain powered in an effort to keep temperature loss to a minimum. After the final refill with helium, the reaction vessels are re-evacuated to a pressure of less than 10 microns and closed off from the vacuum pump. Upon completion of the start-up procedure, the oven door is closed and the power returned to the oven (temperature setting is preset). The samples are heated at 100 °C for a total of 2910 minutes (30 minutes to reach 100 °C plus 2880 minutes). During this 2910-minute time period, pressure and temperature data are grabbed every 5 minutes by the computerized data acquisition system. At the completion of the test, the reaction vessels are cooled to approximately -15 °C by use of a salt/ice bath. This latter procedure ensures that all energetic material is removed from the dead volume and condensed into the reaction vessel.

4. Gas Analysis

a. The gaseous content of each post-test reaction vessel is analyzed by gas chromatography by using a Varian Model 3400 gas chromatograph equipped with a thermal conductivity detector. The stainless steel column, 9 feet long by 0.125 inch in diameter is packed with Porapak Q (100/120 mesh). Helium, flowing at a rate of 40 cm^3/min, is used as the carrier gas. The total volume of gas evolved during the 2910-minute heating period is flushed onto the column by passing the carrier gas through the reaction vessel. The column is maintained at -98 °C for the first 8 minutes of the operation, then heated at 5 °C/min to 200 °C. The data are reduced by using a Hewlett Packard 3365 Series II ChemStation equipped with a Hewlett Packard LaserJet III printer.

b. The decomposition gases typically observed during MVTS testing with energetic materials were calibrated by using the external standard method and a 1.052 cm^3 sample loop. Standard calibration gases, acquired from Scott Specialty Gases, are: H_2

(4.03 %), N_2 (4.98 %), O_2 (5.01 %), CO (4.98 %), CH_4 (4.03 %) and CO_2 (4.99 %) as a mixture in helium and N_2O (10.00 %) in helium and NO (100.00%). The volume of water generated/desorbed from the energetic sample during the test (not considered a decomposition gas for this operation) is calculated by difference ($Volume_{pressure}$ - Total Volume of Decomposition $Gases_{GC}$). Water is readily detected by GC analysis, but quantification is not possible due to the current configuration of the non-heated, gas entry system. This system is composed of a multiport valve, considerable stainless steel tubing and the reaction vessel. All of the entry system components adsorb water during the flushing of the gases from the reaction vessel into the GC. NO_2, if evolved, is not detected by this operation due to its reaction with Porapak Q.

5. Thermogravimetric Analyses (TGA)

Both dynamic and isothermal-TGA calibration verification experiments were carried out by using a DuPont Instruments 951 Thermogravimetric Analyzer. Nitrogen, flowing at 60 cm^3/min, was used as the purge gas.

6. Calibration Verification

The material used to verify the volume calibration procedure/calculation was sodium molybdate (VI) dihydrate [Na_2MoO_4 $2H_2O$], A.C.S. Reagent Grade (+99 %), purchased from Aldrich Chemical Co., Inc, Milwaukee, WI, and was used as received.

7. Volume Calculation Procedure

The total gas volume, obtained at 100 °C then reduced to standard conditions, is calculated from the total pressure by using equation (1):

$$V_{STP} = (P_f - P_i)(273.2)(V_{rt} - V_s)/(760)(T_{oven} + 273.2) \qquad (1)$$

Where P_f is the final pressure (mm), P_i is the initial pressure (mm), V_{rt} is the reaction tube volume (cm^3), V_s is the sample volume (cm^3) and T_{oven} is the oven temperature (°C).

8. Differential Scanning Calorimetry (DSC)

Dynamic DSC experiments are carried out at a heating rate of 10 °C/min on all samples prior to MVTS testing. Isothermal DSC experiments lasting 48 hours are carried out at 100 °C on samples of suspected low thermal stability, e.g, PBX-type samples with binder systems containing nitrate esters. DSC experiments at this facility are carried out by using a TA Instruments, Dual Differential Scanning Calorimeter, Model 912, equipped with a standard Dual Sample (DSDSC) cell and a 2100 Thermal Analyzer Data System. Standard aluminum sample pans and lids, TA Instruments Part Nos. 072492 and 073191, respectively, are generally used for all DSC operations.

RESULTS AND DISCUSSION

1. MVTS Reaction Vessel Volume Calibration Experiments

Three samples of sodium molybdate (VI) dihydrate, 10.17, 10.11 and 10.05 mg, were heated in MVTS reaction vessels at 100 °C under vacuum for 278 minutes. They generated 89.46, 86.63 and 87.07 mm of pressure in internal volumes of 22.48, 22.71 and 22.63 cm^3, respectively. The number of waters determined for each sample was 2.05, 2.02 and 2.04, respectively, for an average value of 2.04 ± 0.01. The average absolute error is +2.00 percent.

The presence of two molecules of water per molecule of the anhydrous salt was confirmed by thermogravimetric analyses. Four samples of the dihydrate were heated at 100 °C under a nitrogen purge until a constant weight was attained. The data, shown in Table 1, confirm the presence of two molecules of water.

2. Comparison of MVTS and Standard VTS Data (RDX and HMX)

a. RDX

Fifteen samples of RDX (Class 1), obtained from Holston Army Ammunition Plant (AAP) (Lot # HOL86E515-086), were subjected to MVTS testing. Eight tests were carried out by using one-gram

TABLE 1. Summary of Thermogravimetric Analyses

Type Expt	Sample Weight (mg)	Percent Water Calc'd	Percent Water Found	No. Waters	Rxn Time (min)
ITGA	96.666	14.88	14.87	2.00	40
DTGA	31.407	14.88	14.59	1.96	17
DTGA	10.272	14.88	15.07	2.03	18
DTGA(1)	12.237	14.88	14.56	1.96	18
Average No. Waters				1.99±0.02	

(1) Under vacuum at room temperature for 15 min. prior to DTGA.

samples (Table 2) and seven by using quarter-gram samples (Table 3). Five samples from the former and four from the latter weight classes were dried under vacuum. The remainder from each weight class were not dried prior to testing. Decomposition gases detected and quantified from both weight classes were N_2, O_2, CO_2 and N_2O. Water was the major component of the evolved gases from all samples. The source of O_2 is believed to be trapped air desorbed from open microporosity during the test period.

The average total volume of decomposition gases (GC) from the one-gram samples was 0.032 ± 0.003 cm^3/g, where the deviation is of the mean (s_m). The average total volume of gas reported by Holston AAP[3] from standard (mercury manometric) VTS tests with RDX (Class 1) is 0.08 cm^3/g.

The average volume of decomposition gases (GC) from quarter-gram samples is 0.025 ± 0.003 cm^3, where the deviation is of the

TABLE 2. MVTS Data for One-Gram Samples of RDX (Class 1).

Expt #	Sample Weight (g)	Gas(1) Volume (GC) (cm^3/g)	Gas(2) Volume (P) (cm^3/g)	Water(3) Volume (cm^3/g)
656(4)	1.0020	0.026	0.35	0.32
657(4)	1.0033	0.032	0.40	0.37
668(5)	1.0005	0.030	0.12	0.09
669(5)	1.0003	0.023	0.12	0.10
670(5)	0.9999	0.027	0.13	0.10
650(6)	1.0024	0.025	0.39	0.36
653(6)	1.0032	0.044	0.79	0.75
654(6)	1.0034	0.046	0.88	0.83

(1) Volumes not corrected for the assumed presence of air.

(2) Volumes computed from gas pressures measured at 100 °C, include all volatiles (H_2O, solvents, etc.).

(3) H_2O volumes determined by difference.

(4) Dried at 33 °C for 72 hours under vacuum.

(5) Dried at 40 °C for 72 hours under vacuum.

(6) Not dried.

mean (s_m). As can be seen from Table 3, the decomposition gas volumes (GC) normalized to unit mass are considerably larger than those obtained from one-gram samples of RDX from the same lot. The average of these normalized volumes is 0.099 ± 0.012 cm^3/g, where the deviation is of the mean (s_m). While the volumes normalized to unit mass are well within the acceptable limit of 2 cm^3/g, the data suggest the normalization procedure is not linear

TABLE 3. MVTS Data for Quarter-Gram Samples of RDX (Class 1).

Expt #	Sample Weight (g)	Gas[1] Volume (GC) $cm^3/0.25$ g	Gas[1] Volume (GC) (cm^3/g)	Gas[2] Volume (P) (cm^3/g)	Water[3] Volume (cm^3/g)
658[4]	0.2510	0.030	0.120	0.28	0.25
665[5]	0.2508	0.017	0.068	0.07	0.05
666[5]	0.2501	0.016	0.064	0.07	0.05
667[5]	0.2502	0.020	0.080	0.07	0.05
651[6]	0.2510	0.028	0.112	0.33	0.30
652[6]	0.2510	0.025	0.100	0.27	0.25
655[6]	0.2502	0.038	0.151	0.63	0.59

(1) Volumes not corrected for the assumed presence of air.

(2) Volumes computed from gas pressures measured at 100 °C, include all volatiles (H_2O, solvents, etc.).

(3) H_2O volumes determined by difference.

(4) Dried at 33 °C for 72 hours under vacuum.

(5) Dried at 40 °C for 72 hours under vacuum.

(6) Not dried.

and one should use one-gram samples or report the volume for the actual sample mass used.

b. HMX Class 2

Nine samples of HMX, obtained from Holston AAP, were subjected to MVTS testing. Six samples were Class 2 from Lot #

HOL77G240-002, while the Lot # and Class designation for the remaining three samples are not known. All samples were subjected to pre-test drying under vacuum. The average decomposition gas volumes (GC) for the first six and for the last three samples are 0.052 ± 0.006 and 0.028 ± 0.004 cm^3/g, respectively, where the deviation is of the mean (s_m). These data are shown in Table 4. Gases detected and quantified by gas chromatography were N_2, O_2, CO_2 and N_2O except for sample number 528, where NO was found and O_2 was not detected. As with the RDX samples described previously, the source of the O_2 is believed to be trapped air that desorbed from open microporosity during the 48-hour test. The average volume of gas per unit mass of HMX (Class 1) reported by Holston AAP[3] is 0.06 cm^3/g.

A compilation of the individual decomposition gas volumes(GC) and associated volumes attributed to water, the latter obtained by difference, is shown in Table 5. The volumes of water obtained from the samples yielding the largest average volume of decomposition gases are significantly larger than the water volumes obtained from the samples yielding the smaller volumes of decomposition gases. These data suggest that the rate of the HMX decomposition process may be affected by the amount of water associated with the specific sample that is subjected to the MVTS test.

TABLE 4. Modified Vacuum Thermal Stability Data for HMX.

Expt #	Sample Weight (g)	Gas(1) Volume(GC) (cm^3/g)	Gas(2) Volume(P) (cm^3/g)	Water(3) Volume (cm^3/g)	Drying (hrs/°C)
528(4)	1.0010	0.059	0.45	0.39	96/57
529(4)	1.0030	0.043	0.62	0.58	96/57
530(4)	1.0005	0.052	0.65	0.60	96/57
659(5)	1.0022	0.047	0.72	0.67	72/33
660(5)	1.0006	0.054	0.76	0.71	72/33
661(5)	1.0009	0.057	0.74	0.68	72/33
	Average:	0.052	s_m: ± 0.006		
671(5)	1.0009	0.024	0.19	0.17	144/40
672(5)	1.0005	0.032	0.20	0.17	144/40
673(5)	1.0010	0.028	0.19	0.16	144/40
	Average:	0.028	s_m: ± 0.004		

(1) Gas volumes are not corrected for the presence of air.

(2) Gas volumes are computed from pressure data (100 °C) and include all volatiles (H_2O, solvents, etc.).

(3) H_2O volumes are calculated by difference.

(4) Class 2 (Holston AAP Lot # unknown).

(5) Class 2 (Holston AAP Lot # HOL77G240-002).

3. General Observations

The typical pressure/time curve associated with most energetic samples is characterized by a rapid pressure rise during the first 100 minutes of the test (see Figure 2). This initial rapid pressure rise is associated with the desorption of water and solvents not removed during any drying operation that may have been applied. This is demonstrated in Figure 3, where gas chromatograms acquired at 90, 270 and 1440 minutes into a MVTS experiment show only trace decomposition gas (CO_2) after 90 minutes at 100 °C. The N_2 and O_2 seen in this initial gas chromatogram are believed to result from desorbed air. The N_2/O_2

TABLE 5. Volumes of Gases Evolved from HMX During MVTS Testing.

	Gas/Volume (cm^3/g)(1)					
Expt #	N_2	O_2	NO	CO_2	N_2O	H_2O(2)
528	0.024	---	0.004	0.006	0.025	0.39
529	0.024	0.003	---	0.003	0.013	0.58
530	0.027	0.004	---	0.004	0.017	0.60
659	0.021	0.006	---	0.005	0.015	0.67
660	0.027	0.008	---	0.005	0.014	0.71
661	0.028	0.009	---	0.006	0.014	0.68
671	0.009	0.002	---	0.002	0.011	0.17
672	0.014	0.005	---	0.002	0.011	0.17
673	0.012	0.003	---	0.002	0.011	0.16

(1) All footnotes from Table 4 apply.

(2) No solvents detected.

area ratio is obviously increasing with time thereby suggesting that N_2 is being generated via the energetic material decomposition process.

The remainder of the pressure/time curve (> 100 min), when associated with samples that are thermally well-behaved, is characterized by a descending rate pressure rise. Energetic samples that are not thermally well-behaved may begin to self-heat at some point during the test. This will be shown as an ascending rate pressure rise (see Figure 4).

CONCLUSIONS

A modified vacuum thermal stability test apparatus with associated computerized data acquisition system that provides a complete pressure/time history for the energetic sample has been developed. The total volume of gas (STP) evolved during the exposure to elevated temperature is computed from the pressure data (at the test temperature). Subsequent gas chromatographic analysis of the evolved gaseous mixture provides identification and individual volumes of the mixture components for which a calibration has been acquired. Water volume is determined by difference. The presence of solvents evolved along with water from open microporosity can be confirmed and their identity and volume obtained provided calibration data have been acquired.

REFERENCES

1. MIL-STD-1751A (Draft), Safety and Performance Tests for the Qualification of Explosives (High Explosives, Propellants, and

Pyrotechnics), Test Procedure #: VTS/A-109.001, A-107-A-112, 1 December 1992.

2. M. Benchabane, The Discontinuous Vacuum Stability Test (DVST), J. Energetic Materials, 11 (2), 89-100, June 1993.

3. Personal communication from Mr. Charles Smith of Holston Defense Corporation, Kingsport TN dated 11/796.

4. D.T. Knutson and K.E. Newman, Processing and Vulnerability Evaluation of Batch Manufactured RDX, IHTR 1802, Indian Head Division, Naval Surface Warfare Center, Indian Head, MD, 24 March 1995.

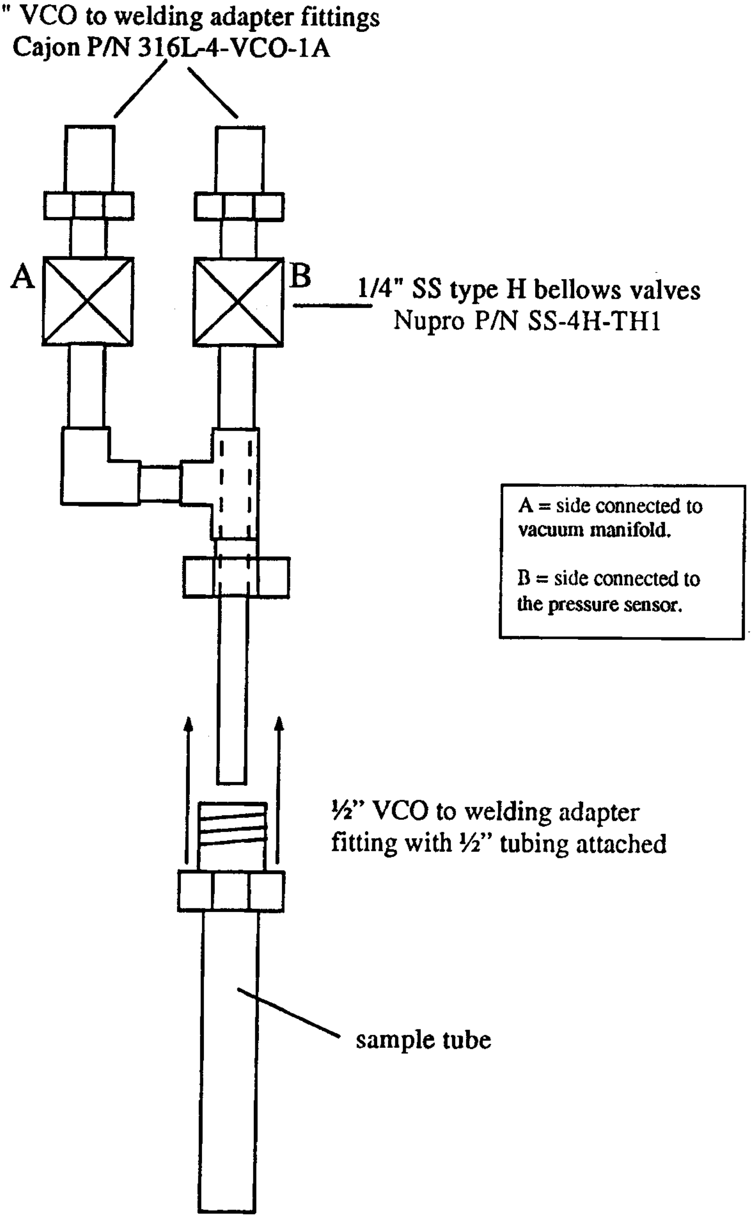

FIGURE 1.

Schematic Diagram of the Modified Vacuum Thermal Stability (MVTS) Sample Reaction Vessel.

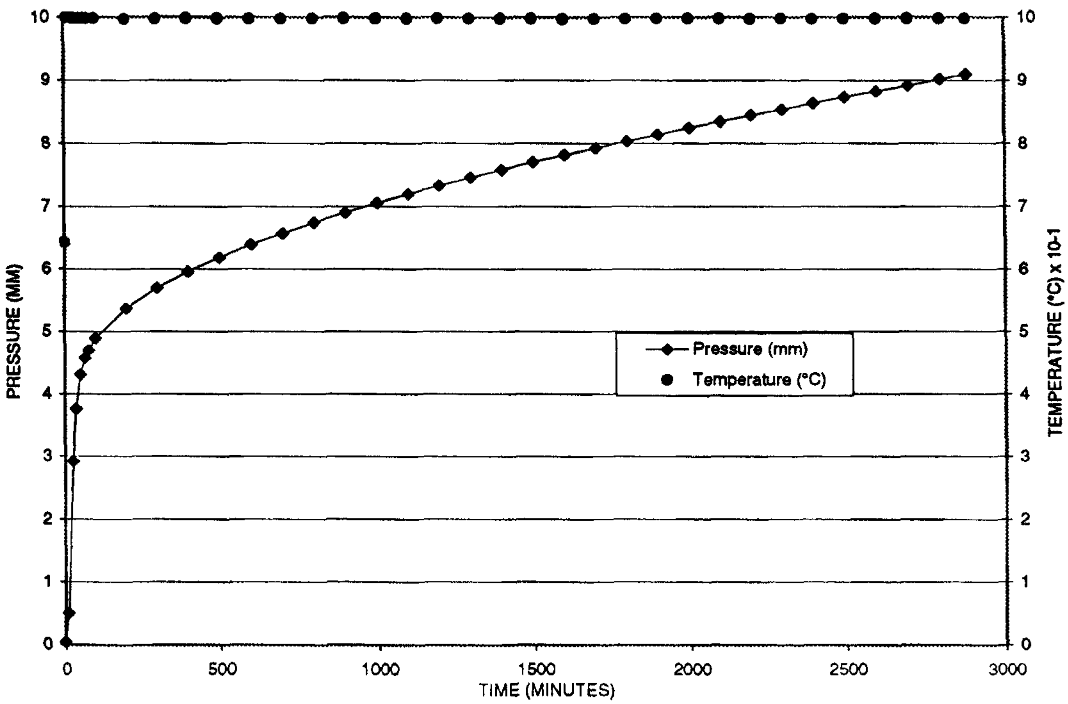

FIGURE 2.

Pressure/Time History for HMX Class 2.

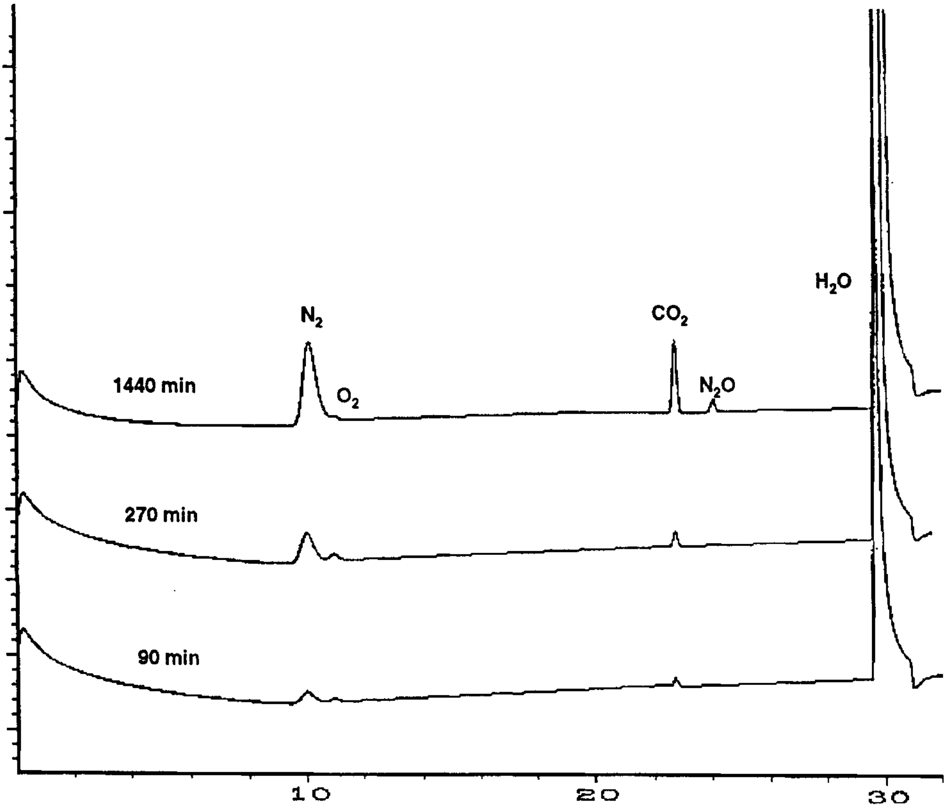

FIGURE 3.

Early Time Analysis of Gases Evolved During a Typical MVTS Test.

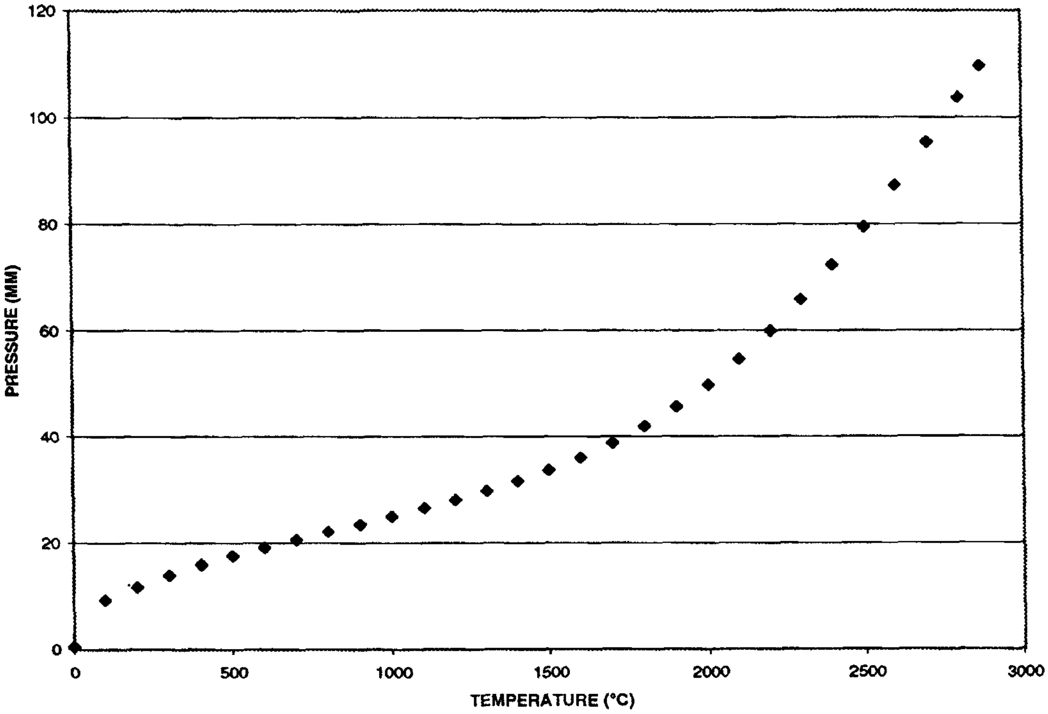

FIGURE 4.

Pressure/Time History for a Thermally Unstable Energetic Material.