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HAZARD ANALYSIS OF EXPLOSIVES BY ACCELERATING RATE CALORIMETRY

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ABSTRACT

This work aims at one important aspect of hazard analysis: compatibility testing of explosives with other materials. We discuss preliminary testing of the Accelerating Rate Calorimeter (ARC) for use in determining compatibility of a widely used military plastic bonded explosive (PBX), PBXN-106, with a material of known incompatibility. A series of tests was done to determine: that the ARC can maintain a typical polyurethane/RDX based PBX in an adiabatic environment; precision of repeat runs; effect of sample size; effect of testing the PBX in contact with an alkaline material. Relative precision for onset of exotherm for six runs was +/-1.24%. Over the mass range tested, 100-400mg, effect of sample size was small (6% change in exotherm onset). Testing the PBX in contact with an alkaline substrate significantly reduced the onset of temperature of exotherm onset.

Safe, but energetic PBXs can become unstable when in contact with a seemingly inert material. This is important over the short term during processing, but sensitive incompatibility detection methods are needed in light of the fact that weapons systems are often expected to store safely for 20-30 years in a variety of climates. It is well known that heat accelerates deteriorative chemical reactions, some of which may already be the result of unfavorable combinations of materials. New PBXs contain many new components for which we have no long term storage data. Our work parallels efforts in the chemical industry to use adiabatic calorimetry to study thermal runaway reactions and to develop criteria for predicting instability. One primary screening method, vacuum thermal compatibility (VTC), uses gassing as a measure of reactivity caused by incompatibility, although some reactions do not produce gas. Differential scanning calorimetry (DSC) is another technique in which lowering of exotherm onset temperature and activation energy or changes in endotherm/exotherm curves suggest incompatibility. Using the ARC, we can expect greater sensitivity of several orders of magnitude and detection of exotherms at lower levels. We anticipate some materials will fit a window of incompatibility detectable on the ARC but not on VTC. As we compare data for materials routinely placed in contact with explosives, our ability to assess incompatibilities of materials on the basis of empirical results may lead to structural and compositional criteria for predicting hazards.

INTRODUCTION

The stability of high explosives is affected not only by the intrinsic stability of the energetic chemicals in use but by the materials in contact with the explosive. Table (1) gives some basic definitions that will be used throughout this paper. Rogers [1] defines thermally incompatible materials as those which, when combined with an explosive, lower the thermal stability of that explosive. A major responsibility of this organization is the development and documentation of safe loading procedures for in service Naval weapons and explosive loading of weapons and shapes for development work. We often select materials of construction, select coatings and liners, sealants, gaskets, and design loading fixtures that will touch the explosive. These materials can affect the stability of the explosives over the short mixing cycles often at elevated temperatures, during loading and special test programs and over the long term - maybe twenty to thirty years or more. Some underwater mines are over forty years old. Elevated storage temperatures, notorious for accelerating deteriorative chemical reactions, may reach over 130 degrees F. inside a weapon in the sun. As a guideline, a chemical reaction doubles in rate for each ten deg. C. rise in temperature. Reference (2) describes an amine-cured epoxy system in use with propellants for twenty years which showed signs of incompatibility depending on which test was used. Thus, we seek new, more sensitive ways to predict incompatibility of materials with explosives. The Accelerating Fate Calorimeter (ARC) is a relatively new instrument developed about 1980 and used in the chemical process industry to predict runaway chemical reactions, basically, reactions generating heat faster than either reaction vessel or storage container can draw it away. References [3], [4] and [5] describe some uses of the ARC in the chemical industry.References [6] and [7] describe recent applications in the explosives industry. Because of parallels between the need to accurately predict runaway chemical reactions in the chemical industry and to detect unsafe material combinations in weapons, paricularly over the long term, we performed preliminary testing of a typical PBX to evaluate the ARC. The aim is to eventually detect latent incompatible combinations of materials and explosives, none of which by themselves are is especially unstable. Since reactions of explosives are complex and don't follow consistent rate laws, we evaluated data for empirical indicators of incompatibility, not for kinetics or reaction mechanisms.

WHY EVALUATE PBXs?

PBXs are mixtures of explosives, plasticizers, energetic plasticizers, stabilizers, polymeric binders and sometimes metals. Initially PBXs satisfied requirements to load weapons of various shapes and resisted aerodynamic heating. Then, they satisfied insensitive munitions objectives. The number of formulations is

rising, and because these explosives are so new and complex, we know little about long term storage stability in contact with various materials. In the current set of experiments, PBXN-106 was chosen since it is in several weapons and it is one of the best characterized.

WHY EVALUATE THE ARC?

References [3], [4] and [8] show that the ARC typically detects onset of an exothermic reaction (used as a measure of incompatibility) at lower temperatures than the differential scanning calorimeter (DSC) and may be a more sensitive predictor of incompatibility. Figure (1) shows this graphically in a plot of log heat rate versus 1/T. The ARC determines self heating usually 50-100 deg. C. lower than the DSC. The ARC automatically records a number of parameters including pressure as a reaction proceeds. The closed, adiabatic system approximates the internal environment of a weapon which is undergoing self heating, keeps

gasses which may catalyze the reaction in contact with the reactants and permits easy collection of gasses and solid reactants. Thus, the ARC may provide more information than other methods.Sample size is larger than that of DSC techniques giving a more representative sample. Finally the metal bomb and outer vessel are ideally suited to contain heat tests on explosives. The instrument is described in more detail below.

COMPARISON OF THE ARC TO OTHER METHODS OF DETERMINING INCOMPATIBILITY

Table (2) lists many of the stability methods now in use. These are compatibility methods if materials are put in contact with the explosives. The two most commonly used methods are the vacuum stability or vacuum thermal compatibility (VTC) test and differential scanning calorimetry (DSC). In the VTC method the sample is heated to about 100 deg. C. for 48 hours under a vacuum in a glass manometer system. The volume of evolved gas is used as a compatibility criterion after correction to standard conditions. NATO Standard Agreement 4147 and OD 44811, among others, describe variations of this test. Figure (2) shows typical apparatus. The test is inexpensive, a number of them can be run simultaneously and it is fairly reliable. However, some reactions do not produce gas, volatiles may interfere with results, toxic mercury is used in the manometer and the glass does not contain the occasional violent overgassing. Figure (3) shows the lump form of the samples with probably little actual contact area, but this problem exists with many methods. The DSC technique uses a reference and a sample, heats the two and monitors the heat needed to maintain constant temperature between the two. Figure (4) shows sample size comparison among several methods. note that the DSC sample size is very small, possibly leading to inhomogeneous samples. Unless a pressure DSC is used, reaction gasses escape. Also, increases in pressure cannot be monitored.

WHAT IS THE ARC?

References [9] and [10] Describe the ARC and its theory in detail. Columbia Scientific Industries of Austin, TX, makes the commercial instrument used in these experiments. Briefly, the ARC is an adiabatic calorimeter which heats the sample in the pattern shown in Figure (1). The sample, typically 0.1-0.5 grams, is sealed in the 0.032 inch walled Hastelloy bomb shown in Figure (5). Figures (6) and (7) show the entire assembly of bomb to instrument which is programmable for parameters such as an isothermal cycle, heating rate changes or start/stop temperatures. The ARC heats the sample in increments looking at preset intervals for onset of exotherm. When a self sustaining reaction starts generating heat at over 0.02 deg. C. per minute, the ARC adds heat to the calorimeter to match the calorimeter temperature to the bomb temperature, thus the true adiabatic nature of the test. Several parameters are monitored including heat rate, pressure increase and time to explosion. The instrument has a correction factor for the thermal mass of the bomb. Evolved gas can be routed to other instruments and the sample residue collected from the bomb and analyzed. A sample run generally takes an hour to prepare and overnight to run so the ARC is best used after a prescreening of samples. Sample bombs are expensive, about $75 each and cannot be cleaned and reused, but they are strong and inert. Development of an inert but less costly bomb is feasible.

Experimental

Three experiments were performed using a PBXN-106 cured production lot B/P 966 dated Mar 1986:

1. Determine repeatability of runs on constant mass of a PBX. Note if the ARC can follow the exotherm generated by the explosive. Results are summarized in Table (3). TA and TB indicate start and finish of the exotherm.

2. Change the sample mass and thus the thermal inertia of the sample bomb and note the effects. Results are summarized in Table (3).

3. Combine the PBXN-106 with solid sodium hydroxide dispersed on reagent grade aluminum oxide (alumina) and note effects. Compare to VTC and DSC data. Table (4) compares ARC and DSC data. Figure (8) shows effect of sodium hydroxide on DSC results. Table (5) compares ARC and VTC data. The sodium hydroxide was used as a material of known incompatibility with nitro groups. The aluminum oxide was an inert diluent.

The sodium hydroxide/aluminum oxide mixtures were prepared by coating the alumina powder with known masses of sodium hydroxide dispersed in water. Dried samples were used in the experiment. The PBX was mashed between fingers only to avoid affecting RDX size. Mixtures prepared were 0, 1, 5, 10, 25 and 50 percent sodium

hydroxide on alumina. A melting point capillary and stainless steel push rod were used to fill the bombs to the desired weights. Figure (9) shows the filling setup. Sample masses for experiments 1 and 2 were as shown. Explosive mass for experiment 3 was 0.2 grams. Total mass of alumina and sodium hydroxide was 0.2 grams to keep a constant thermal mass of 0.4 grams in the bombs.

Bombs were .032 inch wall Hastelloy C with 1/16 inch neck. Thermocouple was held in place at bottom by a manufacturer supplied clip. The original spring was removed.

Instrument settings were:
Start Temp 100, End Temp 350, Slope Sens, Heat Step 2.00, Data Step 0.50, Wait Time 10.00, Burst Diff 100.

The DSC was a Perkin Elmer DSC 4. Sample mass was about 3mg; heating rate was 10 deg. cent per min.

Vacuum thermal compatibilities were run for 48 hours at 100 deg. C. Sample size was 0.2gram of each component.

DISCUSSION

1. Overall aim in comparign various ARC parameters is to evaluate data not dependent on kinetics, and not affected by auto catalysis or changes in reaction order. Heat rate curves (not shown) suggest auto catalysis. Data show that the exotherm onset and exotherm maximum are stable indicators of neat PBXN-106 self heating. The pressure variations indicate that the system had periodic leaks. As delivered, the ARC has no self-check for the pressure transducer plumbing.

2. Effect of sample mass over the range tested of 0.1 to 0.43 grams showed a variation onset of 6.4 percent. The PBXN-106 had a range of 0.2 to 0.3 grams which shows little variation. The main criteria for sample mass were to limit pressures to the 2500 PSI max for the transducer, to enable the calorimeter to follow the exotherm and to avoid disastrous explosions. Some explosives will no doubt generate heat faster than the instrument can track. An inert filler may dampen the exotherm rate by acting as a heat absorber.

3. The comparison between ARC and DSC data shows that the ARC sees the onset of exotherm for neat PBXN-106 55 degrees before the DSC detects it. This difference holds for each concentration of alkaline sodium hydroxide. The DSC 'sees' the 0.5 percent sodium hydroxide shown by an exotherm drop of 2.06 degrees. However, the exotherm onset temperatures reverse with the next increase in concentration by 1.79 degrees.Vacuum thermal compatibility also detects the 0.5 percent sodium hydroxide by gassing more than the arbitrary 2.0 g per cubic centimeter cutoff. At higher concentrations, the reactions were so severe we stopped the tests after about 10-20 minutes. Other materials must be tested to show that the ARC can detect incompatibilities undetected by DSC or VTC.

CONCLUSIONS

1. Based on the preliminary study of PBXN-106 the ARC can supplement other methods in compatibility testing.

2. The ARC can follow the self heating of at least one PBX, and because of formulation similarities, will work on others. Pure explosives such as RDX have not been evaluated.

3. The ARC proved to be more sensitive than the DSC in detecting exotherm onset, but more experiments are necessary to find if there is a window of incompatibility detectable by the ARC but not by DSC or VTC.

PLANNED WORK

1. Evaluate more systems of known incompatibility. Demonstrate that improved sensitivity is significant.

2. Correlate ARC data to VTC data.

3. Improve ARC sample bomb system and pressure system.

4. Incorporate modern microcomputer hardware and software to process data.

5. Develop hazard index.

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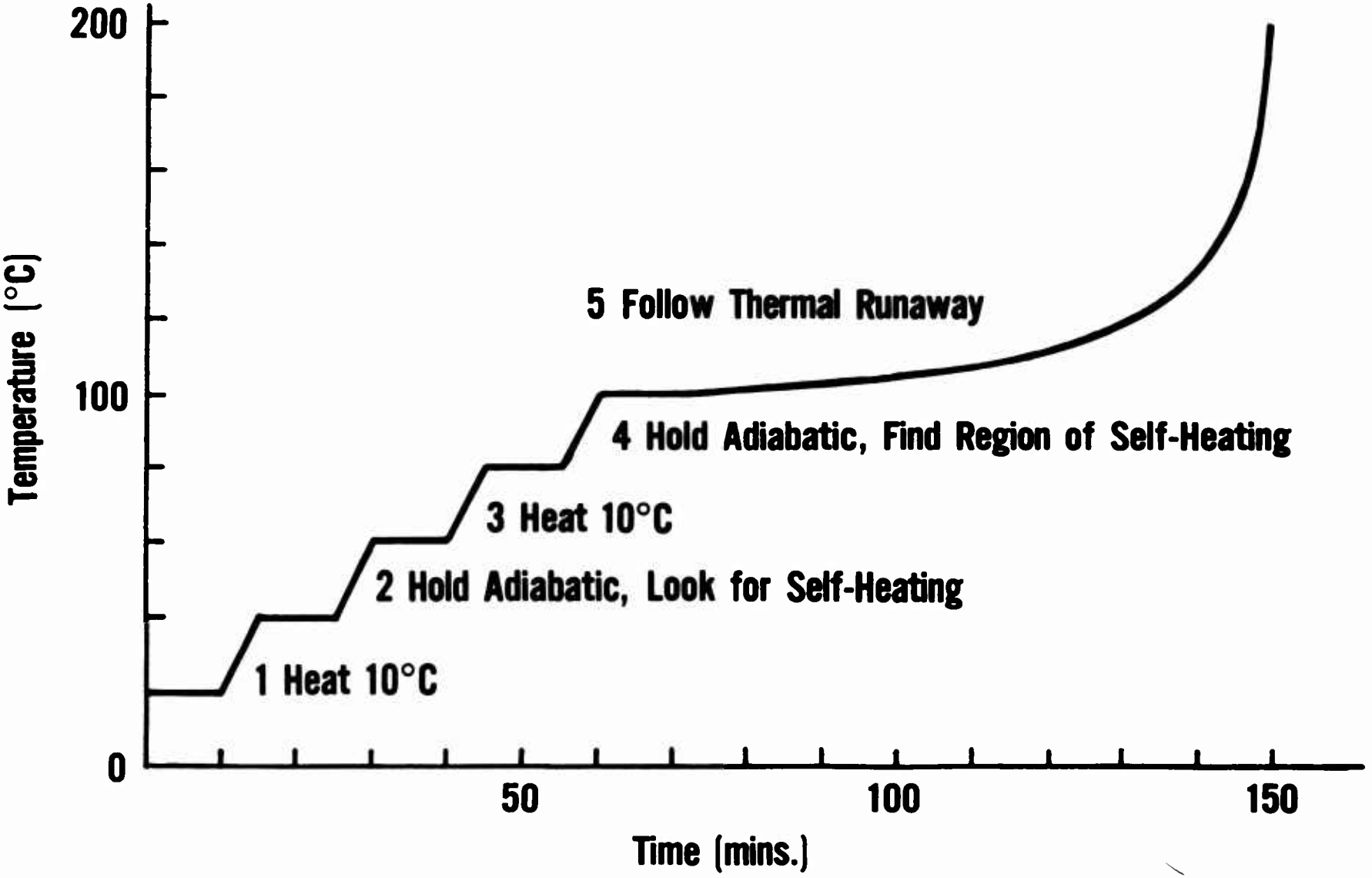


Typical ARC Experiment

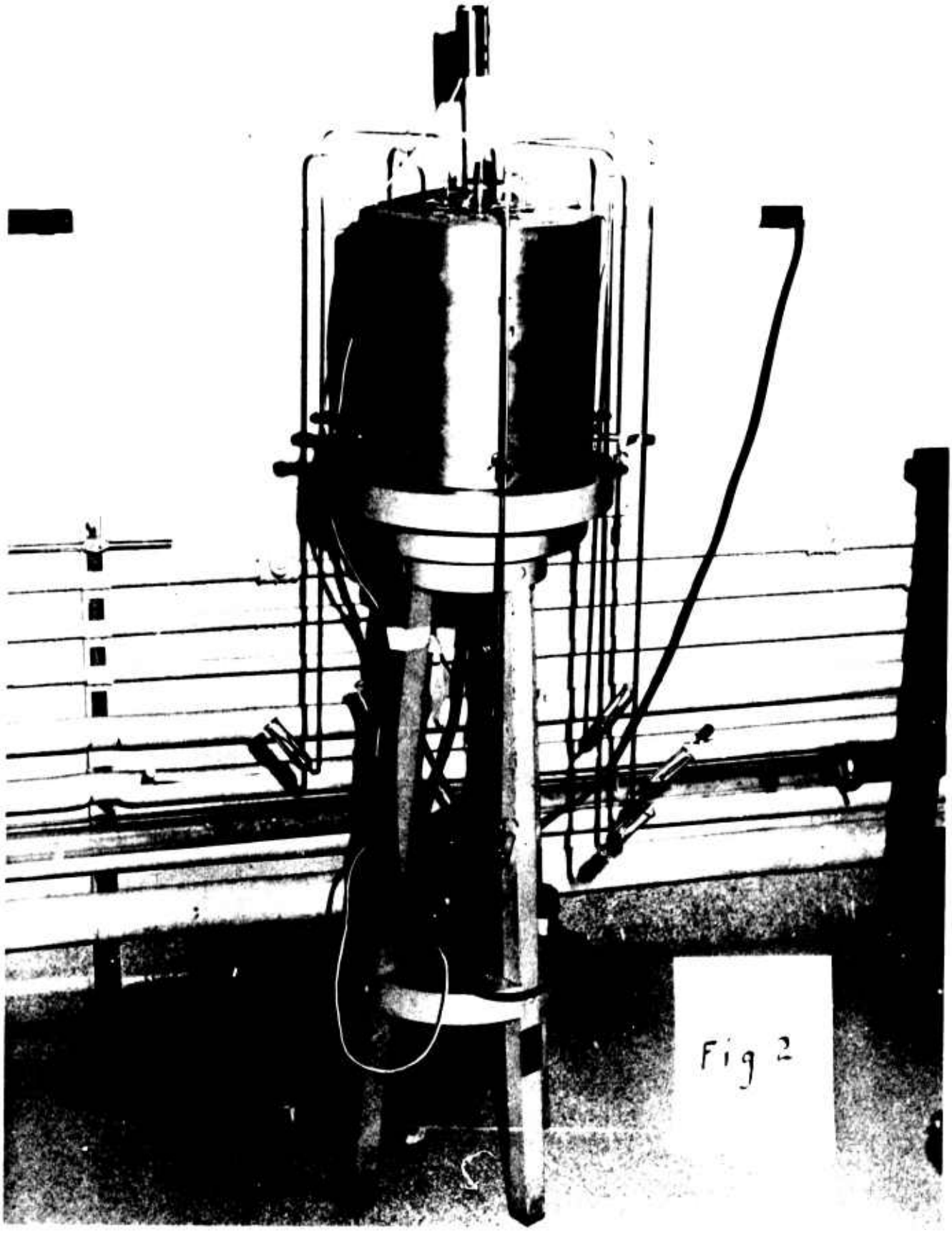


Fig 2

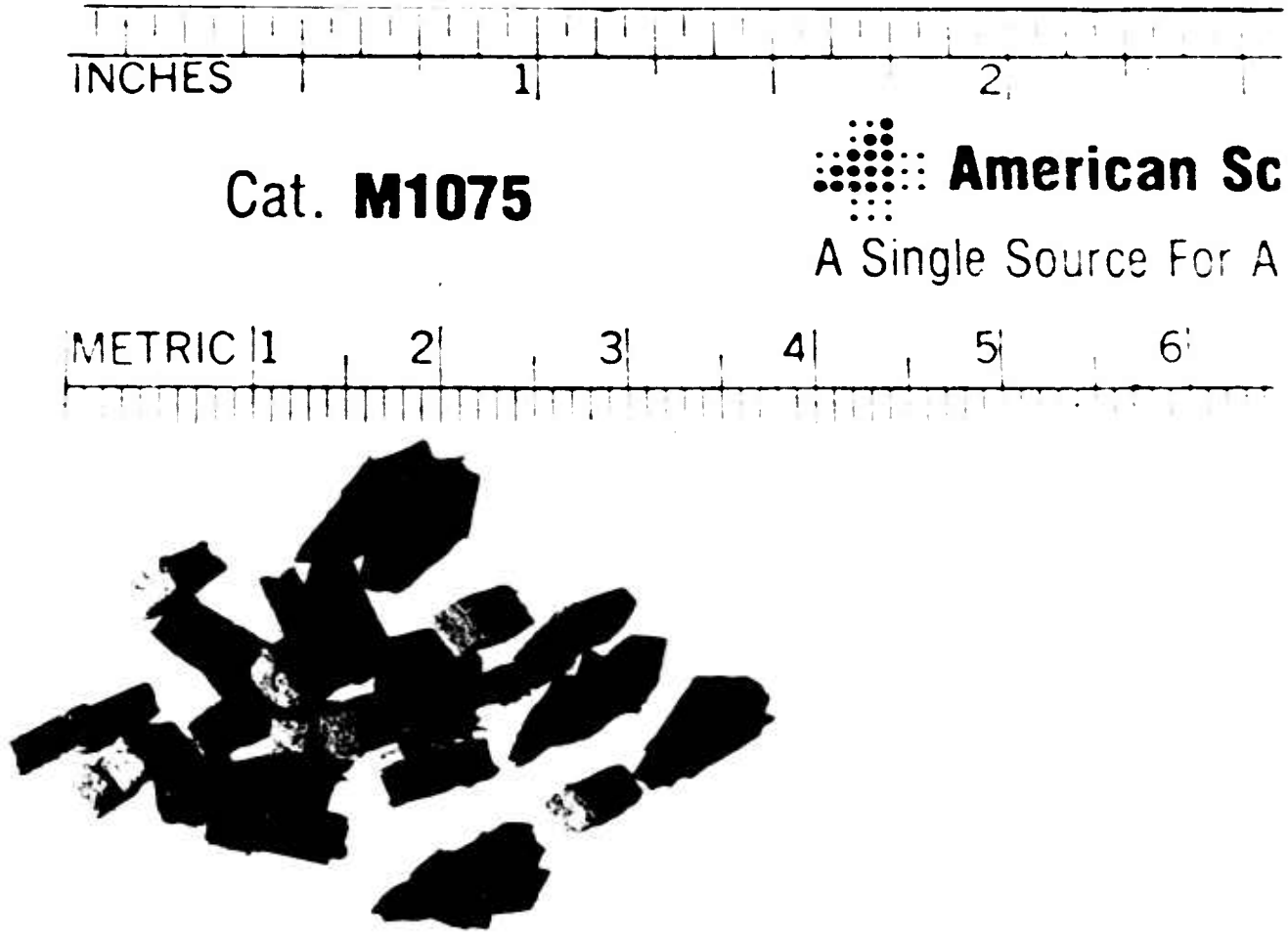
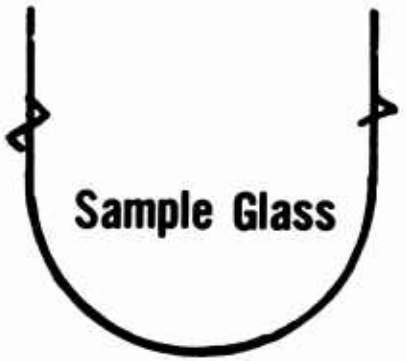

INCHES
1
2
Cat. M1075
American Sc
A Single Source For A
METRIC 1
2
3
4
5
6

Fig 3

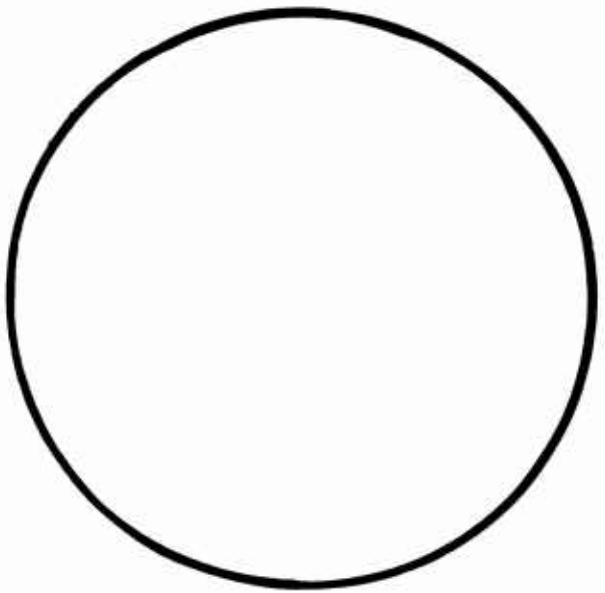
Relative Size Of Sample Holders And Samples

DSC/DTA
1 mm × 6 mm
Sample 2-5mg
(0.002 - 0.005g)
Aluminum



VTC
15 mm dia × 40 mm high
Sample 0.2 to 1g

DTA
2 mm × 5 mm
Sample 10m (0.5-2 Ideal)
Aluminum



ARC
25.4 mm dia
Sample 0.1 to 0.5g
SS, Ti, H stelloy

Fig 4

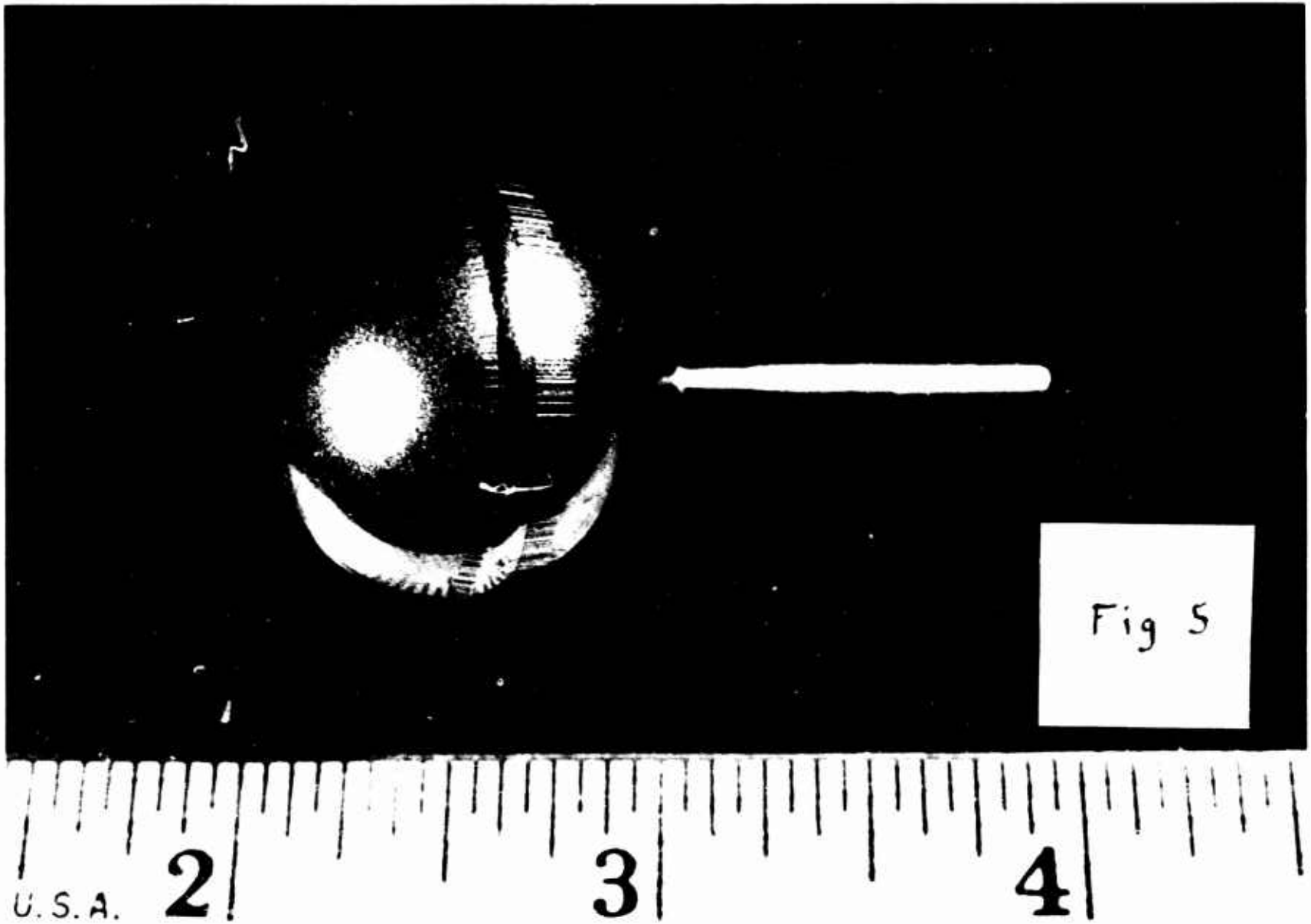
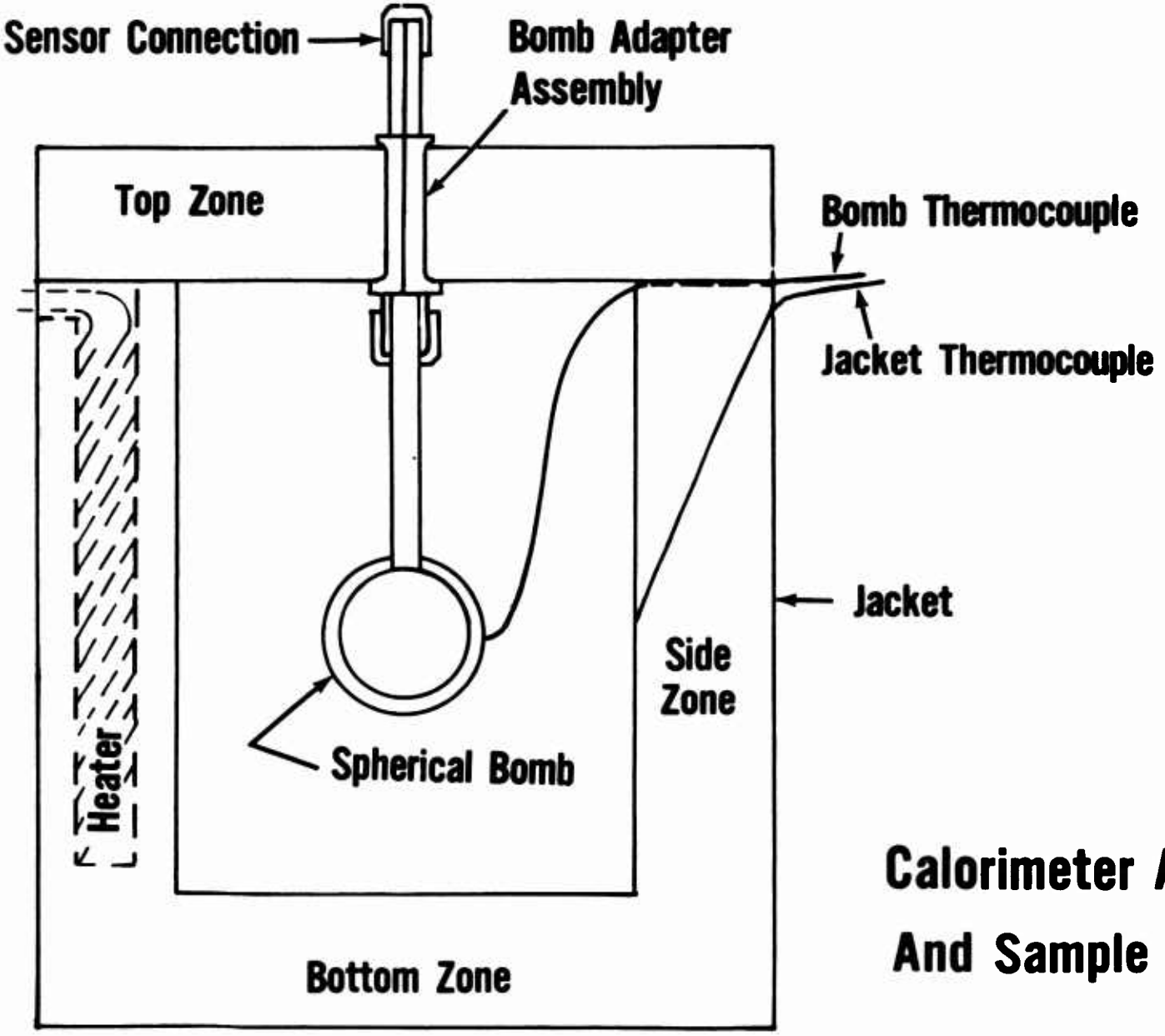


Fig 5

Fig 6



2097

Fig 7

Calorimeter Assembly And Sample System

Fig 8

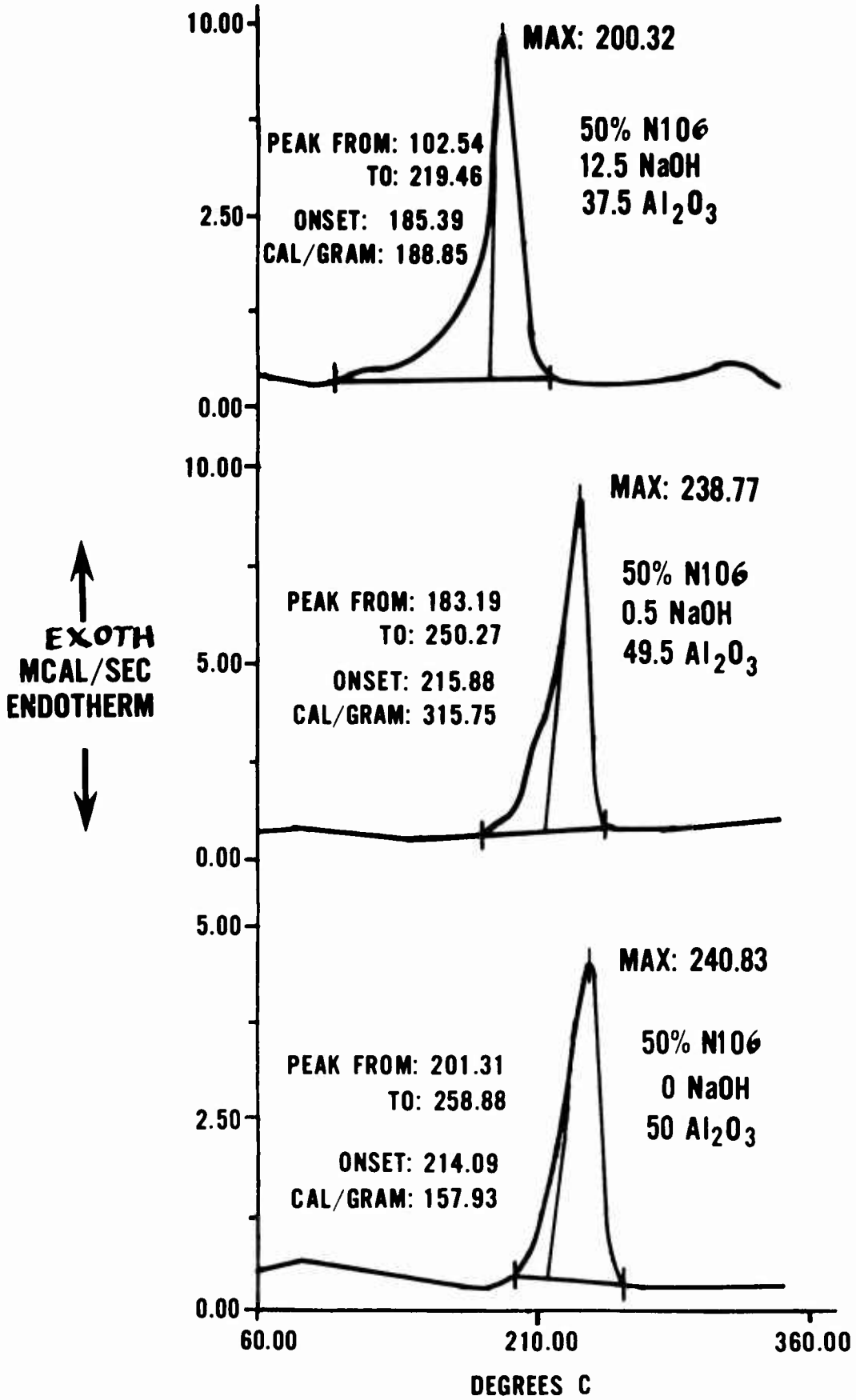

DSC SCANS PBXN 106 WITH Al_2O_3/NaOH
10.00
2.50
0.00
MAX: 200.32
PEAK FROM: 102.54
TO: 219.46
ONSET: 185.39
CAL/GRAM: 188.85
50% N106
12.5 NaOH
37.5 Al_2O_3
10.00
5.00
0.00
MAX: 238.77
PEAK FROM: 183.19
TO: 250.27
ONSET: 215.88
CAL/GRAM: 315.75
50% N106
0.5 NaOH
49.5 Al_2O_3
EXOTH
MCAL/SEC
ENDOTHERM
5.00
2.50
0.00
MAX: 240.83
PEAK FROM: 201.31
TO: 258.88
ONSET: 214.09
CAL/GRAM: 157.93
50% N106
0 NaOH
50 Al_2O_3
60.00
210.00
360.00
DEGREES C
SCAN RATE 10°C/MIN.

Fig 9

BASIC DEFINITIONS

- **EXPLOSIVE** - Substance capable, by chemical reaction, of producing gas at such a temperature, pressure and rate as to be capable of causing damage to the sur roundings.

- **HIGH EXPLOSIVES** - Substances which, in their applica tion as primary, booster or main charges are required to detonate. Examples, RDX, HMX and TNT

- **PBX** - Plastic Bonded Explosive

2100

Table 1

BASIC DEFINITIONS cont'd . . . . .

- **PBXN 106**

  Nitramine High Explosive - RDX Or Hexogen Or Cyclonite

  Energetic Plasticizer Mixture - Bis(2.2 Dinitropropyl) Acetal/Formal

  Crosslinked Polyurethane Binder

  Stabilizer

  Catalyst

- **RDX**

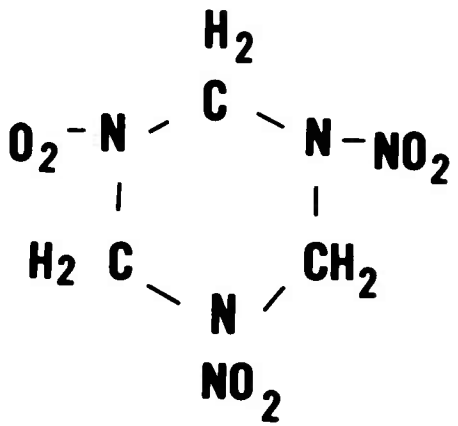


Table 1

COMPATIBILITY METHODS NOW IN USE

- DSC
- DTA
- VACUUM STABILITY
- TALIANI
- TGA
- ASTM E 698-79 ARRHENIUS KINETIC CONSTANTS
- HENKIN TIME TO EXPLOSION TEST
- ASTM E 476-73 THERMAL INSTAB. OF CONFINED CONDENSED PHASE SYSTEMS
- ARC

Table 2

ARC-PBXN 106
REPRODUCIBILITY AND EFFECT OF SAMPLE MASS

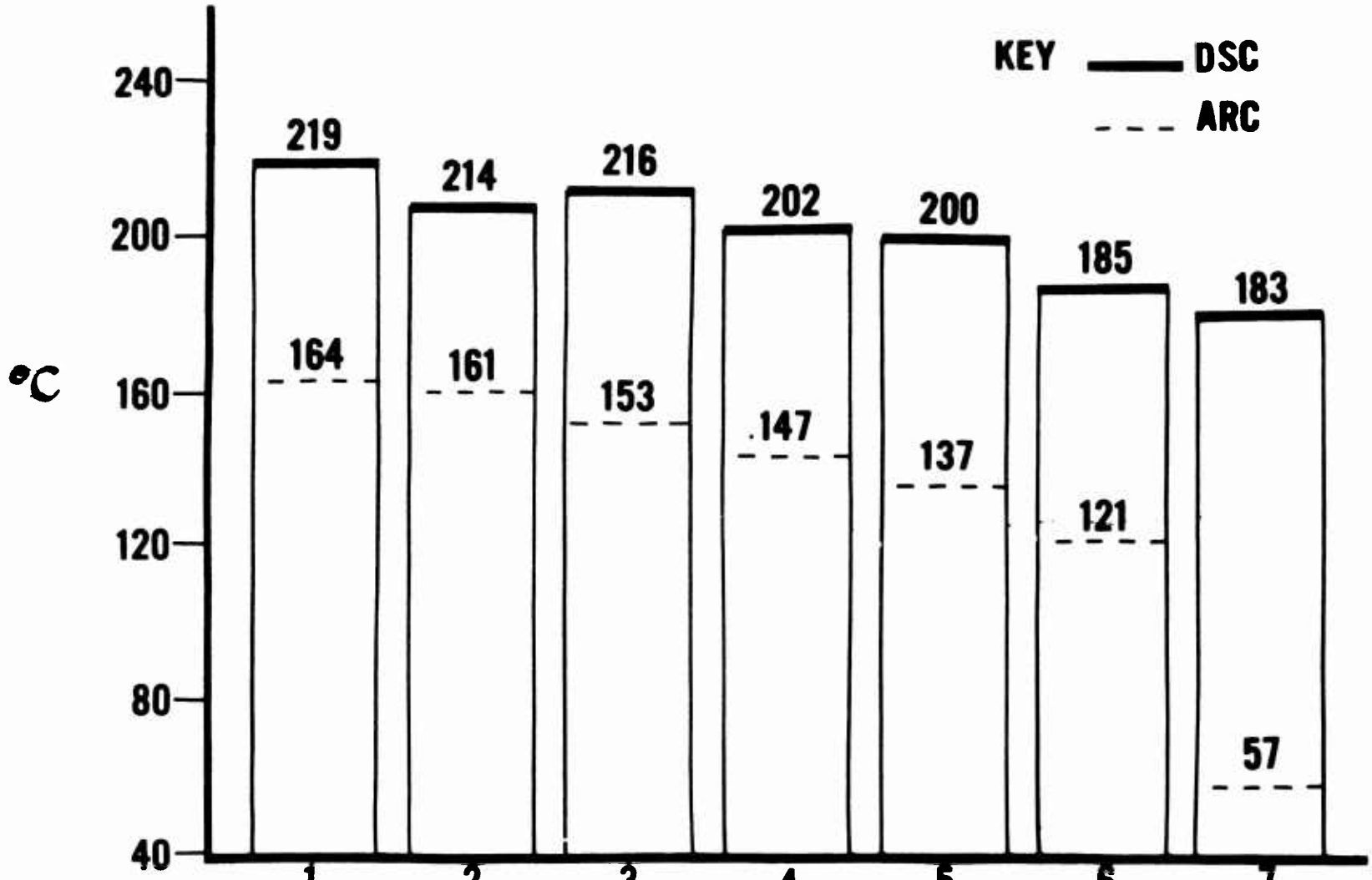
●REPRODUCIBILITY

	SAMPLE MASS GRAMS	PRESSURE PSI	EXOTHERM ONSET, °C TA	EXOTHERM MAX, °C	TA-TB
	0.2002	511	165.9	223.1	63.3
	0.2000	513	161.2	226.7	67.9
	0.1998	350	163.1	223.1	64.1
	0.1998	503	163.9	225.6	66.2
	0.2003	476	167.0	227.7	60.2
	0.1998	525	162.2	230.3	66.9
MEAN	0.2000	475	163.9	226.1	64.7
PREC	± 0.11%	± 16.3%	± 1.13%	± 1.24%	± 4.29%

●EFFECT OF SAMPLE MASS

0.1001	148.2	167.1	208.6	41.5
0.2000	513	161.2	226.7	67.9
0.3155	694	161.0	240.9	79.5
0.3945	1089	158.7	239.2	99.9
0.4207	1362.1	157.2	206.9	49.6
0.4309	1171.4	156.7	245.9	109.0
		△ 6.2%	Table 3	

EXOTHERM ONSET PBXN 106/NaOH ARC VS DSC



	1	2	3	4	5	6	7
PBXN 106 %	100	50	50	50	50	50	50
Al_2O_3	0	50	49.5	47.5	45	37.5	25
NaOH	0	0	0.5	2.5	5.0	12.5	25

Table4

2104

ARC-VTC DATA FOR PBXN 106/NaOH

	PERCENT	EXOTHERM ONSET °C	EXOTHERM MAX °C	TIME TO MAX TEMP	VAC COMP CC/G
PBXN 106	100	163.90	226.09	967.24	0.2
PBXN 106 NaOH Al_2O_3	50 0 50	160.94	207.14	1293.15	TEST ABORTED
	50 0.5 49.5	152.98	171.07	1337.69	3.4
	50 2.5 47.5	147.19	169.78	1159.56	TEST ABORTED
	50 5.0 45	137.18	142.78	1226.87	TEST ABORTED
	50 12.5 37.5	121.12	133.63	1075.99	GASSED THROUGH
	50 25 25	57.01	66.07	158.94	GASSED THROUGH

Table 5