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Ti/PETN Accident Investigation

Final Report

D. Ingersoll, W. J. Andrzejewski, D. E. Mitchell, J. E. Dotts

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Ti/PETN ACCIDENT INVESTIGATION

FINAL REPORT*

D. Ingersoll and W. J. Andrzejewski
Explosive Subsystems

D. E. Mitchell
Detonating Components Division

J. E. Dotts
Safety Engineering Division I

Sandia National Laboratories
Albuquerque, NM 87185-5800

ABSTRACT

During a routine mixing operation, a 1:1 mixture of titanium and pentaerythritol tetranitrate (PETN) powders accidentally ignited. This prompted an investigation into the cause of the accident. Friction, impact, thermal, and electrostatic stimuli, as well as incompatibility between the powders, were evaluated for their potential to serve as the ignition mechanism. Although a definitive determination of the mechanism was not made, the operation that is believed to have imparted the requisite energy to cause ignition has been identified. The results of these studies, as well as recommended changes to the mixing operations, are described.

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ACKNOWLEDGMENTS

We gratefully acknowledge the technical contributions made by J. W. Fronabarger of Unidynamics/Phoenix. His work, which was performed under contract, is reported in its entirety in Appendix E. We also acknowledge the contributions made by T. M. Massis who performed some of the DSC and isothermal calorimetry experiments.

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Ti/PETN Accident Investigation

Introduction

On February 22, 1989, a 1:1 by weight mixture of titanium and pentaerythritol tetranitrate (PETN) powders was accidentally ignited during a routine mixing procedure. The ensuing explosion resulted in personnel injury and minor property damage.

The titanium metal powder involved in the incident had a nominal particle size of approximately 2 μm, and a surface area of 6450 $cm^2\ gm^{-1}$. The PETN is designated RR5K, and has a nominal surface area of 5000 $cm^2\ gm^{-1}$. Both materials have been safely used in many other studies. In these other studies, the titanium and PETN powders have been used alone, and in mixtures with many other materials. (At least to our knowledge, prior to the accident, these materials had not been used together.)

Five potential ignition sources were studied in this work. These were: (1) friction; (2) impact; (3) thermal; (4) electrostatic discharge (ESD); and (5) chemical incompatibility. The results of these studies indicated that a compatibility problem did not exist, since mixtures of these materials could be prepared and stored for prolonged periods without evidence of degradation. In addition, the mixture was not unduly sensitive to friction, thermal, or impact stimuli. In the case of an electrostatic discharge, the powder was found to be extremely sensitive. However, on the basis of a series of experiments designed to evaluate the characteristics of the decomposition process, and in comparison to the actual incident, the likelihood of the operator being the source of the ESD is virtually nonexistent. Although another possible source of the ESD was identified, it was not possible to experimentally evaluate this process.

In addition to these studies, a cursory evaluation of the effect of the state of the powder, i.e., whether the powder was wet or dry, on the ignition characteristics was performed. These studies indicated that the powder was more sensitive when dry.

For a variety of reasons, including being able to reproduce the ignition of the powder mixture under conditions similar to the accident in only a few isolated instances, a definitive identification of the exact ignition mechanism was not made. However, that step in the mixing process which we feel did impart the requisite energy was identified. This operation is the breaking of the small glass capillary tube which is used to mix the powder, while it is still immersed in the powder mixture.

In order to prevent a future recurrence of this incident, we have recommended that this step be performed only after the capillary tube has been completely removed from the sample container. We further recommend that the sample container not be held by the operator during this process.

After reviewing the procedures being utilized, we have identified another area of concern, although this is not believed to have contributed to the accidental ignition. This other area focuses on the possibility of a true, chemical incompatibility between the constituents of the various mixtures that are, or will be, tested. In this event, the amount of materials normally mixed might pose an undue risk. Consequently, we have recommended that an initial compatibility screening of all new mixtures using minimal amounts of material be performed.

With these changes, we feel that the processes under consideration can be performed safely. What follows is a brief summary of the accident, a description of the work performed to determine the ignition mechanism, the results of these studies, and the proposed changes to the Safe Operating Procedures (SOPs).

Accident Description

Two hundred milligrams of PETN and 200 mg of titanium metal powder were mixed in a 10 mm diameter by 75 mm long glass test tube using a 1.5-1.8 mm diameter by 90 mm long capillary tube. After mixing, the top portion of the capillary tube was broken off while the mixing end of the capillary tube was still in the test tube containing the powder sample. This was done by partially withdrawing the capillary tube from the test tube, and placing that portion of the capillary tube which emerged from the test tube on the lip of the test tube. The end of the capillary tube that was still in the test tube was positioned on the opposite wall of the test tube. The end of the capillary tube that emerges from the test tube was then firmly grasped by the operator and snapped off. Ignition of the mixture occurred when the capillary tube was broken. A witness to the incident has stated that she distinctly heard the glass capillary tube break just prior to the explosion.

A more complete description of the incident can be found in Appendices A and B.

Accident Investigation Team And Activities

An Accident Investigation Team was formed to investigate the incident and to identify the cause of the accidental ignition. This team was composed of:

D. E. Mitchell, Team Chairman, Organization 2513
W. J. Andrzejewski, Organization 2512
D. Ingersoll, Organization 2512
J. E. Dotts, Organization 3215

The committee performed the following activities:

1. Documentation review.
2. Interview of personnel and walk-through of the accident scenario.
3. Experimental investigations.
4. Evaluate information and prepare recommendations.

The details and results of these activities are described in the remainder of this document.

Documentation Review, Personnel Review, and Walk-Through

A review of the SOPs (Appendix C) and other documentation, together with interviews of T. M. Massis, L. Maestas (the principals involved in the accident), P. J. Rodacy, and D. Ingersoll (the first to arrive at the accident scene and the first to render assistance) and the walk-through, showed that the operating procedures in effect were being followed, as required.

Appendix 1 and Addendum 5 of the SOP in question (Appendix C of this report) enumerate the relevant procedural guidelines for performing aging and compatibility experiments [1]. The explosive quantity limit for these operation is set at 500 mg in Sections 2.3 of Appendix 1 and Addendum 5. The amount of explosive, i.e., PETN, involved in the accident was 200 mg, well below the mandated quantity limits [2,3].

A review of the SOP used at Pantex (Appendix D) shows that the Pantex procedure is very similar to the one used at Sandia at the time of the accident. The SOPs used at Sandia have been routinely reviewed, and both sets of SOPs have been in use at both Sandia and Pantex for some time. There has never been any indication that these operations pose any undue risk to either personnel or equipment.

There were no indications of carelessness, or of an attitude that would lead to a dangerous situation.

Experimental Results and Discussion

A series of experiments were designed and performed in order to determine the probable cause of the accident. These experiments included an initial compatibility screening of the mixture, differential scanning calorimetry (DSC) analysis, and a series of qualitative experiments designed to assess the behavior of the separate constituents and the mixture to various stimuli. A quantitative determination of the effect of friction, impact, and electrostatic stimuli were carried out under contract at Crane Unidynamics/Phoenix (UPI) by J. W. Fronabarger. In addition to these experiments, a series of experiments simulating the incident were performed at both Sandia and UPI with mixed results. Also studied at UPI was the effect of various ignition conditions on the decomposition process. A copy of the final report prepared by UPI is included in this report as Appendix E.

Compatibility Studies.

The initial experimental work was designed to determine if there was a true compatibility problem between the titanium and PETN powders, and if this conjectured compatibility problem was the source of the explosion. Varying amounts of the 1:1 mixture, from approximately 10 mg to 2 g, were prepared and stored as loose powders, as well as in glass capillary tubes and test tubes. On the basis of this work, we have determined that the mixture is stable for months in the absence of other ignition sources.

The DSC traces of the PETN, titanium, and the mixture, shown in Figures 1 and 2, and Appendix E, reveal a lowering of the onset temperature and the peak temperature of the exotherm of the mixture, in comparison to PETN. In addition, isothermal calorimetry carried out at temperatures close to 170°C, well above the melting point of PETN, shows an approximately two-fold increase in the rate of PETN decomposition in the mixture [4].

In addition, as pointed out by Fronabarger, there is an increased calorific output from the mixture in comparison to the pure materials. One plausible explanation for the increased calorific output is based on the titanium serving as a heat transfer medium [Appendix E]. Alternatively, a change in the reaction mechanism, as postulated by one reviewer, or a true chemical incompatibility could be the reason for the increased heat output. However, it should be noted that the amount of heat liberated is still significantly less than that which could be theoretically obtained from the amount of PETN present in these experiments.

Taken together, these data suggest that there may be an underlying incompatibility between PETN and/or its thermal decomposition products, and titanium. However, because of the extreme conditions used in these series of experiments and based on the behavior of the mixture under ambient conditions, a true compatibility problem between the constituents can be ruled out as the accidental ignition source. (In this context the term "compatible" refers to the absence of a spontaneous, rapid, exothermic reaction occurring soon after mixing the powder constituents.)

Thermal Initiation Studies.

The effect of a thermal stimulus on the pure materials and mixture depends primarily on the heating rate. For the most part, at low heat rates, such as those used in a DSC experiment, the mixture behaved like PETN, as previously described. That is, as the temperature is slowly increased, the PETN first melts at around 141°C, and then begins to decompose starting at about 193°C, as seen by the DSC traces shown in Figures 1 and 2 and Appendix E. After decomposition of the PETN, the remaining

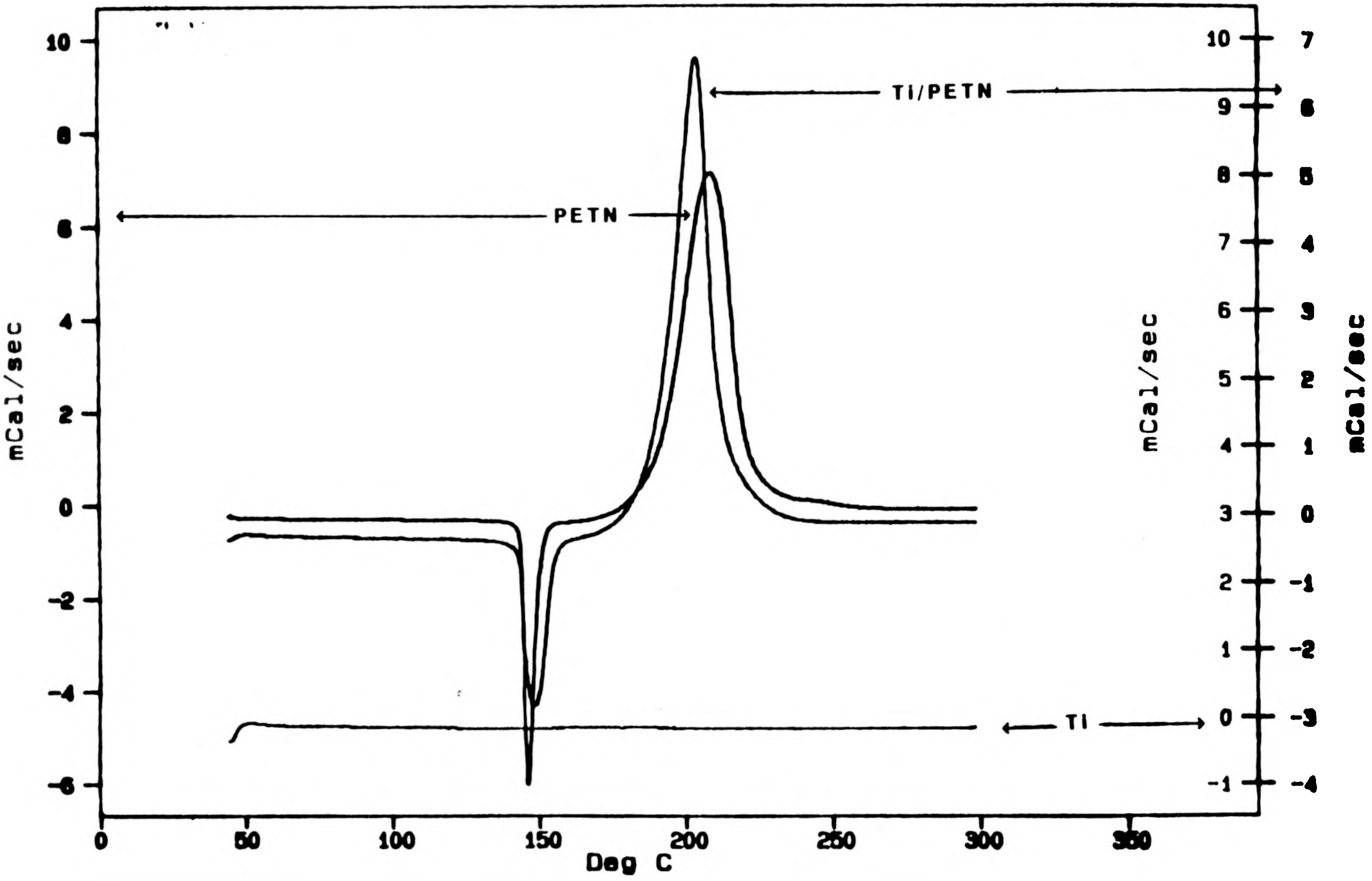

Figure 1. DSC traces of Ti, PETN, and the Ti/PETN mixture. These data were collected using a heating rate of 10C/min.

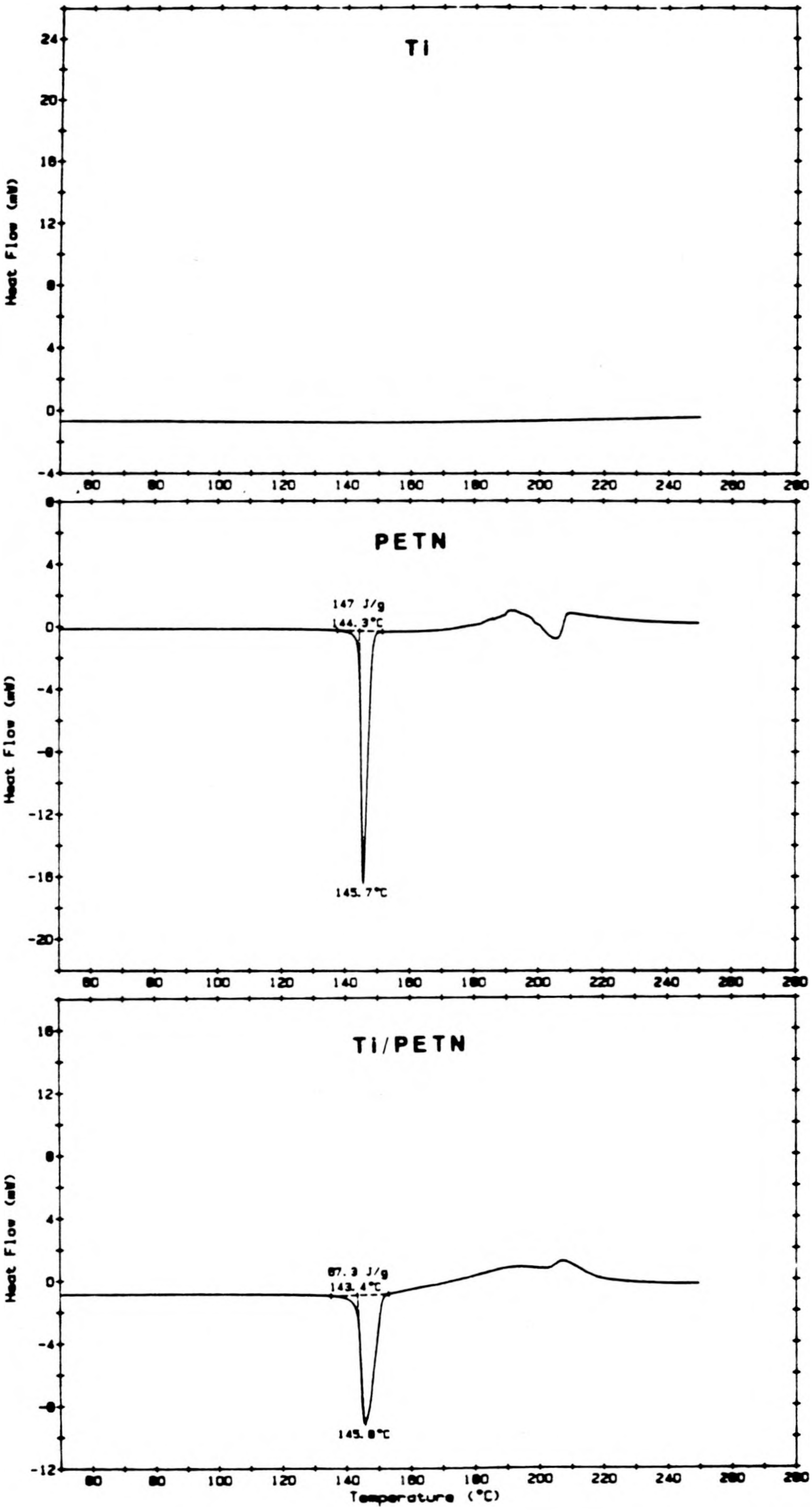

Figure 2. DSC traces of Ti, PETN, and the Ti/PETN mixture. These data were collected using a heating rate of 10C/min in air in open DSC cups.

residue appeared to be unreacted titanium powder, indicating that under these conditions the titanium did not participate to any great extent in the decomposition reaction. Furthermore, although the decomposition process is exothermic, it did not react as fast, or as violently, as when the titanium participates in the reaction. In fact, the decomposition can be described as relatively mild.

The effect of high heating rates on the behavior of the powders was also investigated. Subjecting the mixture to a flame ignition test results in ignition and reaction of the mixture in a fashion similar to, or perhaps somewhat more energetically than, pure titanium . In this case there is a significant amount of gas evolution, as evidenced by the numerous burning titanium particles propelled through the air, and emission of a bright light.

The effect of high heating rates was also studied by dropping a portion of powder onto a surface heated to temperatures between 250-300°C. In this temperature range the pure titanium is unreactive, and after the initial evaporation of adsorbed water, the heated titanium powder sits on the hot surface. Two routes for PETN decomposition under these conditions were observed. If the PETN was dispersed, it would first melt, and then decompose with gas evolution. There was no evidence of explosive decomposition. If the PETN was deposited in a clump on the heated surface, some melting did occur, followed by a rapid exothermic reaction, presumably resulting from heating of the powder past its autoignition temperature. There was occasionally some evidence of explosive decomposition, i.e., an extremely rapid reaction accompanied by a popping noise.

The mixture behaved similarly to PETN under these high heating rate conditions. If the black powder was dispersed on the heated surface, it appeared to first get wet and then evolve gas. The material remaining after gas evolution looked like pure titanium . If the powder was not dispersed but was instead deposited as a clump, a violent exothermic reaction was observed. In this case the PETN was presumably heated to its autoignition temperature, which in turn initiated the reaction between the constituents of the mixture. The resulting exothermic reaction was more violent than that observed in the case of pure PETN.

Finally, a series of tests were performed in order to determine the effect of even higher heating rates on the powder. In this case the three powders, PETN, titanium, and the Ti/PETN mixture, were placed onto an unheated aluminum surface so that each was dispersed into a powder trail having a cross sectional diameter of approximately 1/8" and a length approximately 2". (In this configuration each line of powder looked like a fat string or wire.) One end of the dispersed material was then rapidly heated by touching it with a spatula that had been heated to redness. (The temperature of the spatula is estimated to be approximately 700-800°C.)

Presumably because of the way the powder was dispersed, it was not possible to heat the PETN to its autoignition temperature. What was observed was that wherever the PETN was touched with the hot spatula, it decomposed with some gas evolution. The remainder of the power remained unaffected. In the case of titanium , the temperature of the hot spatula was sufficient to ignite the titanium powder, and a relatively slow burn of the entire powder trail ensued. In the case of the mixture, ignition resulted in an extremely fast burn of the powder trail with evidence of gas evolution (sparks of reacting material were projected into the air, much in the same way as a pyrotechnic sparkler behaves). In this unconfined configuration, the mixture did not explode. (In this context the term "explode" means a rapid exothermic reaction accompanied by a loud report and emission of light.)

The autoignition temperature of titanium is reported to be 250-600°C [5] depending on its physical state (e.g., fine powder, dust layer, dust cloud, etc.), and is as high as 1200°C for the bulk metal [6]. Based on its color, the temperature of the heated spatula is estimated to be greater than 600°C, as previously mentioned. Consequently, under these conditions it is believed that the titanium metal powder is ignited, and this results in the rapid exothermic reaction of the powder mixture.

As a result of these studies, it is apparent that the powder mixture is no more sensitive to thermal initiation than either of the components. It is also apparent that in order to thermally initiate the powder mixture, thermal conditions necessary to initiate either of the constituents must be attained. We believe that heating the powder mixture to initiate the decomposition process could not have occurred under the conditions of the accident, since no heat source of the requisite magnitude exists in the mixing process. Consequently, thermal initiation of the powder mixture leading to explosive decomposition seems unlikely.

Friction Initiation Studies.

The friction sensitivity tests that were performed at UPI shows that the mixture is not unduly friction sensitive. The largest weight used on the BAM Friction Tester for these studies was 1 kg, and no ignition of the powder mixture occurred [Appendix E].

In addition to these quantitative experiments, a series of qualitative studies were performed which also indicate that the powder is not unduly friction sensitive. In this case a small sample of the powder mixture was placed onto a glass plate, and capillary tubes were ground into, and almost always broken off in, the powder. In no case did the powder ignite. A metal spatula was then used to break the capillary tubes and forcefully grind the powder and glass shards together. This was done by sandwiching the powder and glass shards between the supporting glass plate and the flat side of the spatula, and then rotating and pulling the spatula while applying enough down force to scratch the surface of the supporting glass plate. The powder did not ignite.

On the basis of this work, it is felt that the frictional energy generated during the breaking of the glass capillary was insufficient to have led to the accidental ignition of the powder mixture.

Impact Initiation Studies.

The studies performed at UPI demonstrate that the mixture is more sensitive to impact ignition than is PETN. The first initiation of the Ti/PETN powder mix occurs at a height of 35 cm when using a modified 2 kg Bureau of Mines Impact Tester. By way of comparison, the first initiation of PETN occurs when the weight is dropped from a height of 80 cm. Nevertheless, it is felt that the powder mixture is not unduly sensitive to an impact initiation mechanism, and that the energy required for this initiation mechanism could not have been achieved under the conditions of the accident.

Electrostatic Discharge (ESD) Initiation Studies.

In contrast to the other initiation mechanisms studied, it has been determined that the powder mixture is sensitive to an electrostatic discharge (ESD), presumably as a result of the ESD sensitivity of the titanium powder.

It has been demonstrated by UPI that PETN is insensitive to a 25 kV ESD obtained using a UN-326-E ESD tester equipped with a 600 pF capacitor discharged through a 500 Ω series resistor (the classical "standard man" model) using a dull copper point and aluminum electrodes. The powder mixture, on the other hand, can be initiated using a charge voltage of only 1 kV (0.6 mJ), the lowest charge voltage that could be reliably tested. It was also shown that pure titanium can also be occasionally ignited at 1 kV. The minimum energy required for ignition of titanium powder by an electrical spark is 10 mJ for a dust cloud and 0.008 mJ for a dust layer [7]. Consequently, it is expected that initiation of the mixture with this minimal amount of energy is possible.

This amount of electrostatic energy can be easily obtained from the "standard" person. In fact, it has been experimentally demonstrated that the electrostatic charge that can develop on a person is sufficient to ignite the powder mix. This was done by having an individual repeatedly sit down onto a laboratory chair and stand up while holding a metallic rod that terminated in a fine point.. The combination of clothing and chair materials resulted in a buildup of static charge on the investigator. The fine point of the metallic conductor was then slowly moved up to a small pile of the powder mixture which was placed on an electrically grounded aluminum plate. The resulting static discharge was sufficient to ignite the powder, although not in every case.

On the basis of these results, it appears that the most likely initiation mechanism is an electrostatic discharge. Although the most likely source of the ESD in this situation would appear to be that derived from a person, some additional studies were performed that seem to rule out the operator as the source of the ESD.

As described in the UPI final report, 400 mg of the powder mixture was placed into a test tube of the type involved in the accident, and then initiated. Two initiation mechanisms were studied, a thermal initiation mechanism and an exploding bridgewire mechanism. In addition, two different points of ignition of the powder mix were also studied. These locations were just at the top surface of the powder bed, and down at the bottom of the powder bed.

It was observed that if the ignition occurred at the top of the powder bed, regardless of the ignition source, the powder did not explosively decompose. Instead what was observed upon surface ignition was "rapid deflagration with no explosive force." This was evidenced by the fact that in all cases studied, a rapid burn of approximately one second duration and bright plume were observed, and the test tube was intact after ignition. In addition, the loud report often associated with an explosion was absent.

On the other hand, when the point of ignition was at the bottom of the powder bed, a violent explosion and fireball resulted, irrespective of the ignition mechanism. In this case the test tube shattered and a loud report was heard [8].

On the basis of these results then, if the operator had been the source of the ESD, the discharge would presumably have been to the top of the powder bed, and the powder would have deflagrated, and not exploded. UPI also concluded that "the Sandia incident resulted from ignition in the interior of the Ti/PETN blend."

The results of one other set of experiments further demonstrates that the operator was probably not the ESD source. These studies, which successfully recreated the incident, will be described in the following section.

On the basis of the work presented in this section, it is reasonable to conclude that the initiation of the powder mix occurred down in the powder bed. Since we have ruled out the operator as the ignition source, we are forced to consider other possible sources of ESD that might have occurred in the powder bed as the capillary tube is broken.

One such possible source of ESD is found associated with tribolominescence, i.e., the emission of light which occurs as a result of fracturing of crystals. Although it has been demonstrated that an ESD occurs when some materials are cracked or crushed [9-11], it has not been demonstrated that these processes occur in this situation. It is also conceivable that an electrostatic charge could have developed on the glass capillary during mixing, and breaking the glass resulted in a static discharge. Because of the circumstances of the accident and the sensitivity of the Ti/PETN mixture to an ESD, this, or other similar mechanisms, cannot be ruled out as possible ESD ignition sources.

Simulation of Accident.

Numerous attempts to safely reproduce the incident at both Sandia and UPI were successful in only one case. In this one case, a test tube was placed into a boom box so that the lip of the test tube just protruded through a hole in the box. The tube was held in place in the box using a rubber stopper. Approximately 200 mg of the powder mixture was poured into the test tube, and a glass capillary tube inserted into the powder mix with some stirring. A sheet of 3/32" thick aluminum having a hole slightly larger than the capillary tube was fitted over the protruding capillary tube, and rested on the lip of the test tube. The aluminum was held in place by the investigator using a leather gloved hand. The investigator and boom box were electrically grounded with a grounding strap. The aluminum plate was then slowly moved so that the capillary tube was pinched between the lip of the test tube and the aluminum plate, and was canted at an angle which was believed to be comparable to that in the actual accident situation. The aluminum plate was then quickly pushed away from the investigator with enough force to crack the capillary tube. When this occurred, the mixture exploded.

Because the top of the test tube was outside of the boom box and the aluminum sheet was over the open end of the tube, the aluminum sheet was exposed to blast effects. Subsequent examination of the aluminum sheet revealed discoloration and severe damage in a circular pattern corresponding to the position of the aluminum plate over the test tube at the time of explosion. Since we know the original position of the aluminum plate from the location of the small hole for the capillary tube, we can determine that the plate moved approximately 8 mm before the sample exploded. Although we do not know the rate of travel of the aluminum plate, it is clear that there was a slight delay between the breaking of the capillary tube and the explosion. This observation is consistent with the actual incident, i.e., the breaking of the capillary tube was distinctly heard by one witness. This would not have been possible had there not been a slight delay.

It is clear from the results of these studies, as well as from some work described in the next section, that some process associated with the breaking of the capillary tube in the mix imparts the requisite energy to initiate the explosive decomposition. Furthermore, since the experimentalist was electrically grounded with a grounding strap and electrically insulated from the aluminum plate by a leather glove, an ESD from the operator was not responsible for the ignition of the mix in this case. Although it can be argued that there was a charge on the aluminum plate that may have caused the ESD since the plate was not electrically grounded, this possibility seems unlikely since no discharge occurred when the plate was initially placed over the test tube. Since the aluminum plate was flat and smooth, the probability of a discharge occurring from a different part of the aluminum surface to the mixture in preference to its original position(s) is unlikely. Furthermore, even if an ESD from the plate to the powder did occur, one would expect deflagration with no explosive force and not an explosion, as previously discussed.

The other tests attempting to recreate the incident, totaling approximately 16 in number and being performed at both Sandia and UPI, were unsuccessful.

Other Considerations.

It is known that titanium metal powders having a particle size less than 200 mesh are pyrophoric [12]. As described by E. L. Stout [13], tests at the Bureau of Mines have demonstrated spontaneous ignition of dust clouds in air at 330 to 590°C, and dust layers at 380 to 510°C. Stout also reports that spontaneous ignition of fine, oil-covered titanium chips have occurred. Despite the pyrophoric nature of titanium, on the basis of the studies so far described, neither the mixture nor the pure metal powder are pyrophoric under the conditions existing in our laboratories.

In a separate study, Attalla has reported that water is reversibly and rapidly taken up and released by titanium powder [14]. At equilibrium in an atmosphere of 50% relative humidity (RH), the amount of adsorbed water is approximately 0.5% by weight. Attalla also reported that one of a number of titanium samples having a surface area of 6.45 $m^2 g^{-1}$ spontaneously ignited when exposed to atmosphere after being dried for 72 hours in a vacuum oven at 200°C and 1.33 mPa. On the basis of this information, additional ignition studies simulating some aspects of the accident conditions were performed using dried powders.

The powder mixture was dried in a vacuum desicator containing Drierite under a reduced pressure for varying periods of time between 24 and 72 hours. Upon exposure to atmosphere, the sample did not spontaneously self ignite. The dried sample was then transferred to a dry, glass petri dish, and a dry capillary tube was broken in the powder. This was done by grasping one end of the capillary tube in a gloved-hand, and placing the other end of the capillary tube in the powder. Forceps were then used to push down on the capillary tube, causing it to break in the powder. These experiments were similar to those previously described in the section titled Friction Initiation Studies.

Using the dry powder, it was possible to ignite the mixture in this fashion, although not with a high degree of reliability. In the first instance, when a small amount of powder was present and the capillary tube was not completely covered, an incandescent flash of short duration was observed at the broken end of the capillary tube. In the second instance, a significantly larger amount of powder was used which completely covered the capillary tube. Upon breaking the capillary tube, the entire mass of powder ignited and burned rapidly. Since the powder was not confined in this instance, it did not explode.

Comparing these results with those obtained using powder that was not dried, it appears that the dried powder is more sensitive than the undried powder. The state of the powder at the time of the accident is not known. At 2:50 p.m., February 22, 1989, 20 minutes before the accident, the outside RH was 17% and the outside temperature was 57°F, (both readings were made at the Albuquerque International Airport, just a few miles away from the scene of the accident). It is also know, on the basis of Attalla's work, that the titanium powder rapidly equilibrates with the prevailing humidity conditions. However, we do not know the functional relationship between the RH and amount of adsorbed water. Furthermore, we do not know how wet or dry the PETN powder was, or how its condition will effect the condition of the titanium powder. Consequently, we do not know how wet or dry the sample was at the time of the accident, nor whether its condition at the time of the accident contributed to the accidental ignition. Nevertheless, it is conceivable that this may have been a contributing factor to the accident, as described below.

An inert oxide layer is present on titanium surfaces, and it is this protective oxide film which effectively passivates the active underlying metal [15], and insulates the zero valent titanium from the PETN. When the oxide layer is broken, as might happen when the material is mechanically abraded, it is quickly repaired by reaction of the zero valent titanium with either water or oxygen [15]. Consequently, under conditions of high humidity, a significant amount of adsorbed water is present. If this water were uniformly distributed over the titanium surface, it is conceivable that this intervening layer would allow for the immediate reformation of the protective oxide layer. In this case the presence of water on the titanium surface, and the mechanism and rate of reformation of the oxide layer is such that PETN is never in direct contact with the zero valent metal.

Under low humidity conditions when the amount of adsorbed water is low, it is conceivable that PETN may come into direct contact with the underlying metal when the oxide layer is disrupted since there is little if any adsorbed water present, and since the rate of transport of oxygen to the defect site is relatively slow. When the oxide layer is disrupted, PETN may begin to react with the zero valent metal, thereby producing a localized hot spot. This process could then result in propagation of the reaction throughout the powder mixture, ultimately resulting in explosive decomposition of the mixture.

It should be reiterated that this proposed mechanism is purely speculative, and that there are other equally plausible mechanisms that can be proposed which can account for the observed behavior. It should also be reiterated that it has not been conclusively demonstrated that the moisture content of the powder at the time of the incident was a contributing factor to the accident. Nevertheless, we felt it necessary to mention this possibility.

Conclusion

Although the fundamental ignition mechanism has not been determined, on the basis of the experimental work performed, the most probable cause appears to be an ESD. Alternatively, it could be some other unrecognized stimulus, or combination of stimuli, e.g., friction/thermal, friction/impact, thermal/impact, etc. In addition, the state of the powder at the time of the incident, e.g., its moisture content, may be a contributing factor. In any case, since we have neither the capabilities or resources to test all of these possible combination of factors, it is not possible, or practical, to make a definitive statement as to the fundamental cause of the accidental ignition.

It is felt, however, that the breaking of the capillary tube while it is in the test tube did impart the requisite energy through some unidentified mechanism. Consequently, by breaking the capillary tube away from the mixture, any energy that is liberated in this process will not be transferred to the powder, thereby eliminating this process as a possible ignition source. Furthermore, we feel that by performing a preliminary compatibility study on any new mixtures using minimal amounts of material, we can reduce the chance of other accidents that might occur as a result of a true chemical compatibility problem. Also, since the sensitivities of new mixtures of energetic species to various stimuli is generally not known, we feel that these mixtures of unknown sensitivity must be handled as if they were extremely sensitive, i.e., primaries.

Recommendations

On the basis of the foregoing information and considerations, the following changes and additions to the SOPs are recommended when performing aging and compatibility studies.

1. Prior to mixing or blending energetic materials which result in formation of more than 20 mg of a mixture of unknown sensitivity, a preliminary compatibility screening should be done. This can be done in the manner described below.

   Initially limit the amount of energetic materials in the mixture to a maximum of 10 mg each until it has been demonstrated that a true compatibility problem does not exist; i.e., no readily observable spontaneous exothermic reaction of the mixture occurs.

2. Paragraph 4.6, Page 3 of SOP 26500 8806, dated May 1988, reads "new or unknown energetic material shall be handled as a primary explosive until sensitivity tests indicate otherwise." It should be explicitly stated in this paragraph that mixtures in which one or more of the constituents is a primary explosive shall be handled as a primary explosive. In all other cases, appropriate safety precautions must be taken [16].

3. During CRT sample preparation, the capillary tube will not be broken while it is in the sample tube. Furthermore, the tube containing the sample should not be hand held while the capillary tube is being broken. The residual sample adhering to the capillary tube can then be placed back in the test tube.

4. Whenever possible a roll mixer, or other mechanical remote mixer, should be used to blend powders. If possible, the powder mixture in question should be contained in an electrically conductive container that is electrically grounded during this process to reduce the possibility of static charge build-up.

With these modifications, we feel that the laboratory operations involving use of novel mixtures of unknown sensitivity can be performed safely.

Finally, one general comment regarding SOPs is included to emphasize the importance of thorough review. Several ambiguities were noted in our review of the SOP, as described in References 1--3. Although none of these led to the accident, they do point out the need for careful review of the entire document, including addendums and appendices. It is important that during the review process any and all ambiguities or contradictory statements be resolved. In the event of a conflict, e.g., the quantity limit specifications in the main SOP versus those found in an addendum, a clear, concise statement describing the conflict and explicitly stating which procedures or guidelines take precedence must be made.

References

1. In reviewing the SOP, a number of ambiguities were noted, including the basis of classification of novel mixtures composed of materials of known sensitivities.

   Section 4.6 of the main portion of the SOP specifically states that "Any new or unknown energetic material shall be handled as a primary explosive until sensitivity tests indicate otherwise. Quantity, limitation of a primary explosive shall also apply." For these materials, the quantity limit is 200 mg.

   The committee feels that this statement does not apply to the titanium/PETN mixture. Neither PETN nor titanium are new energetic materials, and the materials being used are known. Although some members of the committee do not agree with this literal interpretation of the SOP, based on personnel interviews it is clear that such mixtures were thought to be excluded from these guidelines. Consequently, both the letter and spirit of the operational guidelines are being observed with this interpretation.

   The committee finds that the quantity limits governing the activities in question are set in the appendices and addendums. As stated in Appendix B, the "compatibility" aspects of this mixture were being evaluated using the chemical reactivity test (CRT). Since Appendix 1 of the SOP covers the operations involving the CRT, it can be reasonably concluded that these are the procedures that should be followed. However, the title of the appendix states that this procedure is to be used for "aging" explosives. No mention is made of "compatibility" studies. Addendum 5, on the other hand, describes procedures that will be used for "aging and compatibility" studies. In this case, however, the test vehicle to be utilized is a cold weld pinch off tube, and not a CRT. Consequently, there is some ambiguity regarding which procedure should most appropriately be followed.

   It is the position of this committee that the apparent ambiguity is entirely semantic in nature. It is also our opinion that the terms "aging" and "compatibility", at least in the context of this investigation, are synonymous. We further find that the operations being performed are covered by both of these procedures. Addendum 5 provides the requisite procedural information for sample preparation for compatibility testing, and Appendix 1 describes the CRT procedure. In any case, the quantity limits set by both procedures is the same. Consequently, a quantity limit of 500 mg is found to apply.

   We strongly recommend that these issues be rectified by defining terminology where necessary. We further recommend that a single procedure for sample preparation be written, and that this procedure be referenced in all other relevant documents.

2. Since, some of the novel mixtures of energetic materials prepared will be handled as primary explosives, there will be an apparent conflict between the quantity limits set for primaries in the main SOP, and those set in the appendices and addendums. It is the opinion of this group that a clear, unambiguous statement be made in the main SOP regarding which set of safety procedures take precedence, e.g., the main SOP limits or the appendix limits, while performing an appendix (addendum) task. Furthermore, in the event of an apparent conflict between the guidelines of the main SOP and any appendices or addendums, a clear and concise statement that unambiguously resolves the apparent conflict must be made.

3. In reviewing the main SOP, an apparent conflict for the limits for primary explosives was identified. The relevant sections are 3.6 and 5.1. As stated in Section 5 Precautions, "Do not bring into the laboratories primary explosives . . . in quantities greater than 50 milligrams." Section 3.6 states that "primary explosives may be weighed and tested . . . provided their quantities are less than 200 milligrams." It is recognized that the operation specified in Section 3.6 and 5.1 are different, i.e., bringing materials into the laboratory versus weighing and testing. Nevertheless, clarification of this issue is warranted.

4. T. M. Massis, Sandia National Laboratories, unpublished results.

5. L. Bretherick, Handbook of Reactive Chemical Hazards, 2nd ed. Butterworths, London, 1979, pp. 1156-1159.

6. N. Irving Sax and Richard J. Lewis, Sr., Hazardous Chemicals Desk Reference, Van Nostrand Reinhold Co., NY, 1987, p. 820.

7. Private communication from D. E. Mitchell, Sandia National Laboratories, Albuquerque, NM.

8. Private communication with J. W. Fronabarger.

9. L. M. Sweeting and A. L. Rheingold, J. Am. Chem. Soc., **1987**, *109*, 2652.

10. J. Raloff, Sci. News, **1988**, *134*, 78.

11. Sci. News, **1987**, *131*, 360.

12. L. Bretherick, Handbook of Reactive Chemical Hazards, 3rd ed., Butterworths, London, 1985, pp. 1403-1405.

13. E. L. Stout, Safety Considerations for Handling Plutonium, Uranium, Thorium, the Alkali Metals, Zirconium, Titanium, and Calcium, Los Alamos Scientific Laboratory, LA-2147, 1957.

14. A. Attalla, "Characterization of Titanium Metal Powder by Pulsed NMR." Proceedings of the Fifth Annual DOE Compatibility Meeting Held at the Mound Facility, Miamisburg, Ohio, October 4-6, 1977.

15. Kirk-Othmer Encyclopedia of Chemical Technology, Vol. 23, John Wiley & Sons, NY, 1983, pp. 109-112.

16. In making this recommendation, the committee was attempting to address what it perceived as a serious deficiency in the existing SOP. Namely, classifying energetic materials on the basis of their identity or their newness. We attempted to do this by composing a statement which would address our concerns, and which could be substituted into the existing document in place of the objectionable statement. We were unsuccessful.

    The statements composed by the committee were unacceptable because they were either so restrictive that even routine laboratory operations that are performed every day in chemistry laboratories across the country could not be performed, or they were so loosely worded that many, potentially hazardous materials, were excluded.

    It is not the intent of the committee to impose unreasonable restrictions that would unduly hamper the laboratory operations, nor is it within our charter to give the investigators carte blanche for any and all operations. Consequently, all author(s) and reviewer(s) of an SOP must use their own discretion when addressing this issue.

Appendix A

Unusual Occurrence Report
Sandia National Laboratories

UNUSUAL OCCURRENCE REPORT
SANDIA NATIONAL LABORATORIES

Page 1 of 3

1. UOR Number 89-3
2. Status and Date:

Initial March 1, 1989
Interim ______
Final ______

---

3. **Division or Project:**

Initiating and Pyrotechnic Components Division 2515

Programmatic Office - DP

4. **Facility, System or Equipment:**	5. **Date of Occurrence:**	6. **Time of Occurrence:**
Bldg. 807/Room 3041	2/22/89	3:10 p.m.

7. **Subject of Occurrence:**

An explosion of an explosive compatibility sample.

8. **Apparent Cause:** **Design** ______ **Material** ______ **Personnel** ______

Procedure ______ **Other** X **(Explain in Item 14.)**

9. **Description of Occurrence:**

While preparing a mixture of the materials, titanium metal powder and the explosive PETN, for an evaluation of their compatibility with each other, the sample "exploded" during the final stages of this preparation. The sample (total weight = 400 milligrams) had been completely mixed and the last stage (breaking of a long glass tube to shorten its length) prior to sealing was taking place when the sample exploded in the employee's left hand.

The employee's left palm suffered severe injury. In the immediate area below the ring finger, a severe laceration exposing the underlying muscular tissue occurred, it was about one inch in diameter. The palm area below the index finger and thumb had a contusion over one inch in diameter. The inside index finger at the palm had a contusion approximately one-half inch in diameter. The inside small finger at the rear of the palm had a small contusion plus numerous shallow cuts in the skin in back of the finger tip area. There were other shallow cuts on each of the fingers from the flying glass.

The employee and his assistant had extensive ringing in their ears from the report of the explosion. There were no other immediate observable injuries.

No damage to the facilities occurred.

UOR No. 89-3
UOR Date ______

---

0. Operating Conditions of Facility at Time of Occurrence:

The facility is an explosives chemistry lab. Conditions were normal for this type of chemistry lab. The accident occurred while holding the sample between a sink and special bench. There were no obstructions or other unusual conditions on the floor or in the immediate area.

---

1. Immediate Evaluation:

During the breaking of the glass melting point tube, the sample ignited. A sensitization of the mixture by the individual materials may have occurred. Ignition could have been the result of friction or static electricity during this last procedural step (breaking of the melting point tube). No damage to the facilities occurred.

The only short-term effect will be during the evaluation by the accident investigation team which will temporarily delay further studies for compatibility of this system. This was to be a long-term study and will have no effect on the system or program.

---

2. Immediate Action Taken and Results:

The employee looked at his left hand, knew it was seriously injured, and had his assistant call the emergency phone number. The assistant sat the injured employee in a chair. Help from two other employees was immediate as they heard the explosion next door. One gave the injured employee paper towels so he could minimize loss of blood. The other went for supervisory assistance. This all took place in less than two minutes. Security and medical help arrived in less than 5 minutes and the employee was transported to Sandia Medical for further assistance.

---

3. Is Further Evaluation Required?:

Yes X No ______
If Yes, Before Further Operation: Yes ______ No X
If Yes, By Whom? Accident evaluation team headed by D. E. Mitchell, Supervisor Org. 2513.
When? To be determined.

---

4. Final Evaluation and Lessons Learned:

An accident investigation team has been formed and will provide a final evaluation and recommendations.

---

5. Corrective Action:

To be determined.

Taken: ______
Recommended: ______
To Be Supplied: X

---

16. **Programmatic Impact:**

None or Minimal. A slower approach to this compatibility question will be taken.

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17. **Impact Codes and Standards:**

None

---

18. **Similar Unusual Occurrence Report Numbers:**

None

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19. **Signatures:**

Originator Thomas M. Massis, 2515 **Date** 2-28-89
Thomas M. Massis, Member Technical Staff

Approved by: P. D. Wilcox / [illegible], 2515 **Date** 2/28/89
Paul D. Wilcox, Supr., Initiating & Pyrotechnic Components Div.

Approved by: David H. Anderson, 2510 **Date** 2/28/89
David H. Anderson, Mgr., Explosive Components Dept.

Approved by: W D Burnett Date 3/1/89
W. D. Burnett, Mgr., Health & Safety Dept., 3210

Appendix B

Memo--Accident on February 22, 1989

Sandia National Laboratories

Albuquerque, New Mexico 87185

date: March 13, 1989

to: P. D. Wilcox, 2515

Thomas M Massis

from: T. M. Massis, 2515

subject: Accident on February 22, 1989

BACKGROUND

A request was made by D. E. Hoke, 2513, about the compatibility of PETN and titanium. Titanium alloys are being considered for a detonator redesign and this was to be an initial compatibility study between PETN and these materials. Pure titanium was to be used because there were no known compatibility data between PETN and titanium plus the actual titanium alloys to be considered for the redesign had not been chosen. These data would provide baseline information on the compatibility between PETN and pure titanium to compare future data against in case compatibility problems with various titanium alloys were encountered.

The Chemical Reactivity Test (CRT) procedure was to be used for the compatibility study. The CRT procedure is our main screening test for compatibility. This test is done using mixed powdered materials at moderately elevated temperatures for short time periods. The use of powders provides a great deal of surface contact between the materials in question, which in turn results in measurable quantities of gas being evolved if reactions take place. For this test, a standard 48 hour aging period at 100°C was to be used. The samples are first mixed in a glass test tube and placed in a valved stainless steel CRT aging fixture. The stainless steel CRT fixture is then evacuated, backfilled with helium, the valves closed and aged. Following aging, the evolved gaseous contents in the stainless steel CRT fixture are analyzed by gas chromatography.

ACCIDENT EVENTS

After lunch on February 22, 1989, Lori Maestas and I started to assemble the necessary compatibility samples for the PETN and titanium study. The total assembly operation was done in room 3041. The titanium to be used was a standard 2 micron material purchased from Ventron in the middle 1970's (Ventron Lot J-4705). Lot J-4705 was used extensively during the development of the pyrotechnic $Ti/KClO_4$ and the MC3004 actuator. The PETN used was detonator grade RR5K powder.

Two-200 milligram samples of PETN followed by two separate 200 milligram samples of titanium were initially weighed into individual glass test tubes for use as baseline CRT samples. Lori did the weighings while I assembled the individual samples in the stainless steel CRT apparatus and started the evacuation/ backfill procedure. The evacuation/backfill procedure is used to eliminate air from the internal CRT volume and to backfill it with helium. This was done on the gas chromatograph also located in room 3041.

For the mixtures, Lori weighed 200 milligrams of PETN, then 200 milligrams of titanium into the same test tube. Duplicate samples were made. By the time this occurred, the PETN CRT assemblies had been evacuated, backfilled and taken over to room 3003 for placement in the thermal aging oil bath. While the first sample of titanium was being evacuated and backfilled, I started mixing the first PETN/titanium sample.

This entailed physically mixing the sample in the test tube using a small melting point tube that is sealed on one end. The test tube is held by the lip with my left hand and mixed with the melting point tube with my right hand. The sample is mixed by this procedure until the sample appears homogeneous to the eye. It took between 5 and 10 minutes to mix it properly due to the low bulk density and "fluffiness" of the PETN. During this time period, I set the sample down a number of times to go to the gas chromatograph and continue the evacuation/backfill procedure for the titanium CRT sample. I probably set the PETN/titanium test tube on the wood top bench around the corner from the balance or in the hood so I could do the evacuation/backfill procedure on the first titanium sample since two hands are needed.

After the sample appeared to be mixed, I went over to Lori to show her how homogeneous it looked. She had just completed the weighing of the materials for the second sample and was preparing to get another melting point tube to mix it when I showed her how well mixed the first sample looked. Lori then got up from the chair with the second sample in her hand along with a melting point tube. The melting point tube was not in the sample. She was walking toward the surface area analyzer and making a turn to go down that aisle.

I turned away from Lori and was facing the corner sink. At this point in the sample preparation, the melting point tube is too long for the CRT apparatus and must be broken. One then leaves the remaining piece in the test tube. The breaking operation is done by raising the melting point tube in the test tube, holding it against the test tube wall with the left hand index finger and breaking it off with the right hand. As I broke the melting point tube, the sample exploded into my hand. The time was 3:10 p.m. not the 2:50 p.m. initially thought. Note that Lori remembers hearing the melting point tube break (it has a distinct sound when broken) and a split second later hearing the explosion. From the corner of her eye, Lori also saw a flash of light and smoke as the sample exploded. I only heard the explosion.

I turned my hand over and it looked bad; blood was already coming out and I could see flesh hanging. I immediately told Lori to call the doctor. Both my ears and Lori's were ringing intensely from the report of the explosion. Lori went to my phone and while holding the unmixed sample in her left hand called the emergency 144 number. While on the phone she told me to sit down and not move until emergency help came. Please note the importance of the sticker on the the telephone with the emergency numbers. She did not have to look it up.

Dave Ingersoll and Phil Rodacy, who were working next door, heard the explosion and came over immediately. Dave got me some Kim Wipes to hold in my hand while Phil went to find supervision. Jere Harlan was available and came to the lab with Phil. Dave was handed the still unmixed sample from Lori and placed it in a red ammo can on the static free bench. This all happened within two minutes from the time of the explosion. Within five minutes a team of three security inspectors arrived. I had calmed down considerably from initial excitement of the explosion and the intense ringing in my ears had decreased considerably. I felt I could walk to the arriving ambulance which I did. Lori and I walked to the elevator with the security inspectors and rode down to the ambulance at the dock area with the medical team who were in the elevator. Again within five minutes from the time of the explosion.

We were taken to Sandia medical where my injuries were examined, X-ray'd, washed and initially dressed. Paul Wilcox took me to Presbyterian Hospital where I was admitted through the emergency room, examined by a plastic surgeon (Dr. R. C. Gobeille) and taken to surgery. I was in the hospital until 8:00 p.m. the next day, released and returned to work on Friday, February 24, 1989 for a couple of hours.

INJURIES

My ears stopped ringing by 11:00 p.m. on February 22, 1989. Lori's ears continued to ring for at least 24 hours after the explosion.

According to my observations these were my injuries. My left palm area suffered almost all the injury. In the immediate area below my left hand ring finger, a severe laceration exposing the underlying muscular tissue occurred. It was about one inch in diameter. The palm area below index finger and thumb suffered a contusion which was over one inch in diameter. The inside index finger at the palm had a contusion approximately one-half inch in diameter. Both the back side ring finger at the palm and the inside small finger at palm had small contusions. There were also numerous shallow cuts in the skin in back of the finger tip area of the small finger. There were also numerous shallow cuts on each of the other fingers from the flying glass.

There were no cuts or other injuries to my right hand. The only other injuries were found later at the hospital where it was discovered that my chest had twenty one (21) "pepper" marks from the glass that penetrated both my shirt and tee shirt. These broke the skin and left small dried blood spots on my chest. Dr. Gobeille confirmed there was no glass imbedded in these areas on my chest.

Copy to:

2510	D. H. Anderson
2512	J. H. Harlan
2512	W. J. Andrzejewski
2512	D. Ingersoll
2513	D. E. Mitchell
2514	L. L. Bonzon
2515	L. M. Maestas
3315	J. E. Dotts
2515	T. M. Massis
2515	Day File

Appendix C

Safe Operating Procedure for the Physical and Chemical Testing of Explosive Materials in Room 3041 of Building 807

SOP Number 26500 8806

SOP # 26500 8806
Org.: 2515
Supercedes: 00100
00104
00106

SAFE OPERATING PROCEDURE FOR THE PHYSICAL AND CHEMICAL TESTING OF EXPLOSIVE MATERIALS IN ROOM 3041 OF BUILDING 807

MAY 1988

David H Anderson 6/23/88
D. H. Anderson, 2510 Date

J. R. Doyle 6/23/88
J. R. Doyle, 3441 Date

Paul Wilcox 6/23/88
P. D. Wilcox, 2515 Date

J E Dotts 6/23/88
J. E. Dotts, 3441 Date

Thomas M Massis 6-22-88
T. M. Massis, 2515 Date

J G Harlan 6/23/88
J. G. Harlan, 2512 Date

W. Andrzejewski 6-22-88
W. J. Andrzejewski, 2512 Date

I have read, clearly understand, and will follow the safety procedures outlined in the attached SOP, and the attached Addenda to the SOP.

Division 2512

Phil Rodacy 6-22-88
Date

6/22/88
Date

R.G. Jungst 6/22/88
Date

W. Andrzejewski 6/22/88
Date

Date

Date

Division 2515

Thomas M. Massis 6-22-88
Date

6/22/88
Date

J.L. Schlobohm 6/22/88
Date

Date

Date

Date

Date

SAFE OPERATING PROCEDURE FOR THE PHYSICAL AND CHEMICAL TESTING OF EXPLOSIVE MATERIALS IN ROOM 3041 OF BUILDING 807

1. Purpose

1.1 The purpose of this procedure is for the handling of explosive and pyrotechnic materials during physical and chemical testing by Organizations 2512 and 2515 in Room 3041 of Building 807.

2. Scope of Activities

2.1 Laboratory equipment and/or experimental techniques included in this safe operating procedure are: differential thermal analysis (DTA), differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), thermal mechanical analysis (TMA), effluent gas analysis (EGA), pyrolysis, isothermal kinetics gas analysis, calorimetry, chromatography, wet analysis, microscopy, spectroscopy, surface area, particle analysis and other related laboratory experiments or techniques that involve the testing of individual quantities or explosive or pyrotechnic materials of less than one gram. Standard operating procedures as outlined by the respective manuals and techniques shall be followed.

2.2 Individual procedures for experiments and techniques that involve more than one gram of explosive or pyrotechnic material will be written as an addendum to this procedure.

2.3 This procedure shall apply only to Room 3041 of Building 807.

2.4 This SOP will be used by 2512 and 2515 personnel only when explosive or pyrotechnic materials are utilized.

2.5 Personnel from Organizations 2512 and 2515 signing this SOP will not be permitted to operate any of the laboratory equipment or perform experiments until they are completely familiarized with the procedures involved and have been checked out by the individuals responsible for operations in Room 3041 of Building 807.

2.6 Paragraph 2.4 may be waived for other personnel provided the involved organizations and the Safety Department are in agreement and that these personnel are completely familiarized with this procedure.

3. Quantity of Bulk Explosive Materials

3.1 The total amount of explosive or pyrotechnic materials stored in the room shall not exceed 100 grams.

3.2 A readily available inventory of each stored material will be kept for Room 3041.

3.3 The amount of explosive or pyrotechnic stored in any one bottle shall not exceed 20 grams.

3.4 Energetic materials stored in Room 3041 will be limited to: secondary explosives, pyrotechnics, propellants, high energy fuels, and MDF. Explosives being worked on may be left out in the open on the static free bench or hood. Otherwise, they must be stored per 3.7.

3.5 Primary explosives **WILL NOT** be stored in Room 3041.

3.6 Primary explosives may be weighed and tested in Room 3041 provided their quantities are less than 200 milligrams (0.200 grams).

3.7 Secure storage of explosives.

3.7.1 A four-door combination safe and a locked explosive cabinet can be used for the storage of explosives. The total quantity cannot exceed 100 grams.

3.7.2 The four-door combination safe will be used for storage of classified bulk explosives and components only.

3.7.3 No flammable materials are to be stored in either the safe or explosives storage cabinet.

3.7.4 The top and bottom drawer of the safe can be used for storage of 20 grams each of explosive materials and devices (40 grams total storage limit). The middle drawers will be used as buffers with no explosive storage in these two drawers.

3.7.5 All storage of explosives in the safe will be in approved containers (for example ammunition boxes or suitcases). Bulk explosives and components will be stored in separate containers.

3.7.6 The safe shall be labeled accordingly to what drawers may contain explosives.

3.7.7 Both the safe and explosives cabinet will be connected to the room ground line. This will be checked every year for proper grounding.

3.7.8 Storage of explosives in the cabinet will be according to the DOE Explosives Safety Manual in regards to separation of explosive classes. Separation will be on shelves or in approved containers according to explosives classes.

3.7.9 An inventory will be maintained as to the description and quantity of explosives stored in the safe and storage cabinet.

3.7.10 The safe and storage cabinet will be locked during non-operational time periods.

4. Handling Procedure

4.1 Safety glasses will be required during **ALL** operations involving explosives.

4.2 A second person must be in a secure location in the immediate vicinity to give aid and assistance if needed.

4.3 No smoking will be permitted in Room 3041; **NO SMOKING** signs will be posted.

4.4 Grounding straps and conductive equipment will be used whenever possible during explosive and pyrotechnic handling operations.

4.5 Explosive waste shall be disposed of by washing into sawdust or vermiculite filled cans with appropriate solvent.

4.6 Any new or unknown energetic material shall be handled as a primary explosive until sensitivity tests indicate otherwise. Quantity limitation of a primary explosive shall also apply.

4.7 Sample sizes shall be kept to a reasonable and practical minimum and shall not exceed limitation as described in paragraph 3.

4.8 All samples of explosives shall be in a hood or other protective enclosure when heat or other known initiating stimuli are being applied.

4.9 Laboratories shall be kept in a clean and orderly condition.

4.10 Spilled samples of explosives will be cleaned up immediately.

5. Precautions

5.1 Do not bring into the laboratories primary explosives or new materials with unknown sensitivities in quantities greater than 50 milligrams.

5.2 Do not flush waste explosives down drains.

5.3 Do not place explosives on desks.

5.4 Do not store or mix explosives with materials that may cause an accidental incompatible situation to occur. Have the compatibility of unknown materials checked.

5.5 Do not block exits or congest paths to them.

5.6 Know the location, use and operability of safety equipment prior to use of laboratory equipment and experimental techniques.

6. Special Precautions

6.1 When pressurized gas cylinders are used, approved safety relief valves must be installed on gas regulators to relieve the flow of excess gas pressures during failure. Flow restrictors are recommended whenever possible. This precaution must be adhered to so as to prevent an accidental overpressure from causing a hazardous situation on equipment that cannot take cylinder tank pressure. The only time this precaution will be waived is if it can be demonstrated to the Pressure Safety Committee that the apparatus or equipment utilizing pressurized gas can safely withstand tank pressures. Safety relief valves must be approved by the Pressure Safety Committee prior to use.

7. Only individuals reading and understanding the above procedures and addenda will be authorized to handle bulk explosives and test them in the specified areas mentioned above. Signatures acknowledging the above are required and can be found at the beginning of this SOP.

ADDENDUM 1

Safe Operating Procedure for Calorimetric Analysis of Pyrotechnics, Propellants, and Explosive in the PARR Macro Bomb

1. General

   1.1 This procedure is for use in Room 3041 of Building 807.

   1.2 This procedure is to be used in conjunction with all other procedures pertaining to Room 3041 of Building 807.

   1.3 Quantities of explosive material tested at times will exceed one gram during calorimetric analysis.

   1.4 This procedure pertains to the PARR Macro bomb only. The PARR micro bomb CANNOT safely accommodate 1 gram quantities or greater.

   1.5 Samples for the PARR Micro bomb shall not exceed 1,800 calories output.

2. Apparatus Assembly and Analysis for PARR Macro Bomb

   2.1 Accurately weigh into a calorimeter sample cup sufficient sample of explosive materials so as not to exceed an estimated 10,000 calories when burned.

   2.2 Attach the ignition wire to the terminals in the head of the calorimeter bomb. The head of the bomb will be grounded with an alligator clip to the approved building ground system prior to the placement of the explosive cup to the ignition wire.

   2.3 Place the sample cup and sample in the retainer ring of the bomb and insert the grounded ignition wire into the sample.

   2.4 With the grounding wire still attached, insert the head into the bomb cylinder, secure the screw cap, and tighten the overpressure screws into the bomb head.

   2.5 Attach the calorimeter bomb to the gas cylinder, (oxygen, nitrogen, or inert gas, depending upon the test) fill the bomb with 30 atmospheres of gas, purge three times leaving bomb filled with gas on the third purge.

2.6 With the key interlock ignition system in OFF position and the key removed, disassemble the grounding wire from the bomb and immerse the bomb into the calorimeter bucket previously filled with 2,000 grams of H_2O.

2.7 Attach the ignition leads to the terminals in the calorimeter bomb head and close the cover over the bucket and jacket.

2.8 Insert the temperature measuring system into the water jacket, turn on the stirrer motor, and record the temperature of the water jacket until equilibrium has been reached.

2.9 Turn on the key interlock system and fire the ignition wire in the bomb. After ten seconds, turn key to the OFF position and remove the key.

2.10 If ignition occurs, observe the temperature rise until temperature equilibrium; turn off the stirrer; remove the temperature measuring apparatus; open cover; remove the bomb and clean the bomb on inert residues.

2.11 If ignition does not occur, wait five minutes, turn off stirrer; remove temperature measuring apparatus; open cover, remove the bomb and attach the grounding wire to the head. Disassemble the bomb and discard the explosive residue as outlined in 4.5.

ADDENDUM 2

Safe Operating Procedures for the Surface Area Measurements of High Explosives in Building 807, Room 3041

1. General

1.1 This procedure is to be used in conjunction with all other procedures pertaining to Room 3041 of Building 807.

1.2 Quantities of explosive materials in most cases will exceed one gram during surface area measurements.

2. Testing Procedures

2.1 Gas adsorption surface area will be done by the Digisorb Surface Area Analyzer.

2.2 Sample preparation

2.2.1 Digisorb analyzer. Accurately weigh 0.1 to 15.0 grams explosive material (depending upon expected surface area) into a tube being careful to observe high explosive loading precautions.

2.3 Degassing analysis tubes

2.3.1 Digisorb analyzer. Heat analysis tube on degas side of apparatus to desired temperature until outgassing pressure is less than 0.5 microns per minute. Maximum temperature is 100°C for explosives.

2.3.2 Cool to room temperature, remove and reweigh tubes.

2.4 Assembly of surface area tubes to apparatus

2.4.1 Digisorb analyzer. Attach the tube to the manifold by use of swagelock fittings and "O" rings. Assemble to finger-tightness. Do not tighten with wrench.

2.5 Follow procedures for automatic operation as outlined in the Digisorb manual until analysis is completed. Remove and discard.

ADDENDUM 3

Safe Operating Procedures for the Determination of Properties of Barium Styphnate in Building 807, Rooms 3041 and 3053

1. General

   1.1 This procedure is for use in Rooms 3041 and 3053 of Building 807.

   1.2 This procedure is to be used in conjunction with all other procedures pertaining to Rooms 3041 and 3053 of Building 807.

   1.3 Quantities of barium styphnate in Room 3041 will not exceed 200 milligrams (0.2 grams) at any one time.

   1.4 Additional quantities of barium styphnate to be tested will be stored in Room 3003 of Building 807 and brought to Room 3041 as needed in a red ammo can (not to exceed the 200 milligram limit).

   1.5 Only storage and removal of appropriate samples will be conducted in Room 3003.

   1.6 Barium styphnate will be stored in a separate cubicle of the hood in Room 3003 with NO other explosives.

   1.7 Excess quantities of barium styphnate will be disposed of in a one gallon paint can with vermiculite and water. No more than 2.0 grams of barium styphnate will be disposed of in each paint can. The paint can with waste barium styphnate will then be shipped and sent to the SNLA igloo area for destruction.

2. Testing Procedures

   2.1 The following types of barium styphnate are to be tested.

      Bulk barium styphnate
      Free standing barium styphnate pellets
       (0.1 - 0.12 grams each)
      Free standing barium styphnate pellets
       (0.2 grams each)
      Ceramic chargeholders loaded with barium styphnate
       (0.1 gram maximum)

2.2 The following are the barium styphnate properties to be determined with appropriate procedures in Room 3041.

Caloric Output - Parr Bomb Calorimeter
Thermal Conductivity - DSC Procedure
Heat Capacity - DSC Procedure
Expansion Coefficient - TMA Procedure
Powder/Chargeholder Decoupling Characteristics - TMS Procedure
Thermal Decomposition Profiles and Kinetics - DSC and TG Procedures
Microscopy

2.3 Standard operating procedures for each property measurement as used by Organization 2515 or described in respective instrument manuals will be followed.

2.4 Barium styphnate samples sub-divided in Room 3003 for use in Room 3041 will be performed by the operator who is attached to an appropriate wrist band/grounding system.

2.5 Barium styphnate samples for use in Room 3041 will be transported from Room 3003 in a red ammo can.

2.6 All barium styphnate handling and assembly operations in Room 3041 will be performed by an operator wearing a wrist band which is attached to an approved grounding system. This wrist band/grounding system will be worn until the samples are placed in the appropriate instrument for testing.

2.7 The wrist band/grounding system will be worn during all weighing operations involving barium styphnate.

2.8 The wrist band/grounding system will be worn during all disassembly and disposal operations where residual barium styphnate remains. Exceptions are successful calorimetric, DSC and TG analyses, where a barium styphnate is reacted or decomposed.

ADDENDUM 4

Safe Operating Procedures for Gas Analysis of Explosive Components in Building 807, Rooms 3041, 3051, and 3053

1. Purpose

The purpose of this procedure is to describe a piercing device and the operations necessary to collect and analyze decomposition gases from sealed explosive components.

2. General

2.1 The operations described below can represent an abnormal safety hazard.

2.2 This procedure will be used in conjunction with all other safe operating procedures for Rooms 3051, 3041, and 3053.

2.3 The quantities of explosive material analyzed using this procedure may not exceed 200 mgs.

2.4 Explosive means secondary explosives and pyrotechnic material.

3. Description of Sample Piercing Device

3.1 The sampling device consists of a bellows sealed valve which has been modified to contain an explosive component. The modifications include heavy wall construction throughout (except metal bellows) and teflon seals to permit evacuation of the internal volume. A carbide piercing tip has been added to the valve stem so that upon closure of the valve the carbide tip pierces the closure disk of the component. The valve is opened, and decomposition gases are allowed to expand into the internal volume of the piercing device. Helium carrier gas will be used to sweep the internal volume of the device and transfer decomposition gases to a liquid nitrogen trap.

3.2 Refer to Appendix A for the containment test of a similar detonator piercing device.

4. Operation of Sample Piercing Device

4.1 This procedure assumes the unloaded device is connected to a vacuum manifold and GC carrier gas flow. A liquid nitrogen flow trap is also installed on the carrier gas line.

4.2 The device is electrically grounded by conduction through 1/8" ss tubing (carrier gas flow lines) to the mainframe of the GC.

4.3 With the piercing device in the full open position, load a component into the device. Seal the piercing device using the capping nut.

4.4 Evacuate the piercing device by opening the rough vacuum valve, then backfill with helium. Do this a total of four times.

4.5 Close the vacuum valve, and divert the helium carrier gas to the piercing device using the gas sampling valve.

4.6 Place a lexan shield between the operator and the piercing device as an additional safety precaution.

4.7 Manually actuate the piercing device valve and return the valve to full open position. Allow the carrier gas to sweep the decomposition gases into the liquid nitrogen trap.

4.8 After a suitable time has elapsed, remove the liquid nitrogen and rapidly heat the trap using a heat gun.

4.9 Continue gas analysis using standard GC techniques.

5. Disassembly of Piercing Device

5.1 Remove helium carrier flow from piercing device.

5.2 Loosen capping nut and remove component.

APPENDIX A

CONTAINMENT TEST OF DETONATOR PIERCING DEVICE

A piercing device, consisting of a modified bellows sealed valve, was tested for the GAMS program by detonating an actual detonator, containing 133 mgs of PETN, in the device.

The test device was loaded with a live detonator and sealed by tightening the capping nut. The valve ports were "shorted" together with 1/8" ss tubing to simulate connection to the GC. The capping nut contained a hole to permit electrical connection to the detonator.

The results of the tests indicate complete containment of the detonator and gases produced. The predicted failure mode of the device was rupture of the ~ .003" thick ss bellows with subsequent gas escape through the leak check ports of the valve. Visual observation of the detonation using remote camera did not reveal any gas jets or motion of the device. After detonation, the device was disassembled for visual inspection. The inspection showed fragmentation of the valve stem and carbide tip with bulging of the ss bellows. The "throat" of the valve body also showed some scarring. A 200 fr/s film of the containment test was also taken.

Due to the results of the above testing, we feel that our modified bellows sealed valve will adequately contain an accidental detonation or burning pressure of the components we will be piercing for gas analysis (e.g., MC3479 and MC3753). The output pressure of the titanium subhydride components we will be analyzing has been calculated and is less than that calculated for the above detonated PETN component.

ADDENDUM 5

Standard Operating Procedure for the Preparation and Analysis of Cold Weld Pinch Off Tubes (POT) for Aging and Compatibility Experiments

1. Purpose

This procedure describes a method for the aging and compatibility of explosive materials with various sealants, encapsulants, and adhesives.

2. General

2.1 The operations described may represent an unknown safety hazard.

2.2 This procedure will be used in conjunction with all other safe operating procedures for Rooms 3051, 3041, and 3053.

2.3 Quantities of explosive material analyzed may not exceed 500 mgs.

3. Sample preparation

3.1 The test material may exist in different physical and chemical forms (i.e., bulk powder, thin wafers, cured, and uncured resins). The explosive material may exist as a bulk powder, pressed wafer, or pellet.

3.2 Sample preparation may take either of two forms depending on the materials being tested. Various amounts of explosive and test material (up to 500 mgs) typically in a 1:1 ratio, will be intimately mixed and then transferred to a pyrex thimble or pressed into a charge holder while behind a protective shield.

3.3 The compatibility mixture or explosive pellets are then placed in a POT, which has one end pinched off, with the tube in a vertical orientation. Inserts may be used to hold the sample and/or decrease the free volume of the POT. The various configurations of a POT are shown in Figure 1 (A, B, and C).

3.4 At this point, the POT is ready for evacuation, backfill, and sealing.

3.5 Place a spacer block on the POT to maintain a constant tube length as shown in Figure 2.

3.6 Ensure that the flat "edge" of the insert (if used) is parallel to the jaws of the pinch off tool by visually checking the alignment of the insert. Place the POT on a suitable gas manifold for evacuation and backfill using a Cajon o-ring fitting.

3.7 Evacuate and/or backfill the POT as required using necessary gas manifold control valves.

3.8 Place the pinch off tool in position on the spacer block and make the final pinch off by actuating the pinch off tool. The POT and spacer block will separate from the manifold at this point. Do not allow the POT to drop to the floor while making the final pinch off.

3.9 Remove the spacer block, and the POT is ready for aging. A vertical orientation should be marked on the tube.

4. Gas analysis

4.1 Remove the POT from the aging oven and allow it to cool to room temperature.

4.2 Carefully lower the POT into the piercing device so as not to damage the cold weld, and seal the device as shown in Figure 3.

4.3 Evacuate or purge the piercing device with the helium carrier gas from the gas chromatograph manifold.

4.4 The gas in the POT is sampled by turning the piercing device valve handle. The turning action drives a pointed valve stem into the cold weld of the POT which ruptures the weld and allows the gas to escape.

4.5 Normal gas chromatographic procedures are followed from this point.

5. Disassembly of POT

5.1 Remove the POT from the piercing device, maintaining a vertical orientation.

5.2 Place the POT in a vise, and using a jeweler's saw, cut through the wall of the aluminum tube (360° around the tube) at the midpoint of the tube.

5.3 The POT is now in two pieces, and the inserts or samples may be removed.

① Pinch off tube
(9mm O.D. x 45mm)

② Insert

③ Charge holder

④ Explosive

⑤ Glass thimble

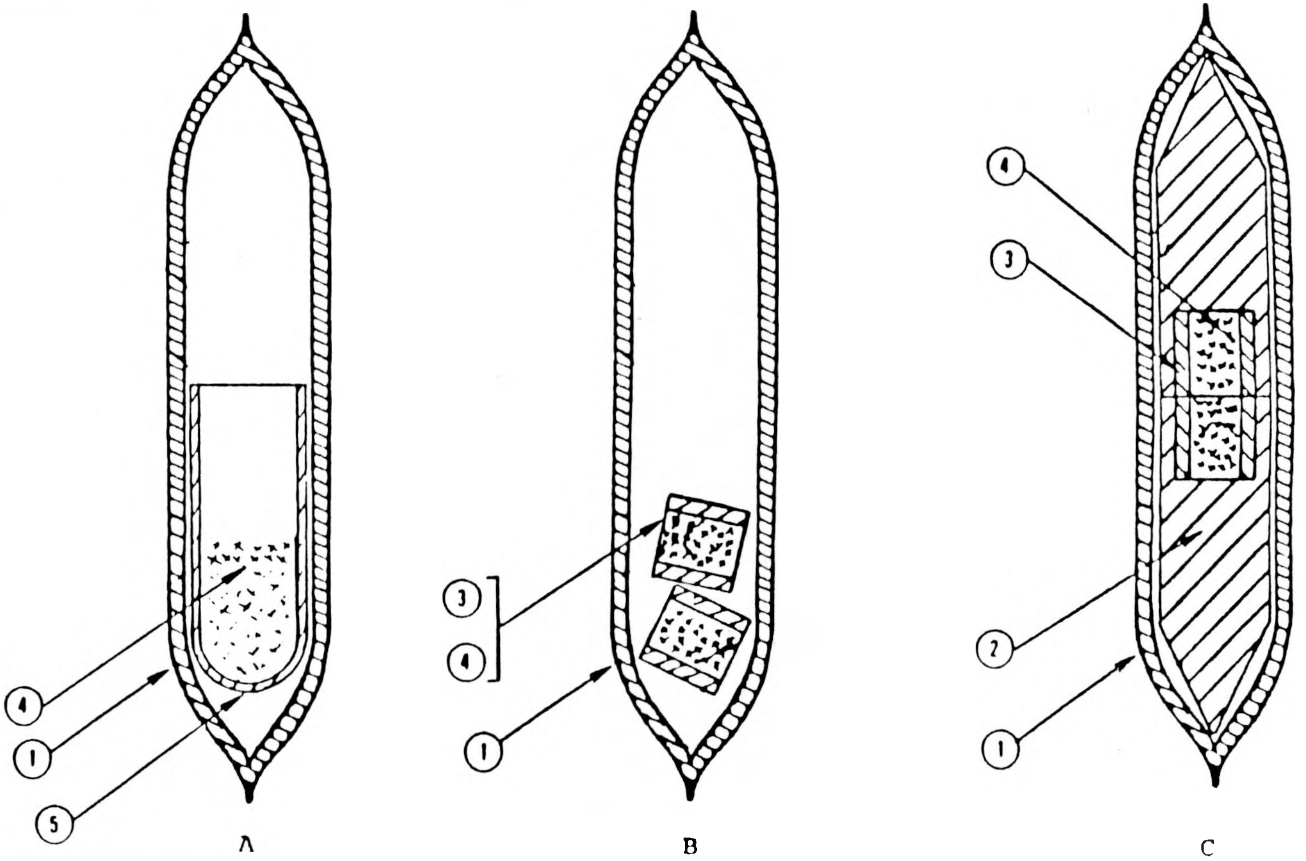

Figure 1. Various sample configurations used for pinch off tube experiments.

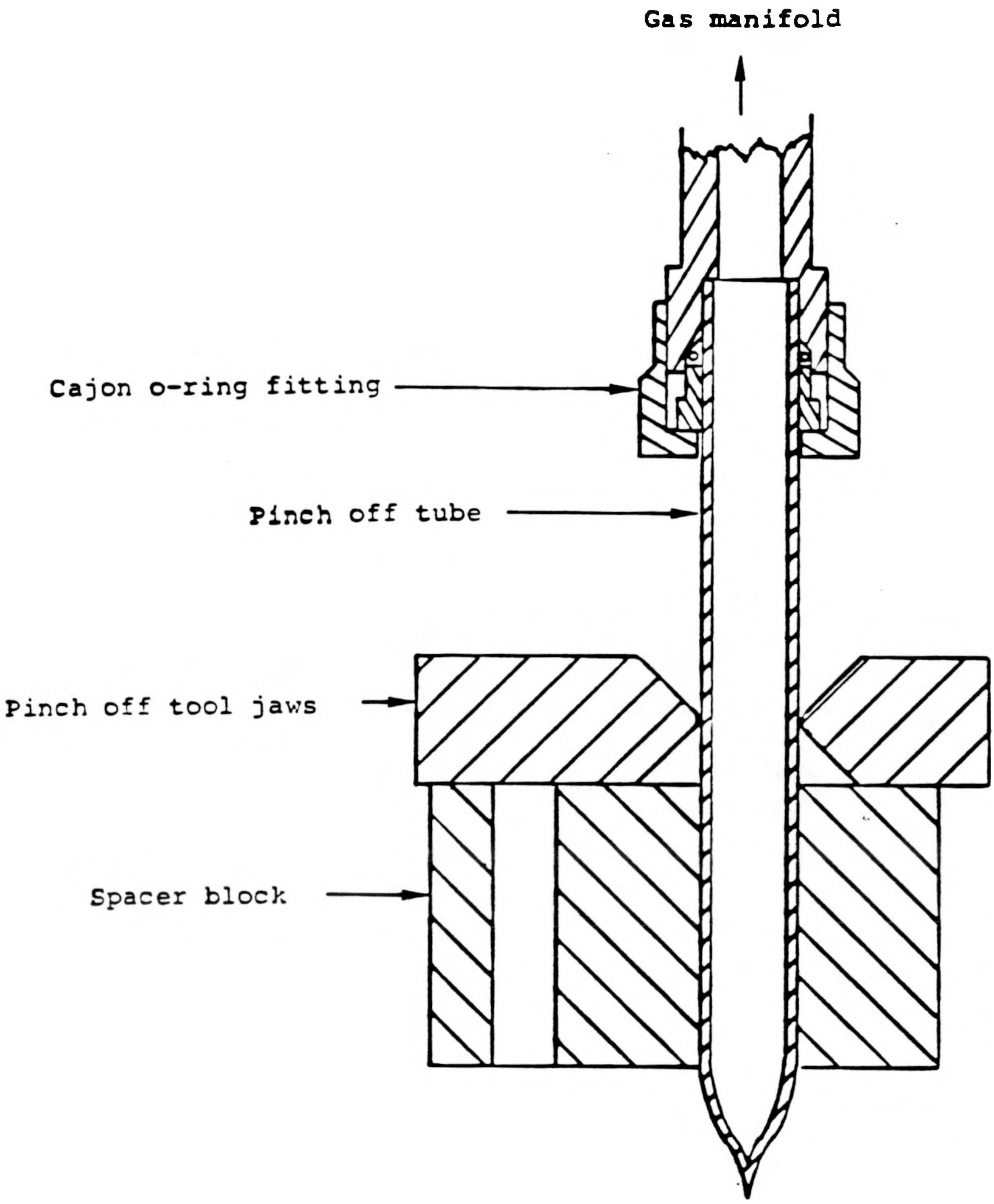

Figure 2. Pinch off tube showing gas manifold connection prior to final pinch off.

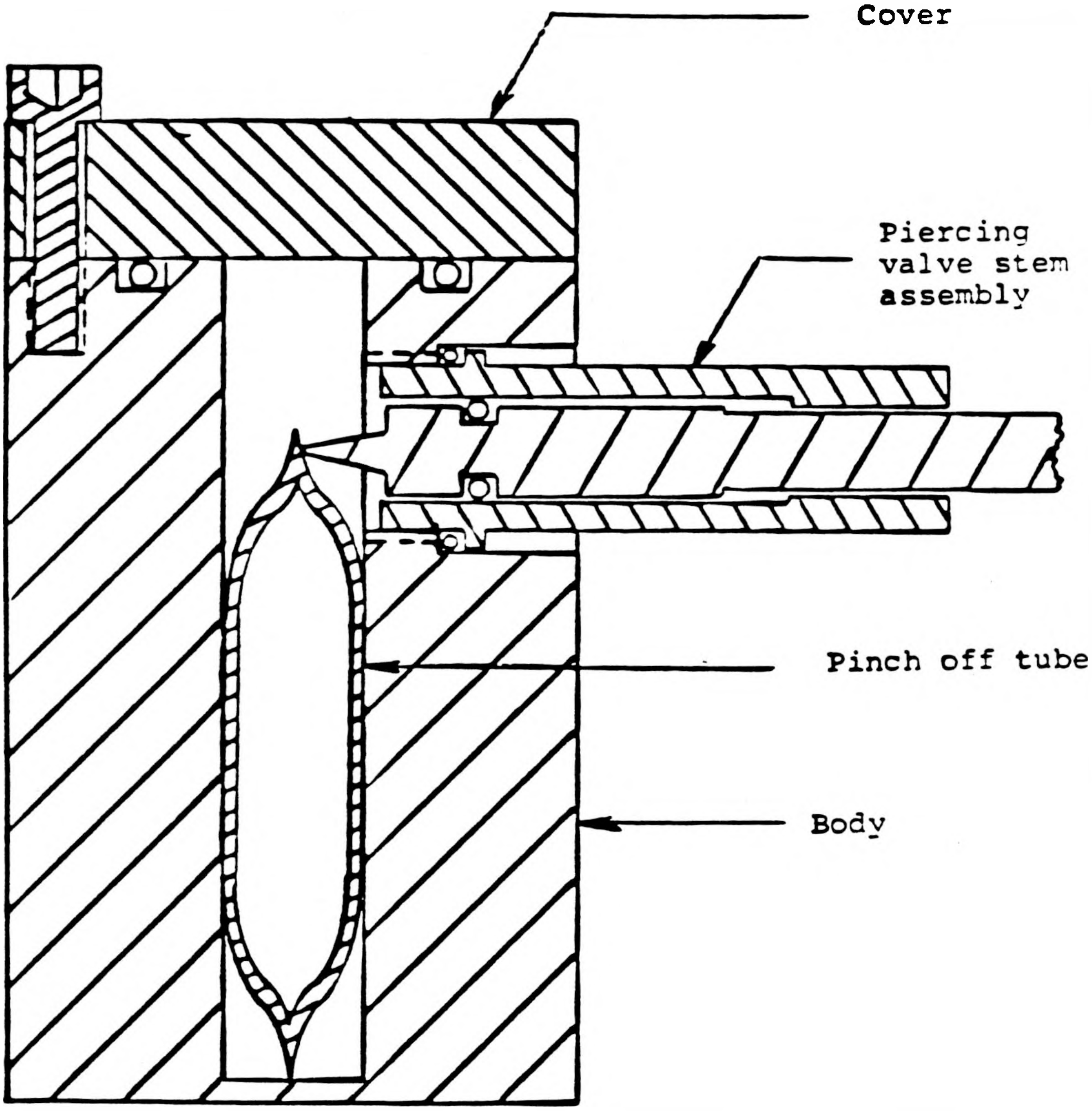

Figure 3. Piercing device for pinch off tube. (Gas inlet and outlet ports not shown.)

APPENDIX 1.

SAFE OPERATING PROCEDURE FOR GAS ANALYSIS OF CHEMICAL REACTIVITY TUBES (CRT) USED FOR AGING EXPLOSIVE MATERIALS

1. Purpose

The purpose of this procedure is to describe the operations necessary to age and analyze explosive materials.

2. General

2.1 The operations described below are not considered to represent an abnormal safety hazard.

2.2 This procedure will be used in conjunction with all other safe operating procedures specified for Rooms 3051, 3041, and 3053 of Building 807.

2.3 Quantities of explosive materials analyzed may not exceed 500 mgs.

3. Assembly of CRT

3.1 Weigh the required amount of explosive material into a pyrex thimble. The explosive may be a free standing pressed pellet.

3.2 Carefully load the glass thimble into a chemical reactivity tube maintaining a vertical orientation. This orientation should be maintained throughout procedure.

3.3 Using the necessary cajon or varian fittings and gasket, seal the thimble in the CRT by tightening the cajon nut or flange (see Fig. 1).

3.4 The sample may now be connected to a vacuum manifold and evacuated slowly to prevent explosive powder from entering the manifold. The CRT may subsequently be backfilled with gas to atmospheric pressure.

3.5 The CRT may now be placed in an oven for aging, according to the SOP specified for that laboratory.

4. Gas manifold operation

WARNING! Do not mix fuel and oxidizing gases in the manifold at the same time.

CHEMICAL REACTIVITY TUBE TYPE 1

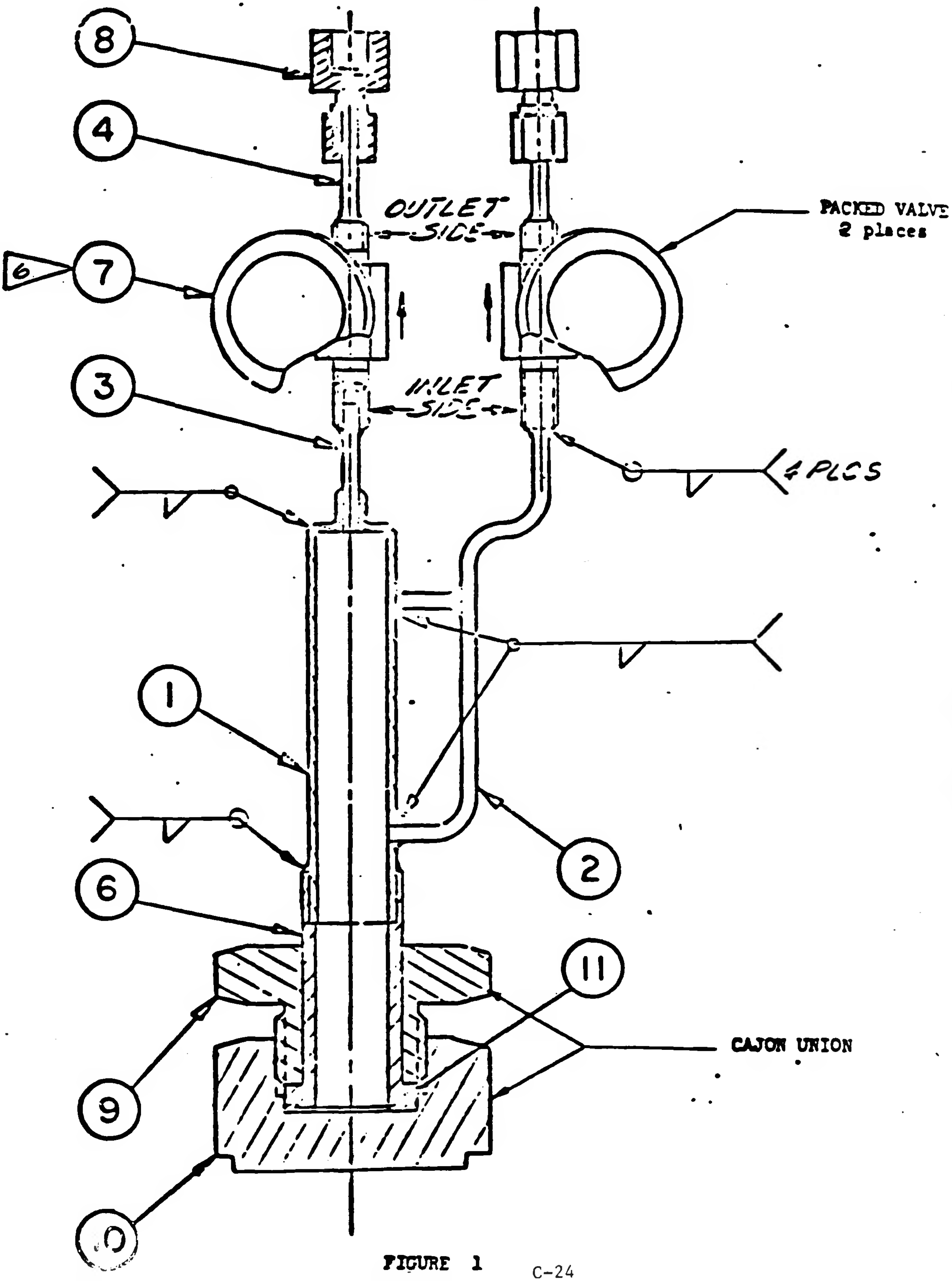

FIGURE 1

4.1 All gas cylinders valves are to remain closed during non-operational hours and when the GC-MS instrument is in stand-by mode.

4.2 All pressure relief valves must use a leak rating of 20-to-30 psig. (All delivery pressures must be less than relief valve setting.)

4.3 All gas cylinders are to be replaced when the cylinder pressure drops below 100 psig.

4.4 Only one gas cylinder valve may be opened at a time for introducing that particular calibration gas into the manifold.

4.5 The following step-by-step operation assumes the gas cylinders and manifold valves are closed and the rough vacuum pump is running.

4.6 Evacuate the gas manifold, supply lines, and regulator by opening the vacuum valve and the gas selection valve. Allow the manifold to evacuate until a pressure reading of 0.1-to-0.3 torr is obtained.

4.7 Close the cylinder selection valve.

4.8 Open the gas cylinder valve and pressurize the supply line to 20 psig using the regulator low pressure adjustment, then close the gas cylinder valve.

4.9 Pressurize the manifold to the desired pressure (zero to 1200 torr max.) by closing the vacuum valve and slowly opening the gas selection valve. Then close the gas selection valve.

4.10 Inject the gas sample into the chromatograph by rotating the sample injection valve 90°.

4.11 Re-evacuate the manifold by opening the vacuum valve and return the injection valve to its original position.

4.12 Steps 6 through 11 may now be repeated for introducing a second calibration gas.

5. Gas analysis of CRTs by GC/MS

5.1 This procedure assumes the experimenter is familiar with standard GC/MS techniques.

5.2 Fill helium carrier gas trap with liquid nitrogen.

5.3 Connect the aged CRT to the gas sample manifold using the appropriate fittings and evacuate the manifold.

5.4 Divert the helium carrier gas flow to the manifold with the CRT and slowly open the CRT valves.

5.5 Allow the helium gas to purge the CRT, trapping the decomposition gases in the liquid nitrogen trap.

5.6 After a suitable time has elapsed, remove the liquid nitrogen and rapidly heat the trap using heat gun.

5.7 Follow standard GC/MS analytical techniques for the remainder of the analysis.

6. Disassembly of CRTs

6.1 Remove the helium carrier gas flow from the manifold and CRT.

6.2 Close CRT valves and remove the CRT from the manifold.

6.3 Slowly open the CRT valve(s) in a hood to vent any excess helium pressure.

6.4 Loosen the cajon nut and remove glass thimble containing the explosive materirl.

6.5 Dispose of explosive material according to SOP.

SOP No. 35600 8809
Org. 2515
Supersedes SOP 08600 8704

SAFE OPERATING PROCEDURE FOR THE ANALYSIS OF EXPLOSIVE MATERIAL BY SCANNING ELECTRON MICROSCOPY (SEM) AND ELECTRON MICROPROBE (EMP)

David H Anderson 6/27/88
D. H. Anderson, 2510 Date

R E Whan 8/29/88
R. E. Whan, 1820 Date

6/22/88
J. G. Harlan, 2512 Date

1822 8/29/88
K. H. Eckelmeyer, 1822 Date

P. D. Wilcox 6/23/88
P. D. Wilcox, 2515 Date

9/1/88
J. R. Doyle, 3315 Date

8/31/88
J. E. Dotts, 3315 Date

Paul F Hlava 880829
P. F. Hlava, 1822 Date

David H Huskisson 8/26/88
D. H. Huskisson, 1822 Date

Thomas M Massis 6-22-88
T. M. Massis, 2515 Date
Author

W. Andrzejewski 6-22-88
W. J. Andrzejewski, 2512 Date

SAFE OPERATING PROCEDURE FOR THE ANALYSIS OF EXPLOSIVE MATERIAL BY SCANNING ELECTRON MICROSCOPY (SEM) 805/124 AND ELECTRON MICROPROBE (EMP) 805/120

1. General

1.1 This procedure becomes effective June 1, 1988.

1.2 This procedure is issued solely for the use of department 2510 to have explosives analyzed by organization 1822 and is not to be loaned or transferred to any other organization except as it applies to 1822 to do the analyses.

1.3 This procedure is to be considered a general outline for the analysis of explosive material by SEM and EMP and covers areas such as the type of samples and storage, transportation, preparation, and analysis of the samples.

1.4 Analysis of explosive material by SEM or EMP gives useful information regarding powder characterization (particle size and morphology), contaminants, and powder alteration due to environmental changes. This information is vital for component failure analysis and aging and compatibility studies.

2. Type of Samples

2.1 Explosive materials are primary explosives, secondary explosives, pyrotechnics, propellants, heat powders, and priming compositions.

2.2 These samples can be present either as bulk powders or pressed charges.

2.3 Bulk powder samples are typically less than 10 milligrams, of which only a few milligrams are used for analysis. The sample should be dispersed as well as possible.

2.4 Pressed charges come in a wide variety of sizes and materials, and the needs are constantly changing. The following serves as a list of typical examples and is not intended to be all-inclusive:

MC3478	40 mg	$TiH_{1.68}/KClO_4$
MC3479	110 mg	$TiH_{1.68}/KClO_4$
MC3804	20 mg	HNS
MC3041	38 mg	PETN
MC2949	110 mg	$TiH_{0.65}/KClO_4$
MC3004	100 mg	$Ti/KClO_4$

2.5 Compounds which contain mercury (e.g., mercury fulminate) may damage the instrument due to outgassing of mercury and may, therefore, be refused for analysis using SEM or EMP.

The following guidelines apply to pressed charges:

a. Analysis of primary explosives in pressed charges will not be conducted using this SOP.

b. The amount to be analyzed shall be kept at a minimum which is consistent with the material's tendency to decompose under an electron beam.

c. Various means of reducing the amount in a pressed charge can often be used. These consist of submitting fragments of a pellet instead of the whole pellet or removing part of the powder in a charge holder. These techniques shall be done when advisable and shall be done by 2512 or 2515 personnel before a sample is submitted.

3. Storage and Transportation

3.1 The samples shall be stored in department 2510 laboratories. The samples will not be stored overnight or on a long-term basis in organization 1822 laboratories.

3.2 The samples will be transported between buildings 807 and 805 in a Sandia approved container that is marked as containing explosives.

3.3 Transportation can be done by appropriate 1822 or 2510 personnel.

3.4 Enough samples for an estimated one day's work will be brought to either the SEM or microprobe lab and will be returned to department 2510 at the end of the day.

4. Sample Preparation and Analysis

4.1 Sample preparation consists of mounting the sample on a block and coating it with conductive material. These procedures will be done by appropriate 1822 personnel. Please note that explosive material which is very heat sensitive may not be suitable.

4.1.1 These procedures will be done by appropriate 1822 personnel. Sample preparation consists of mounting a well dispersed sample on a block and coating it with a conductive material. NOTE: This procedure is not suitable for explosive materials which are very heat sensitive.

4.1.2 A separate addendum to this SOP will be written to cover special procedures if primary explosives are to be prepared for evaluation. Primary explosive samples will be prepared only by department 2510 personnel.

4.2 Because of the wide variety of explosive materials and their correspondingly diverse response to various stimuli, it is not practical to specify details of the analysis. It is, therefore, important that the analysis be done by an experienced operator or that an experienced operator be present.

4.3 The following explosive properties are an example of what should be considered prior to SEM or EMP analysis: sensitivity to heat, electrostatic sensitivity, friction and impact sensitivity, brisance, etc.

4.4 The following analysis condition are an example of considerations to be taken by the SEM or EMP operator: beam energy, magnification, dwell time, working distances, KeV, scanning rates, anything that contributes to heat concentration in the sample, etc.

4.5 The power used in the microprobe is about three orders of magnitude greater than that used in the SEM. Therefore, samples which are suitable for SEM may not be at all suitable for EMP.

4.6 Safety glasses and wristbands for static ground shall be worn.

5. Signatures

I have read, understand, and will abide by the safety procedures in this SOP.

N/A

W. A. Andrzejewski, 2512 — Date

N/A

N. A. Creager, 1822 — Date

L. M. Maestas — 8/26/88

L. M. Maestas, 1822 — Date

R. E. Semarge — 8-26-88

R. E. Semarge, 1822 — Date

Appendix D

Standard Operating Procedure for Performing the Chemical Reactivity Test

Pantex

PX-428A
Rev. 4-82

OPERATIONS AND INSPECTIONS STANDARD
PANTEX PLANT

[redacted]

Index No.	7-9822
Page No.	1 OF 15
Issue	E (ALL PAGES)
Date	June 27, 1989

CHEMICAL REACTIVITY TEST BY GAS CHROMATOGRAPHY (U)

Reason For Change (when applicable): To incorporate CR #218794 completely revising this standard. Destroy previous issues of this standard by placing them in the classified waste. Add pgs 11-15.

SOURCE DOCUMENTS: RM251808

OTHER STANDARDS REFERENCE: 7-5000, 7-5008, 7-5059, 7-9976

SAFETY REQUIREMENTS:

1. Refer to General Standard 7-5000, 7-5008, and 7-5059.
2. Wear appropriate gloves for the solvents used to clean the CRT sample containers. (For toluene and acetone, use Viton gloves.)
3. Wear or use appropriate personal protection devices as instructed by the MSDS of the materials being tested.

RA1196: Issue E - Approved per TWX 002313, W. H. Hubbell to R. L. Johnson, dated July 25, 1989.

SCOPE: This procedure evaluates the chemical reactivity of material in contact with high explosive components in a weapon or during fabrication of a weapon or weapon component.

Office

Distribution:
C File 1 Proc 2 Qual (QAF-1, QCF-1) Fab (CL-3) MER-1
LLNL (W Div-1, W. H. Hubbell-L-125-1)

Tech Writer R. L. Johnson
Lab Dept Hd L. C. Myers
Chem/Sci
ES&H Engr

Plant Manager

* * * * * * * * * *

/// NOTES: 1. All numerical values given in this standard shall be considered approximations unless otherwise specified.

2. All calculations required in this standard may be made manually, by use of a calculator, or by use of a computer.

1. Equipment Needed:

1.1 Instrumentation:

1.1.1 The instrument needed to measure the effluent gases from the CRT sample containers is a gas chromatograph (GC) (a HP-5700 or equivalent) with a thermal conductivity detector (TCD).

/// NOTE: These parameters are guidelines only. The instrument being used, the individual columns used, the age of the equipment, etc., all affect the resolution of the chromatograph. These parameters will need to be adjusted to achieve maximum peak resolution.

1.1.1.1 Chromatographic Parameters:

Carrier: Helium
Carrier flow: 80 ml/minute
Carrier pressure: 60 psig
Column: The sample column shall be Porapak Q, packed in a 1/4 inch OD by 10 feet, stainless steel column. If a reference column is used, it should be identical to the sample column.
Detector temperature: 225°C
Injector temperature: ambient
Oven temperature: -90°C for 4 minutes, then, increased to 200°C at 25°C/minute rate and held until the peaks of interest have all evolved (approximately 25 minutes total run time)

///

NOTE: If the carrier gas flow is interrupted while the TCD is on, damage may result to the TCD. Some GC's do have a safety shutoff device that detects loss of carrier flow and shuts the TCD off to protect it from damage if the carrier flow is lost.

1.1.1.2 There shall be installed onto the GC an inlet manifold system capable of introducing the gases from the CRT sample containers into the chromatographic system. This inlet manifold system shall also be used to calibrate the GC by using one calibration loop or two calibration loops of different sizes to introduce the calibration gases into the GC. This inlet manifold system shall also have the capability of having a vacuum pump connected to it to evacuate the inlet manifold system. This inlet manifold system, when being used, shall have minimal interference with the GC's carrier flow. This inlet manifold system shall have mounted in the system a pressure gauge to measure the pressure of the chromatographic system.

1.1.1.3 There shall be installed onto the detector an integrator, integrating computer, or computer data processor that will integrate the peak areas of the components of interest.

1.2 CRT Sample Container Preparation Manifold System:

1.2.1 This manifold system shall have the capability to evacuate the CRT containers, purge the containers with carrier gas, and then fill the containers with carrier gas to a desired pressure.

1.2.2 This manifold system shall be connected to a vacuum pump to evacuate the system.

1.2.3 This manifold system shall have necessary gauges to monitor the pressure in the manifold system at all times.

1.3 Heating Bath:

1.3.1 The CRT sample containers shall be thermally soaked in a constant temperature heating block or oil bath.

1.3.2 This constant temperature heating block or oil bath shall have the capability of heating the CRT sample container to a depth of 100 ± 5 mm.

1.3.3 The constant temperature heating block or oil bath shall have the capability of maintaining the prescribed temperature to ± 1°C.

1.4 All vacuum pumps used shall be capable of pumping down to 10 mtorr (microns) of vacuum.

2. Instrument Calibration:

2.1 The GC system shall be calibrated using a two point multilevel calibration method.

2.1.1 This shall be accomplished for the calibration gases by using either one calibration loop (100 μL) and filling it to two different pressures or using two calibration loops of different sizes (between 100 and 500 μL) filled to a uniform pressure.

2.1.2 This shall be accomplished for the calibration liquids by injecting two different volumes of the liquid by chromatographic syringe.

2.2 The GC system shall be calibrated using pure N_2, CO, NO, CO_2, and N_2O.

2.2.1 The individual gases shall be calibrated at the following temperatures.

Gas	Temperature, °C
N_2	-20
CO	0
NO	20
CO_2	115
N_2O	130

2.2.2 Single Loop Calibration:

*** 2.2.2.1 After the inlet manifold and calibration loop have been evacuated, fill the loop with the gas being calibrated to a pressure of approximately 650 mm of Hg. Record the room temperature to the nearest 0.1°C and the pressure to the nearest 0.1 mm of Hg. After the loop is filled, the gas is injected into the GC system. This step is repeated five times.

*** 2.2.2.2 The inlet manifold and calibration loop are evacuated again, filled to a pressure of approximately 350 mm of Hg, then injected into the GC system. Record the room temperature to the nearest 0.1°C and the pressure to the nearest 0.1 mm of Hg. This step is repeated five times.

2.2.3 Double Loop Calibration:

/// NOTE: It does not matter what order the calibration loops are run.

*** 2.2.3.1 After the inlet manifold and calibration loop have been evacuated, fill the loop with the gas being calibrated to a pressure of approximately 650 mm of Hg. Record the room temperature to the nearest 0.1°C and the pressure to the nearest 0.1 mm of Hg. After the loop is filled, the gas is injected into the GC system. This step is repeated five times.

2.2.3.2 Step 2.2.3.1 is repeated with the next size calibration loop.

/// NOTE: All calculations shall be recorded in notebooks for historical record.

2.2.4 Calculations:

2.2.4.1 The volume of the gases must be corrected to standard temperature and pressure (STP). This is accomplished by using the following equation.

$$V_{(STP)} = \frac{PV\ (273.16)}{(T + 273.16)\ (760)}$$

Where: $V_{(STP)}$ - Volume of the calibration corrected to STP
P - Pressure of the calibration loop
V - Volume of the calibration loop
T - Temperature of the calibration loop

///

NOTE: The sensitivity is not the response factor in a multilevel calibration. The response factor for a multilevel calibration is calculated from the best fit curve of a plot of volume or mass (the independent variable) vs. the area (the dependent variable) as determined by the method of least squares.

2.2.4.2 The sensitivity of the detector to the gases shall be calculated using the following equation.

$$S = \frac{\text{Area}}{V_{(STP)}}$$

Where: S = Sensitivity of the detector to the component
Area = Integrated peak area
$V_{(STP)}$ = Volume of calibration loop corrected to STP

2.2.4.3 The best fit curve for the plot of volume or mass versus area shall be determined. This can be manually calculated by the following equation.

Equation 1:

$$Y = mX + b$$

Equation 2:

$$m = \frac{E - (AB/N)}{D - (A^2/N)}$$

2.2.4.3 (Continued)

Equation 3:

$$b = \frac{B - A\left(\frac{[E - (AB/N)]}{[D - (A^2/N)]}\right)}{N}$$

Where: Equation 1 is the equation of the best fit curve:

m = the slope of the best fit curve

b = the Y-intercept of the best fit curve

Y = the area of the component

X = the volume or mass of the component

$A = \Sigma X_n$

$B = \Sigma Y_n$

$D = \Sigma X^2_n$

$E = \Sigma X_n Y_n$

N = number of values

2.2.4.4 The average sensitivity (S), the standard deviation (SD), and the relative standard deviation (RSD) of the runs for each of the gases shall be calculated.

NOTE: The Relative Standard Deviation (RSD) is also called the Coefficient of Variation (%).

2.2.4.5 The RSD shall not be over 1%. If the RSD runs over 1%, rerun the calibration. If the RSD still runs over 1%, notify the Supervisor.

2.3 The GC system shall be calibrated using reagent grade water (or deionized) and acetone.

2.3.1 The individual liquids shall be calibrated at the following temperatures.

Liquid	Temperature, °C
Water	165
Acetone	200

2.3.2 A liquid shall be calibrated by injecting 0.5 µL of the liquid into the GC at the injection port. This step shall be repeated until five injections have been made.

2.3.3 The liquid shall then be calibrated by injecting 1 µL of the liquid into the GC at the injection port. This step shall be repeated until five injections have been made.

2.3.4 Calculations:

2.3.4.1 The sensitivity of the liquids shall be calculated using the following equation.

$$S = \frac{\text{Area}}{V}$$

Where: S = Sensitivity of the detector to the liquid
Area = Integrated Peak Area
V = volume of liquid injected
= Density of the liquid (1.00 for water and 0.7899 for Acetone)

2.3.4.2 The average sensitivity, standard deviation, and relative standard deviation shall be determined for each of the liquids.

2.3.4.3 The RSD shall not be over 1%. If the RSD runs over 1%, rerun the calibration. If the RSD still runs over 1%, notify the Supervisor.

3. Quality Assurance:

/// NOTES: 1. A blank run (no sample) shall be made prior to any samples to clear the CRT system.

2. All QA calculations shall be recorded in appropriate notebooks for historical record. Control charts shall be maintained.

3. Any size calibration loop may be used for the Quality Control runs.

3.1 Daily N_2 Sensitivity Check:

3.1.1 The N_2 sensitivity shall be determined by running N_2 five times at -20°C. The calibration loop shall be filled to approximately 300 mm of Hg. It does not matter what size loop is used as long as the same size is used for all five daily runs and for the control chart. If a different size loop is used, a new control chart shall be generated.

3.1.2 The average sensitivity, standard deviation, and relative standard deviation shall be determined. The average sensitivity shall be control charted.

3.1.3 If the daily N_2 runs are out of control, notify the Supervisor for corrective action. This needs to be done before any samples are run. If the RSD is over 1%, notify the Supervisor.

3.2 Daily Gas Mixture Check:

3.2.1 A mixture of any of the concerned gases shall be run daily before any samples and after the N_2 check. This is accomplished by filling the calibration loop with the gas mixture to a pressure of approximately 300 mm Hg. The run is performed using the parameters stated in 1.1.1.1.

3.2.2 The percentages of the gases shall be control charted. There shall be control charts for every gas mixture used.

3.2.3 If any control chart is out of control, notify the Supervisor.

3.3 Monthly PBX-9404 Check:

3.3.1 PBX-9404 shall be tested in duplicate every month. The PBX-9404 shall be prepared as described in Step 4.

3.3.2 The amount of each gas shall be control charted.

3.3.3 If the control chart is out of control, notify the Supervisor.

4. High Explosive (HE) and Inert Material Preparation:

/// NOTES: 1. HE standard lots may be established in order to facilitate testing. This will eliminate the need of running the HE by itself with every inert material. The HE standard lot shall be run every time the CRT system is recalibrated. The PBX-9404 shall be run not only after recalibration, but shall be rerun every month.

2. CRT testing of any HMX-Viton explosives (LX-04, LX-07, LX-10, and LX-11) with any material certifies that material with all those explosives.

3. CRT testing of either LX-17 or PBX-9502 with any material will certify that material with both explosives.

4. Resins and curing agents shall be mixed and allowed to cure before any testing is performed. Any adhesive or potting compounds shall be allowed to cure before any testing is performed. Any paints, inks, etc., shall be allowed to air dry before any testing is performed.

4.1 The HE shall be ground or microtomed, as appropriate, for testing and shall conform to the specifications in Appendix A of RM251808.

4.2 The inert material shall be ground, microtomed, chopped, or shredded as finely as possible.

4.3 All tests shall be run in duplicate unless otherwise notified.

4.4 Sample size, for both HE and Inert, shall be 250 ± 10 mg measured into glass vials of a size that will fit into the CRT container.

4.5 Mixtures of HE and Inert shall contain 250 ± 10 mg each and shall be mixed thoroughly by any convenient method, ie. shaking or stirring with a small glass rod which may be left in the vial.

4.6 The glass vials containing the sample shall be placed in a CRT container with a glass spacer rod on top of the vial.

4.7 A Viton O-ring shall be placed into the VCO fitting and the container assembled hand tight.

4.8 The CRT container is then mounted onto the container preparation manifold, the valves are opened on the container, and the container shall be evacuated for two minutes at a vacuum of 150 mtorr (microns) or less.

4.9 The CRT container shall then be purged with carrier gas for two or more minutes.

4.10 The vacuum shall be shut off and the CRT container backfilled with carrier gas to the pressure that the CRT system is reading.

4.11 The CRT container valves shall then be closed hand tight, the CRT containers removed from the manifold, and small corks placed into the tops of the CRT containers to prevent entry of foreign material.

4.12 The CRT containers shall be placed into the heating bath to a depth of 100 ± 5 mm. If an oil bath is used, make sure that the oil level is below the threads of the VCO fitting.

4.13 The CRT containers shall be removed from the heating bath after 22 to 23 hours of heat soaking. If an oil bath is used, rinse the CRT containers with organic solvents to remove the oil.

4.14 The CRT containers do not necessarily have to cool to be able to run them.

5. Gas Analysis of Chemical Reactivity Samples:

5.1 The CRT container shall be mounted onto the inlet manifold of the CRT system hand tight.

5.2 With the carrier gas running through the calibration side of the inlet manifold and the bypass valve above the CRT container opened, the system shall be evacuated to less than 100 mtorr (microns).

5.3 The vacuum shall be shut off, the carrier gas switched to the sample side of the inlet manifold, and the bypass valve left opened.

5.4 When the GC system is in the ready state, both valves on the CRT container shall be opened, the bypass valve shall be closed, and the GC and data processor shall be started.

5.5 When the run is complete, switch the carrier back to the calibration side of the inlet manifold, open the bypass valve, and remove the CRT container.

5.6 Calculations:

5.6.1 The data processor should print out the results of the CRT runs.

5.6.2 If the results need to be manually calculated, use the best fit equation as calculated in 2.2.4.3.

5.6.3 The results shall be recorded on the appropriate forms [Request Material Analysis (RMA)] and entered into the computer historical files.

6. Disassembly and cleaning of CRT containers:

6.1 The CRT containers shall be disassembled, removing the spacer and sample vial and discarding the viton O-ring.

*** 6.2 The sample shall be inspected and record any abnormalities. The Supervisor shall also be notified. If there are no abnormalities, discard the sample.

6.3 The CRT container parts, along with the spacer, shall be washed in toluene followed by acetone. Make sure that the inside of the container is flushed with acetone several times, allowing the acetone to stand a few minutes inside the CRT container.

6.4 The CRT container parts shall be heated in a 60°C vacuum oven under vacuum for two hours to remove any trace of solvent.

3-1-01

Pantex (Development CRT procedure)

Chemical Reactivity Test (CRT)

The CRT operation is limited to 600 milligram samples with no more than 18 samples on hand at any time. Samples awaiting test shall be in approved closed containers. Maximum temperature during the conditioning period is 150° C.

Samples are weighed on a four place Mettler balance. A stainless steel spatula is used to place .250 ± .001 g of the material being tested into a glass sample vial (9 x 30 mm, 1/4 dram).

For reactivity testing, .250 ± .001 g of HE powder is placed in the same vial, and maximum surface contact between the two materials is normally obtained by shaking the vial to mix the two materials.

The vial is placed in a stainless steel container (using stainless steel spacers), evacuated below 50 microns, backfilled with helium, and placed in a oil bath (using Ucon heat transfer fluid) normally at 120° C for a period of 22 hours.

Development Division
Standard Operating Procedure
Pantex Plant

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Page No.: **1**
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Date: **3/06/89**

THERMAL ANALYSIS LAB

Reason for Reissue *(when applicable)*: **To incorporate changes as indicated by a "C" in left hand margin and reformat. Destroy previous issues of this standard.**

OTHER STANDARDS/REFERENCES: 6-5000, 6-5021, 6-5051, 7-5080,
Safety Standard 328,
Final Safety Assessment Document (FSAD),
and DOE Explosives Safety Manual

POSTING LOCATIONS: Bldg 11-51

1.0 INTRODUCTION

This procedure covers the general safety rules for operations carried out in the Thermal Analysis Lab *(Bldg 11-51, Room 112)*. The Chemistry Department supervisors are responsible for the operations conducted in this room.

PAGES:	1	2	3	4	5	6
ISSUE:	C	C	C	C	C	C

DISTRIBUTION: C File (1) Development (6) EP (1) FP (1) Safety (1) Technical Documents (1)

Originator
Department Head
Safety Engineer
Dev. Div. Manager
Plant Manager ____________________

clr

2.0 MATERIAL AND EQUIPMENT

Not applicable.

3.0 SAFETY

3.1 The operation conducted in the Thermal Analysis Lab shall conform to the safety guidelines for laboratory operations as given in Section 2.19 of the DOE Explosives Safety Manual and Standard Operating Procedures (SOP) 6-5000 and 6-5021.

3.2 Explosive Limits

3.2.1 The explosive limits for Bldg 11-51 are established in the Final Safety Assessment Document (FSAD).

3.2.2 The quantity of explosive present in the laboratory shall be the minimum required for the experiment and in all cases shall be at or below assigned limits.

/// NOTE: Five gram quantities within a laboratory shall have a minimum of 15-cm spacing between samples to eliminate possibility of propagation.

3.2.3 The administrative limits established for the Thermal Analysis Lab are as follows:

(1) Maintaining the amount of explosive at or below room limits.

(2) Prompt disposal of waste explosive samples.

(3) Adjusting log books for samples consumed and/or disposed of in waste containers.

3.3 There shall be no explosive samples *(except those in process)* left out in the laboratory during non-working hours. In process includes CRT samples which are being aged.

3.4 Personnel Limits

3.4.1 The maximum personnel limit for the Thermal Analysis Lab is 5 operators and 5 casuals.

3.4.2 Form PX-100-35 will not be required for touring personnel who may exceed the posted limit, provided the tour has been coordinated with the Development Division Manager and explosive operations cease while the visitors are present.

3.5 The operations conducted in the Thermal Analysis Lab shall conform to the general requirements described in SOP 6-5150.

3.6 If an operation involves an explosive hazard, personnel shall be protected by a safety shield. A 20-mm thick Lucite shield is approved for 10 grams or less of TNT equivalent.

3.6.1 Shields approved for smaller quantities of explosives can be found in Appendix B of SOP 6-5150.

3.6.2 The shield shall be anchored to the wood frame or bench top when it is being used for protection against more than 5 grams of TNT equivalent.

3.7 All operations involving solvents shall be performed under the exhaust hood.

3.8 All spillage shall be cleaned up as soon as possible.

3.9 HE-contaminated solvents shall be disposed of in HE solvent waste cans.

4.0 OPERATIONS

4.1 Any problems or questions concerning these operations shall be referred to one of the following individuals:

4.1.1 Building supervisor for questions or problems related to the general building services or utilities and to the interrelation of the operations in the Thermal Analysis Lab *(Room 112)* to operations in other parts of Bldg 11-51.

4.1.2 The supervisor for whom the work is being performed for questions or problems related to individual test procedures, instrument operations, or malfunctions.

/// NOTE: This section covers only the general directions for operations conducted in the Thermal Analysis Lab. Detailed instructions for each operation are covered in individual operations standards or instrument operation manuals.

4.2 The following operations may be conducted concurrently in the Thermal Analysis Lab:

/// NOTE: Analysis of DTA is limited to 20-milligram samples.

4.2.1 Differential Thermal Analysis (DTA)

C--- (1) This operation is limited to 20-milligram explosive samples with no more than five samples on hand at any one time.

(2) Samples awaiting test shall be in closed sample containers.

4.2.2 Thermogravimetric Analysis (TGA).

/// NOTES (1) This analysis is limited to 20-milligram explosive samples with no more than five samples on hand at any one time.

C--- (2) This operation is limited to 20-milligram explosive samples with no more than two samples on hand at any one time.

(3) Samples awaiting analysis shall be in closed containers.

4.2.3 Differential Scanning Calorimeter (DSC)

/// NOTES (1) Each analysis is limited to two milligrams of HE with no more than five samples on hand at any one time.

(2) Samples awaiting analysis shall be in a closed container and shall be properly labeled as to contents.

4.2.4 Gas Chromatography and/or Chemical Reactivity Test (CRT)

C--- /// NOTES (1) This operation is limited to 600-milligram samples with no more than 18 samples on hand at any one time.

(2) Samples awaiting test shall be in approved closed containers.

4.2.5 Weight of Samples with Analytical Balance and Recording Microbalance

(1) Weigh toxic materials in a closed container, preferably under a hood.

(2) For weighing corrosive material, carefully place the sample into a dish outside the balance, then cover the dish before placing it on the balance pan.

(3) Return all cleaned containers to the storage desiccator.

(4) Clean up all spillage at the end of each weighing.

4.2.6 Microscopy and Hot-Stage Microscopy

(1) Store slides for future analysis in a slide holder.

(2) Conduct hot-stage microscopy with a heat absorbing glass between the operator and the sample.

(3) When microscopes are not in use, keep them covered and clean.

4.2.7 Melting Point Apparatus

(1) Front the apparatus with an approved shield when HE samples are run.

(2) Sample size shall be limited to 10 milligrams.

(3) No more than three samples shall be tested at one time.

(4) The maximum temperature for explosives shall not exceed the melting point by more than 20°C.

4.2.8 Thermal Mechanical Analysis (TMA)

C--- /// NOTE: Explosive samples for TMA shall be limited to 20 milligrams.

CAUTION: Do not allow the final temperature for TMA runs to exceed a temperature which is 50°C less than the onset of the lowest exotherm as measured by DSC or DTA.

Appendix E

Crane Unidynamics Final Report on the Sensitivity Characteristics of a 50/50 Titanium/PETN Blend

CRANE UNIDYNAMICS

06 December 1989

FINAL REPORT ON THE SENSITIVITY CHARACTERISTICS OF A 50/50 TITANIUM/PETN BLEND

(SANDIA CONTRACT 42-0398)
(UNIDYNAMICS/PHOENIX ACCOUNT F0304-01)

Prepared for:

Sandia National Laboratories
P. O. Box 5800
Albuquerque, New Mexico 87185
Attention: A. A. McConnell
Orgn. 3714

Prepared by: John Fronabarger
J. W. Fronabarger
Staff Scientist

Approved by: R D Smith
R. D. Smith
Staff Scientist

Unidynamics/Phoenix
P. O. Box 46100
Phoenix, Arizona
85063-6100

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SECTION **PAGE NUMBER**

INTRODUCTION

This report covers the investigation conducted under Sandia Purchase Order 42-0398. The study involved determination of the safety characteristics of a blend of titanium/PETN and also attempted simulation of an incident occurring at Sandia/Albuquerque involving a very similar blend. The following portions of this report summarize the work performance and data generated.

DISCUSSION

An incident at Sandia involved the accidental ignition of a 50/50 blend of titanium (~2 micron) and PETN. The latter material was an EBW grade (needle crystals). Specifically, the incident occurred during a blending operation of the materials in a 10 mm diameter by 75 mm long glass test tube. Actual ignition occurred when the blending aid, a 1.6 mm diameter capillary, was intentionally broken off in the sample to avoid loss of sample. As a consequence of this event it was decided to investigate the sensitivity characteristics of the subject blend. The following testing was selected for the evaluation of the blend:

- Flame ignition
- Electrostatic discharge (ESD) sensitivity
- Impact sensitivity
- Friction sensitivity
- Attempt to simulate the incident
- Ignition of the blend in test tubes

The mixture used in the evauation was a dry mechanical blend of Sandia furnished titanium (same lot as involved in the the incident) and lot ER-17022 PETN. The blend, four grams, was prepared by rolling a closed aluminum cup at 30 rpm for four hours. The blend appeared quite homogeneous.

Regarding senitivity chatracteristics, the following table provides the data obtained for the blend and for neat PETN.

SENSIVITY CHARACTERISTICS OF PETN AND 50/50 TITANIUM/PETN BLEND

METHOD	DESCRIPTION	RESULTS					
		PETN			50/50 PETN-Ti		
ESD	Instrument: UN-326-E, 600 pfd, 500 Ω series, loose powder, dull copper point and AL plate electrodes	No-Fire 25KV			Fire 1 KV		
Impact Sensitivity	Modified 2 Kg Bureau of Mines Impact Machine	h,cm	Fire	No-Fire	h,cm	Fire	No-Fire
		40	0	1	30	0	2
		50	0	1	35	3	1
		60	0	4	40	4	3
		70	0	3	45	3	0
		80	1	1	50	1	0
		90	1	3	60	1	0
Friction Sensitivity	Julius Peters One Kg BAM Friction Tester	>1 Kg			>1Kg		

It is evident that the ESD sensitivity of the blend would represent a safety problem. Impact or friction sensitivities however, would not suggest unusual safety problems for the blend.

While the Ti/PETN blend is quite ESD sensitive, the study also showed that neat titanium will occassionally ignite at one kilovolt. The sensitivity of titanium can be attributed to this high surface area material reacting with oxygen (and possibly nitrogen) in the region of the arc plasma.

In addition, some open flame (match) ignition testing was performed. The blend burns with a rapid bright white flash but does not produce an audible sound. Confinement under a metal disk and the slate bench top quenched the burning. Quenching also occurred between microscope slides. Titanium alone burned brightly at a moderate rate but with no plume (sintering action).

Differential scanning calorimetry (DSC) showed the titanium has little or no effect on the temperature response of PETN (c.f.Figures 1 through 4 at the conclusion of this section). However, the titanium does result in an enchanced calorific output for the exotherm as can be seen by comparison of Figures 5 and 6. The blend value is more than twice of that for neat PETN. One explanation for the increased heat detected is the reaction of titanium with decomposing PETN or its decompostion products. However, there is an alternative more pluasible explanation. The response of 72 calories/gram for the neat PETN is only about five percent of the reported heat of explosion for PETN, 1385 calories/gram (1). Undoubtably most of the heat produced is dissipated in the PETN decomposition gases and not detected by the DSC sensor.

The increased output from the blend is probably due to the titanium acting as a heat sink and transfer media. The similarily between the curves in Figures 5 and 6 would suggest the titanium did not react with the PETN: An experiment was devised to confirm this lack of reaction. A moderate amount of the blend was heated between two cover glasses on a Fisher-John meeting point apparatus to 280°C (15 to 20°C/minute). No ignition of the mix occurred, and microscopic examination indicated the residue was quite similar to the original blend except the needle form PETN was absent. ALso, the residue burned from flame ignition much like the original titanium (see above). It then appears as previously stated that the titanium merely acts as a heat transfer medium for the energy released by the decomposing PETN. Of course titanium will undoubtably react with

PETN or its decompostion products at higher temperatures, e.g. deflagration or detonation. Adjusting for percentage, the measured PETN output for the blend would be 309 calories/gram versus 72 calories/gram for the neat explosive. Regarding accuracy of the DSC, the measured heat of fusion of PETN (Figure 5) is 11.6 kcal/mole, which compares with a literature value of 11.8 kcal/mole (2).

Some experiments were conducted in attempts to simulate the incident that occurred at Sandia. A bomb arrangement was available that was adapted to simulate the incident. Figure 7 shows the 10 mm by 75 mm bomb and modifications made for simulation. The test sample, 400 milligrams of the blend, was contained in a test tube, and a 1.6 by 90 mm capillary was inserted with the closed end in the test sample. A strong cotton string was arranged around the capillary as shown in the upper portion of Figure 7, the entire setup being behind a shield in a laboratory hood. The string was pulled from outside the hood until the capillary broke. This operation was performed four times with no reaction. The operation was then repeated three times with a 147 gram weight resting on top of the capillary. Still no reaction occurred.

It was then decided to attempt to establish the effects of different modes of ignition of the blend. A 400 milligram sample contained in the above described test tube was ignited by several means as indicated in the following table with results being given in the right hand column.

RESULTS OF IGNITION OF 50/50 TITANIUM/PETN BLEND IN TEST TUBE

	MODE OF IGNITION	OBSERVATIONS
1.	Firecracker fuze on <u>top</u> of powder.	Rapid burn, bright plume, burn time ~1 second, test tube intact.
2.	Electric match header* (Atlas M100) at <u>bottom</u> of sample. Pulsed with a 10 cap blasting machine.*	Explosion, bright fire ball, test tube shattered.
3.	Electric match header at <u>bottom</u> of sample. Pulsed with 4 amps.**	Explosion bright fire ball, test tube shattered.
4.	Electric match header at <u>top</u> (~1/8" below top surface) of sample. Pulsed with 10 cap blasting machine.	Rapid burn, bright plume, burn time ~1 second (possibly slightly slower than test No. 1. Test tube intact.

From these tests it is apparent that ignition of the blend well beneath the surface results in an explosion similar to that encountered in the incident at Sandia. Surface ignition results in a rapid deflagration with no explosive force.

*Match head mix removed from header with acetone to provide bare bridgewire.

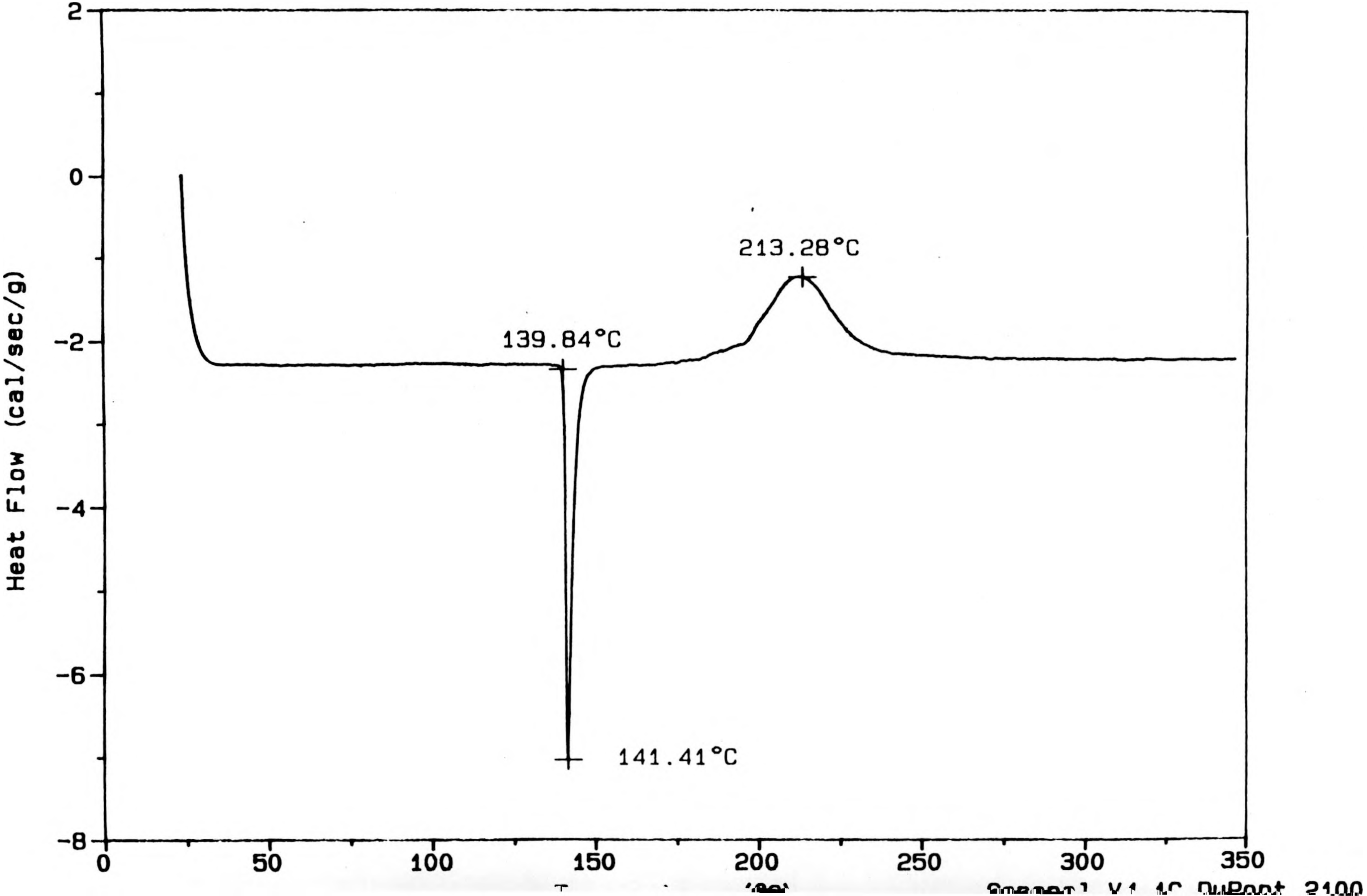
**Ten cap machine was found to explode the bridgewire, thus the reason for using 4 ampere firing current in test No. 3 in order to obtain a pure thermal ignition.

FIGURE 1

Sample: PETN ER-17022
Size: 0.5600 mg
Method: HEAT @ 20°C/MIN
Comment: ARGON @ 55; 20°C/MIN

DSC

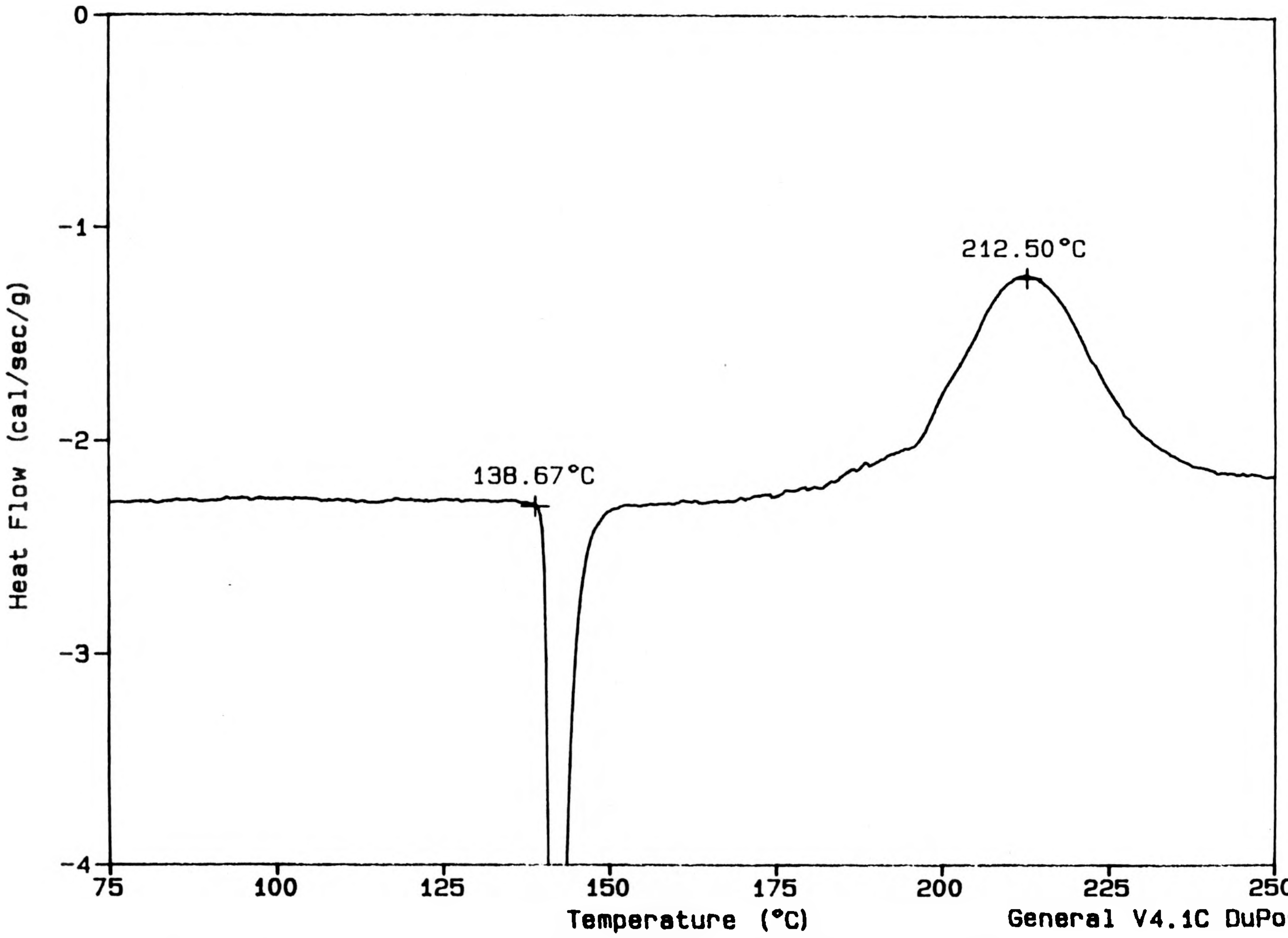
File: PETN.01
Operator: JWF
Run Date: 26-Jul-89 15:30



Sample: PETN ER-17022
Size: 0.5600 mg
Method: HEAT @ 20°C/MIN
Comment: ARGON @ 55; 20°C/MIN

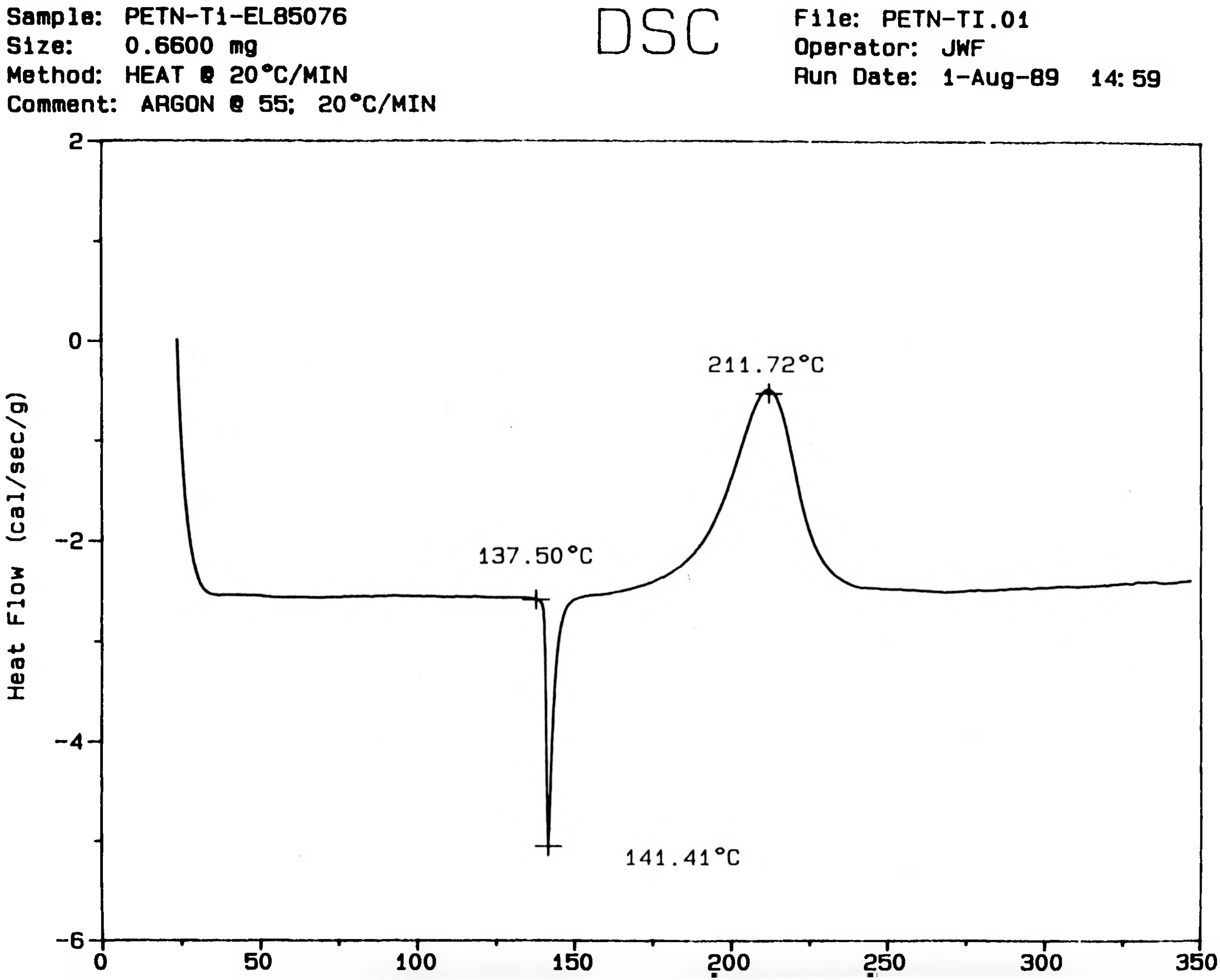
DSC

File: PETN.01
Operator: JWF
Run Date: 26-Jul-89 15:30



General V4.1C DuPont 2100

FIGURE 3



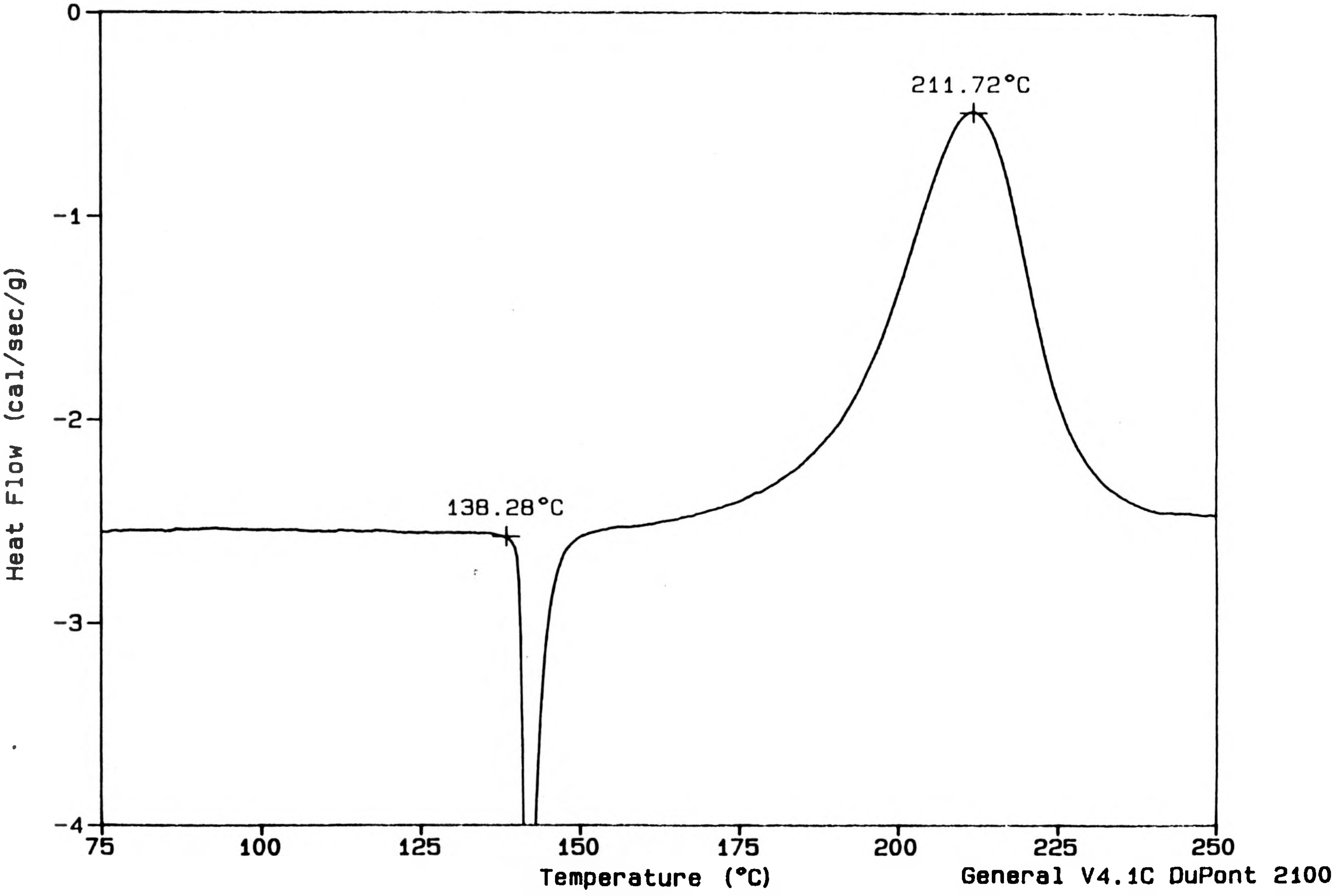
Sample: PETN-Ti-EL85076
Size: 0.6600 mg
Method: HEAT @ 20°C/MIN
Comment: ARGON @ 55; 20°C/MIN

File: PETN-TI.01
Operator: JWF
Run Date: 1-Aug-89 14:59

Sample: PETN-Ti-EL85076
Size: 0.6600 mg
Method: HEAT @ 20°C/MIN
Comment: ARGON @ 55; 20°C/MIN

DSC

File: PETN-TI.01
Operator: JWF
Run Date: 1-Aug-89 14:59



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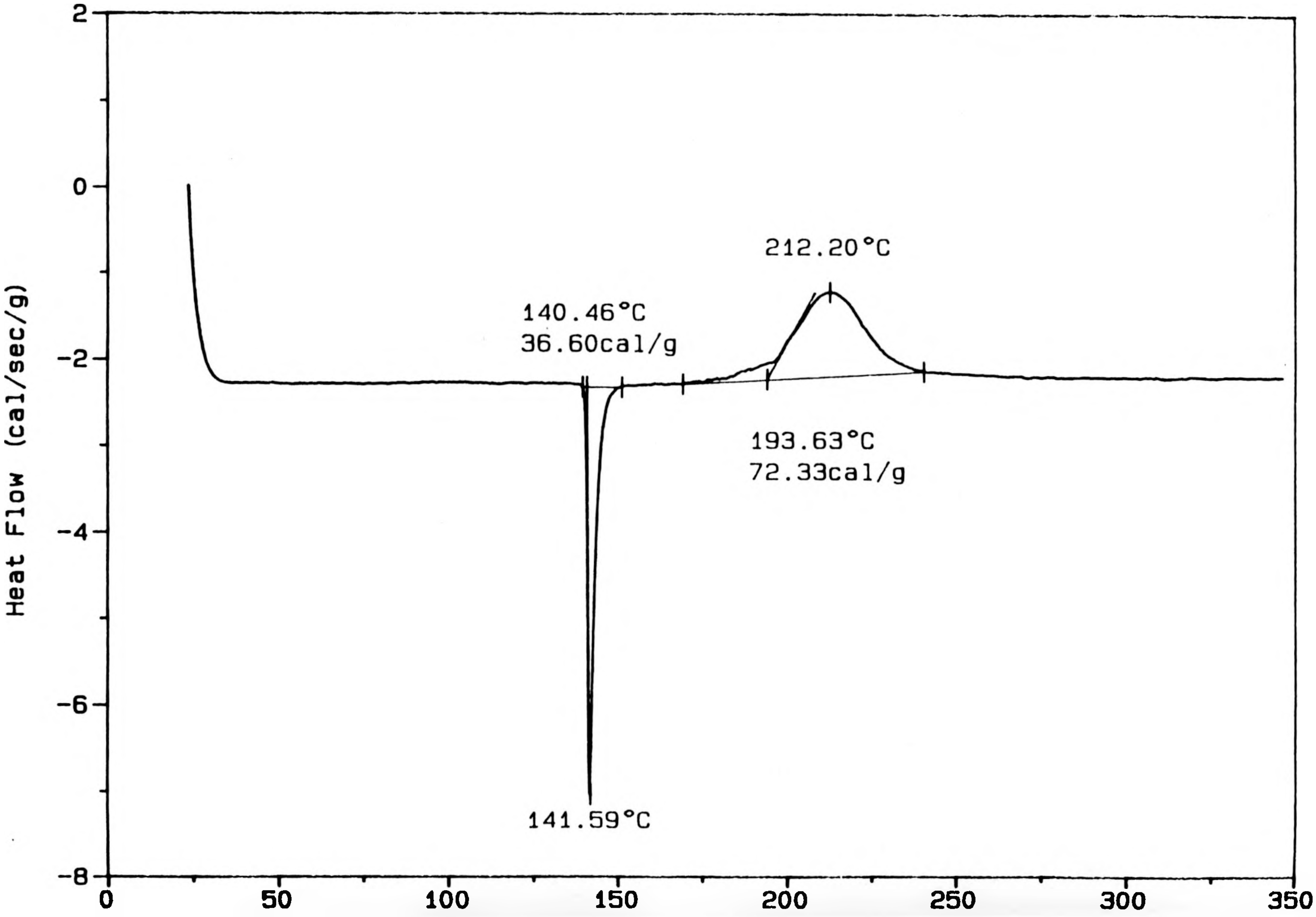
FIGRUE 5



DSC

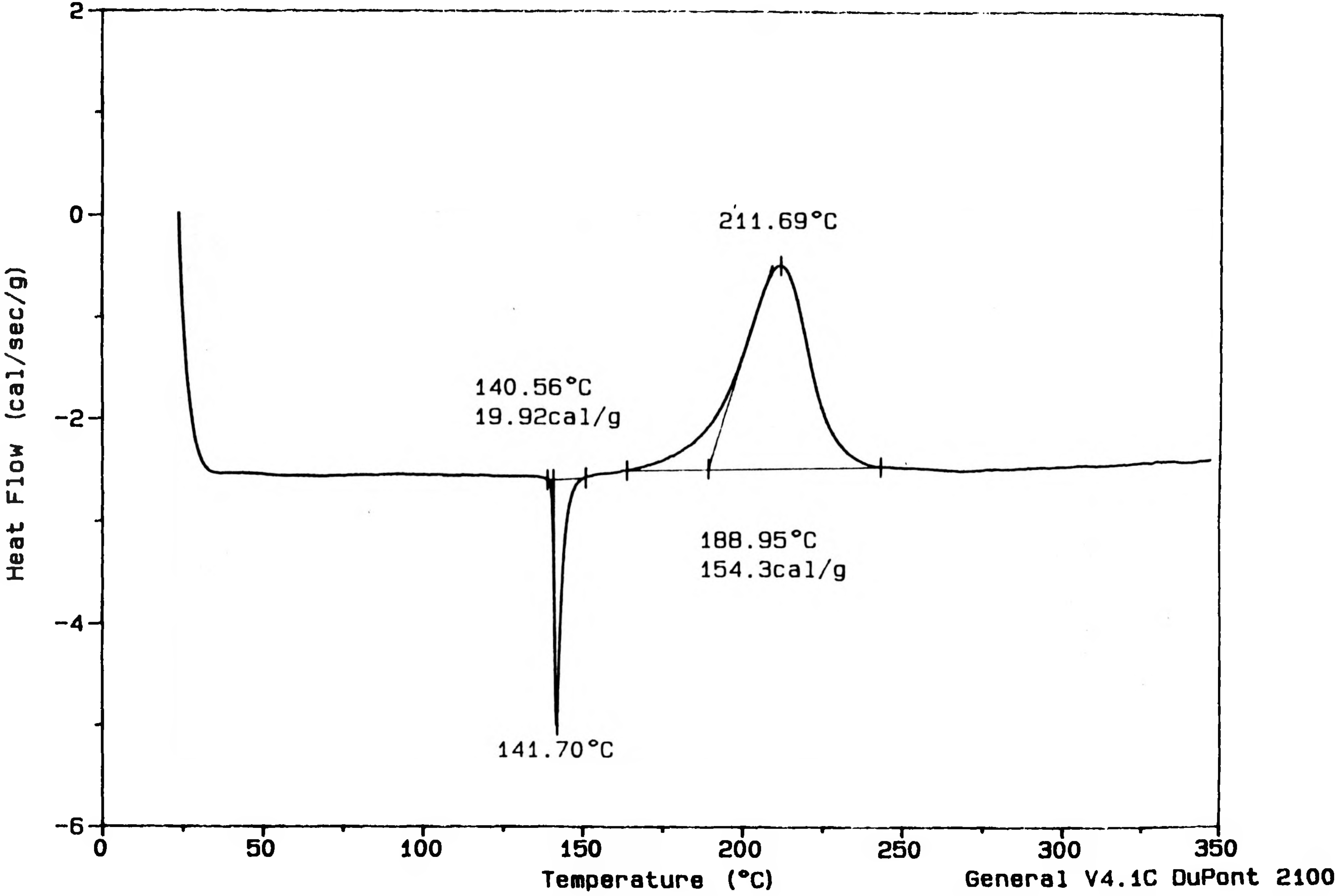
Sample: PETN ER-17022
Size: 0.5600 mg
Method: HEAT @ 20°C/MIN
Comment: ARGON @ 55; 20°C/MIN

File: PETN.01
Operator: JWF
Run Date: 26-Jul-89 15:30

Sample: PETN-Ti-EL85076
Size: 0.6600 mg
Method: HEAT 20°C/MIN
Comment: ARGON @ 55; 20°C/MIN

DSC

File: PETN-TI.01
Operator: JWF
Run Date: 1-Aug-89 14:59



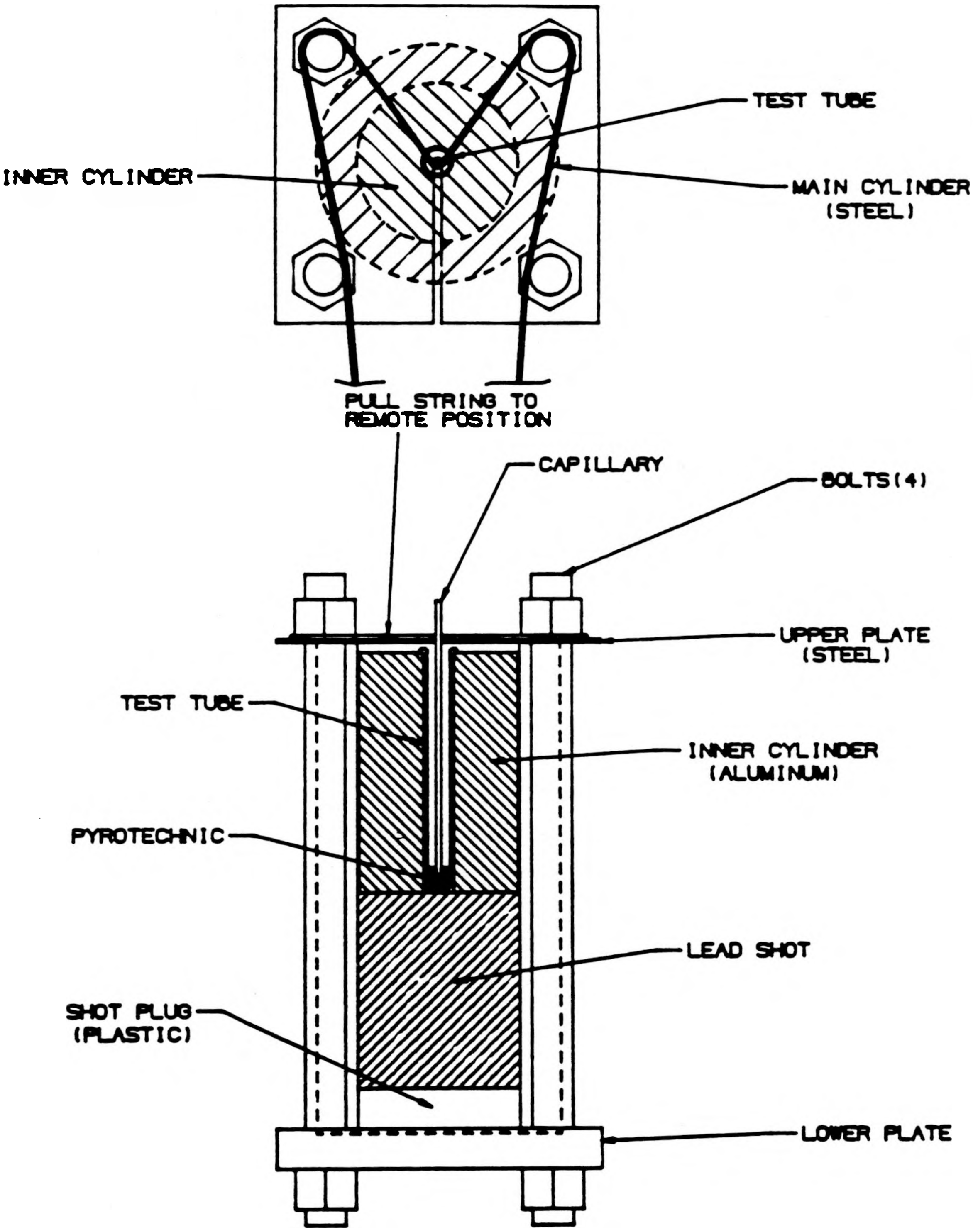


FIGURE 7

TEST BOMB ARRANGEMENT

CONCLUSIONS

1. The titanium/PETN blend is quite electrostatic sensitive but is relatively insensitive to impact and friction. Neat titanium is also quite ESD sensitive, apparently reacting with the elements of air under the spark influence.

2. Open flame testing revealed only deflagrating action. Confinement of thin layers results in quenching.

3. An attempt was made to use an existing bomb arrangement to simulate the Sandia incident. Seven trials resulted in no ignition.

4. Differential scanning calorimetry (DSC) indicates titanium has no effect on the temperature response of PETN. The metal does not react with the PETN under these test conditions but probably acts as a heat transfer media for DSC response.

5. Fuze and hot wire ignition testing of the blend in small test tubes has shown that surface ignition results in rapid deflagration, and internal ignition results in explosion. It is therefore concluded the Sandia incident resulted from ignition in the interior of the titanium/PETN blend.

REFERENCES

1. Engineering Design Handbook, Explosive Series. Properties of Explosives of Military Interest. AMCP 706-177, January 1971.

2. R. N. Rogers and R. H. Dinegar, Thermochemica Acta 1972, 3, 367.

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