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# HEAT RESISTANT EXPLOSIVES, XXI THE THERMAL STABILITY OF DIPAM, 3,3'-DIAMINO-2,2',4,4',6,6'-HEXANITROBIPHENYL (C)

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# HEAT RESISTANT EXPLOSIVES, XXI THE THERMAL STABILITY OF DIPAM, 3,3'-DIAMINO-2,2',4,4',6,6'-HEXANITROBIPHENYL (C)

by

Herbert T. Simmons, Sr.

ABSTRACT: The gas produced per unit weight of DIPAM in the 260°C vacuum stability test is dependent upon the size of the sample used. This lack of scaling is the result, in part, of decomposition of DIPAM vapor as well as from solid DIPAM. DATB showed the same lack of scaling as DIPAM. However, TATB, HNS and NONA scale quite well. A unique pressure effect was found while investigating the thermal stability of DIPAM. (C)

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NOLTR 65-206

18 January 1966

DIPAM is a heat resistant explosive recently released for service use. This report covers an investigation of its thermal stability characteristics at 260°C (500°F). Previous DIPAM studies are reported in NOLTR 62-82, NOLTR 62-175, and NOLTR 64-94. The evaluation of DIPAM for use in various applications is described in NOLTR 63-16 and NOLTR 63-258. The work reported herein was carried out under RUME 4E000 F008 08 11 Problem 012, Explosives Properties.

J. A. DARE
Captain, USN
Commander

ALBERT LIGHTBODY
By direction

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## INTRODUCTION

DIPAM, 3,3'-diamino-2,2',4,4',6,6'-hexanitrobiphenyl, is a heat resistant explosive discovered at the Naval Ordnance Laboratory in the Bureau of Naval Weapon's supported Foundational Research Program on High Energy Chemistry (1). It melts at 306°C and has good thermal stability at 260°C (500°F). Further, it is not complicated by crystalline phase transitions from ambient up to the melting point. A number of successful chemical studies (2),(3),(4) have made DIPAM a practical explosive. It has been accepted for use in the Navy's F-111 aircraft and has been given serious consideration for other applications (5).

In the course of measuring the thermal stability of pre-production material, a sample size effect was found. That is, the computed volume of gas evolved per unit weight of sample somehow was dependent upon the sample weight used in the measurement. Because of the considerable interest in DIPAM, this phenomenon was investigated.

## RESULTS AND DISCUSSION

In evaluating DIPAM quality during the research and development stages, a 0.2 g sample was used rather consistently for the determination of thermal stability. It was thought that a 0.5 g sample might be more representative of production material. The sample size-thermal stability effect was first observed when a 0.5 g sample was used in place of the 0.2 g.

Table I clearly shows the effect of changing sample size. The computed volume of gas evolved per gram per hour varies by a factor of three in changing from a 0.5 to a 0.1 g sample. Detailed procedures are given in the experimental section. All DIPAM stability measurements reported herein are of the same large sample. The reproducibility of replicate measurements, Table I, is about average for stability measurements of this type.

TABLE I

260° VACUUM STABILITY; 10 ml SAMPLE TUBE

| DIPAM Sample Wt | ml gas/gram/hour at NTP |
|---|---|
| 0.1 | 2.97 |
| 0.1 | 3.06 |
| 0.2 | 1.94 |
| 0.2 | 2.01 |
| 0.2 | 1.96 |
| 0.5 | 0.85 |
| 0.5 | 1.08 |
| 0.5 | 1.03 |

In the normal procedure, the stability tube was evacuated to 0.5 to 1.0 mm. It was postulated that residual oxygen might have some effect on the stability of DIPAM at 260°C. An oxygen effect was found, Table II, although it was not a very large one. The oxygen pressure in the two sample tubes containing added oxygen was at least 50 times greater than the oxygen pressure in a sample tube evacuated in the normal manner. Further removal of residual air by evacuation and by sweeping with nitrogen produced no change in the DIPAM stability, Table II.

TABLE II

260°C VACUUM STABILITY; 10 ml SAMPLE TUBE

| DIPAM Sample Wt | ml gas/gram/hour at NTP | Comments |
|---|---|---|
| 0.2 | 1.99 | evacuated to 0.003 mm |
| 0.2 | 1.98 | purged 3 times with nitrogen |
| 0.2 | 1.94 | purged 3 times with nitrogen; |
| 0.5 | 0.94 | run under a partial pressure of nitrogen |
| 0.2 | 2.43 | 11 mm oxygen pressure |
| 0.5 | 1.61 | 20 mm oxygen pressure |

It was thought there might be a glass interface effect. To test this, Vigreux type sample tubes were made which contained numerous indentations in the side walls. This additional surface contact had no effect on the stability-sample size relationship, Table III.

TABLE III

260°C Vacuum Stability; 10 ml Vigreux Type Tube

| DIPAM Sample Wt | ml gas/gram/hour at NTP |
|---|---|
| 0.1 | 2.71 |
| 0.2 | 1.85 |
| 0.5 | 0.88 |

No surface effect was found with other types of sample tubes. In addition, there appeared to be relatively little difference in the results when fused silica sample tubes were substituted for Pyrex.

A rather unique characteristic of DIPAM was observed while investigating the possibility of a surface reaction. Because of the difficulty on controlling surface contact, a pressed DIPAM sample was prepared for a thermal stability comparison with a like weight of loose crystals. The experiment was designed to minimize and maximize surface contact. The result obtained was completely contrary to our expectation as the pressed DIPAM (60,000 psi) produced at least eight times as much gas as the loose powder. Further, pressure (60,000 psi) had no effect on the 260°C stability of DATB, TATB, HNS and NONA. This work will be the subject of another technical report.

In reviewing some of our work, there appeared to be evidence that the sample tube volume might be related to the problem of non-scaling. For example, a 0.1 g sample in a 31 ml sample tube produced more than 4 ml of gas per gram per hour. However, a 0.1 g sample in a 10 ml tube gave only 3 ml of gas, Table I, under the same experimental conditions. The difference between the two values, although not large, was believed to be greater than an experimental error.

The sample tube volume could play a part in the thermal stability measurement if decomposition takes place on the surface of the sample as well as in the vapor phase in the free volume above the sample. If this is the case, then the stability measurement is a function of not only sample size but also sample tube volume.

This explanation was tested by measuring DIPAM stability as a function of sample tube volume, Table IV. About four times as much gas was produced in a 48 ml sample tube as compared to a 2 ml tube. The effect of free volume was further demonstrated by using a sample in a stability tube with as little free volume as possible. This was the case with a 0.5 g sample in a 2.2 ml sample tube, Table IV. Only 0.51 ml of gas per gram per hour was produced.

TABLE IV

260°C VACUUM STABILITY

| DIPAM Sample Wt. | Sample Tube Volume, ml | ml gas/gram/hour at NTP |
|---|---|---|
| 0.1 | 2.00 | 1.52 |
| 0.1 | 10.75 | 3.06 |
| 0.1 | 31.00 | 4.17 |
| 0.1 | 48.05 | 6.15 |
| 0.1 | 2.00 | 1.52 |
| 0.2 | 2.00 | 0.88 |
| 0.5 | 2.20 | 0.51 |
| 0.1 | 48.05 | 6.15 |
| 0.2 | 48.80 | 5.17 |
| 0.5 | 48.45 | 2.60 |

Table IV shows the measured vacuum stability of DIPAM is dependent not only upon sample weight, but also on sample tube volume. The results can be explained in part by assuming the decomposition of DIPAM vapor in the free volume above the sample. With a small free volume, the contribution of vapor decomposition would be less than with a large free volume.

A typical time-pressure plot of DIPAM heated at 260°C is shown in Figure 4. Although scaling is improved at the longer times of heating, it is not true scaling. The time-pressure curve has a rather peculiar shape. After about 50 minutes of heating there is an increase in the pressure rate. This is followed by a decrease in the pressure rate after about 110 minutes.

Our work implies that DIPAM used in a confined space would be more stable than indicated by the vacuum stability measurement. Further, the vacuum stability method in quality control work must clearly define the test conditions.

We have only a partial explanation for the lack of scaling of DIPAM. Additional work underway on the decomposition of DIPAM may provide some further insight into this problem.

Stability measurements were made on DATB, TATB, HNS and NONA to determine whether they showed a sample size effect. DATB acted in the same manner as DIPAM while TATB, HNS and NONA scaled very well, Table V.

TABLE V

VACUUM STABILITY; 10 ml SAMPLE TUBE

| Compound | Sample Wt., g | Temperature, °C | ml gas/gram/hour at NTP |
|---|---|---|---|
| DATB | 0.1 | 260 | 5.03 |
| | 0.2 | 260 | 4.33 |
| | 0.5 | 260 | 2.75 |
| TATB | 0.1 | 260 | 1.23 |
| | 0.2 | 260 | 1.04 |
| | 0.5 | 260 | 1.14 |
| HNS | 0.1 | 260 | 0.38 |
| | 0.2 | 260 | 0.34 |
| | 0.5 | 260 | 0.40 |
| HNS | 0.1 | 280 | 2.71 |
| | 0.2 | 280 | 2.74 |
| | 0.5 | 280 | 2.78 |
| NONA | 0.1 | 280 | 0.99 |
| | 0.2 | 280 | 0.94 |
| | 0.5 | 280 | 0.89 |

## EXPERIMENTAL

The vacuum stability test is carried out in a single piece all glass unit consisting of a sample tube and manometer, Figure 1. One mm (nominal) diameter Pyrex capillary tubing is used for the manometer. Generally a 10 ml sample tube volume is used. These units are made in our Laboratory and each is calibrated before use. Additional detailed information on the construction and calibration of these stability tubes has been reported (6), (7).

Vacuum stability measurements are made in a constant temperature test chamber, Figure 2, which is capable of maintaining 260 $\pm$ 0.5°C or better for several days. This apparatus has been described in some detail by Rosen and Simmons (6).

## TEST PROCEDURE

A weighed sample is introduced through the open end of the tube. The tube is then sealed off just above the point where the manometer is sealed onto the tube, Figure 1. The glass unit is placed in the evacuating rack and evacuated down to a pressure of 0.5 - 1.0 mm of mercury. Four ml of mercury are added to the mercury well of the manometer, following which the manometer is opened to the atmosphere. The sample contained in the sealed glass unit is ready for the test.

The sample tube is placed in the constant temperature test chamber after an initial room temperature reading (zero time) has been recorded along with the barometric pressure. Ten and twenty minute readings are taken. The sample is heated for an additional two hours. We report the volume of gas evolved per gram of sample during the first twenty minutes and the average volume of gas evolved per hour per gram during the following two hour period. Pressure readings are corrected for changes in the barometric pressure between the beginning and end of the test. Frequently, samples are heated beyond the two hour and twenty minute period to gain additional information.

The gas evolved during the first twenty minutes is not a true measure of the stability of the sample because of the time required to reach block temperature, Figure 3. However, the gas evolved during this initial period of heating often provides useful diagnostic information. Figure 4 shows a typical gas pressure-time plot of DIPAM heated at 260°C.

## CALCULATIONS

All calculations are corrected to standard temperature and pressure conditions (0°C and 760 mm). The volume of gas in ml evolved per gram during the 2 hour period is calculated by the following formula:

$$V = \frac{(x)(y)(z)}{W(t)}$$

where:

V = ml gas/gram explosive/hour

X = volume in ml of hot zone of tube and manometer

Y = conversion factor

$$\frac{273}{(533)(760)}$$

Z = corrected pressure increase in mm

W = sample weight

t = test time in hours.

## ACKNOWLEDGEMENT

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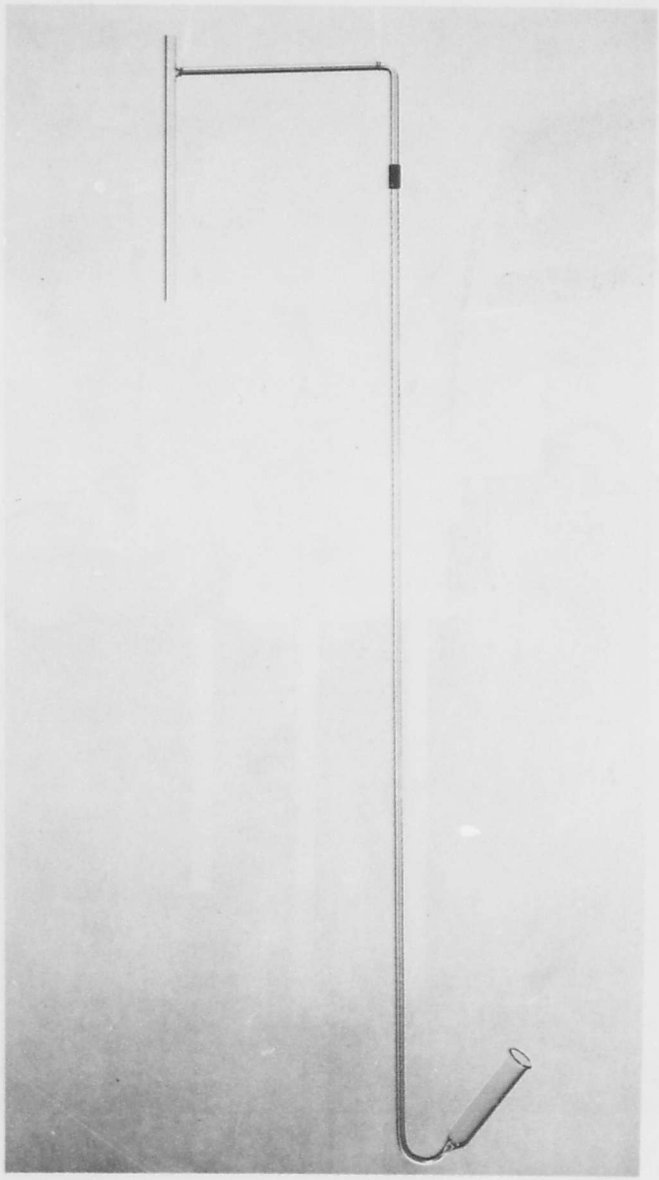

FIG. 1 VACUUM STABILITY TUBE AND MANOMETER

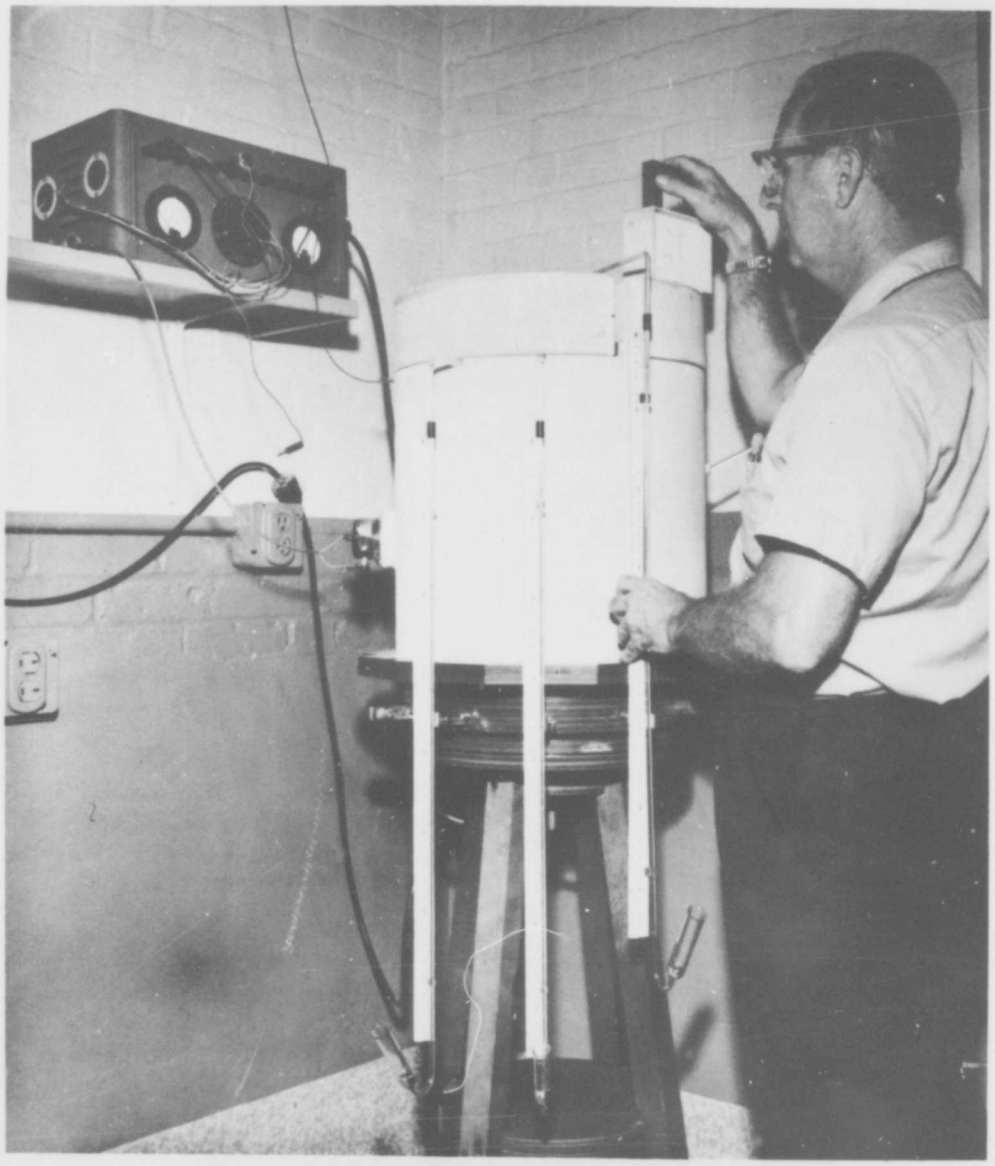

FIG. 2 VACUUM STABILITY BLOCK

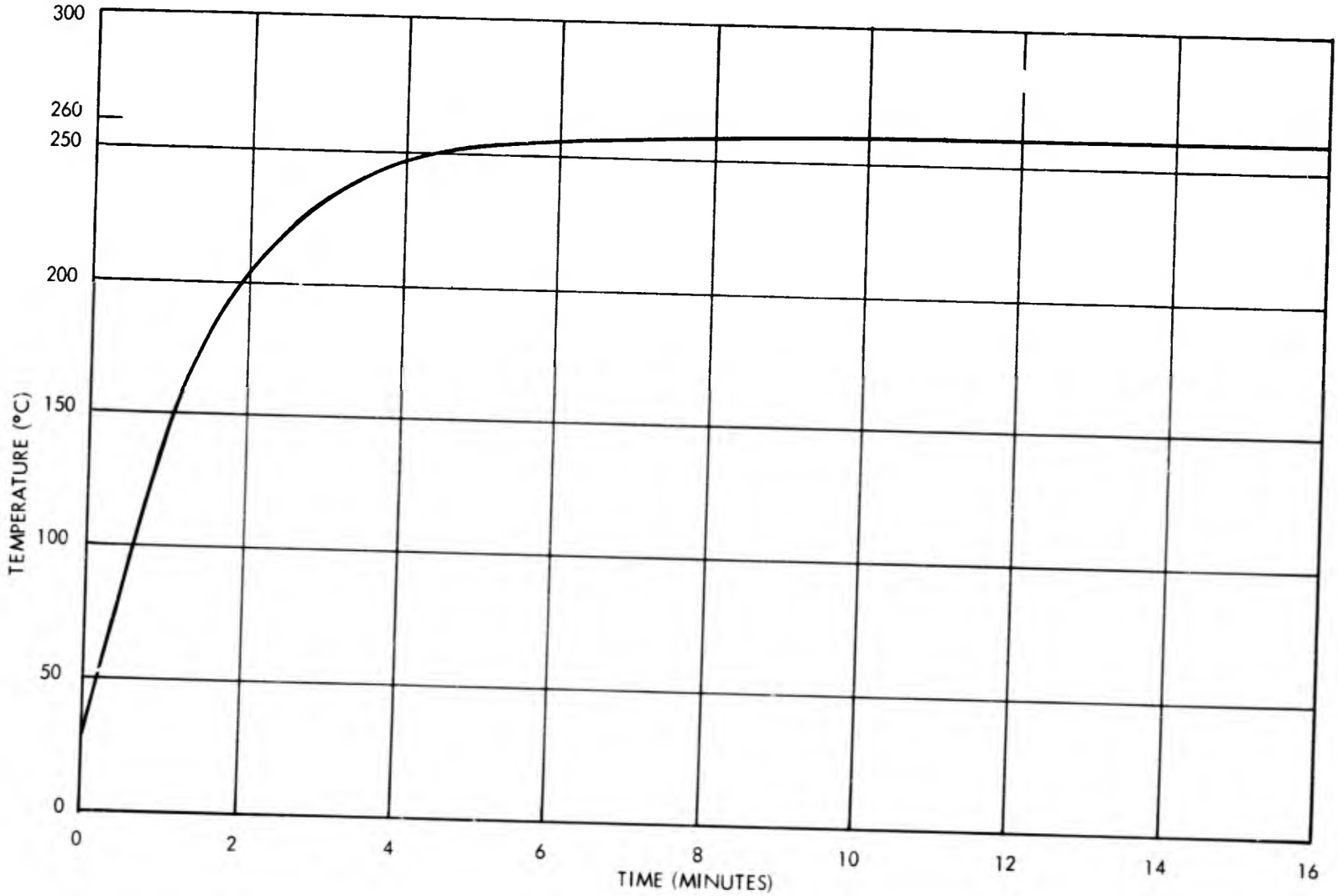


FIG. 3 INITIAL TEMPERATURE RISE OF DIPAM
(THERMOCOUPLE EMBEDDED IN 0.2g SAMPLE)

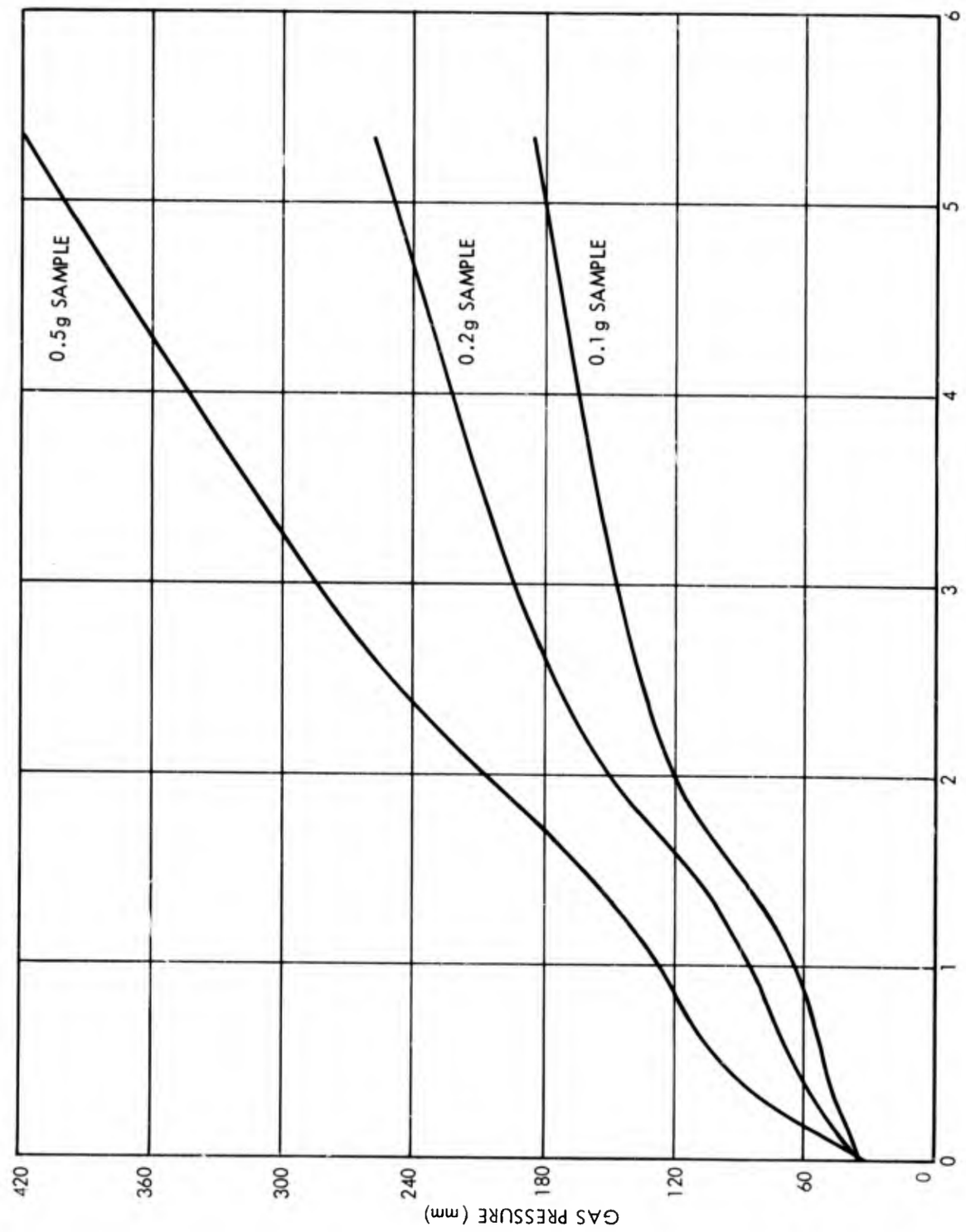


FIG. 4 DIPAM VACUUM STABILITY AT 260° C, 10 ML SAMPLE TUBES