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TECHNICAL AND ECONOMIC ANALYSES TO ASSESS THE FEASIBILITY OF USING PROPELLANT - NO. 2 FUEL OIL SLURRIES AS SUPPLEMENTAL FUELS

September 1991

Prepared for:
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Maryland 21010-5401

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FINAL REPORT

TECHNICAL AND ECONOMIC ANALYSES TO ASSESS THE FEASIBILITY OF USING PROPELLANT-NO. 2 FUEL OIL SLURRIES AS SUPPLEMENTAL FUELS

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The military currently has a large inventory of obsolete conventional munitions and waste propellants generated during the manufacturing process. The current alternatives to storage are open burning/open detonation (OB/OD) and incineration to slowly reduce the inventory of these materials. The impact of OB/OD operations on the environment is under intense scrutiny by regulatory agencies and whether or not they will be allowed to continue in their current form is unknown. Incineration is costly and does not utilize the energy content of the propellants. The United States Army Toxic and Hazardous Materials Agency (USATHAMA) is currently conducting a program with Tennessee Valley Authority's National Fertilizer and Environmental Research Center to determine the feasibility of utilizing propellants as supplemental fuels for the U.S. Army's industrial combustors. Disposing of obsolete and waste propellants in this manner could be both cost-effective and environmentally sound, and as an added benefit, would utilize the energy value of these materials.

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The second project in the supplemental fuels program was undertaken by Tennessee Valley Authority-National Fertilizer and Environmental Research Center to assess the technical, economic, and safety aspects of using propellant-No. 2 fuel oil slurries as supplemental fuels. The materials studied during this project were nitrocellulose, nitroguanidine, and AA2 double-base propellant. Once again, a series of laboratory tests were conducted to evaluate the physical and chemical characteristics, as well as the chemical compatibility, of propellant-No. 2 fuel oil slurries. Wet-grinding of the AA2 propellant with No. 2 fuel oil was required to prepare slurries suitable for testing since the AA2 propellant was received in the form of paper-thin shavings. The nitrocellulose and nitroguanidine were received as finely-divided powders that were easily dispersed in No. 2 fuel oil without grinding to prepare slurries suitable for testing. The physical characteristics of the propellant-No. 2 fuel oil slurries studied during this project were solubility, density, viscosity, and particle-size distribution. Chemical characteristics studied were flash and fire points, heat of combustion, and emissions, while differential scanning calorimetry was used to assess the chemical compatibility of the propellant-No. 2 fuel oil slurries. The results from these laboratory tests, as well as from an economic analysis of the process, will be discussed in this report. Propagation of reaction testing of various propellant-No. 2 fuel oil slurries is currently being conducted and will be published separately.

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ABSTRACT

The military currently has a large inventory of obsolete conventional munitions and waste propellants generated during the manufacturing process. The current alternatives to storage are open burning/open detonation (OB/OD) and incineration to slowly reduce the inventory of these materials. The impact of OB/OD operations on the environment is under intense scrutiny by regulatory agencies and whether or not they will be allowed to continue in their current form is unknown. Incineration is costly and does not utilize the energy content of the propellants. The United States Army Toxic and Hazardous Materials Agency (USATHAMA) is currently conducting a program with Tennessee Valley Authority's National Fertilizer and Environmental Research Center to determine the feasibility of utilizing propellants as supplemental fuels for the U.S. Army's industrial combustors. Disposing of obsolete and waste propellants in this manner could be both cost-effective and environmentally sound, and as an added benefit, would utilize the energy value of these materials.

The propellant studied during the initial project in this program was a nitrocellulose containing 13.15 percent nitrogen by weight. A series of laboratory tests were conducted to evaluate the physical and chemical characteristics, as well as the chemical compatibility, of nitrocellulose-solvent-No. 2 fuel oil solutions. These tests were based on previous work by USATHAMA to determine the feasibility of using explosives as supplemental additives to fuels for the recovery of energy from these compounds. Preliminary testing on the explosives TNT and RDX were encouraging. The methods used to introduce these explosives as a fuel additive included solvation and mixing with No. 2 fuel oil. Unfortunately, the tests outlined above using the propellant nitrocellulose indicated that such solvation

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I. SUMMARY

1.1 Objectives

The objective of this project is to assess the technical and economic feasibility, as well as the safety aspects, of using waste propellants as supplemental additives to fuels for the recovery of energy from these compounds. This project represents a logical extension of a previous program conducted by the United States Army Toxic and Hazardous Materials Agency (USATHAMA) to develop methods and procedures for utilizing waste explosives [primarily TNT and Composition B (60 percent RDX, 39 percent TNT, and 1 percent wax)] and propellants (nitrocellulose) blended with a solvent and No. 2 fuel oil as a supplemental fuel in the United States Army's industrial combustors. Preliminary testing on the explosives TNT and RDX have been encouraging. Preliminary testing using the propellant nitrocellulose indicated that such solvation and mixing with No. 2 fuel oil was not cost effective. Only relatively small amounts (2-3 percent by weight) of nitrocellulose could be incorporated in the solvent-No. 2 fuel oil mixture without increasing the viscosity of the resulting nitrocellulose-solvent-No. 2 fuel oil solution beyond the maximum value which a conventional oil burner could conceivably handle. However, economic analysis did indicate potential cost effectiveness using propellant-No. 2 fuel oil slurries as supplemental fuels. There is no data to confirm the technical feasibility of using such a slurry as a feed to an industrial combustor.

1.2. Laboratory Tests

In order to fill this data gap, an extensive series of laboratory tests were conducted during the course of this project to evaluate the physical and chemical characteristics, as well as the chemical compatibility, of propellant-No. 2 fuel oil slurries. Based on the results obtained from the laboratory tests, an economic analysis was performed using the propellant-No. 2 fuel oil slurries which possessed the most desirable physical and chemical characteristics for use as supplemental fuels. The safety aspects of the process, including propagation of reaction testing on propellant-No. 2 fuel oil slurries, will be published separately.

1.3 Propellants

The propellants studied during this project were nitrocellulose, nitroguanidine, and AA2 double-base. The nitroguanidine was supplied as a dry (<1 percent H_2O), finely-divided powder. The nitrocellulose was received as a water-wet (28-29 percent H_2O), finely-divided powder, while the AA2 propellant was supplied as paper-thin shavings of various lengths. Nitrocellulose-No. 2 fuel oil slurries containing 5-15 percent by weight of the propellant were prepared from water-wet material, as well as from nitrocellulose that was dried to <1 percent H_2O content. Nitroguanidine-No. 2 fuel oil slurries were prepared that contained 5-15 percent by weight of the propellant. The AA2 propellant was wet-ground with No. 2 fuel oil to produce slurries containing 5-30 percent by weight of the propellant. The particle-size distributions of the AA2 propellant-No. 2 fuel oil slurries were similar to those reported previously for explosives-No. 2 fuel oil slurries.

1.4 Characteristics

1.4.1 Physical Characteristics

The physical characteristics of the propellant-No. 2 fuel oil slurries described above were evaluated by measuring the solubilities, densities, and viscosities of these samples at 25°C, 45°C, and 65°C. AA2 propellant is slightly soluble in No. 2 fuel oil (0.016 g/ml @ 65°C), while nitrocellulose and nitroguanidine are insoluble (<0.010 g/ml @ 65°C). Densities were measured and this data was used to calculate viscosities and certain parameters in the economic analysis. Viscosity measurements at 65°C indicated that for nitrocellulose (dried)-No. 2 fuel oil slurries, the viscosity of the supplemental fuel would exceed that capable of being fed to a conventional oil burner (i.e., approximately 30 centistokes) when the weight percent nitrocellulose content in the No. 2 fuel oil exceeded 7.5 percent. Similarly, for nitrocellulose (water-wet)-, nitroguanidine-, and AA2 propellant-No. 2 fuel oil slurries, the viscosities of these supplemental fuels exceeded that capable of being fed to a conventional oil burner when the weight percent propellant content in the No. 2 fuel oil exceeded 10 percent.

1.4.2 Chemical Characteristics

The chemical characteristics of the propellant-No. 2 fuel oil slurries described above were evaluated by measuring the flash points, fire points, heats of combustion, and emissions from these materials. The flash and fire point measurements showed that each propellant-No. 2 fuel oil slurry may be classified as "combustible". The heat of combustion values measured experimentally for each propellant studied averaged approximately 4,300 Btu/lb; when these materials were added to No. 2 fuel oil, the heat of combustion calculated for the resulting propellant-No. 2 fuel oil slurry was less than that for No. 2 fuel oil only. Finally, the major emissions to be expected from burning propellant-No. 2 fuel oil slurries as supplemental fuels, assuming complete combustion of the No. 2 fuel oil component, are carbon dioxide (CO_2) and water (H_2O).

Small amounts of nitrogen oxides (NO_x), ammonia (NH_3), hydrogen (H_2), nitrogen (N_2), carbon monoxide (CO), and lead oxides are also expected to be emitted from the propellant components.

1.4.3 Compatibility

The chemical compatibility of selected propellant-No. 2 fuel oil slurries was assessed by a thermal analysis technique known as differential scanning calorimetry. This technique showed that the chemical stability of the propellants was only slightly affected by blending them with No. 2 fuel oil. Propagation of reaction testing on the propellant-No. 2 fuel oil slurries is currently being performed by Hercules, Inc. As mentioned earlier, the results from these tests will be published separately.

1.5 Economic Analysis

The economic analysis showed that fueling combustors with 10 percent by weight nitrocellulose-, nitroguanidine-, or AA2 propellant-No. 2 fuel oil slurries as supplemental fuels could be a cost effective process; costs per ton for burning these slurries averaged $350, while the cost per ton for open burning/open detonation (OB/OD) disposal of propellants currently ranges from $300-$813. The limit of 10 percent by weight concentration of propellant in the slurry is based on the viscosity that could be handled by a conventional, unmodified oil burner. In addition, the economic analysis also indicated that burning propellant-No. 2 fuel oil slurries as supplemental fuels could be a cost-effective, viable option for disposing of large quantities of these materials if the Army's industrial combustors were retrofit with burners capable of handling a fuel with a viscosity double that capable of being fed to a conventional, unmodified oil burner.

1.6 Conclusions and Recommendations

The major conclusion of this project and recommendations for additional work, based on the chemical and physical characteristics tests, the chemical compatibility tests, and the economic analysis of using various propellant-No. 2 fuel oil slurries as supplemental fuels is as follows:

1. From a technical standpoint of using a conventional oil burner, it would be feasible to use 7.5 percent by weight nitrocellulose-, 10 percent by weight nitroguanidine-, and 10 percent by weight AA2 propellant-No. 2 fuel oil slurries as supplemental fuels for the Army's industrial combustors. If a modified oil burner could be identified that could burn a supplemental fuel with, for example, twice the viscosity that a conventional oil burner could handle, then it might be feasible to burn 15 percent by weight nitroguanidine- and 20 percent by weight AA2 propellant-No. 2 fuel oil slurries as supplemental fuels. The economic advantage of using these latter slurries as fuels could easily offset the costs associated with retrofitting the Army's industrial combustors to handle more viscous feeds than is currently possible with conventional oil burner technology.

1.7 Future Work

As stated in the test plan for this project, future work will include testing to find suitable means for incorporating single- (nitrocellulose) and double-base (AA2) propellants into a propellant/coal matrix stable under storage and firing. Tennessee Valley Authority's extensive experience with granulation technology as applied to fertilizer materials will be utilized during this phase of the project. In addition, we recommend that modified oil burners capable of burning supplemental fuels with viscosities greater than the 30 centistoke upper limit for a conventional burner should be identified and the technical and economic feasibility of applying them to the supplemental fuels project should be assessed.

II. INTRODUCTION

2.1 General

This report provides a technical and economic evaluation of the feasibility for using waste propellant-No. 2 fuel oil mixtures as supplemental fuel for burning in military combustors. The study was conducted under contract TV-79416 by the Tennessee Valley Authority during the period of November 19, 1990 to May 15, 1991.

The military currently has a large inventory of acceptable propellants which are obsolete due to changes in the weapon systems for which the propellants were originally produced. Additional quantities of waste propellants, i.e., propellants that do not conform to ballistic, chemical, or physical specifications, are generated during the normal process of manufacturing these materials. For example, according to the Environmental Conference proceedings of the "Hazardous Waste Minimization Interactive Workshop" sponsored by the Army Materiel Command in November 1987, 158,000 metric tons of obsolete conventional munitions are in the demilitarization inventory with a total of 249,000 metric tons projected by the year 1993.

Currently available options for disposing of obsolete or out-of-specification propellants are open-air burning, open-air detonation, or incineration (1,2). At the Radford Army Ammunition Plant alone, 88 metric tons of solvent-based propellants (single-, double-, or triple-base) are slowly being disposed of by Open Burning/Open Detonation (OB/OD) or incineration. However, these options are being severely constrained due to increased pressure from local, state, and national environmental groups and agencies. For example, disposing of waste energetic compounds has come under scrutiny as a consequence of the end in interim status for incinerators under the Resource Conservation and Recovery Act (RCRA). OB/OD of energetic wastes requires a Subpart X permit. Subpart X operations remain under interim status until November 1992. At that time, whether or not OB/OD operations will be allowed to continue in their current form is unknown (3).

The United States Army Toxic and Hazardous Materials Agency (USATHAMA) is currently conducting a program to develop methods and procedures for utilizing waste explosives and propellants as supplemental additives to fuels for the recovery of energy from these compounds. Preliminary testing on the explosives TNT and RDX have been encouraging. The method used to introduce these explosives as a fuel additive involves solvation and mixing with No. 2 fuel oil (4). Preliminary testing using the propellant nitrocellulose indicates that such solvation and mixing with No. 2 fuel oil is not cost effective due to the fact that only relatively small amounts (approximately 2-3 weight percent) of nitrocellulose can be incorporated in the solvent-No. 2 fuel oil mixture without increasing the viscosity of the resulting nitrocellulose-solvent-No. 2 fuel oil solution beyond the maximum value which a conventional oil burner could conceivably handle (5). However, an economic analysis did indicate potential cost effectiveness of an alternative process using propellant-No. 2 fuel oil slurries as supplemental fuels. There is no data to confirm the technical feasibility of using such a slurry as a feed to an industrial combustor.

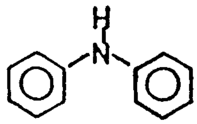
The following introductory sections will describe the manufacturing process and the chemical and physical characteristics of each type of propellant and the common base ingredients found in each formulation.

2.2 Composition and Methods of Preparation and Properties of Propellants

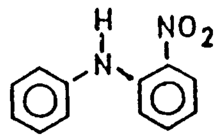
2.2.1 Major Components of Typical Propellants

Three types of propellant are used in military ordnance: single-, double-, and triple-base. These propellants contain at least one of three common base ingredients: nitrocellulose, nitroglycerin, and/or nitroguanidine. Single-base propellant contains predominantly nitrocellulose; double-base propellant is a solution of nitroglycerin plasticizer in nitrocellulose; and triple-base propellant contains nitrocellulose, nitroglycerin, and nitroguanidine. Different grades of nitrocellulose, containing different weight percent nitrogen contents are used in the manufacture of each type of propellant. For example, triple-base propellant is manufactured with 12.6 percent nitrogen nitrocellulose, while single-base propellant is manufactured from a blend of 12.5- and 13.4-percent nitrogen nitrocellulose. For a single-base propellant, 85-98 percent of the composition consists of nitrocellulose; for a double-base propellant, the fraction of nitrocellulose decreases to 55-78 percent, while for a triple-base propellant, only about 20-28 percent of the composition consists of nitrocellulose.

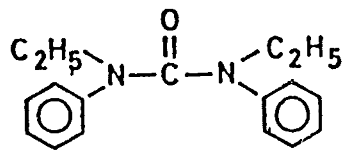
Stabilizers are frequently incorporated into nitrocellulose-based propellants to promote long-term stability and prolong the safe storage life of these materials. The chemical compounds which have traditionally been used for this purpose are basic compounds such as amines or ureas. Typical examples include diphenylamine (DPA), 2-nitrodiphenylamine (2-NDPA), and 1,3 diethyl-1,3-diphenyl urea (Ethyl Centralite). The structures of these compounds are shown on the following page. Alkali salts are sometimes added to suppress "afterburning" (in rockets) and "muzzle flash" (in guns) caused by the subsequent burning in air



DPA



2-NDPA



Ethyl Centralite

Structures of Typical Amine and Urea Stabilizers

of the combustion products CO and H_2. Examples of these alkali salts include barium nitrate, potassium nitrate, potassium sulfate, and lead carbonate.

The chemical analyses of various propellant types may be found in the literature. Since the only true propellant used in this study is the AA2 material, we were mainly interested in the chemical analyses of double-base propellants. A list of multi-base propellant ingredients and their functions is presented in Table 2-1.

General solubility characteristics for various propellant ingredients were also compiled from the literature. Based on this information, the propellant ingredients may be separated into four groups: hydrophilic, organophilic, insoluble, and others as shown in Table 2-2.

2.2.2 Nitrocellulose

2.2.2.1 Chemical and Physical Properties of Nitrocellulose (6).

Nitrocellulose is a cellulose derivative and its solid structure strongly resembles the cellulose from which it is derived. In the manufacture of military-grade propellants, the cellulose

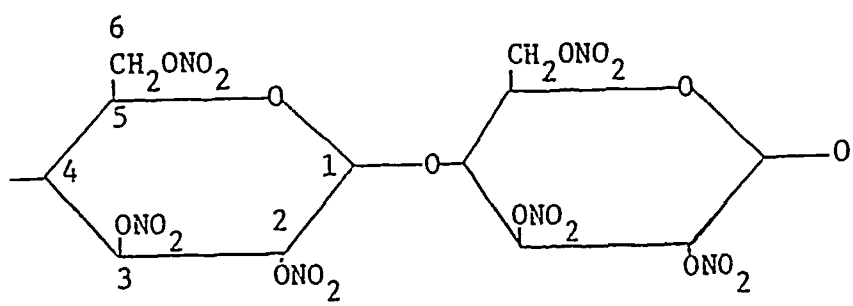
Table 2-1. Multi-Base Propellant Ingredients and Functions

Ingredient	Function
Nitrocellulose	A base ingredient that is a binder. Yields gaseous decomposition products and energy.
Nitroglycerin	A base ingredient that yields gaseous decomposition products and energy.
Nitroguanidine	A base ingredient that yields gaseous decomposition products and energy. Gases are cool and much less gun barrel erosion is obtained than with other propellant bases.
Dibutylphthalate (DBP)	Plasticizer. Peptizes binders such as nitrocellulose so that fibers form plastics such as propellant. Improves mechanical properties such as promoting increased elongation. Decreases energy. Decreases hygroscopicity.
2-nitrodiphenyl-amine (2-NDPA)	Stabilizer. Acquires decomposition products to inhibit decomposition and decreases energy. (Also acts as rate modifier.)
Ethyl centralite (EC)	Stabilizer. Acquires decomposition products to inhibit decomposition and decreases energy.
Potassium sulfate Barium nitrate	Flash and smoke reducers to inhibit completion of combustion and reduce flash (associated with radar detection). Particle size is important. Provides some energy.
Cryolite	Flash reducer, insoluble in water. Therefore, cryolite is good for slurry mix operations.
Graphite (glaze)	Acts as a lubricant, thereby increasing loading density. Also acts as a conductor for static electricity.
Carbon black	Increases rate of burning. Opacifies and prevents subsurface burning.
Acetone	Gelatinizes (peptizes) nitrocellulose so that other ingredients can be bound into it.
Water	Used in propellant manufacturing to keep nitrocellulose wet and to purify. Keeps nitrocellulose fibers from becoming tightly knit. Aids in cross linking nitrocellulose so that processing is facilitated.

Table 2-2. Separation of Propellant Ingredients into Groups

Hydrophilic	Organophilic
Potassium nitrate	Dinitrotoluene
Barium nitrate	Dibutylphthalate
Potassium perchlorate	Diphenylamine
Lead carbonate	2-nitrodiphenylamine
Potassium sulfate	Ethyl centralite
Insolubles	**Others**
Graphite	Nitrocellulose (12.6% N)
Carbon black	Nitrocellulose (13.15% N)
Cryolite	Nitroguanidine

source from which the nitrocellulose is prepared is cotton linters. Cotton linters are the material remaining on or attached to cotton seeds after the more valuable cotton hairs have been removed. Typical nitrocelluloses are high molecular weight (10^5-10^6 g/mole) polymer chains composed of anhydroglucose units, each containing up to three nitrate groups. Two such units for fully nitrated cellulose are shown below.



Fully Nitrated (14.15 Percent Nitrogen) Nitrocellulose

The chemical reaction which converts the cotton linters to nitrocellulose is actually not a nitration but an esterification reaction. In each glucose residue of the cellulose chain, there are three hydroxyl (-OH) groups, two secondary and one primary, which theoretically could result in the formation of one or more definite compounds corresponding to the successive nitration of each type of hydroxyl group in each residue. In practice, however, no such distinction of mono- or dinitrate can be made with certainty and there is no valid evidence to suggest that even the primary hydroxyl group is different from the two secondary groups in regard to their relative reactivity with nitric acid. A representative formula for nitrated cellulose may be written as $C_6H_7(OH)x(ONO_2)y$ where $x + y = 3$. The mononitrate, $x = 2$ and $y = 1$, has a nitrogen content of 6.76 percent; the dinitrate, $x = 1$ and $y = 2$, has a nitrogen content of 11.11 percent; and the trinitrate, $x = 0$ and $y = 3$, has a nitrogen content of 14.14 percent.

The nitrogen content determines the chemical and physical properties of any particular nitrocellulose. In fact, the great majority of nitrocelluloses which are useful for industrial purposes have nitrogen contents not very far removed from 12.0 percent. The more highly nitrated variety containing from 12.9- to 13.5-percent nitrogen content, which is made for incorporation into military propellants, is known by the traditional name of "guncotton". Nitrocelluloses used in propellants contain 12-13.2 percent nitrogen by weight and consequently, still have a significant number of unnitrated hydroxyl groups randomly distributed along the polymer. In nitrocellulose with less than 14.14 percent nitrogen, the NO_2 groups are distributed randomly along the entire length of the cellulose polymer, so x and y should be regarded as average values over the entire length of the chain. These unreacted hydroxyl groups strongly affect the physical and chemical properties of the nitrocellulose polymer.

2.2.2.2 Manufacture of Nitrocellulose and Single-Base Propellants (6)

In the manufacture of nitrocellulose, the first step is the pretreatment of the cellulose. Cotton linters that have been suitably purified by washing with water are dried until the moisture content is reduced from 6-7 percent to about 0.5 percent. The linters are then nitrated by the mechanical dipper process which has displaced other, more hazardous processes. The composition of the mixed acid used in this process varies depending on the type of cellulose nitrate, the degree of nitration desired, and the season of the year. A typical mixed acid composition for the preparation of guncotton from cotton linters is 60.5 percent sulfuric acid, 24.5 percent nitric acid, 4.0 percent nitrosylsulfuric acid, and 11.0 percent water.

About 1,500 pounds of mixed acid are placed in a stainless-steel nitrator at a temperature of 30°C. The nitrator is equipped with two vertical agitators revolving in opposite directions that impart motion toward the center. Approximately 32 pounds of cotton linters are added. The paddles of the agitator are designed to immediately draw the linters below the surface of the acid, away from the fume exhaust line. Nitration is exothermic, so provisions must be made to prevent the temperature from rising above 30°C. When nitration has been completed (about 20 minutes), the slurry is discharged through a valve in the bottom to a centrifuge, where most of the mixed acid is removed. The acid-wet, crude nitrocellulose is then forked through an opening in the bottom of the centrifuge into a drowning basin where rapid submersion in cold water takes place. The nitrocellulose must then be stabilized and purified.

Five different grades of nitrocellulose are recognized and used in the preparation of military propellants (Table 2-3). Pyroxylin, which contains from about 8- to 12.3-percent nitrogen, consists of light yellow, matted filaments. When dissolved in 3 parts ether and 1 part alcohol, the solution is pale yellow and viscous. Pyroxylin is also soluble in acetone or glacial acetic acid and is precipitated from solution by water. Pyroxylin is very flammable and is decomposed by light. The pyroxylin used for military purposes contains 12.2±0.10 percent of nitrogen. Pyroxylin is the type of nitrocellulose that was used in the manufacture of the AA2 propellant used in this study.

Table 2-3. Military Grades of Nitrocellulose

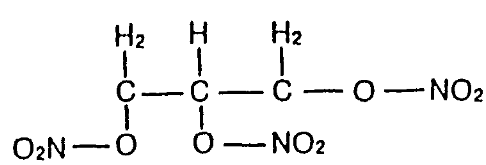
	Class	Nitrogen, Percent
Grade A	Pyrocellulose	
Type I		12.60±0.10
Type II		12.60±0.15
Grade B	Guncotton	13.35 minimum
Grade C	Blended	
Type I		13.15±0.05
Type II		13.25±0.05
Grade D	Pyroxylin	12.20±0.10
Grade E		12.00±0.10

In the manufacture of single-base propellants, wet nitrocellulose from the manufacturing process described above is dehydrated. Dehydration is accomplished by pressing the nitrocellulose at low pressure in order to squeeze out water, adding 95 percent ethanol, and pressing at about 3,500 pounds per square inch. A block containing 25 pounds of dry nitrocellulose and about one-third that much of 90 percent ethanol is obtained. The wet block is broken into small lumps by means of a rotating drum containing iron prongs and a screen. The nitrocellulose is transferred to a water-cooled dough mixer and, while in this operation, ether equal to approximately two-thirds of the weight of dry nitrocellulose is added. Any plasticizing agents and stabilizers to be included in the composition are dissolved in or mixed with the ether prior to addition to the nitrocellulose. After addition of the ether is complete, materials such as potassium nitrate are added. Mixing of the ingredients is continued for about one hour. A partially colloided mixture which resembles dry oatmeal is produced. After pressing this mixture into a block, extruding it through a macaroni press, and re-pressing it into a block again, a well colloided material is obtained. This is placed in a graining press and extruded through a carefully designed die by the application of pressure. The material emerges as a cord with one or more cylindrical performations. The cord is cut into pieces of predetermined length. Removal of the volatile solvent, with shrinkage of the grains to their final dimensions, completes the manufacture of most common single-base propellants.

2.2.3 Nitroglycerin

2.2.3.1 Chemical and Physical Properties of Nitroglycerin (6)

Nitroglycerin, glycerol trinitrate, or 1,2,3-propanetriol trinitrate, shown below, is a clear, colorless, odorless, oily liquid with a theoretical maximum density of 1.596 grams per cubic centrimeter. Nitroglycerin has a sweet, burning taste and a molecular weight of 227.1.



Structural Formula for Nitroglycerin

Nitroglycerin can be used as a solvent for other explosives; 35 grams of dinitrotoluene dissolve in 100 grams of nitroglycerin at 20°C and 30 grams of trinitrotoluene dissolve per 100 grams at 20°C. Nitroglycerin is used extensively in propellant compositions as gelatinizing agent for nitrocellulose as well as in dynamites and for the shooting of oil wells.

2.2.3.2 Manufacture of Nitroglycerin and Double-Base Propellants (6)

Nitroglycerin is manufactured by nitrating glycerin with a mixed acid. Several processes are currently used in the United States and Europe. The processes can be generally classified according to whether they are continuous or batch production.

In batch production, high grade glycerol is added to mixed acid that consists of 45- to 50-percent nitric acid and 50- to 55-percent sulfuric acid. The reaction between the glycerol and mixed acid is carried out in a nitrator equipped with a mechanical agitator and cooling coils that carry a brine solution of calcium chloride at -20°C. A 6,800 pound charge of mixed acid is placed in the nitrator and the glycerol is added in a small stream. Stirring is continued for a few minutes after the 50 to 60 minutes required to add the glycerol. Then the nitroglycerin is allowed to separate completely. The lower layer of spent acid is drained off to be recycled or otherwise disposed of and the nitroglycerin is run off into a neutralizer. An initial 40°C water wash removes most of the acid. Then a wash with a 2- to 3-percent sodium carbonate solution neutralizes the residual acid. Washing with water is continued until the water is free of alkali and the nitroglycerin is neutral to litmus. The yield of nitroglycerin is 230±5 parts by weight per 100 parts of glycerin.

The chemistry involved in the continuous manufacture of nitroglycerin is basically the same as that described for batch processing except the equipment is designed to allow nonstop production. The advantages of continuous processes are: faster production, better process control, lower labor costs, and, perhaps most important, safety, as a result of the smaller accumulations of nitroglycerin at any given plant location. In the United States the common practice is to nitrate mixtures of glycol and glycerol. The nitration proceeds in the same manner as with pure glycerol.

Double-base propellants are manufactured by two methods. The solvent process is similar to that used for single-base propellants except that a mixture of ethanol and acetone is used as the solvent and the solvent recovery procedure is omitted because of the hazard involved in recovering solvents containing nitroglycerin.

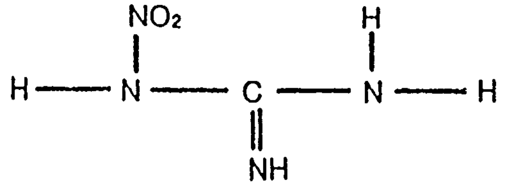
The solventless process is used when the nitroglycerin and any other colloiding agents constitute approximately 40 percent of the composition. The AA2 propellant used in this study is manufactured using the solventless process. In this process the wet nitrocellulose (e.g., pyroxylin for AA2) is blended with the nitroglycerin in a tank filled with water. Ethyl centralite is mixed in and the bulk of the excess water is removed by centrifuging. The resulting paste is put in cotton bags and subjected to heated air currents to reduce the moisture content. The remaining constituents are then blended with the partially dried paste. Repeated rolling between heated steel rollers removes the rest of the water and completes colloiding of the nitrocellulose. The thickness of the sheet formed is controlled carefully and varies with use. If the sheet is to be cut into flakes for use in small arms or mortars, the thickness is between 0.08 and 0.32 millimeter (0.003 and 0.0125 inch).

Sheets to be extruded in the form of large grains for use in rockets may be as thick as 3.18 millimeters (0.125 inch). The AA2 propellant shavings used in this study are the waste material resulting from the latter extrusion process.

2.2.4 Nitroguanidine

2.2.4.1 Chemical and Physical Properties of Nitroguanidine (6)

Nitroguanidine, shown below, is also known as picrite or guanylnitramine. The compound has a nitrogen content of 53.84 percent, an oxygen balance to CO_2 of -30.8 percent, a theoretical maximum density of 1.81 grams per cubic centimeter, and a molecular weight of 104.1. The melting point of nitroguanidine varies somewhat with the rate of heating. The pure material melts with decomposition at 232°C, but values from 220°C to 250°C are obtainable with various heating rates.



Structural Formula for Nitroguanidine

Because of the low temperature of explosion, about 2,098°C, nitroguanidine is used in triple-base propellants that are practically flashless and less erosive than nitrocellulose-nitroglycerin propellant of comparable force. When used by the Germans in World War II in antiaircraft guns, a nitroguanidine propellant increased the barrel life from 1,700 firings to about 15,000 firings.

2.2.4.2 Manufacture of Nitroguanidine and Triple-Base Propellants (6)

Several methods for the preparation of nitroguanidine are known. The earliest method was by the direct nitration of guanidine thiocyanate with mixed acids. Guanidine thiocyanate is one of the cheapest and easiest to prepare of the guanidine salts. However, this method of production also produced sulfur compound impurities which attacked and degraded the nitrocellulose component. This lowered the stability of propellant compositions to an unacceptable degree, thus precluding early use of the compound as an ingredient in nitrocellulose based propellants. A more pure form of nitroguanidine that does not contain the sulfur compound impurities can be prepared in one of several known ways. In one method, equimolecular quantities of urea (H_2NCONH_2) and ammonium nitrate (NH_4NO_3) are fused. The product is then recrystallized from boiling water. The yield of this method is approximately 92 percent of the theoretical.

Another method of preparation involves heating a solution of equimolecular quantities of cyanamide (H_2NCN) and ammonium nitrate (NH_4NO_3) to 160°C at a pressure of 200 pounds. The product is then recrystallized from boiling water. The yield of this method is approximately 88 percent.

A third method involves the production of guanidine nitrate as a precursor to the nitroguanidine. Two reactions can be employed to produce guanidine nitrate. The first reaction is the reaction between guanidine ($H_2NC(=NH)NH_2$) and nitric acid (HNO_3). The second reaction is the reaction between dicyandiamide ($H_2NC(=NH)NHCN$) and ammonium nitrate (NH_4NO_3). As the guanidine or dicyandiamide can be produced from the raw materials coke, limestone, atmospheric nitrogen, and water, the production of nitroguanidine does not involve the use of special natural resources. However, a very large amount of electrical energy is required for the production of dicyandiamide or guanidine. Dehydration of guanidine nitrate to nitroguanidine is affected by adding 1 part of the nitrate to 2.3 parts by weight of sulfuric acid (95 percent), so that the temperature does not rise above 10°C. As soon as all the nitrate has been dissolved, the milky solution is poured into seven and one-half parts of ice and water. The mixture is kept ice-cold until precipitation is complete, when the nitroguanidine is filtered, washed with cold water, and redissolved in 10 parts of boiling water. The nitroguanidine recrystallizes when the solution cools. The yield is approximately 90 percent of the theoretical.

The manufacturing process used for the nitroguanidine triple-base propellants in the United States has been uniformly solvent extrusion. The amount of solvent used is quite low so the propellant is very soft during extrusion. The soft strands may require partial drying before cutting in order not to deform the cross section at the cut. Removal of solvent from the triple-base propellant is rapid, possibly due to diffusion of solvent within the grain along the crystal-plastic interfaces. In order to make a good quality grain, lower drying temperature gradients are used in order to avoid steep solvent gradients which result in distortion and cracking.

III. DISCUSSION OF RESULTS

3.1 Physical Characteristics of Propellant-No. 2 Fuel Oil Slurries

The first series of tests in this project were conducted to determine the physical characteristics of propellant-No. 2 fuel oil slurries. Initially, tests were conducted to determine the feasibility of wet-grinding the AA2 propellant shavings with No. 2 fuel oil to produce slurries suitable for subsequent physical testing. The nitrocellulose and nitroguanidine propellant samples did not require wet grinding prior to dispersing them in No. 2 fuel oil to form slurries suitable for testing. The solubility of each propellant in No. 2 fuel oil at 25°C, 45°C, and 65°C was then measured. Next, the particle-size distributions of representative AA2 propellant-No. 2 fuel oil slurries were measured. The settling rate for each propellant-No. 2 fuel oil slurry was recorded. Finally, the density and viscosity of each propellant-No. 2 fuel oil slurry was measured at 25°C, 45°C, and 65°C.

3.1.1 Characterization and Composition of Each Propellant Sample

Each propellant sample used in this project was supplied by the Naval Ordnance Station in Indian Head, Maryland. Nitroguanidine was supplied as a dry (<1 percent H_2O), finely-divided powder. As Figure 3-1 shows, some aggregation of the nitroguanidine occurred during shipping and handling, however, these aggregates were easily broken up when the nitroguanidine was dispersed in the No. 2 fuel oil. A chemical analysis for percent carbon, hydrogen, and nitrogen content confirmed the purity of the nitroguanidine sample as greater than 99 percent.

The nitrocellulose was received as a water-wet (28-29 percent H_2O), finely divided powder that contained 13.3 percent nitrogen by weight. A photograph of this material at 2X magnification

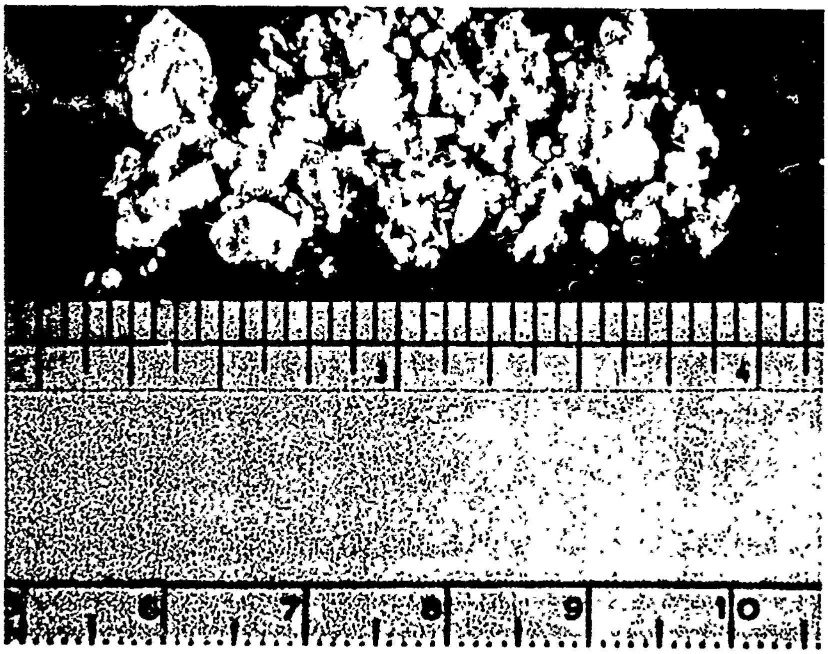


Figure 3-1. Photograph of Nitroguanidine Propellant (2 x Magnification).

shows the finely-divided nature of this material (Figure 3-2). Finally, the AA2 propellant was supplied as paper-thin shavings of various lengths (Figure 3-3), resulting from the extrusion of the propellant sheets through a die to form large grains for use in rockets. The composition of this propellant was kindly supplied by Hercules, Inc., Rocket Center, West Virginia (Table 3-1). This composition was confirmed by a chemical analysis.

Table 3-1. Composition of the AA2 Propellant Formulation

Ingredient	Weight Percent in the Formulation
Nitrocellulose (12.2 percent nitrogen)	51.0
Nitroglycerin	38.6
Triacetin	2.7
Lead Salt	4.0
Dinitrophenylamine	1.6
2-Nitrodiphenylamine	2.0
Wax	0.1

3.1.2 Solubility Tests

Nitrocellulose was found to be insoluble (<0.010 g/ml) in No. 2 fuel oil at 25°C, 45°C, and 65°C. As was noted in a previous report (5), the common paraffin hydrocarbons are very poor solvents for nitrocellulose since they are practically devoid of any polar groups within their molecular structure. As a general rule, no substance is a solvent for nitrocellulose unless its molecular structure contains a polar group. For example, acetone, which contains a polar carbonyl oxygen (C=O) group, has been shown to be one of the most effective solvent for nitrocelluloses of various nitrogen contents.

Nitroguanidine was also found to be insoluble (<0.010 g/ml) in No. 2 fuel oil at 25°C, 45°C, and 65°C. Nitroguanidine is

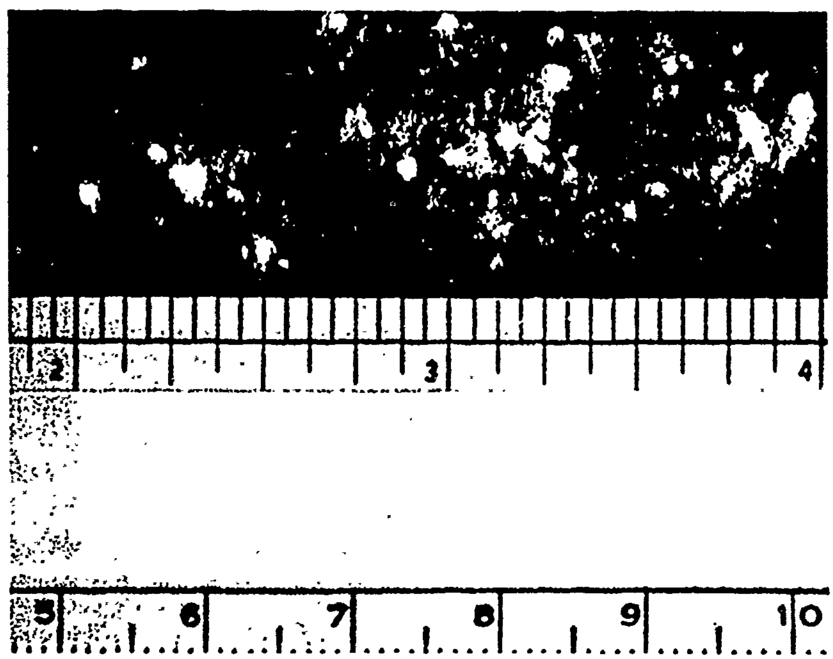


Figure 3-2. Photograph of Nitrocellulose (Dried) Propellant (2x Magnification).

Figure 3-3. Photograph of AA2 Propellant Shavings (2x Magnification).

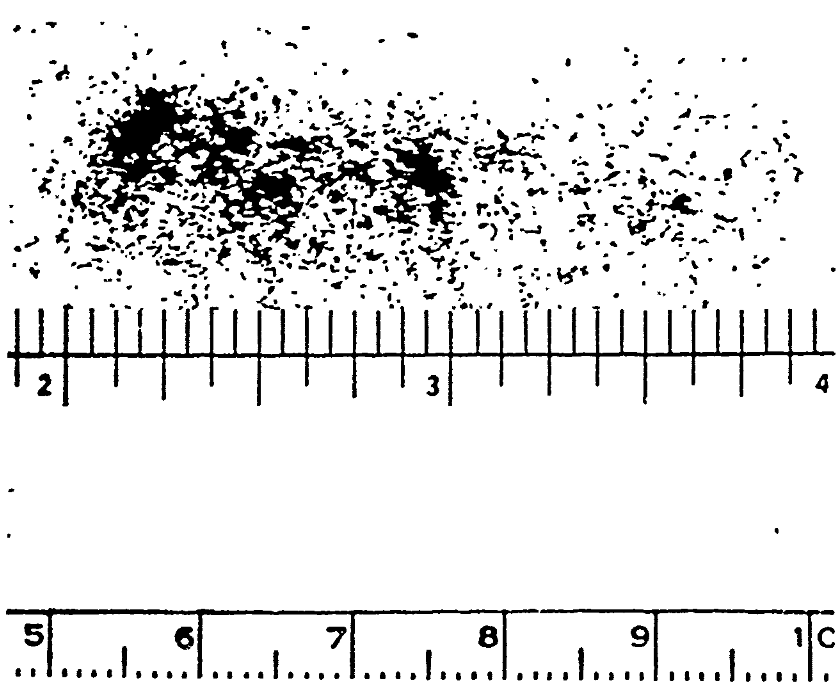


Figure 3-4. Photograph of AA2 Propellant Shavings After Grinding in Fuel Oil (2x Magnification).

slightly soluble in water and alcohol at 25°C, but nearly insoluble in ether at this temperature. The AA2 propellant was found to be slightly soluble in No. 2 fuel oil at 25°C, 45°C, and 65°C, the solubility values being 0.0145, 0.0154, and 0.0163 g/ml, respectively. As was noted in Table 2-2, the amine- and urea-based stabilizers 2-nitrodiphenylamine and ethyl centralite are organophilic compounds and may leach from the AA2 propellant into the No. 2 fuel oil.

3.1.3 Size Reduction and Particle-Size Distribution Tests

As was stated earlier, the AA2 propellant was received in the form of paper-thin shavings of various lengths and sizes. In order to produce a slurry suitable for subsequent physical and chemical testing, the AA2 propellant shavings were wet-ground with No. 2 fuel oil using an Ultra-Turrax T-25 grinder fitted with an appropriate dispersing tool (see Section 5.2.2.2 for details). The particle-size distribution from a representative AA2 propellant-No. 2 fuel oil slurry prepared with this grinding apparatus is given in Table 3-2. This particle-size distribution was characteristic of each AA2 propellant-No. 2 fuel oil slurry and did not vary significantly as the weight percent concentration of AA2 propellant in the No. 2 fuel oil was increased from 5 to 30 percent. Figure 3-4 shows a photograph taken at 2X magnification of the ground AA2 propellant after it had been filtered from the No. 2 fuel oil, washed thoroughly with kerosene, and dried. This photograph clearly illustrates the reduction in particle size for the AA2 propellant shavings capable of being attained with the Ultra-Turrax grinder.

Table 3-2. Particle-size Distribution of AA2 Propellant After Wet-Grinding in No. 2 Fuel Oil

Particle Size (micron)	Amount Retained (weight percent)	Sieve Number
420	0.4	40
250	30.5	60
177	29.3	80
125	28.2	120
90	6.0	170
45	3.2	325
<45	2.4	<325

3.1.4 Settling Rates of Propellant-No. 2 Fuel Oil Slurries

Each propellant-No. 2 fuel oil slurry was allowed to settle for approximately one week and the level to which the propellant had settled was marked on the container. The respective slurry was then shaken vigorously for 30 seconds to redisperse the propellant in the No. 2 fuel oil. The amount of time elapsed while the slurry settled to the marked position on the container was then recorded. For the nitroguanidine-No. 2 fuel oil slurries, a minimum of 60 minutes to a maximum of 120 minutes was required for a 5 and 15 percent by weight propellant-No. 2 fuel oil slurry to settle out, respectively. On average, for both the nitrocellulose (dried)- and nitrocellulose (water-wet)-No. 2 fuel oil slurries, 60 minutes was required for the nitrocellulose in the slurries to settle out, irrespective of concentration. Finally, for the AA2 propellant-No. 2 fuel oil slurries, the elapsed time for the propellant to settle out averaged less than 15 minutes.

3.1.5 Densities of Propellant-No. 2 Fuel Oil Slurries

The density of each propellant-No. 2 fuel oil slurry was measured at 25°C, 45°C, and 65°C with a mud balance according to

ASTM D 4380-84 standard procedure (Appendix A). The results obtained at each temperature for each type of slurry are summarized in Table 3-3. The densities of these slurries provide the data required for calculating the viscosity of each slurry and some economic parameters as well. The viscosity data is more informative and will be discussed in the following section.

Table 3-3. Densities[a] of Propellant-No. 2 Fuel Oil Slurries at 25°C, 45°C, and 65°C

		Density (g/ml)		
Propellant	Wt. % Propellant	25°C	45°C	65°C
No. 2 Fuel Oil	0.0	0.851	0.826	0.812
Nitroguanidine	5.0	0.875	0.858	0.846
	7.5	0.883	0.870	0.860
	10.0	0.901	0.885	0.871
	12.5	0.920	0.891	0.885
	15.0	0.933	0.908	0.895
Nitrocellulose (Dried at 70°C)	5.0	0.875	0.855	0.826
	7.5	0.886	0.872	0.840
	10.0	0.898	0.880	0.852
	12.5	0.908	0.886	0.870
	15.0	0.939	0.896	0.883
Nitrocellulose (28% Water Content)	5.0	0.872	0.859	0.847
	7.5	0.880	0.868	0.860
	10.0	0.891	0.878	0.867
	12.5	0.905	0.885	0.874
	15.0	0.910	0.893	0.883
AA2 Propellant	5.0	0.879	0.864	0.854
	10.0	0.899	0.885	0.872
	15.0	0.924	0.903	0.891
	20.0	0.943	0.926	0.911
	25.0	0.968	0.948	0.930
	30.0	0.983	0.966	0.952

[a]All values are the average of three replicates.

3.1.6 Viscosities of Propellant-No. 2 Fuel Oil Slurries

To obtain atomization in a standard, unmodified oil burner, it has been determined that the viscosity of the oil should not exceed a range of 20 to 30 centistokes at the burner tip (4). At temperatures of 25°C, 45°C, and 65°C, the neat No. 2 fuel oil exhibited viscosities of 5.3, 4.5, and 3.4 centistokes, respectively.

The viscosity of each propellant-No. 2 fuel oil slurry was measured at 25°C, 45°C, and 65°C with a Brookfield Model DV-II viscometer according to Method A, ASTM D 2196-86 and ASTM D 1439-83a standard procedures (Appendix A). The viscosity data is summarized in Table 3-4. Two general observations can be made based upon the data given in this Table: (1) the viscosity of each propellant-No. 2 fuel oil slurry increases as the weight percent concentration of propellant in the No. 2 fuel oil increases; and (2) the viscosity of each propellant-No. 2 fuel oil slurry decreases as the temperature is increased from 25°C to 65°C.

Before a more in-depth analysis of the viscosity data from the propellant-No. 2 fuel oil slurries can be presented, some additional points need to be made regarding the accuracy of viscosity measurements obtained from dispersions or slurries. Dispersions or slurries, which are multiphase materials consisting of one or more solid phases dispersed in a liquid phase, display characteristics peculiar to multiphase materials. These characteristics are discussed below.

One of the major characteristics to consider is the state of aggregation of the sample material. Are the particles that make up the solid phase separate and distinct or are they clumped together; how large are the clumps and how tightly are they

Table 3-4. Viscosities[a] of Propellant-No. 2 Fuel Oil Slurries at 25°C, 45°C, and 65°C

Propellant	Wt. % Propellant	Viscosity (cS) 25°C	45°C	65°C
No. 2 Fuel Oil	0.0	5.3	4.5	3.4
Nitroguanidine	5.0	9.3	6.5	5.7
	7.5	12.6	9.8	8.8
	10.0	31.4	18.4	16.0
	12.5	78.2	54.5	49.6
	15.0	128.9	74.4	58.6
Nitrocellulose (Dried at 70°C)	5.0	15.9	10.5	8.7
	7.5	53.5	30.4	25.0
	10.0	156.4	95.6	80.9
	12.5	381.5	203.2	180.5
	15.0	454.8	243.5	220.8
Nitrocellulose (28% Water Content)	5.0	12.4	9.8	7.8
	7.5	29.9	17.7	14.9
	10.0	54.3	40.1	33.6
	12.5	149.9	110.9	98.2
	15.0	341.9	240.5	188.0
AA2 Propellant	5.0	43.8	20.3	17.9
	10.0	51.9	40.5	35.9
	15.0	58.0	52.1	46.4
	20.0	84.7	64.3	54.7
	25.0	92.7	78.3	69.6
	30.0	105.4	87.8	83.9

[a]All values are the average of three replicates.

stuck together? If the clumps (flocs) occupy a large volume in the dispersion, the viscosity of the dispersion will tend to be higher than if the floc volume was smaller. This is due to the greater force required to dissipate the solid component of the dispersion. In fact, this provides support for the first general observation noted above for the propellant-No. 2 fuel oil slurries, namely, that the viscosity of each slurry increases as the weight percent concentration of propellant in the No. 2 fuel oil increases.

The shape of the particles making up the dispersed phase is also of significance in determining a system's rheology. Particles suspended in a flowing medium are constantly being rotated. If the particles are essentially spherical, rotation can occur freely. If, however, the particles are needle- or plate-shaped, the ease with which rotation can occur is less predictable, as is the effect of varying shear rates.

Finally, the stability of a dispersed phase is particularly critical when measuring the viscosity of a multiphase system. If the dispersed phase has a tendency to settle, producing a non-homogeneous fluid, the rheological characteristics of the system will change. In most cases, this means that the measured viscosity will decrease. This was certainly the case with each of the propellant-No. 2 fuel oil slurries measured during this study. Therefore, all the viscosity measurements described below were taken immediately after the slurry sample was shaken vigorously for 10 seconds, in accordance with ASTM D 1439-83a standard procedure (Appendix A).

The viscosities of the nitroguanidine-No. 2 fuel oil slurries at 25°C, 45°C, and 65°C are shown in Figure 3-5. At a concentration of 10 percent by weight nitroguanidine in No. 2 fuel oil at both 45°C and 65°C, the viscosities of the slurries will be below the 30 centistoke upper limit to obtain atomization in a standard, unmodified oil burner. However, if an oil burner could be modified to allow a supplemental fuel with, for example, a viscosity double that allowed in an unmodified burner, then the viscosity data taken at 65°C indicate that a nitroguanidine-No. 2 fuel oil slurry containing

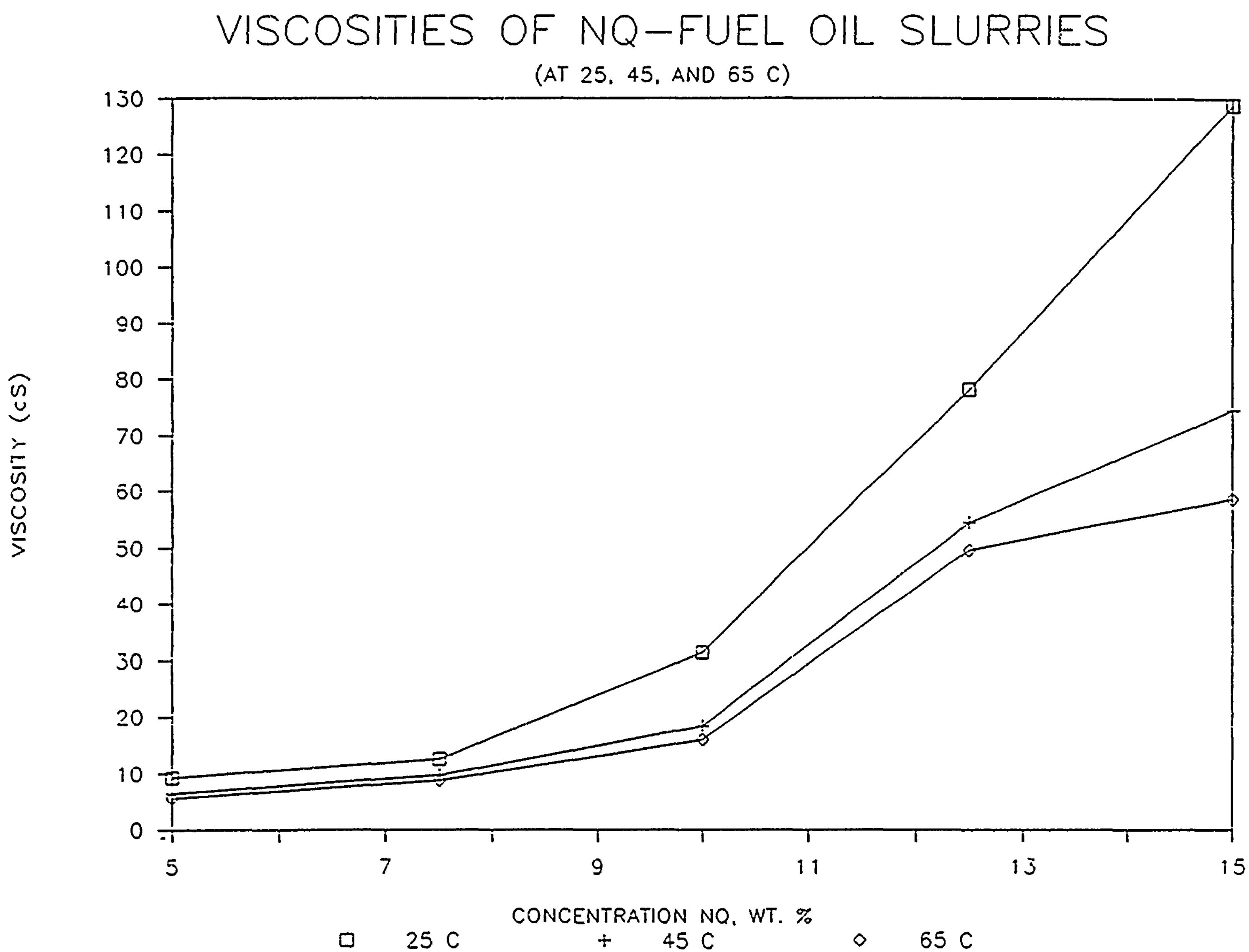


Figure 3-5. The Viscosities of Nitroguanidine-No. 2 Fuel Oil Slurries at 25°C, 45°C, and 65°C.

15 percent by weight nitroguanidine could be burned as a supplemental fuel. In fact, the economic analysis given in Section 4 indicates that it may be cost-effective to consider using a modified oil burner to dispose of propellant-No. 2 fuel oil slurries containing greater than 10 percent by weight propellant.

The viscosities of the nitrocellulose (dried)-No. 2 fuel oil slurries measured at 25°C, 45°C, and 65°C are shown in Figure 3-6. The nitrocellulose was dried to less than 1 percent water content by placing small portions in an oven for 24 hours at 70°C (see section 5.2.2.1). At a concentration of 7.5 percent by weight dried nitrocellulose in No. 2 fuel oil at both 45°C and 65°C, the viscosities of the slurries will be at and slightly below, respectively, the 30 centistoke upper limit to obtain atomization in a standard, unmodified oil burner. By comparison, the viscosities of the nitrocellulose (water-wet)-No. 2 fuel oil slurries at 25°C, 45°C, and 65°C are shown in Figure 3-7. From an inspection of this data at 65°C, it is clear that the viscosity limit to obtain atomization is not exceeded until the nitrocellulose (water-wet)-No. 2 fuel oil slurry concentration increases above 10 percent by weight of the propellant. These limits for the concentration of each propellant in the No. 2 fuel oil, i.e., 7.5 percent by weight for the dried nitrocellulose and 10 percent by weight of the water-wet (28-29 percent H_2O) nitrocellulose, could not be increased since the viscosities of the next highest concentration at 65°C in each case are well above even a 60 centistoke limit postulated for atomization of a 15 percent by weight nitroguanidine-No. 2 fuel oil slurry supplemental fuel in a modified oil burner.

Finally, the viscosities of the AA2 propellant-No. 2 fuel oil slurries measured at 25°C, 45°C, and 65°C are shown in Figure 3-8. At a concentration of 10 percent by weight AA2 propellant

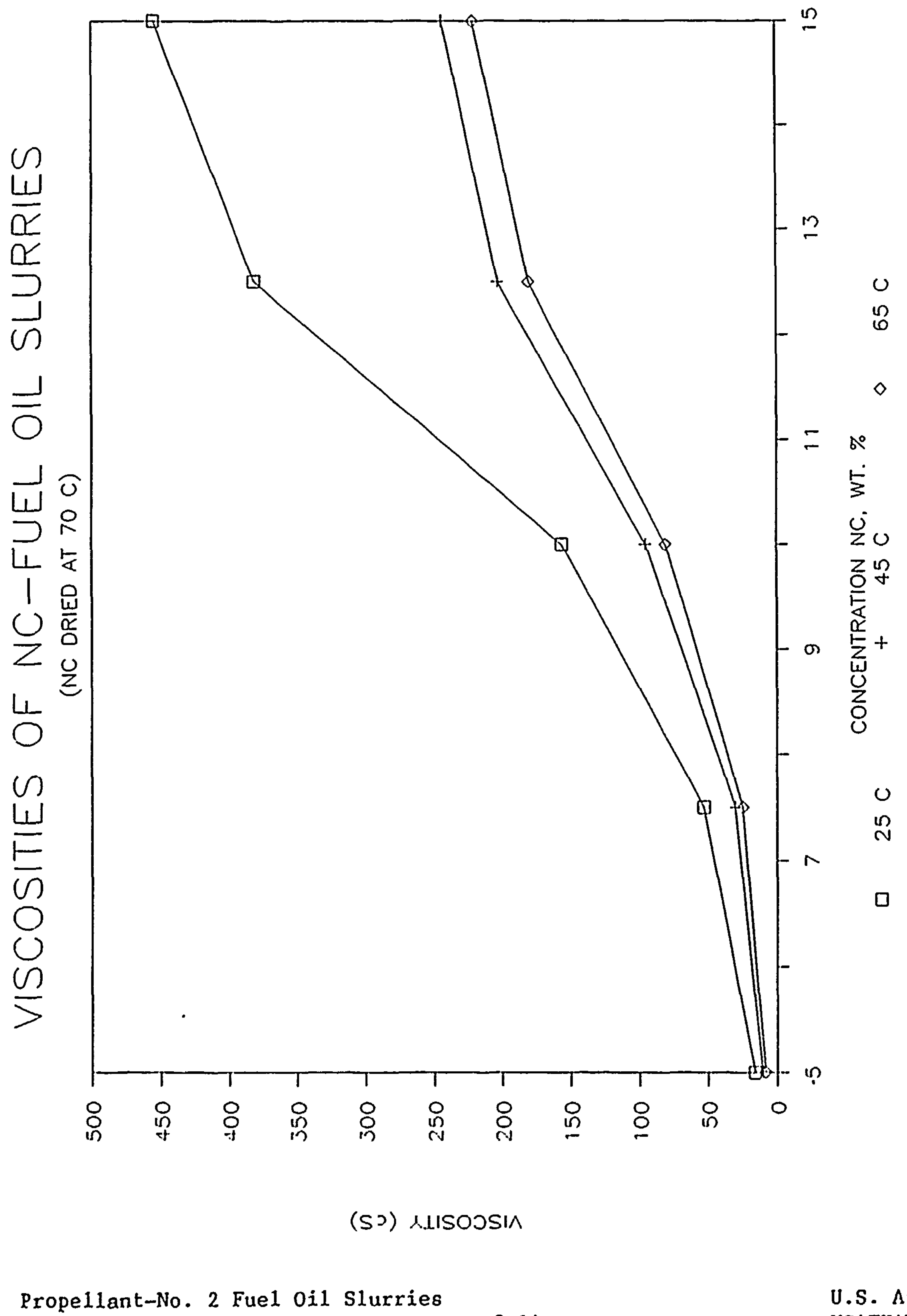


Figure 3-6. The Viscosities of Nitrocellulose (Dried)-No. 2 Fuel Oil Slurries at 25°C, 45°C, and 65°C.

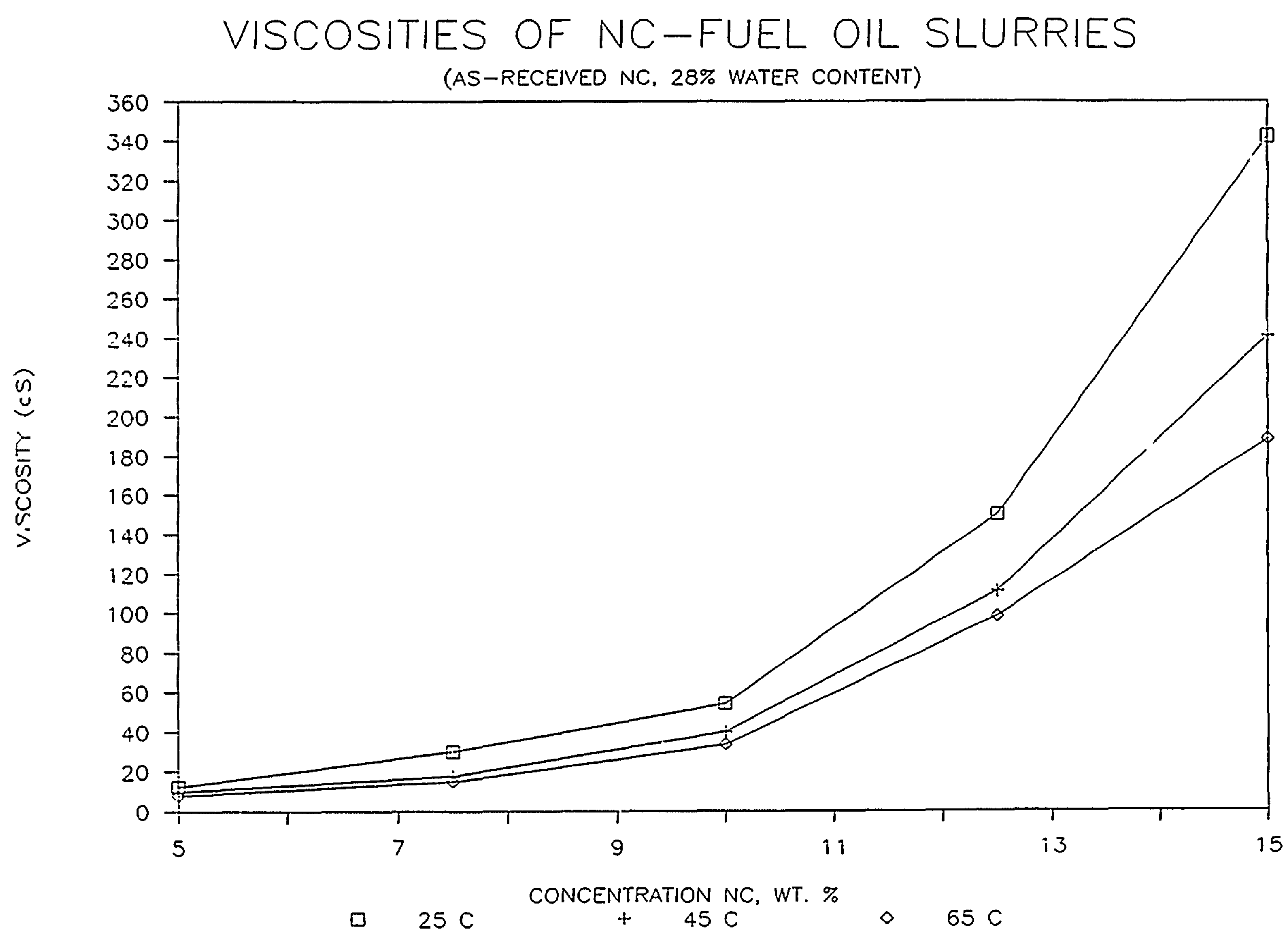


Figure 3-7. The Viscosities of Water-Wet Nitrocellulose-No. 2 Fuel Oil Slurries at 25°C, 45°C, and 65°C.

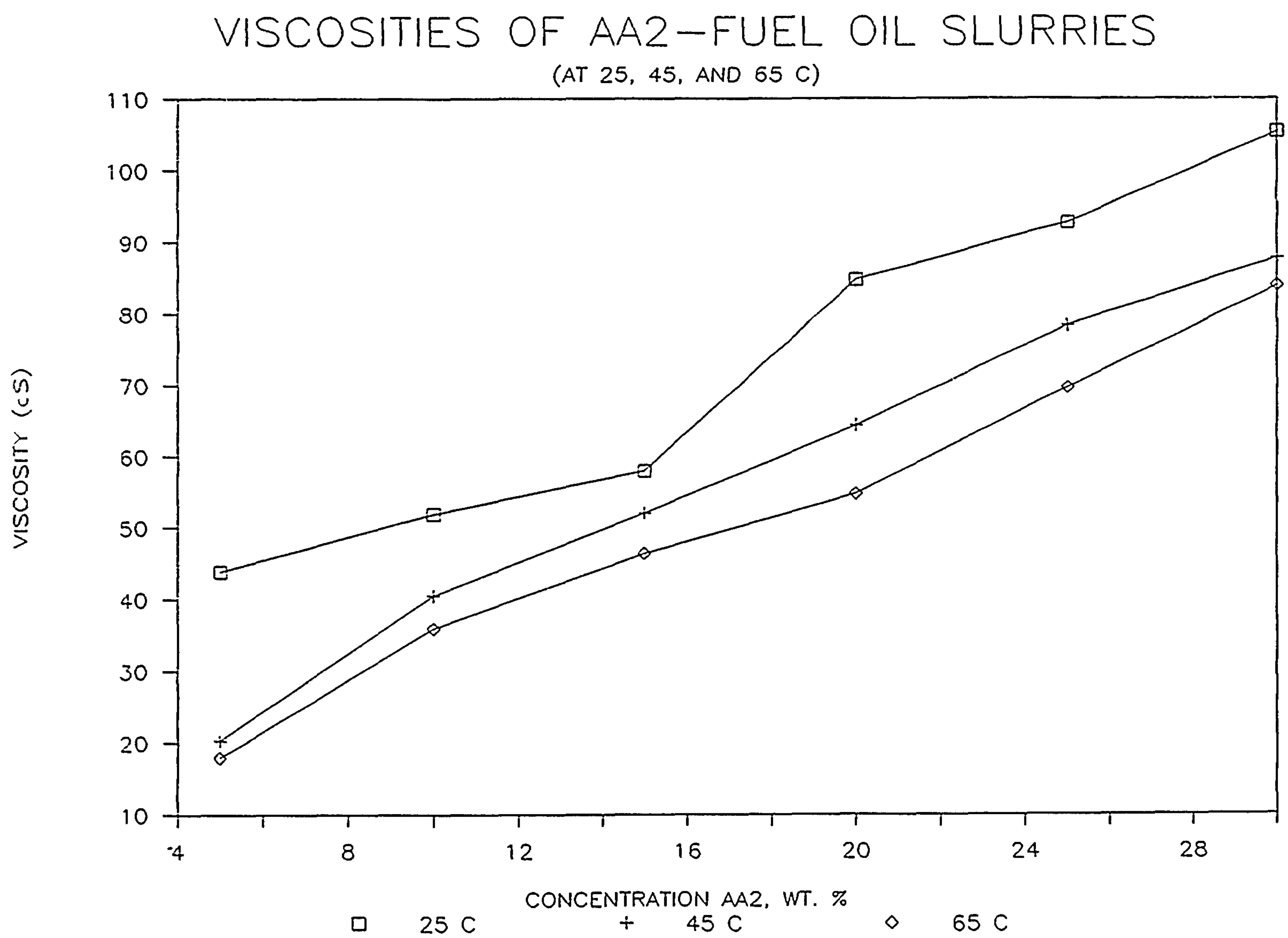


Figure 3-8. The Viscosities of AA2 Propellant-No. 2 Fuel Oil Slurries at 25°C, 45°C, and 65°C.

in No. 2 fuel oil at 65°C, the 30 centistoke upper limit to obtain atomization in a standard, unmodified oil burner will just be exceeded. However, if an oil burner could be modified to allow a supplemental fuel with, for example, a viscosity double that allowed in an unmodified burner, then the viscosity data taken at 65°C indicate that a AA2 propellant-No. 2 fuel oil slurry containing 20 percent by weight AA2 propellant could be burned as a supplemental fuel.

3.2 Chemical Characteristics of Propellant-No. 2 Fuel Oil Slurries

The second series of tests in this project were conducted to determine the chemical characteristics of the propellant-No. 2 fuel oil slurries. Flash point, fire point, heat of combustion, and emissions analysis of No. 2 fuel oil and propellant-No. 2 fuel oil slurries were performed in this phase of the project.

3.2.1 Flash Points of Propellant-No. 2 Fuel Oil Slurries

The flash point measures the tendency of a sample to form a flammable mixture with air under controlled laboratory conditions. It is one of the important properties which must be considered in assessing the overall flammability hazard of a material. The flash point is used in shipping and safety regulations to define "flammable" materials. Three degrees of flammability are commonly used: flammable, combustible and nonflammable. They are defined as follows:

- Flammable - flash point is less than 100°F,
- Combustible - flash point is greater than 100°F,
- Nonflammable - flash point is not measurable.

The flash point can also indicate the possible presence of a highly volatile and flammable component in an apparently nonvolatile or nonflammable material. The following paragraphs describe the results obtained from the determination of the flash points of No. 2 fuel oil and the propellant-No. 2 fuel oil slurries according to ASTM D 92-85 standard procedure (Appendix A).

The flash points of No. 2 fuel oil and propellant-No. 2 fuel oil slurries are summarized in Table 3-5. As stated previously, the maximum concentration of the propellants nitrocellulose and nitroguanidine that could be attained during the preparation of the slurries was 15 percent by weight. However, for the AA2 propellant, the maximum concentration of this material was 30 percent by weight.

Table 3-5. Flash Points[a] of No. 2 Fuel Oil and the Propellant-No. 2 Fuel Oil Slurries

Material	Weight Percent Propellant	Weight Percent No. 2 Fuel Oil	Flash Point (°F)
No. 2 Fuel Oil	0.0	100.0	178.0
Nitroguanidine	5.0	95.0	235.0
	10.0	90.0	219.9
	15.0	85.0	210.2
Nitrocellulose (Dried at 70°C)	5.0	95.0	210.1
	10.0	90.0	195.1
	15.0	85.0	180.0
Nitrocellulose (Water-Wet)	5.0	95.0	195.1
	10.0	90.0	204.8
	15.0	85.0	185.0
AA2 Propellant	5.0	95.0	204.8
	10.0	90.0	195.1
	15.0	85.0	180.0
	20.0	80.0	175.9
	25.0	75.0	170.1
	30.0	70.0	166.7

[a]Measured according to ASTM D 92-85 standard procedure.

The flash points of all the nitrocellulose-No. 2 fuel oil and nitroguanidine-No. 2 fuel oil slurries are higher than the flash point of neat No. 2 fuel oil. In contrast, when the concentration of AA2 propellant in No. 2 fuel oil was increased above 15 percent by weight, the flash point became lower than the flash point of neat No. 2 fuel oil. Finally, the data summarized in Table 3-5 clearly shows that each propellant-No. 2 fuel oil slurry may be classified as "combustible".

3.2.2 Fire Points of Propellant-No. 2 Fuel Oil Slurries

The fire point measures the characteristics of a sample which are required to support combustion. The fire point is defined as the lowest temperature at which a volatile combustible substance vaporizes rapidly enough to form above its surface an air-vapor mixture which burns continuously when ignited by a small flame. The results obtained from determination of the fire points of No. 2 fuel oil and the propellant-No. 2 fuel oil slurries according to ASTM D 92-85 standard procedure (Appendix A) are discussed in the following paragraph.

The fire points of No. 2 fuel oil and the propellant-No. 2 fuel oil slurries are summarized in Table 3-6. With the exception of the nitroguanidine-No. 2 fuel oil slurry containing 5 percent by weight propellant, the fire points of all of the propellant-No. 2 fuel oil slurries are less than the fire point of No. 2 fuel oil. It had previously been a matter of some concern, expressed in the test plan for this project, that measurement of the fire points of the propellant-No. 2 fuel oil slurries might not be possible due to safety considerations. However, during the analysis of these slurries, the observation was made that each propellant-No. 2 fuel oil slurry burned, when initially ignited and allowed to burn for 5 seconds, in an identical manner to the No. 2 fuel oil.

Table 3-6. Fire Points[a] of No. 2 Fuel Oil and the Propellant-No. 2 Fuel Oil Slurries

Material	Weight Percent Propellant	Weight Percent No. 2 Fuel Oil	Fire Point (°F)
No. 2 Fuel Oil	0.0	100.0	237.0
Nitroguanidine	5.0	95.0	250.0
	10.0	90.0	230.0
	15.0	85.0	219.9
Nitrocellulose (Dried at 70°C)	5.0	95.0	219.9
	10.0	90.0	199.9
	15.0	85.0	190.0
Nitrocellulose (Water-Wet)	5.0	95.0	204.8
	10.0	90.0	210.2
	15.0	85.0	204.8
AA2 Propellant	5.0	95.0	215.1
	10.0	90.0	204.8
	15.0	85.0	199.9
	20.0	80.0	196.3
	25.0	75.0	192.2
	30.0	70.0	190.0

[a]Measured according to ASTM D 92-85 standard procedure.

3.2.3 Heat of Combustion of Propellant-No. 2 Fuel Oil Slurries

The heat of combustion is a measure of the energy released when 1 mol of a substance is oxidized at constant pressure or constant volume. A knowledge of this value is essential when considering the thermal efficiency of equipment for producing either heat or power.

The heat of combustion data obtained from No. 2 fuel oil and the propellants according to ASTM D 240-87 standard procedure are given in Table 3-7. Several of the heat of combustion data points calculated for the propellant-No. 2 fuel oil slurries are used in the economic analysis which follows in the next section.

Table 3-7. Heats of Combustion[a] of No. 2 Fuel Oil, Propellants, and Selected Propellant-No. 2 Fuel Oil Slurries

Material	Heat of Combustion (Btu/lb)
Nitrocellulose	4,308
Nitroguanidine	4,016
AA2 Propellant	4,354
No. 2 Fuel Oil	18,947
10% Nitrocellulose-90% No. 2 Fuel Oil	17,483
15% Nitroguanidine-85% No. 2 Fuel Oil	16,707
15% AA2 Propellant-85% No. 2 Fuel Oil	16,758
20% AA2 Propellant-80% No. 2 Fuel Oil	16,029

[a]Heats of combustion for propellants and No. 2 fuel oil were determined experimentally. Heats of combustion for the propellant-No. 2 fuel oil slurries were calculated from these values.

3.2.4 Emissions From the Pyrolysis of Propellant-No. 2 Fuel Oil Slurries

The reaction products (emissions) of propellants are dependent on the pressure and temperature, and therefore also on the confinement under which the combustion reaction proceeds. The knowledge of the reaction products of combustion processes is important for several reasons:

A. To learn more about the reaction kinetics and about equilibrium or non-equilibrium burning,

B. To study the heat output,

C. To evaluate the completeness of reactions and to find out if components of the original propellant or high explosive can still be found in the residue,

D. In connection with the disposal of energetic materials, it is also of interest if the combustion leads to toxic or carcinogenic reaction products that may be emitted to the atmosphere.

Although not specifically ‿ated as such in the test plan for this project, a qualitative determination was made of the emissions from the nitrocellulose, nitroguanidine, and AA2 propellant using a solid probe-mass spectrometry (SPMS) instrument. The SPMS spectrum of each material was obtained and then compared and contrasted to information alrea‿ ‿vailable in the scientific literature. The SPMS spectra were recorded using a procedure similar to ASTM D 2650-88 "Standard Test Method for Chemical Composition of Gases by Mass Spectrometry." Specific details of the procedure are given in Section 5.4.4. The emissions expected from various propellant-No. 2 fuel oil slurries were then calculated from the information already available in the literature. Although this approach differs from that outlined in the test plan, it was approved by USATHAMA at the Interim Project Review meeting in February, 1991.

It is important to emphasize the fact that combustion of the propellant-No. 2 fuel oil slurries will be accomplished at temperatures between 1500°C to 1700°C. The emissions from various propellant-No. 2 fuel oil slurries given in the following sections serve only to theoretically characterize reaction products that might result in the event of incomplete combustion.

3.2.4.1 Typical Emission From the Pyrolysis of Nitrocellulose

Many studies have been reported in the literature regarding the thermal decompositio‿ of nitrocellulose and the analysis of the emissions from this pyrolysis. The emissions expected from the pyrolysis of nitrocellulose based upon the literature are given in Table 3-8. The relevant literature references are also given in the table. To summarize, the predominant (i.e., >10 percent) emissions observed from the pyrolysis of nitrocellulose were NO_2, NO, CO, CO_2, and H_2O. Minor emissions (i.e., 5-10 percent)

Table 3-8. Emissions Expected from the Pyrolysis of Nitrocellulose Based on a Review of the Scientific Literature

Major (>10 %)	Minor (5-10%)	Traces (<5%)
NO_2, Refs. 9-11	Formic acid, HCOOH, Ref. 16	HCN, Refs. 16, 19
NO, Refs. 9-14, 19	Formaldehyde, HCHO, Refs. 9, 16, 19	N_2, Refs. 12-15
CO, Refs. 9, 12-15, 19	Glyoxal, $(HCO)_2$, Ref. 16	N_2O, Refs. 9, 12, 14
CO_2, Refs. 9, 12-14, 19	N_2O, Ref. 19	Acetaldehyde, CH_3CHO, Refs. 15, 17, 19
H_2O, Refs. 9, 12, 15		Acetone, $(H_3C)_2CO$, Refs. 17, 19
		Acrolein, $CH_2{=}CHCHO$, Refs. 17, 19
		CH_4, Refs. 14, 15
		$H_2C{=}CH_2$, Ref. 15
		CH_3OH, Ref. 15
		CH_3CH_2OH, Ref. 15
		Formamide, $HCONH_2$, Ref. 18
		H_2O, Ref. 19
		CH_3CH_2CHO, Ref. 19

were formic acid, formaldehyde, and glyoxal. Trace emissions (i.e., <5 percent) were HCN, N_2, N_2O, acetaldehyde, acetone, acrolein, CH_4, $H_2C=CH_2$, methanol, ethanol, and formamide.

In a recent study by Huwei and Ruonong (19), pyrolysis-gas chromatography was used to study the emissions from nitrocellulose. During this analysis, the nitrocellulose was pyrolyzed at high temperature and high heating rate, and its decomposition reaction was quick and complete. Therefore, the pyrolysis of nitrocellulose during this technique may simulate its combustion. At the high temperatures used in this study, it was observed that NO_2 was changed into NO. Therefore, the predominant emissions detected during this analysis were CO, NO, and CO_2. Minor emissions were N_2O and formaldehyde. Trace emissions were HCN, H_2O, CH_3CHO, CH_3CH_2CHO, CH_3COCH_3, and $CH_2=CHCHO$.

A number of studies on the mechanism of the thermal decomposition of nitrate esters (e.g., nitrocellulose, nitroglycerin, and nitroguanidine) have verified that the decomposition proceeds with homolytic cleavage of nitrate ester groups ($RO-NO_2$) via an autocatalytic-type reaction. The autocatalytic-type reaction is believed to proceed by a complicated series of consecutive radical reactions. Kimura (20,21) and Kubota (22) have shown that, for example, nitrocellulose initially decomposes by rupture of one of the $RO-NO_2$ bonds, since they are the weakest chemical bonds present, to form oxidizers (NO_2) and alkoxy radicals (RO•). Apparently, the decomposition process occurs in the condensed phase or at least at the burning surface. The generated NO_2 oxidizes RO• to form peroxy radicals (ROO•) and nitrogen oxide (NO). Finally, the last stage is the exothermic oxidation of the organic molecules by NO giving N_2, CO_2, CO, H_2O, etc. (22). Fifer (23) has published an excellent review of the chemistry of the decomposition of nitrate ester and nitramine propellants.

The SPMS spectrum obtained from the thermal decomposition of nitrocellulose taken over the temperature range from 40°C to 220°C at 10°C/min is shown in Figure 3-9. As was pointed out in the above discussion, the emissions from the pyrolysis of nitrocellulose are dependent both on the temperature and the pressure at which the pyrolysis takes place. As a further example, DeHaan (24) has pointed out that since nitrocellulose functions as a propellant by generating large quantities of gases while undergoing an explosive burning process, its true behavior is pressure dependent. In most cases, one must be content with evaluating a propellant's behavior at atmospheric pressure.

The explosive burning process mentioned above begins as a normal combustion when the temperature reaches 170°C to 180°C. Heat generated by the combustion of the first "layers" accelerates the combustion of succeeding portions of the sample. The pressure generated by the production of NO_2, CO, H_2, and H_2O vapor causes the reaction to proceed faster and faster. The progressive burning feature of nitrocellulose makes the geometry of the individual sample very important to the behavior of the propellant as a whole.

Therefore, based upon the considerations discussed above, the only conclusion that can be drawn from the fact that the SPMS spectrum shown in Figure 3-9 indicates H_2O (mass 18), HCHO and NO (mass 30), and N_2O and CO_2 (mass 44) as major peaks is that these are the pyrolysis products at 220°C and the pressure within the SPMS capillary analysis tube. For the purposes of identifying and quantifying the major emissions that may result

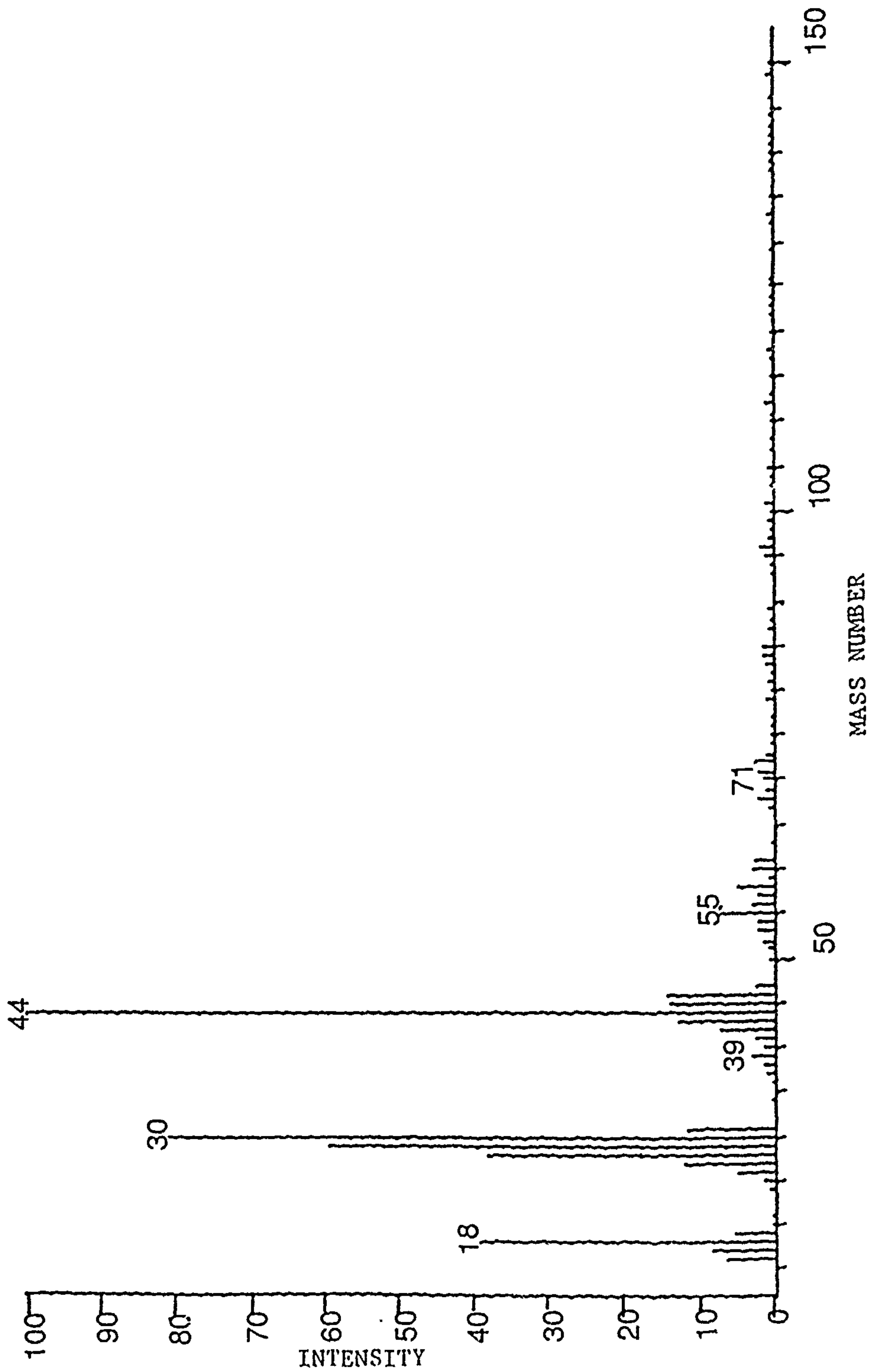


Figure 3-9. The SPMS Spectrum of Nitrocellulose From 40°C to 220°C at 10°C/Minute.

from the incomplete combustion of various nitrocellulose-No. 2 fuel oil slurries, we will rely on the distribution of reaction products from the pyrolysis of a single-base propellant (A 5020), published by Volk (25). The emissions obtained from the pyrolysis of this propellant were as follows: H_2 (18.4 percent), CH_4 (0.1 percent), CO_2 (12.6 percent), N_2 (10.1 percent), H_2O (15.2 percent), and NH_3 (0.85 percent). HCN and NO gases were not found. Quantification of the emissions expected from a 7.5 percent by weight nitrocellulose-No. 2 fuel oil slurry is presented in section 3.2.4.4.

3.2.4.2 Typical Emissions from the Pyrolysis of Nitroguanidine

Nitroguanidine is one of the main components of triple-base propellant and can form large amounts of combustion gases and NH_3 when burning. Since NH_3 gas can react with NO_2, it may consume a large amount of the NO_2 produced during the decomposition of nitrate and connected with an autocatalytic decomposition of the propellant (26).

In a study by Volk (27), the following gaseous reaction products were analyzed by mass spectrometry: NH_3, N_2O, CO_2, N_2, NO, NO_2, and HCN. Temperatures in the range of 180°C-240°C were used during the decomposition stage of the analysis. In the gas mixture evolved, N_2O and NH_3 were the main products. The composition of the decomposition gases was found to vary widely as a function of temperature. At the beginning of the decomposition process at 180°C, NH_3 was the main product. However, at higher temperatures or with extended decomposition time, the formation of N_2O was found to increase. For example, at 220°C the formation rate of N_2O was found to exceed that of NH_3 by 3 to 1. At 240°C, the approximate composition of the emissions from the particular nitroguanidine sample used the this study were: 23 percent NH_3, 66 percent N_2O, 5 percent CO_2, and a combined total of 6 percent of the gases N_2, NO, and HCN.

The SPMS spectrum obtained from the thermal decomposition of nitroguanidine from 50°C to 220°C at 20°C/min for 23 minutes is shown in Figure 3-10. As was pointed out in the above discussion, the emissions from the pyrolysis of nitroguanidine are dependent on the temperature at which the pyrolysis takes place. Therefore, the only conclusion that can be drawn from the fact that the SPMS spectrum shown in Figure 3-10 indicates H_2O (mass 18), NO (mass 30), H_2N-CN (mass 42), and N_2O and CO_2 (mass 44) as major peaks is that these are some of the pyrolysis products at 220°C and the pressure within the SPMS capillary analysis tube. For the purposes of quantifying the major emissions expected from the pyrolysis of 10 and 15 percent by weight nitroguanidine-No. 2 fuel oil slurries (section 3.2.4.4), the information published by Volk (27) will be used.

3.2.4.3 Typical Emissions from the Pyrolysis of Double-Base Propellants

While the literature does not contain any references which specifically describe the emissions from the pyrolysis of the AA2 propellant used in this study, there are several references which deal with other, similar types of double-base propellant (25,28-30). For example, Volk (25) has described the reaction products from the thermal decomposition of the double-base propellant H 518, which contains a high amount of nitroglycerin. The reaction products of this propellant were as follows: H_2 (10.2 percent), CO (28.5 percent), CO_2 (22.3 percent), N_2 (14.4 percent), NO (0.09 percent), HCN (0.03 percent), and H_2O (24.4 percent).

The SPMS spectrum of the AA2 propellant is given in Figure 3-11. Some of the major peaks identified in this spectrum are H_2O (mass 18), NO and HCHO (mass 30), as well as N_2O and CO_2 (mass 44). Using the gaseous product distribution published by Volk (25), the calculated emissions from the

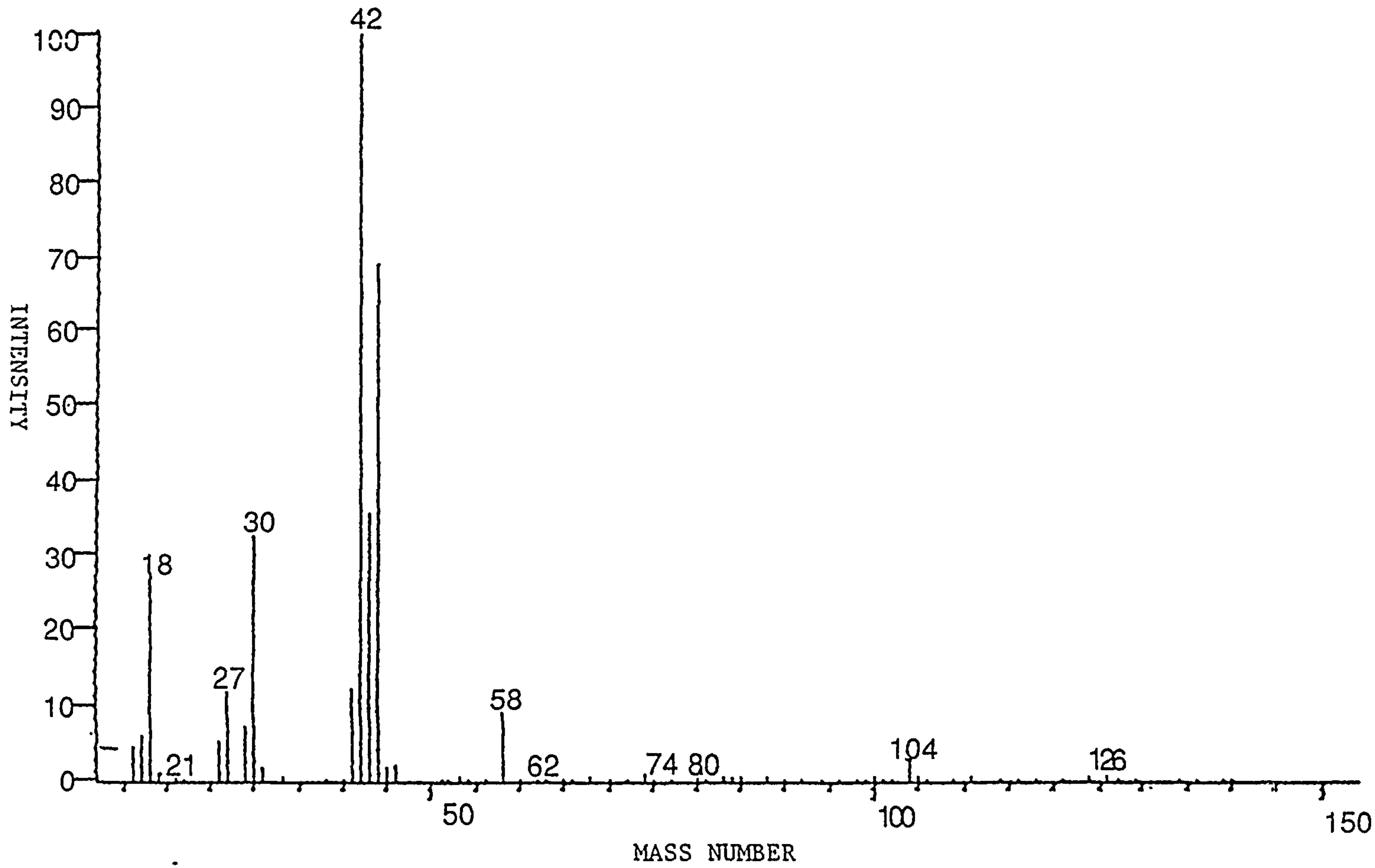


Figure 3-10. The SPMS Spectrum of Nitroguanidine From 50°C to 250°C at 20°C/Minute for 23 Minutes.

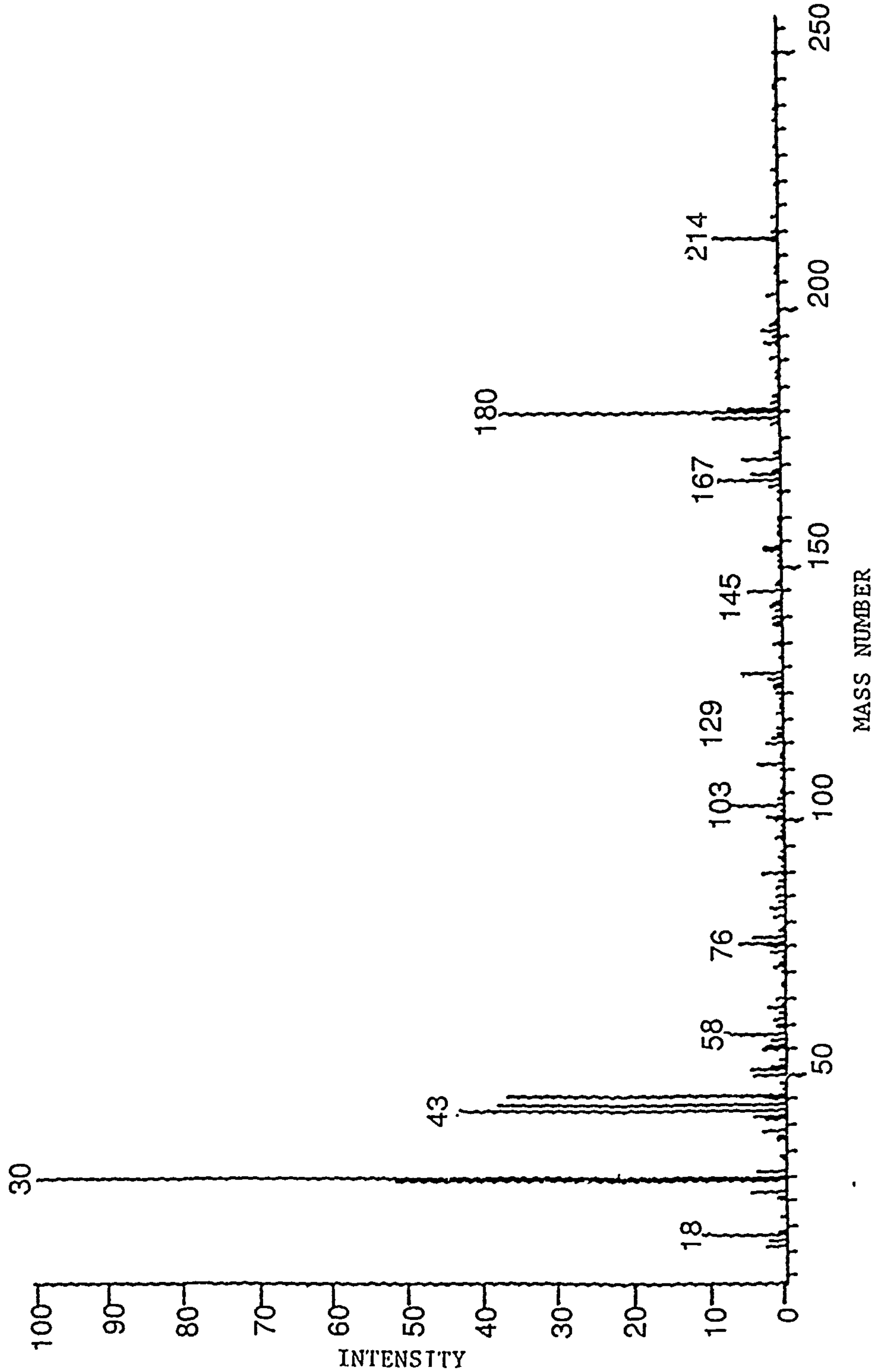


Figure 3-11. The SPMS Spectrum of AA2 Double-Base Propellant.

pyrolysis of 10 and 20 percent by weight AA2 propellant-No. 2 fuel oil slurries are given in the following section.

3.2.4.4 Estimate of Emissions to be Expected From Burning Propellant-No.2 Fuel Oil Slurries as Supplemental Fuels

In the USATHAMA document entitled "Pilot Test to Determine the Feasibility of Using Explosives as Supplemental Fuel at Hawthorne Army Ammunition Plant (HWAAP) Hawthorne, Nevada" it is noted that O_2, CO_2, CO, explosives, lead oxides, NO_x, particulates, and moisture content will be monitored in the emissions from the process. It is assumed that a similar monitoring program would be implemented if propellant-No. 2 fuel oil slurries were burned in a similar pilot plant.

The average formula for No. 2 fuel oil may be given as $C_{7.190}H_{12.619}$. Assuming complete combustion of the No. 2 fuel oil to CO_2 and H_2O, we estimate that 3.16 pounds of CO_2 and 1.15 pounds of H_2O will be released from burning one pound of No. 2 fuel oil. These values form the basis for calculating the emissions that may result from the incomplete combustion of various propellant-No. 2 fuel oil slurries.

Starting with a 10 percent by weight nitroguanidine-No. 2 fuel oil slurry and using the emissions data published by Volk (27) (i.e., 23 percent NH_3, 66 percent N_2O, 5 percent CO_2, and 6 percent total of N_2, NO, and HCN), we estimate that 2.845 pounds of CO_2, 1.040 pounds of H_2O, 0.023 pounds of NH_3, 0.066 pounds of N_2O, and 0.006 pounds combined of N_2, NO, and HCN may be emitted from one pound of combusted slurry. For the combustion of one pound of a 15 percent by weight nitroguanidine-No. 2 fuel oil slurry, the distribution of emissions may be as follows: 2.694 pounds CO_2, 0.978 pounds H_2O, 0.035 pounds NH_3, 0.099 pounds N_2O, and 0.009 pounds combined of N_2, NO, and HCN.

Continuing with a 10 percent by weight AA2 propellant-No. 2 fuel oil slurry and using the emissions data published by Volk (25) for H 518 double-base propellant (i.e., 10.2 percent H_2, 28.5 percent CO, 22.3 percent CO_2, 14.4 percent N_2, 0.09 percent NO, 0.03 percent HCN, and 24.4 percent H_2O), we estimate that 2.866 pounds of CO_2, 1.064 pounds of H_2O, 0.010 pounds of H_2, 0.029 pounds of CO, 0.014 pounds of N_2, <0.001 pounds of NO, and <0.001 pounds of HCN may be emitted from one pound of combusted slurry. For a 20 percent by weight AA2 propellant-No. 2 fuel oil slurry, the distribution of emissions expected from the combustion of one pound of this supplemental fuel may be as follows: 2.528 pounds CO_2, 0.969 pounds H_2O, 0.020 pounds H_2, 0.057 pounds CO, 0.029 pounds N_2, <0.001 pounds NO, and <0.001 pounds HCN.

Finally, for a 7.5 percent by weight nitrocellulose (dried)-No. 2 fuel oil slurry, using the emissions data published by Volk (25) for single-base gun propellant A 5020 (i.e., 18.4 percent H_2, 0.1 percent CH_4, 12.6 percent CO_2, 10.1 percent N_2, 15.2 percent H_2O, and 0.85 percent NH_3), we estimate that 2.932 pounds of CO_2, 1.075 pounds of H_2O, 0.014 pounds of H_2, 0.008 pounds of N_2, <0.001 pounds of CH_4, and <0.001 pounds of NH_3 may be emitted from the combustion of one pound of this supplemental fuel.

However, in conclusion, it must be kept in mind that these estimates for the emissions that may result from the pyrolysis of each propellant-No. 2 fuel oil slurry are based entirely upon the best information available from the scientific literature. The relevance of these estimates to the actual combustion process at 1500°C-1700°C will only come when the propellant-No. 2 fuel oil slurries are burned in a pilot plant, and the emissions from this combustion are measured at that time.

3.3 Chemical Compatibility of Propellant-No. 2 Fuel Oil Slurries

The third and final series of laboratory tests in this project were conducted to determine the chemical compatibility of each propellant dispersed in No. 2 fuel oil. The chemical compatibility of the resulting slurries was evaluated using a thermal analysis technique, differential scanning calorimetry. The propagation of reaction tests on the propellant-No. 2 fuel oil slurries are currently being performed by Hercules, Inc., Rocket Center, West Virginia. The results from these tests, as well as from a preliminary safety analysis of the process of using propellant-No. 2 fuel oil slurries as supplemental fuels, will be published separately.

3.3.1 Differential Scanning Calorimetry (DSC)

3.3.1.1 General

The thermal decomposition of nitrocellulose has been studied for many years (31). Wolfrom et al. (32), analyzed the decomposition products from nitrocellulose by assuming that the thermally initiated rupture of the cellulose nitrate molecule yielded a series of volatile species whose relative importance was inversely proportional to the pressure of the system. Later, using spectroscopic and gravimetric techniques, Phillips et al. (33), showed that the thermal decomposition of nitrocellulose follows, in first approximation, first-order kinetics with two or three branches, suggesting that a more complex reaction process than a simple first-order one might occur.

More recently, Pfeil and Eisenreich (34) studied the thermal decomposition of nitrocellulose by thermogravimetic analysis, differential thermal analysis, and infrared and Raman spectroscopies. Their results revealed the presence of an initial autocatalytic decomposition of nitrate groups and an increase in carbonyl and hydroxyl groups up to a weight loss of 55 percent. Further decomposition turned out to be a second-order reaction, terminating in a charcoal-like residue.

Lemieux and Prud'homme (35) used a DSC apparatus to compare the heats of decomposition of seven nitrocellulose samples, derived from wood and cotton, with various nitrogen contents ranging from 12.6 percent to 13.5 percent. They observed that the average heat of decomposition of nitrocellulose samples increased slightly with nitrogen content, the values ranging between 1711 and 2050 J g-1.

The thermal decomposition of propellants can also be conveniently analyzed using DSC. Singh and Rao (36) have used DSC methods to study the role of lead salts of organic acids in the combustion of double-base rocket propellants. Lead salts affect the reactions taking place in one or more of four distinct reaction zones that occur during the steady state burning of double base propellant, namely, the foam, fizz, dark, and luminous zones.

As another example, House et al. (37), used DSC to compare the decomposition of twelve commercial nitrocellulose-containing propellants. Curiously, these researchers observed two different decomposition pathways for the same propellant, even though each DSC experiment was run in the same fashion. The first decomposition pattern may be represented by the following:

Propellant = volatile products + 12-16 percent residue (1)

while the second decomposition pattern is represented by

Propellant = volatile products + 2-5 percent residue (2)

The results obtained by House et al., indicated that there was no significant difference between the heats of decomposition of most propellants investigated which decompose according to Equation 1. However, for some propellants, decomposition could take place by Equation 1 or 2 with about equal frequency.

3.3.1.2 Results and Discussion-Propellants

The DSC curve obtained from the decomposition of the dried nitrocellulose sample at a heating rate of 20°C/min is given in Figure 3-12. A Perkin-Elmer DSC-7 instrument was used to obtain all the DSC curves shown in this section of the report at a heating rate of 20°C according to ASTM E 537-86 standard procedure. Figure 3-12 shows that the exothermic decomposition peak is asymmetric with decomposition starting at about 205°C and finishing at about 247°C, with the peak maximum located at 219.46°C. These values are identical to those reported by Eisenreich and Pfeil (38) for the decomposition of pure nitrocellulose as monitored by DSC at a heating rate of 20°C.

The DSC curve obtained from the decomposition of nitroguanidine is shown in Figure 3-13. The exothermic decomposition peak is asymmetric with decomposition starting at about 269°C and ending at about 299°C, with the peak maximum located at 279.44°C. These values compare favorably with those previously reported by Rogers (39).

The DSC curve obtained from the decomposition of the AA2 propellant is shown in Figure 3-14. The exothermic decomposition peak is asymmetric with decomposition starting at about 180°C and ending at about 258°C, with the peak maximum located at 208.71°C. These values may be compared with those

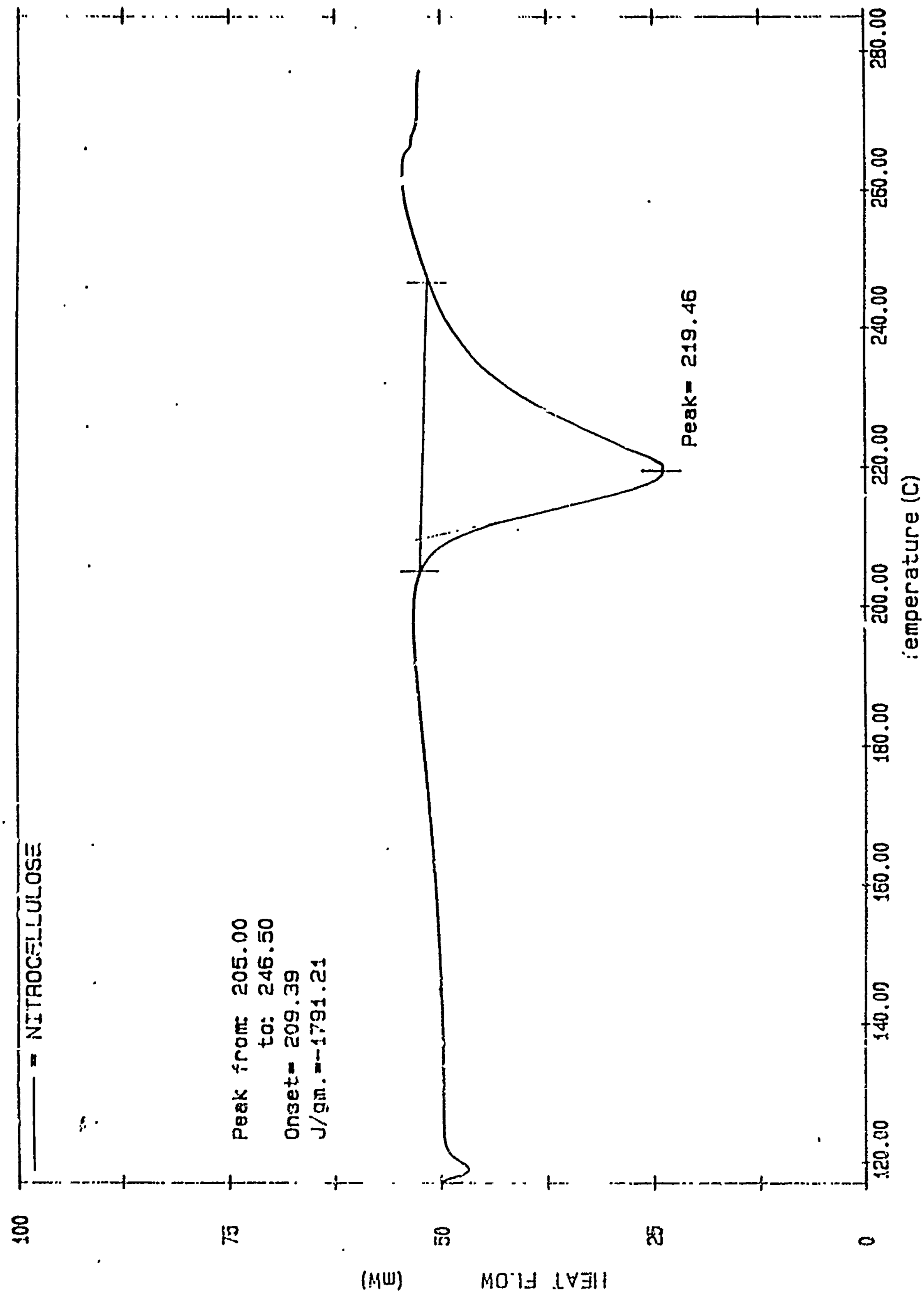


Figure 3-12. The Differential Scanning Calorimetry Curve for the Decomposition of Nitrocellulose.

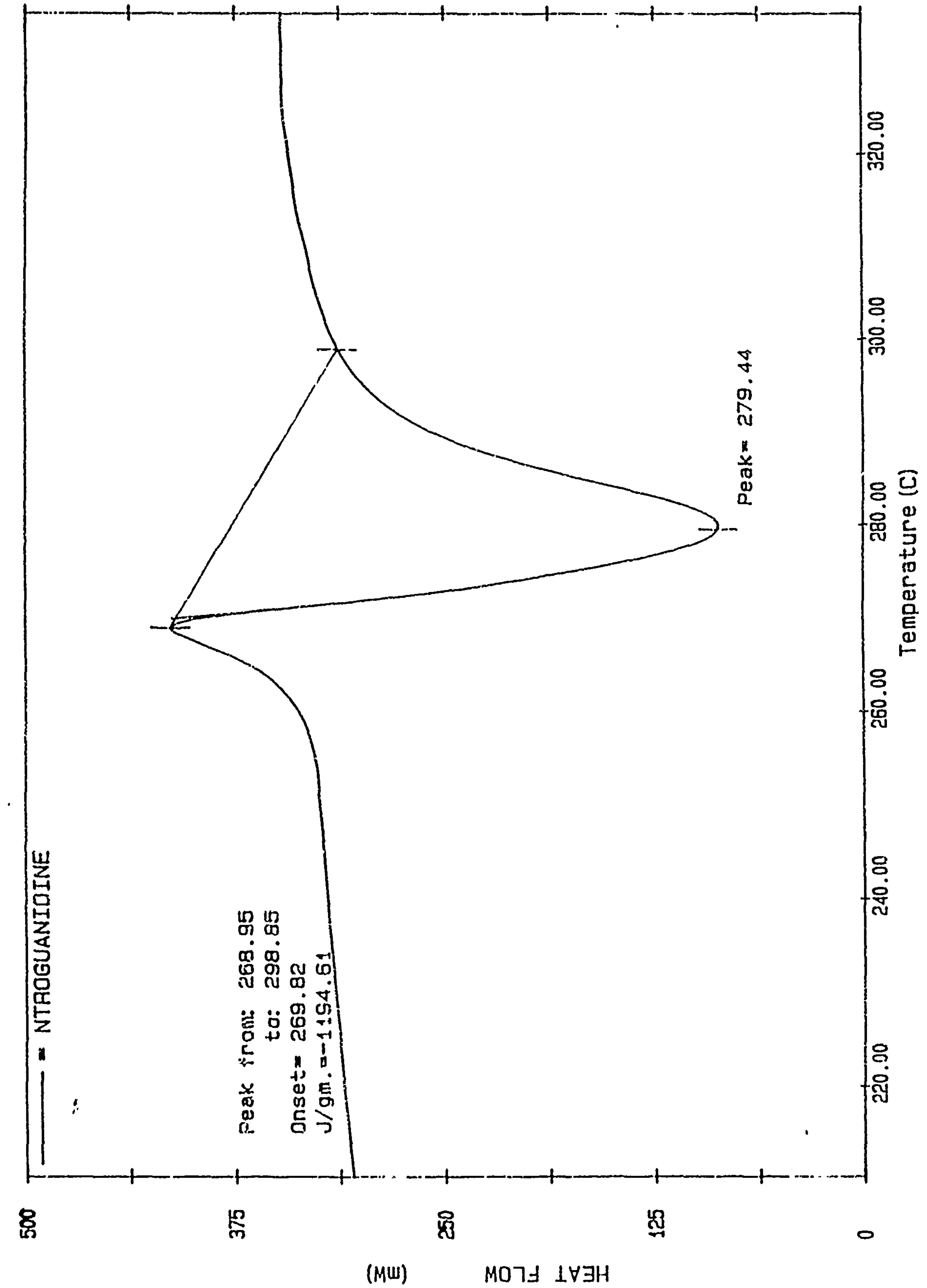


Figure 3-13. The Differential Scanning Calorimetry Curve for the Decomposition of Nitroguanidine.

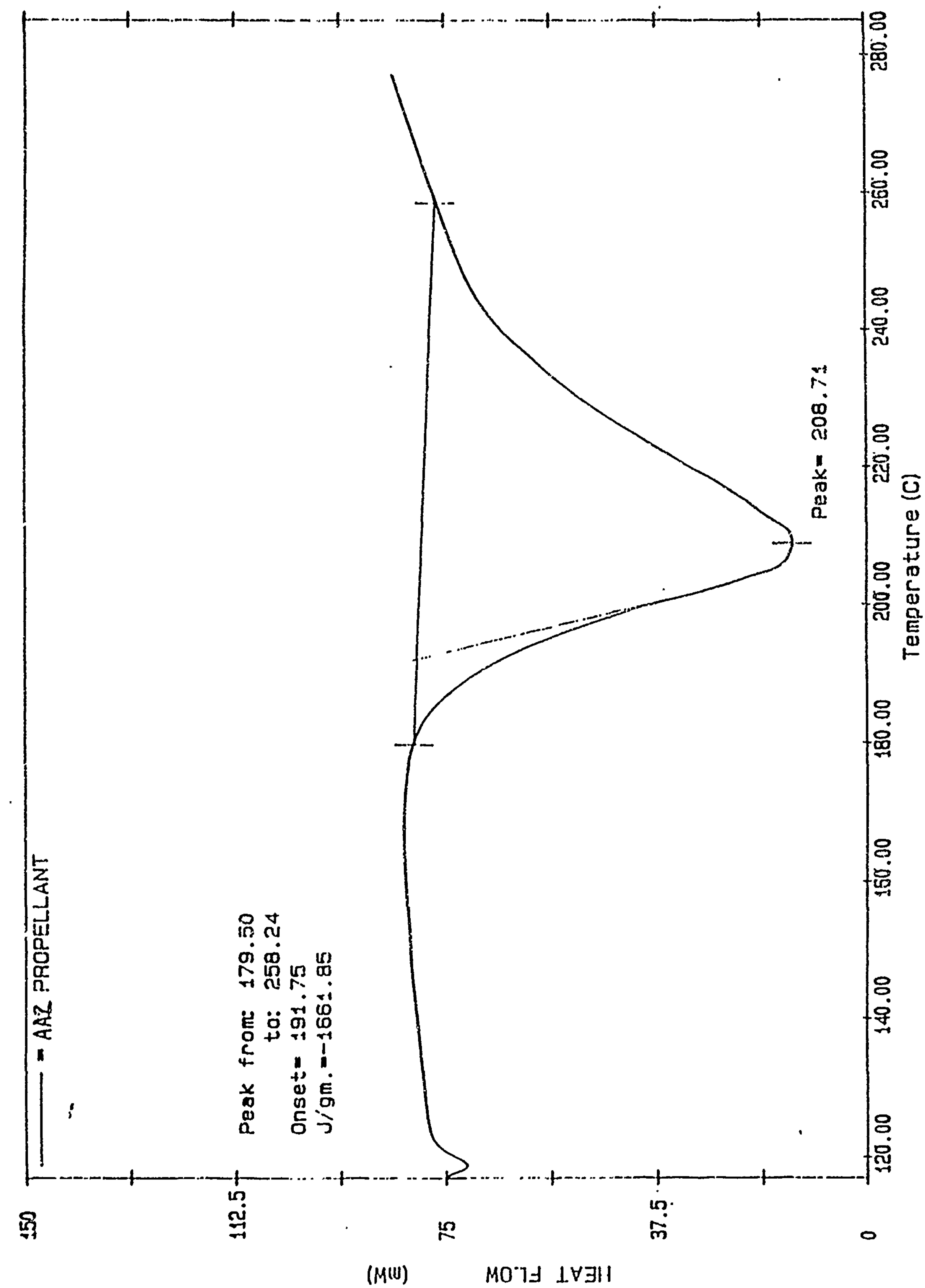


Figure 3-14. The Differential Scanning Calorimetry Curve for the Decomposition of AA2 Propellant.

obtained by De Schor and Toni (40) for a typical double-base propellant (containing nitrocellulose, nitroglycerin, stabilizers, plasticizers, and lead salt) where the decomposition reaction started at about 157°C and ended at about 261°C, with the peak maximum located at 207°C. The differences in the initial and final decomposition temperatures between the two propellants is the slightly different heating rates used in this study (20°C/min) compared with that used in the study published by De Schor and Toni (16°C/min).

3.3.1.3 Results and Discussion-Propellant Slurries

The DSC curve obtained from the decomposition of a representative nitrocellulose (dried)-No. 2 fuel oil slurry is given in Figure 3-15. A Perkin-Elmer DSC-7 instrument was used to obtain all the DSC curves shown in this section of the report at a heating rate of 20°C/min according to ASTM E 537-86 standard procedure. Figure 3-15 shows that the exothermic decomposition peak is much sharper than that shown in Figure 3-12 for nitrocellulose, with decomposition starting at about 208°C and finishing at about 232°C, with the peak maximum located at 213.59°C. The peak maximum for the nitrocellulose (dried)-No. 2 fuel oil slurry is 6°C lower than that obtained from nitrocellulose. The DSC curve obtained from the decomposition of a representative nitrocellulose (water-wet)-No. 2 fuel oil slurry is shown in Figure 3-16. In this case, the peak maximum occurs at 215.01°C, which is only about 4°C lower than that obtained from nitrocellulose.

The DSC curve obtained from the decomposition of a representative nitroguanidine-No. 2 fuel oil slurry is shown in Figure 3-17. Figure 3-17 shows that the exothermic decomposition peak has shifted to a peak maximum of 266.33°C, with decomposition starting at ,ut 260°C and ending at

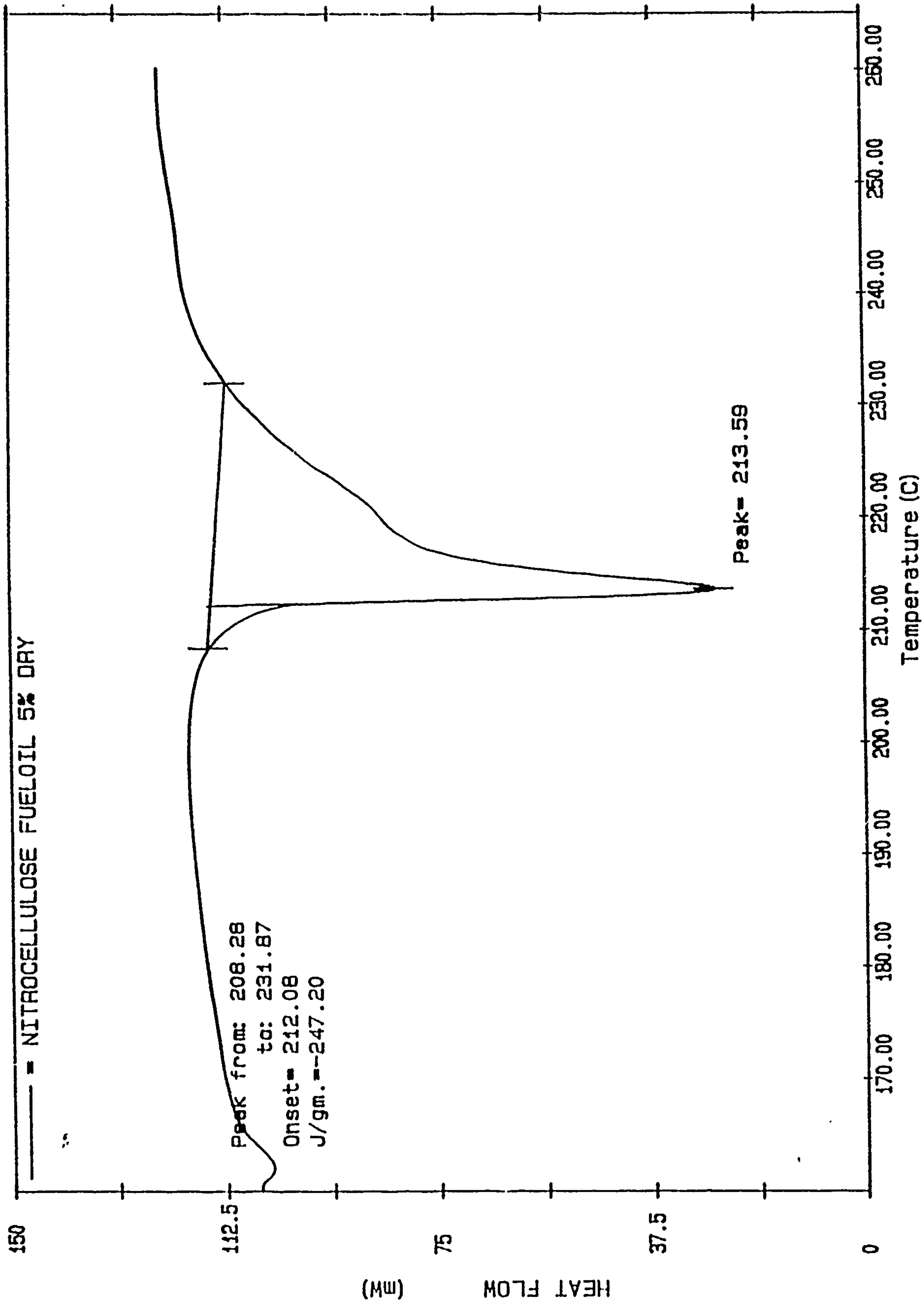


Figure 3-15. The Differential Scanning Calorimetry Curve for the Decomposition of a Nitrocellulose (Dried)-No. 2 Fuel Oil Slurry.

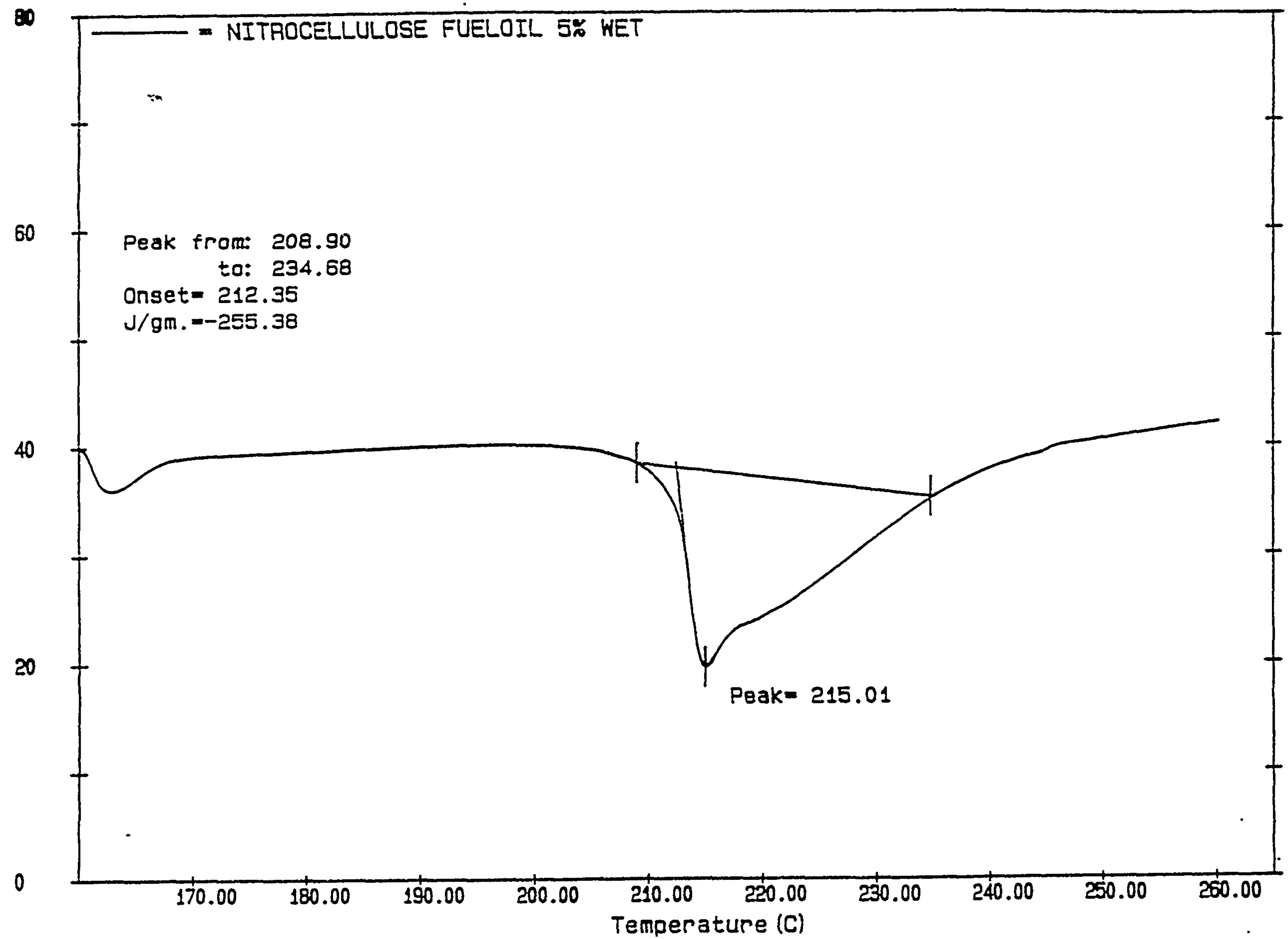


Figure 3-16. The Differential Scanning Calorimetry Curve for the Decomposition of a Nitrocellulose (Water-Wet) No. 2 Fuel Oil Slurry.

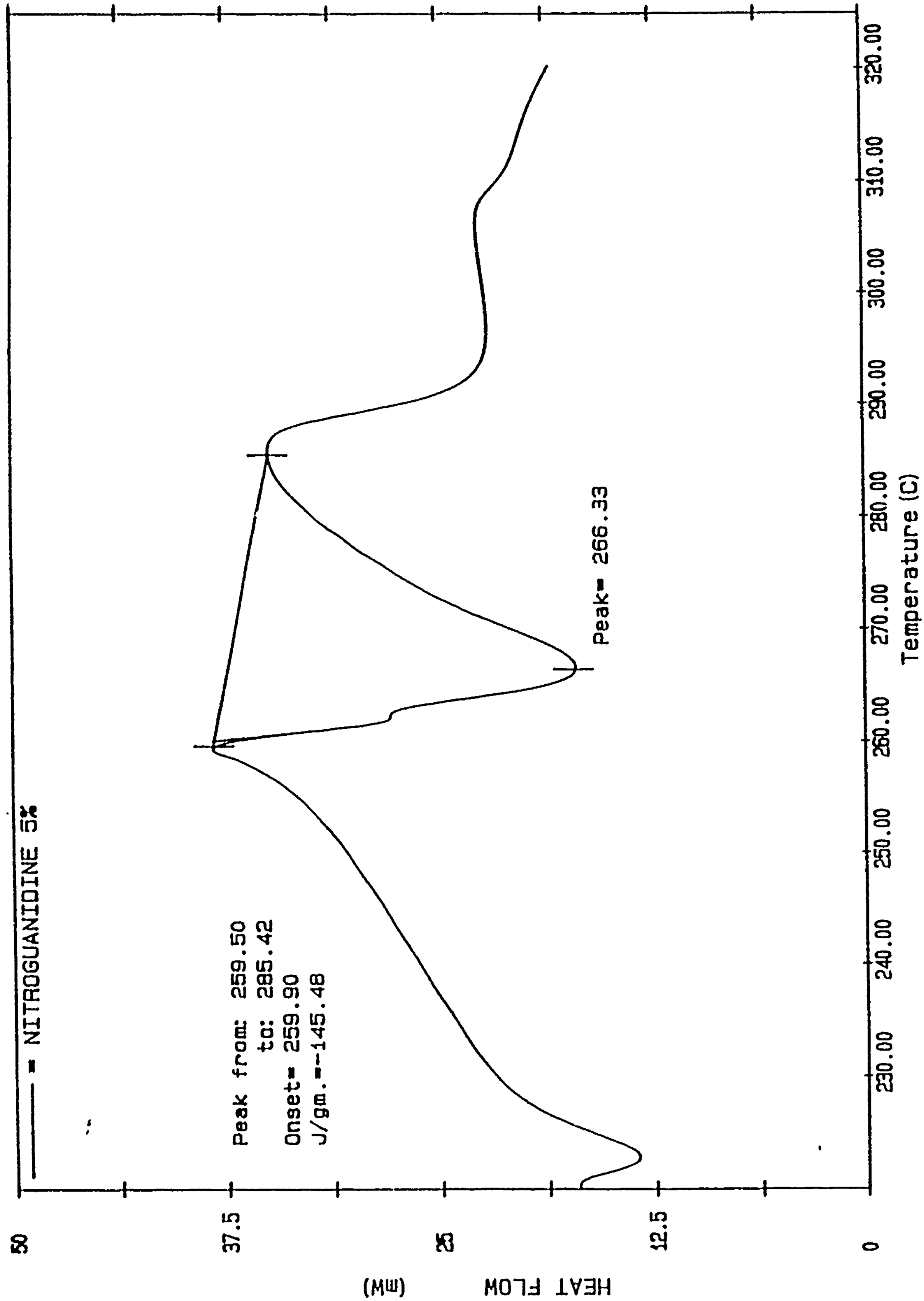


Figure 3-17. The Differential Scanning Calorimetmry Curve for the Decomposition of a Nitroguanidine-No. 2 Fuel Oil Slurry.

about 285°C. As was the case with the nitrocellulose-No. 2 fuel oil slurries, the peak maximum for the nitroguanidine-No. 2 fuel oil slurry is less than that for nitroguanidine alone; however, in this case the difference is much more significant at about 13°C.

The DSC curve obtained from the decomposition of a representative AA2 propellant-No. 2 fuel oil slurry is shown in Figure 3-18. Figure 3-18 shows that the exothermic decomposition peak has shifted to a peak maximum of 224.08°C, with decomposition starting at about 205°C and finishing at about 242°C. However, in contrast to the results obtained from DSC analysis of the nitrocellulose- and nitroguanidine-No. 2 fuel oil slurries, the peak maximum from the decomposition of the AA2 propellant-No. 2 fuel oil slurry has <u>increased</u> by about 16°C compared to the peak maximum from the decomposition of AA2 propellant alone.

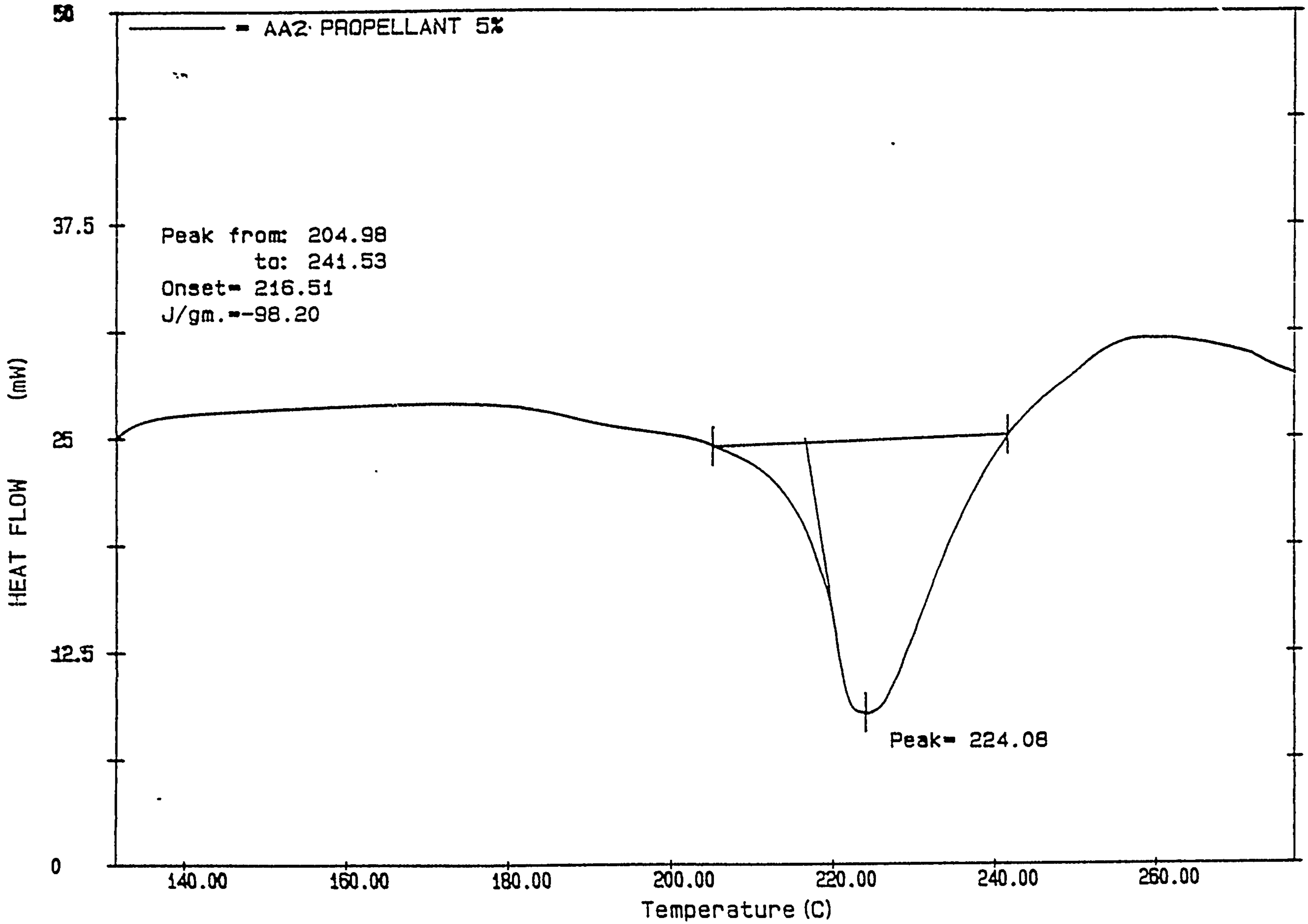


Figure 3-18. The Differential Scanning Calorimetry Curve for the Decomposition of a AA2 Propellant-No. 2 Fuel Oil Slurry.

IV. ECONOMIC ANALYSIS

4.1 Propellant-No. 2 Fuel Oil Slurries

An economic analysis of various propellant-No. 2 fuel oil slurries was performed in this phase of the project. This analysis emphasizes the costs of the propellant-No. 2 fuel oil slurries as well as the amounts of the propellants that could be dispersed in the slurries. The approach used to analyze the economics of propellant-supplemented fuels was to compare them to the current application in which they would be used, namely, industrial combustors. The economic analysis is broken down into three areas, raw materials, capital costs and labor costs.

4.1.1 Fuel Costs

A general process flow diagram for burning propellant-No. 2 fuel oil slurries as supplemental fuels in an industrial combustor is shown in Figure 4-1.

For the production of steam in an industrial combustor, the raw materials will be fuel and water. For the comparison of supplemented to non-supplemented fuels, the water requirements and the electricity are assumed to be the equal. A 20 MM Btu/hr industrial combustor operating 6570 hours per year (75 percent operational) fired with No. 2 fuel oil will be used to provide a baseline case for further comparison with supplemented fuels. The combustor is assumed to be 80 percent efficient for both the supplemented and the non-supplemented fuel. The physical properties and costs for the No. 2 fuel oil and propellants used in this economic analysis are shown in Table 4-1. The baseline fuel cost is $856,812 per year from the following calculation:

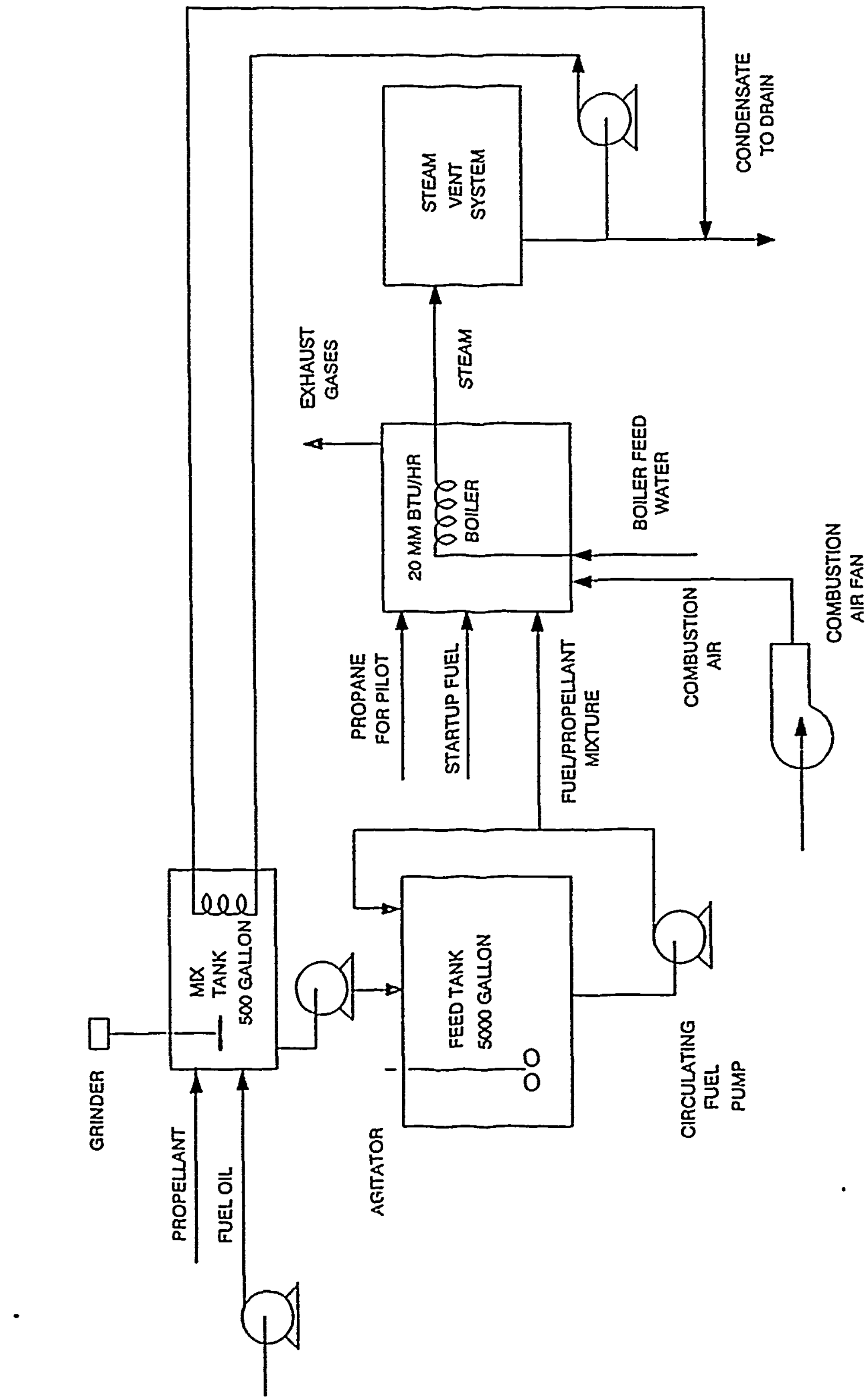


Figure 4-1. Process Flow Diagram for Burning a Supplemental Fuel.

Table 4-1. Physical Properties and Cost of No. 2 Fuel Oil and Propellants Used in the Economic Calculations

No. 2 Fuel Oil	
Heat of Combustion	18947 Btu/lb
Density	7.31 lb/gal
Cost	$0.7225/gal
Nitrocellulose	
Heat of Combustion	4308 Btu/lb
Density	11.68 lb/gal
Nitroguanidine	
Heat of Combustion	4016 Btu/lb
Density	13.44 lb/gal -liquid
	15.63 lb/gal -dry
AA2 Propellant	
Heat of Combustion	4354 Btu/lb
Density	13.69 lb/gal -liquid
	16.02 lb/gal -dry

$2*10^7$ Btu/hr * 6570 hrs/yr * 1 lb No. 2 fuel/18947 Btu * 1 gal No. 2 fuel/7.31 lb No. 2 fuel * $0.7225/gal No. 2 fuel * 1/0.8 (efficiency factor) = $856,812/yr

A No. 2 fuel oil supplemented with nitrocellulose will now be compared to the baseline. Consider a fuel with a composition of 90 percent by weight No. 2 fuel oil and 10 percent by weight nitrocellulose (dried). This supplemented fuel was selected for study because the viscosity of a 10 percent by weight nitrocellulose-No. 2 fuel oil slurry is just below the maximum value capable of being fed to a conventional, unmodified oil burner (see section 3.1.6). The cost of one pound of this supplemented fuel is $0.089 from the following calculation:

0.90 * $0.7225/gal No. 2 fuel oil * 1 gal/7.31 lb No. 2 fuel oil = $0.089/lb supplemented fuel

The heating value of the supplemented fuel is 17483 Btu/lb from the following calculation:

(0.90 * 18947) + (0.10 * 4308) Btu/lb = 17483 Btu/lb supplemented fuel

In the above estimate the heats of solution are assumed to be negligible.

Using the two estimates given above, the yearly fuel cost for operating the same 20 MM Btu/hr combustor as in the baseline case with the 10 percent by weight nitrocellulose-No. 2 fuel oil supplemented fuel can be calculated. The following calculation yields a yearly supplemented fuel cost of $836,141 per year.

$2*10^7$ Btu/hr * 6570 hrs/yr * 1 lb supplemented fuel/17483 Btu * $0.089/lb supplemented fuel * 1/0.8 (efficiency factor) = $836,141/yr

Therefore, the yearly fuel cost differential of operating the baseline combustor with the 10 percent by weight nitrocellulose-No. 2 fuel oil supplemented fuel is:

(836,141 - 856,812) $/yr = - 20,671 $/yr

Figure 4-2 shows that the cost differential is not dependent on No. 2 fuel oil prices since there is zero cost associated with the nitrocellulose.

4.1.2 Capital Cost

The capital cost estimate will assume that the existing combustor will be used with the supplemented fuel without retrofit. This yields a zero cost for the baseline case. The

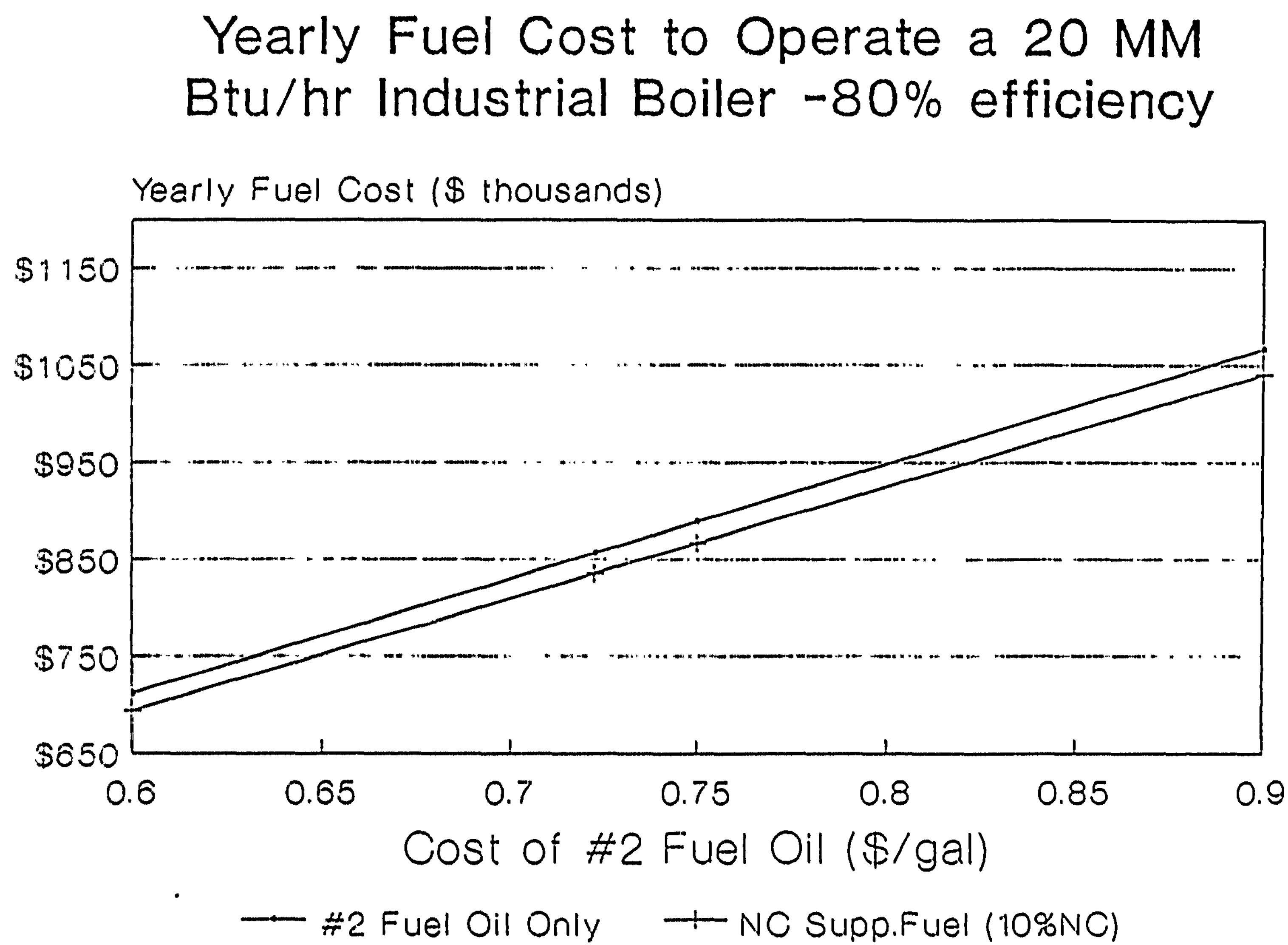


Figure 4-2. Yearly Fuel Cost to Burn Nitrocellulose-No. 2 Fuel Oil Mixture at Various Fuel Oil Prices.

major additional equipment required to burn the supplemented fuel is found in the feed system. The daily volume of supplemented fuel required for operating the 20 MM Btu/hr combustor is 3500 gallons. Therefore, a 5000-gallon feed system is specified for operations. The major equipment and estimated costs for the process are given in Table 4-2 If the final capital cost of $947,400 is considered over a 20 year period at 0 percent interest, the yearly capital cost expenditure is $47,370.

Table 4-2. Capital Cost Estimate for a 5000 Gallon Feed System

Major Equipment Costs

Item	Capacity	Cost, $
Feed tank	5000 gal, SS	64,200
Mix tank	500 gal, SS	10,000
Propellant Storage Tank	2250 gal, SS	47,900
Grinder	20 hp	15,000
Agitator	15 hp	5,000
Pumps (3)	15 gpm	9,000
		Total 151,100

Langs factor for solid-fluid processing plant fixed capital is 4.18(3). A factor of 1.5 is applied to the capital cost as an estimate to account for propellant requirements not included in equipment estimates.

Capital Cost Estimate = $151,000 * 4.18 * 1.5 = $947,400

4.1.3 Labor Cost

The labor cost estimate will assume that a 2 man operation can prepare the supplemental fuel. A supervisor is included at one quarter of the work time. Table 4-3 shows the details of the labor cost estimate, which totals $105,000 per year.

Table 4-3. Labor Cost Estimate for Burning Propellant-No. 2 Fuel Oil Slurries

2 operators (@ $25,000/yr)		$50,000
1 supervisor (@ $40,000/yr) * 0.25		$10,000
	Subtotal	$60,000
Overhead (@ 75 percent labor rate)		$45,000
	Labor Total	$105,000/yr

4.1.4 Overall Cost Comparison

The additional cost to operate the supplemental fuel fired combustor is calculated as $131,699 per year. This cost is based on the sum of the yearly fuel cost differential, capital cost, and labor cost.

(-20,671) + 47,370 + 105,000 $/yr = $131,699/yr

The amount of nitrocellulose consumed per year by burning a 10 percent by weight nitrocellulose-No. 2 fuel oil slurry as a supplemental fuel is calculated as 751,583 pounds. This results in a total cost for nitrocellulose destruction of $0.1752 per pound or $350/ton.

The results of identical calculations for various weight percentages of nitrocellulose-, nitroguanidine-, and AA2 propellant-No. 2 fuel oil supplemental fuels are shown in Table 4-4.

Table 4-4. Cost of Disposal for Various Propellant-No. 2 Fuel Oil Slurries in a 20 MM Btu/hr Industrial Combustor

	Amount of propellant (weight %)	Heating Value (Btu/lb)	Additional Fuel Cost ($/yr)	Propellant Consumed (Tons/yr)	Cost of disposal ($/ton)
No. 2 Fuel Oil	0.0	18947	---	---	---
Nitrocellulose	5.0	18215	142282	180	790
	7.5	17849	136639	276	495
	10.0	17483	131699	376	350
Nitroguanidine	5.0	18201	142933	181	790
	10.0	17454	133088	376	354
	12.5	17081	127145	481	264
	15.0	16707	121380	590	206
AA2 Propellant	10.0	17488	131460	376	350
	15.0	16758	119866	588	202
	20.0	16029	106100	820	129

The current cost of disposal for propellants by open burning/open detonation (OB/OD) ranges from approximately $300/ton to $813/ton of propellant. The cost per ton of incinerating these propellants is estimated at $2,800. Using the data summarized in Table 4-4, a comparison of the cost for destruction by OB/OD versus using 10 percent by weight nitrocellulose-, nitroguanidine-, or AA2 propellant-No. 2 fuel oil slurries as supplemental fuels indicates that OB/OD and incineration are significantly higher in cost in each case. This concentration for the nitrocellulose-No. 2 fuel oil slurry is the highest that could be handled even by a modified oil burner, i.e., the viscosities of nitrocellulose-No. 2 fuel oil slurries increase dramatically as the concentration of nitrocellulose in the No. 2 fuel oil increases above 10 percent by weight.

However, as noted in section 3.1.6, the situation is different for the nitroguanidine- and AA2 propellant-No. 2 fuel oil slurries. If an oil burner could be identified that could burn a supplemental fuel with, for example, a viscosity double that allowed in an unmodified burner, then viscosity data indicate that 12.5 or 15 percent by weight nitroguanidine-No. 2 fuel oil slurries could be burned as supplemental fuels. As Table 4-4 shows, the costs for burning 12.5 and 15 percent by weight nitroguanidine-No. 2 fuel oil slurries as supplemental fuels are $264/ton and $206/ton, respectively. Obviously, these figures are less than the current approximate costs given earlier for disposal of propellants via OB/OD or incineration.

Similarly, if an oil burner could be modified to allow a supplemental fuel with, for example, a viscosity double that allowed in an unmodified burner, then viscosity data indicate that AA2 propellant-No. 2 fuel oil slurries containing up to 20 percent by weight propellant could conceivably be burned as supplemental fuels. Once again, as Table 4-4 shows, the costs for burning 15 and 20 percent by weight AA2 propellant-No. 2 fuel oil slurries as supplemental fuels are $202/ton and $120/ton, respectively. These figures obviously represent a significant cost savings compared to disposal via OB/OD or incineration and may represent enough savings to justify retrofit of combustors with burners capable of burning viscous slurries.

Finally, Figure 4-3 shows that the disposal costs associated with combustor destruction do not fluctuate significantly with changing fuel prices. As discussed in Section 6, the environmental issues associated with OB/OD may increase the upper limit of $813/ton cost for this disposal method in the near future.

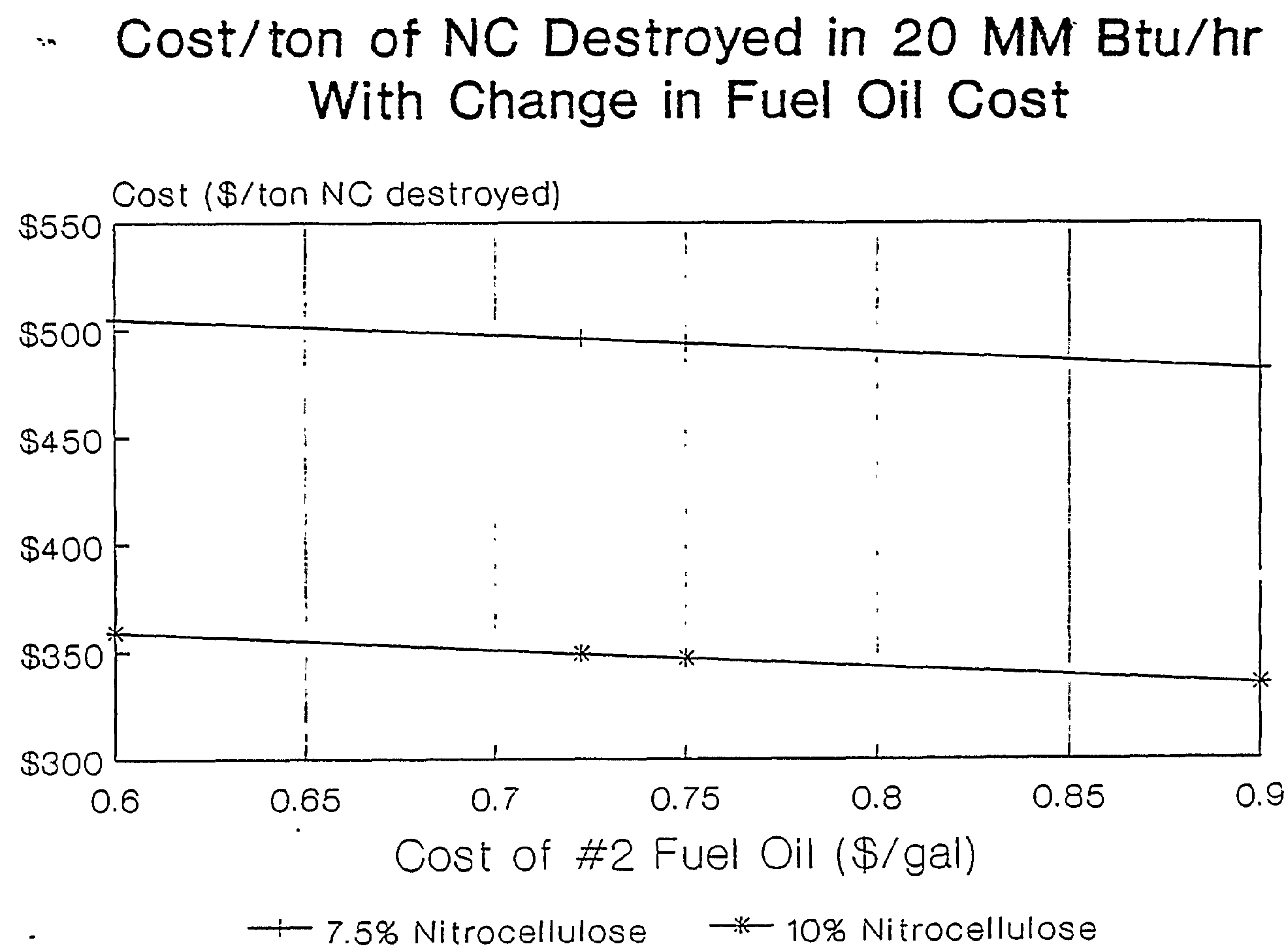


Figure 4-3. Cost of Nitrocellulose Destroyed at Various Fuel Oil Prices.

V. EXPERIMENTAL PROCEDURES

5.1 General

The following sections describe the test plan, selection of test materials, preparation of propellant-No. 2 fuel oil slurries, and the test methodologies to determine the physical and chemical characteristics, as well as the chemical compatibility, of these slurries.

5.2 Overall Test Plan and Procedures

Propellants that require disposal by the U.S. Army primarily consist of single-, double, and triple-base propellants. For a single-base propellant, 85-98 percent of the composition consists of nitrocellulose; for a double-base propellant, the fraction of nitrocellulose decreases to 55-78 percent, while for a triple-base propellant, only about 20-28 percent of the composition consists of nitrocellulose.

To determine whether using propellant-No. 2 fuel oil slurries as supplemental fuels in industrial combustors was feasible, a series of tests were developed to assess the physical and chemical characteristics, as well as the chemical compatibility of nitrocellulose, nitroguanidine, and AA2 double-base propellant slurries in No. 2 fuel oil. These propellants were received for testing from the Naval Ordnance Station in Indian Head, Maryland.

5.2.1 Compositions of Test Sample Materials

5.2.1.1 No. 2 Fuel Oil Component

A commercial grade of No. 2 fuel oil was purchased from a local distributor. A typical analysis of this oil is shown in Table 5-1.

Table 5-1. Analysis of Commercial No. 2 Fuel Oil

	Grade number 2
Element	
Carbon, %	86.35
Hydrogen, %	12.72
Oxygen, %	0.82
Nitrogen, %	<0.01
Sulfur, %	0.10
Ash, %	0.01
Density, lb/gal at 16°C (60°F)	7.208
Heat of Combustion, Btu/lb	19,500
Viscosity, centistokes at 38°C (100°F)	3.7

5.2.1.2 Propellant Components

As stated above, the Naval Ordnance Station supplied samples of nitrocellulose, nitroguanidine, and AA2 double-base propellants (1 lb. each) for use in the tests reported herein. The nitrocellulose was received as a water-wet (28-29 percent H_2O), finely-divided white solid. The nitroguanidine was received as a dry (<1 percent H_2O), finely-divided white solid. The AA2 double-base propellant was received as paper-thin shavings of various sizes and lengths. Photographs of each of these materials were previously shown in Figures 3-1, 3-2, and 3-3. After a particle-size analysis was run on the nitrocellulose and nitroguanidine, it was found that these materials did not require grinding prior to being dispersed in No. 2 fuel oil to form a slurry.

5.2.2 Mix Preparation

5.2.2.1 Drying of Nitrocellulose

Nitrocellulose (20 g) containing 28-29 percent of moisture was dried for 24 h at 70°C until a constant weight was obtained. The oven used for drying the nitrocellulose had the latch removed for safety reasons. Dry nitrocellulose, if ignited by fire, spark, or static electricity, burns very rapidly. Consequently, only enough nitrocellulose required to perform a particular test was dried. Any nitrocellulose left over after a particular test was wet with 28-29 percent water and recombined with the bulk propellant sample.

5.2.2.2 Preparation of Propellant-No. 2 Fuel Oil Slurries

The appropriate amount of No. 2 fuel oil was weighed out on an analytical balance to the nearest 0.1 g in an 8 ounce Nalgene bottle. The amount of propellant required to prepare the desired slurry composition was then weighed out. In the case of the nitrocellulose-No. 2 fuel oil and nitroguanidine-No. 2 fuel oil slurries, an Ika-Works dispersing tool (#S25N-25GM) was inserted into the No. 2 fuel oil and the Ultra-Turrax T-25 drive unit was turned on. The mixing speed required to prepare the 5-10 percent slurries of these materials in No. 2 fuel oil was 8,000-9,500 rpm, while the 10-15 percent slurries required a mixing speed of 9,500-13,500 rpm due to the increased viscosity of these samples. The nitrocellulose or nitroguanidine propellants were added gradually over a period of approximately

3 minutes, then the resulting slurry was allowed to mix for an additional 2 minutes. Each slurry was then transferred to an Eberbach reciprocating shaker.

In the case of the AA2 propellant-No. 2 fuel oil slurries, the #S25N-25GM dispersing tool was initially used to prepare each slurry with the Ultra-Turrax T-25 drive unit operating at 8,000-11,500 rpm. However, in this case, after all the propellant was added to the No. 2 fuel oil and the slurry was allowed to mix for 2 minutes, a #S25N-25F dispersing tool was then substituted for the #S25N-25GM tool and mixing was allowed to continue for an additional 2 minutes at 9,500-11,500 rpm. The use of the #S25N-25F dispersing tool allowed the preparation of AA2 propellant-No. 2 fuel oil slurries with a much finer particle size distribution than was possible with the #S25N-25GM tool.

5.3 Physical Characteristics Tests

5.3.1 Brookfield Viscometer Measurements

Viscosity measurements were performed using a Brookfield digital viscometer (Model DV-II) on each of the propellant-No. 2 fuel oil slurries at temperatures of 25°C, 45°C, and 65°C. The propellant-No. 2 fuel oil slurries were simultaneously heated and agitated in a Lab-Line Orbit Environ-Shaker prior to each measurement. Two standard oils of viscosities differing by at least 50 centipoise were used to calibrate the viscometer. The viscosity tests were performed according to a combination of Method A in ASTM D 2196-86 standard procedure and ASTM D 1439-83a standard procedure. Standard procedure ASTM D 2196-86, Method A, covers the determination of the apparent viscosity of non-Newtonian materials by measuring the torque on a spindle rotating at a constant speed in the material. Standard procedure ASTM D 1439-83a covers the determination of the viscosity of aqueous slurries of sodium carboxymethyl cellulose with the Brookfield viscometer.

For the preparation of the nitrocellulose- and nitroguanidine-No. 2 fuel oil slurries for viscosity measurement, the calculated quantity of No. 2 fuel oil was added to an eight-ounce capacity glass jar. A stainless steel, two-bladed, marine-type propeller attached to a variable speed laboratory stirrer was inserted into the jar allowing minimum clearance between the stirrer and the bottom of the container. Stirring was initiated and the propellant was slowly added to the No. 2 fuel oil. The stirring speed was adjusted to 800±100 rpm and mixing was continued for two hours. The stirrer was then removed and the sample container was transferred to a Lab-Line Orbit Environ-Shaker for one hour. The sample container was then removed and shaken vigorously for 10 seconds. The viscosity was then measured with the Brookfield Model DV-II digital viscometer.

5.3.2 Density Measurements

Density measurements were performed on propellant-No. 2 fuel oil slurries at 25°C, 45°C, and 65°C with a mud balance according to ASTM D 4380-84 standard procedure (Appendix A). The propellant-No. 2 fuel oil slurries were simultaneously heated and agitated in a Lab-Line Orbit Environ-Shaker prior to analysis.

In some cases, particularly with the more viscous slurry samples, the density value obtained with the mud balance was confirmed by measuring the density according to the procedure given in ASTM D 1343-86 standard procedure (Appendix A). In this procedure, the density of the sample in grams per cubic centimeter is determined by measuring the weight of a known volume of the sample contained in a 25-ml tightly stoppered graduated cylinder. In all cases, the density value determined with either method agreed to within 0.002 grams per cubic centimeter.

5.3.3 Particle Size Distribution

The laboratory procedure outlined by Lackey (4) was used to wet-screen a representative AA2 propellant-No. 2 fuel oil slurry to determine its' particle-size distribution. The residual No. 2 fuel oil was washed off the propellant fraction retained on each screen with a solvent in which the oil has a high solubility and the propellant a very low solubility. Kerosene is one example of such a solvent. After drying at 80°C for 24 h, the propellant retained on each screen was weighed on an analytical balance, and the particle size distribution was calculated.

5.3.4 Solubility Tests

The solubility apparatus used in these experiments was invented at TVA-NFERC (41). A 5 percent by weight slurry of the propellant in No. 2 fuel oil was prepared and loaded into a 50-ml Nalgene erlenmeyer flask containing a magnetic stirring bar. The flask was placed in the solubility apparatus and stirred for 24-48 hours at 25°C, 45°C, or 65°C. The resulting mixture was then filtered on a 45-micron filter and washed with kerosene to remove all traces of the No. 2 fuel oil. After drying at 80°C for 24 hours, the propellant was weighed on an analytical balance to the nearest 0.0001 gram, and the solubility value was calculated.

5.4 Chemical Characteristics Tests

5.4.1 Flash Point Tests

The flash points of the propellant-No. 2 fuel oil slurries were measured using a Cleveland Open-Cup apparatus according to ASTM D 92-85 standard procedure (Appendix A). In this test, the sample is heated at a slow, constant rate with continual stirring. A small flame is directed into the cup at regular intervals with simultaneous interruption of stirring. The flash point is defined as the lowest temperature at which application of the test flame causes the vapor above the sample to ignite. Extreme care was exercised during this test to prevent backflash of the flame into the slurry, which might have resulted in explosive decomposition of the propellant-No. 2 fuel oil mixture.

5.4.2 Fire Point Tests

The fire points of the propellant-No. 2 fuel oil slurries were determined using a Cleveland Open-Cup apparatus according to ASTM D 92-85 standard procedure (Appendix A). In this test, the slurry is placed in the cup and heated rapidly at first but then at a slow, constant rate as the flash point is approached. A small test flame is passed at a uniform rate across the cup at specified intervals until application of the test flame causes the specimen to burn for at least five seconds. Due to safety considerations, preliminary tests were performed on selected propellant-No. 2 fuel oil slurries where a small amount was placed in a metal cup and ignited.

5.4.3 Heat of Combustion Tests

The heats of combustion of each propellant and No. 2 fuel oil was measured using a bomb calorimeter according to ASTM D 240-87 standard procedure (Appendix A). The heat of combustion is a measure of the energy available from a fuel. A knowledge of this value is essential when considering the thermal efficiency of equipment for producing either power or heat. The heats of combustion of various propellant-No. 2 fuel oii slurries were then calculated from the values measured from the propellants and the No. 2 fuel oil.

The heat of combustion value for each sample was determined in triplicate by burning a weighed sample of material in an oxygen bomb calorimeter under controlled conditions. The heat of combustion was computed from temperature observations before, during, and after combustion, with proper allowance for thermochemical and heat transfer corrections. These tests were performed by the Tennessee Valley Authority's analytical laboratories in Chattanooga, Tennessee.

5.4.4 Emissions

The emissions from the pyrolysis of the individual propellants, were determined using a Kratos instrument according to a procedure similar to ASTM D 2650-88 standard procedure. This test method covers the qualitative and quantitative analyses of gases containing specific combinations of the following components: hydrogen; hydrocarbons with up to six carbon atoms per molecule; carbon monoxide; carbon dioxide; mercaptans with one or two carbon atoms per molecule; hydrogen sulfide; and air (nitrogen, oxygen, and argon). This test method cannot be used for the determination of constituents present in amounts less than 0.1 mole percent.

Although a standard method does not exist that specifically covers the analysis of propellants via SPMS, ASTM D 2650-88 provides a sufficient amount of guidance for testing these compounds using this analytical technique. As was mentioned in Section 3.2.4, the SPMS spectrum of each propellant sample was obtained, then compared and contrasted to information already available in the scientific literature. The emissions expected from the incomplete combustion of various propellant-No. 2 fuel oil slurries were then calculated from this information. This approach was discussed with USATHAMA personnel, and subsequently approved at an Interim Project Review meeting.

As stated above, the solid propellant materials were analyzed by solid probe mass spectrometry with electron ionization at 70 eV. Just enough sample was placed in a 1.5- to 2-cm capillary tube until the material was visible. With the sample tube positioned in the probe tip, the probe was inserted into the source which was held at 200°C. Nitroguanidine was analyzed using a temperature program of 50°C to 250°C at 20°C per minute. A program of 40°C to 220°C at 10°C per minute was used to analyze the AA2 propellant and nitrocellulose.

The liquid sample (No. 2 fuel oil) was analyzed by gas chromotography/mass spectrometry. A 0.32 mm x 30 m DB-5 column with a temperature program of 40°C to 310°C at 10°C per minute was used. The sample (0.3 µL) was directly injected onto the column. The source temperature was 200°C and electron ionization at 70 eV was used for this sample.

5.4.5 Elemental Analyses (C, H, N)

The carbon (C), hydrogen (H), and nitrogen (N) contents of each propellant sample were determined with a Carlo Erba Model 1108 C, H, N, S analyzer. The instrument was standardized with cysteine. All samples were analyzed in triplicate.

5.5 Chemical Compatibility Tests

5.5.1 Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program. This technique is useful for detecting potentially hazardous reactions including those from volatile chemicals and for estimating the temperatures at which these reactions occur. In addition, this technique is recommended as an initial test for detecting the reactive hazards of an uncharacterized chemical substance or mixture.

The DSC experiments were performed according to ASTM E 537-86 standard procedure (Appendix A) using a Perkin-Elmer model DSC-7 instrument. A heating rate of 20°C/min was used in each experiment with a nitrogen flow rate of 65 cc/min. The apparatus was calibrated in temperature and surface area with indium (Tm = 156°C and Hm = 28.4 J/g). An empty pan was used as the reference material for all measurements. The surface areas were measured by manipulating the decomposition curves and baselines with the DSC-7 computer software.

The method for crimping the pans was identical to that discussed by Lemieux et al. (42). First, the sample (0.5-1.5 mg) was crimped in the usual manner with aluminum pan and cover. Then, the rim of the capsule was pinched with tweezers in a criss-cross way so that decomposition gases could escape easily. This operation leaves the bottom of the capsule uniform to allow a proper thermal contact between the sample holder and the capsule. The sample was then placed in the DSC-7 apparatus, brought rapidly to 117°C, and equilibrated for two minutes. The DSC experiment was then performed at a heating rate of 20°C/min under a nitrogen flow rate of 65 cc/min.

5.5.2 Supplementary Tests

Qualitative analyses of the propellant-No. 2 fuel oil slurries were conducted over the six month course of this project to determine, for example, the rate at which the slurries settled out. Specific results from these observations are discussed in the text of the report.

VI. CONCLUSIONS

Based on the cost comparisons discussed in the economic analysis (Section 4), we conclude that fueling combustors with 10 percent by weight nitrocellulose-, nitroguanidine-, or AA2 propellant-No. 2 fuel oil slurries as supplemental fuels is a cost effective disposal option compared to disposal of these propellants via OB/OD ($300-$813/ton) or incineration ($2,800/ton). The limit of 10 percent by weight concentration of propellant in the slurry is based on the viscosity that could be handled by a conventional, unmodified oil burner. In addition, it should be noted that burning these slurries as supplemental fuels may be considered more environmentally acceptable than disposal of propellants via OB/OD or incineration. For example, Myler and Mahannah (3) have noted that disposing of waste energetic compounds has recently come under regulatory scrutiny in consequence of the end of interim status for incinerators under the Resource Conservation and Recovery Act (RCRA). OB/OD of energetic wastes requires a Subpart X permit. Subpart X operations remain under interim status until November 1992. Whether or not OB/OD operations will be allowed to continue in their current form is unknown. Therefore, burning propellant-No. 2 fuel oil slurries as supplemental fuels may be a viable option for disposal of large amounts of waste and out-of-specification propellants when the status of Subpart X operations is further clarified by November 1992. Moreover, the economic analysis has shown that burning propellant-No. 2 fuel oil slurries with greater than 10 percent by weight propellant contents as supplemental fuels could presently be a viable option for disposing of large quantities of these materials if the Army's industrial combustors could be retrofit with burners capable of handling a fuel with a viscosity, for example, double that capable of being fed to a conventional, unmodified oil burner. We recommend that the existence and cost of these modified burners be surveyed in the next phase of this project.

VII. REFERENCES

Previous work in the scientific literature concerning the physical characteristics, chemical characteristics, and thermal stability of single-, double-, and triple-base propellants were identified using the STN computer database. This database does not provide references published prior to 1964. Therefore, the Chemical Abstracts reference database was searched manually by TVA personnel for pertinent literature articles published prior to 1964.

A total of 1549 references were obtained from the STN computer database using the following search keywords: Propellants (Single-, Double-, and Triple-Base), Reactions, Properties, Chemistry, Decomposition, and Physical Properties. Copies of pertinent literature articles, reports, and patents were obtained and the contents of each reference were reviewed for relevance to the current project. A copy of the original computer printout from the STN database literature search is available from the authors upon request.

Reference material gathered in the literature search included previous work that USATHAMA has sponsored, as well as several studies sponsored by the U.S. Government and by Hercules, Inc. concerning the safety aspects of handling propellants.

7.1 Literature Cited

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APPENDIX A

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM) STANDARD PROCEDURES

ASTM D 2196-86

Standard Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer

Standard Test Methods for Rheological Properties of Non-Newtonian Materials by Rotational (Brookfield) Viscometer[1]

This standard is issued under the fixed designation D 2196; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

These test methods have been approved for use by agencies of the Department of Defense to replace Method 4287 of Federal Test Method Standard No. 141A and for listing in the DoD Index of Specifications and Standards.

1. Scope

1.1 These test methods cover the determination of the apparent viscosity and the shear thinning and thixotropic properties of non-Newtonian materials in the shear rate range from 0.1 to 50 s^{-1}.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Document

2.1 *ASTM Standard:*

E 1 Specification for ASTM Thermometers[2]

3. Summary of Test Methods

3.1 Test Method A consists of determining the apparent viscosity of coatings and related materials by measuring the torque on a spindle rotating at a constant speed in the material.

3.2 Test Methods B and C consist of determining the shear thinning and thixotropic (time-dependent) rheological properties of the materials.[3] The viscosities of these materials are determined at a series of prescribed speeds of a rotational-type viscometer. The agitation of the material immediately preceding the viscosity measurements is carefully controlled.

4. Significance and Use

4.1 Test Method A is used for determining the apparent viscosity at a given rotational speed, although viscosities at two or more speeds better characterize a non-Newtonian material than does the single viscosity measurement.

4.2 With Test Methods B and C, the extent of shear thinning is indicated by the drop in viscosity with increasing viscometer speed. The degree of thixotropy is indicated by comparison of viscosities at increasing and decreasing viscometer speeds (Test Method B), viscosity recovery (Test Method B), or viscosities before and after high shear (combination of Test Methods B and C). The high-shear treatment in Test Method C approximates shearing during paint application. The viscosity behavior measured after high shear is indicative of the characteristics of the paint soon after application.

5. Apparatus

5.1 Rotational-type viscometers having at least four speeds, such as:

5.1.1 *Brookfield Viscometer,*[4] Model LVF, having four rotational speeds, or Model LVT having eight rotational speeds, with set of four spindles; or

5.1.2 *Brookfield Viscometer,* Model RVF, having four rotational speeds, or Model RVT having eight rotational speeds, with set of seven spindles.

5.2 *Thermometer*—ASTM thermometer having a range from 20 to 70°C and conforming to the requirements for Thermometer 49C as prescribed in Specification E 1.

5.3 *Containers,* round 1-pt (0.5-L) can, 3⅜ in. (85 mm) in diameter, or 1-qt (1-L) can, 4 in. (100 mm) in diameter.

5.4 *Shaker,*[5] or equivalent machine capable of vigorously shaking the test specimen.

6. Materials

6.1 *Standard Oils,*[6] calibrated in absolute viscosity, millipascal seconds.

7. Calibration of Apparatus

7.1 Select at least two standard oils of viscosities differing by at least 5 P (0.5 Pa·s) within the viscosity range of the material being measured and in the range of the viscometer. Condition the oils as closely as possible to 25.0°C (or other agreed-upon temperature) for 1 h in a 1-pt (0.5-L) can, 3¼ in. (85 mm) in diameter. Measure the viscosities of each oil as described in Test Method B (Section 13) taking readings only at increasing speeds (13.7). Make certain that the

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[1] These test methods are under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials and are the direct responsibility of Subcommittee D01.24 on Physical Properties of Liquid Paints and Paint Materials.

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[2] *Annual Book of ASTM Standards,* Vol 14.01.

[3] Pierce, P. E., "Measurement of Rheology of Thixotropic Organic Coatings and Resins with the Brookfield Viscometer," *Journal of Paint Technology,* Vol 43, No. 557, 1971, pp. 35–43.

[4] Brookfield viscometers are available from the Brookfield Engineering Laboratories, Inc., 240 Cushing St., Stoughton, MA 02072.

[5] A reciprocating shaker may be obtained from the Red Devil Tools, 2400 Vauxhall Rd., Union, NJ 07083.

[6] Absolute viscosity standards are available in 1-pt samples from The Cannon Instrument Co., P.O. Box 16, State College, PA 16801, or Brookfield Engineering Laboratories, Inc., 240 Cushing St., Stoughton, MA 02072.

spindle is centered in the container prior to taking measurements.

NOTE 1—The Brookfield LV and RV series viscometers are equipped with a spindle guard leg. The spindle/speed multiplying factors (Table 1) are designed for use with the guard leg in place except for the following conditions: RV series when the factors are the same with or without the guard leg for spindles No. 3 through 7, or LV series when the factors are the same with or without the guard leg for spindles No. 3 and 4.

7.1.1 Calibration in a 1-pt (0.5-L) can is always possible with the LV series viscometer with the guard leg attached. Calibration of the RV series viscometer in the 1-pt can must be done with spindles No. 3 through 7 without the guard leg. If the No. 1 or No. 2 spindles are to be used, calibration is carried out in the 1-qt (1-L) can with the guard leg attached.

7.2 Combining the tolerance of the viscometer (±1 %, equal to the spindle/speed factor) and the tolerance of the temperature control (typically ±0.5°C at 25°C) it is reasonable to assume that a viscometer is calibrated if the calculated viscosities are within ±5 % of the stated values (see Table 2 for examples of the considerable change in viscosity with temperature exhibited by standard oils). If measurements are not made at 25°C, then the stated viscosities should be corrected to the temperature at which they are measured. If the viscosities determined in 7.1 differ from the stated values of the viscosity standard by more than 5 %, calculate new factors for each spindle/speed combination as follows:

$$f = V/s \tag{1}$$

where:

f = new factor for converting scale reading to viscosity, cP (mPa·s),
V = viscosity of standard oil, mPa·s, and
s = scale reading of the viscometer.

7.3 Prepare a table of new factors similar to that furnished with the viscometer (Table 1) for the spindle/speed combinations worked out in 7.2. Spindle/speed factors vary inversely with speed.

TABLE 1 Factors for Converting Brookfield Dial Readings to Centipoises (Millipascal Seconds)

NOTE—M = 1000.

Speed, rpm	RV Series Factors Spindles						
	1	2	3	4	5	6	7
0.5	200	800	2000	4000	8000	20M	80M
1	100	400	1000	2000	4000	10M	40M
2	50	200	500	1000	2000	5M	20M
2.5	40	160	400	800	1600	4M	16M
4	25	100	250	500	1000	2.5M	10M
5	20	80	200	400	800	2M	8M
10	10	40	100	200	400	1M	4M
20	5	20	50	100	200	500	2M
50	2	8	20	40	80	200	800
100	1	4	10	20	40	100	400

Speed, rpm	LV Series Factors Spindles			
	1	2	3	4
0.3	200	1000	4000	20M
0.6	100	500	2000	10M
1.5	40	200	800	4M
3.0	20	100	400	2M
6	10	50	200	1M
12	5	25	100	500
30	2	10	40	200
60	1	5	20	100

8. Preparation of Specimen

8.1 Fill a 1-pt or 1-qt can with sample to within 1 in. (25 mm) of the top with the sample and bring it as close as possible to a temperature of 25°C or other agreed-upon temperature prior to test.

8.2 Vigorously shake the specimen on the shaker or equivalent for 10 min, remove it from the shaker, and allow it to stand undisturbed for 60 min at 25°C prior to testing (Note 2). Start the test no later than 65 min after removing the can from the shaker. Do not transfer the specimen from the container in which it was shaken.

NOTE 2—Shake time may be reduced if necessary, or as agreed upon between the purchaser and manufacturer, but, in any case, should not be less than 3 min.

TEST METHOD A—APPARENT VISCOSITY

9. Procedure

9.1 Make all measurements as close as possible to 25°C, or other agreed-upon temperature.

9.2 Place the instrument on the adjustable stand. Lower the viscometer to a level that will immerse the spindle to the proper depth. Level the instrument using the attached spirit level.

9.3 Tilt the selected spindle (Note 3), insert it into one side of the center of the surface of the material, and attach the spindle to the instrument as follows: Firmly hold the upper shaft coupling with thumb and forefinger; screw left-hand thread spindle coupling securely to the upper shaft coupling being very careful when connecting to avoid undue side pressure which might affect alignment. Avoid rotating the dial so that pointer touches the stops at either extreme of the scale.

NOTE 3—Select the spindle/speed combination that will give a minimum scale reading of 10 but preferably in the middle or upper portion of the scale. The speed and spindle to be used may differ from this by agreement between user and producer.

9.4 Lower the viscometer until the groove (immersion mark) on the shaft just touches the material. Adjust the viscometer level if necessary. Move the container slowly in a horizontal plane until the spindle is located in approximately the center of the container so that the test will be run in a region undisturbed by the lowering of the spindle.

9.5 Turn on the viscometer. Adjust the viscometer to the rpm selected (Note 3) for the material under test. Allow the viscometer to run until the pointer has stabilized (Note 4). After the pointer has stabilized, depress the clutch and switch off the motor so that when it stops, the pointer will be in view (Note 5).

NOTE 4—In thixotropic paints, the pointer does not always stabilize. On occasion it reaches a peak and then gradually declines as the structure is broken down. In these cases, the time of rotation or number of revolutions prior to reading the viscometer should be agreed to

TABLE 2 Viscosity Variation of Cannon Viscosity Standards About the 25°C Temperature Point

Cannon Viscosity Standard	Viscosity at 25°C, cP (mPa·s)	Viscosity Change With +1°C at 25°C, cP (mPa·s)
S-600	1 400	87.7 (6.26 %)
S-2000	4 900	332 (6.77 %)
S-8000	20 000	1462.3 (7.31 %)

between user and manufacturer.

NOTE 5—Always release the clutch while the spindle is still immersed so that the pointer will float, rather than snap back to zero.

10. Calculation

10.1 Calculate the apparent viscosity at each speed, as follows:

$$V = fs$$

where:

V = viscosity of sample in centipoises, mPa·s,
f = scale factor furnished with instrument (see Table 1), and
s = scale reading of viscometer.

11. Report

11.1 Report the following information:

11.1.1 The Brookfield viscometer model and spindle,

11.1.2 The viscosity at the spindle/speed utilized,

11.1.3 The specimen temperature in degrees celsius, and

11.1.4 The shake time and rest period if other than specified.

12. Precision and Bias

12.1 *Precision*—See Section 23 for precision, including that for measurement at a single speed.

12.2 *Bias*—No statement of bias is possible with this test method.

TEST METHOD B—VISCOSITY UNDER CHANGING SPEED CONDITIONS, DEGREE OF SHEAR THINNING AND THIXOTROPY

13. Procedure

13.1 Make all measurements with the Brookfield viscometer as close as possible to 25°C, or other agreed upon temperature.

13.2 Adjust the instrument and attach the spindle as in 9.2 through 9.4.

13.3 Set the viscometer at the slowest rotational speed (Notes 5 and 6). Start the viscometer and record the scale reading after ten revolutions (or other agreed-upon number of revolutions).

NOTE 6—When the eight speed viscometers (RVT and LVT) are used, lower or higher speeds than that permitted by the four speed viscometers may be used upon agreement between producer and user.

13.4 Increase the viscometer speed stepwise and record the scale reading after ten revolutions (or equivalent time for each spindle/speed combination) at each speed. After an observation has been made at the top speed, decrease the speed in steps to the slowest speed, recording the scale reading after ten revolutions (or equivalent time) at each speed.

NOTE 7—It is preferable to change speed when the motor is running.

13.5 After the last reading has been taken at the slowest speed, shut off the viscometer and allow it and the specimen to stand undisturbed for an agreed-upon rest period. At the end of the rest period, start the viscometer at the slowest speed and record the scale reading after ten revolutions (or other agreed-upon number of revolutions).

14. Calculations and Interpretation of Results

14.1 Calculate the apparent viscosity at each speed as shown in Section 9.

14.2 If desired, determine the degree of shear thinning by the following method:

14.2.1 *Shear Thinning Index* (sometimes erroneously called the thixotropic index)—Divide the apparent viscosity at a low rotational speed by the viscosity at a speed ten times higher. Typical speed combinations are 2 and 20 rpm, 5 and 50 rpm, 6 and 60 rpm but selection is subject to agreement between producer and user. The resultant viscosity ratio is an index of the degree of shear thinning over that range of rotational speed with higher ratios indicating greater shear thinning.

14.2.2 A regular or log-log plot of viscosity versus viscometer speed in rpm may also be useful in characterizing the shear-thinning behavior of the material. Such plots may be used for making comparisons between paints or other materials.

14.3 If desired, estimate the degree of thixotropy (under conditions of *limited* shearing-out of structure) by one of the following methods:

14.3.1 Calculate the ratio of the slowest speed viscosity taken with increasing speed to that with decreasing speed. The higher the ratio, the greater the thixotropy.

14.3.2 Calculate the ratio of the slowest speed viscosity taken after the rest period to that before the rest period. The higher the ratio, the greater the thixotropy.

15. Report

15.1 Report the following information:

15.1.1 The Brookfield viscometer and spindle,

15.1.2 The viscosities at increasing and decreasing spindle speeds,

15.1.3 The rest period time and the viscosity at the end of that time,

15.1.4 The specimen temperature in degrees celsius, and

15.1.5 The shake time if other than that specified.

15.2 *Optional Reporting:*

15.2.1 *Degree of Shear Thinning*—Shear thinning index and speeds over which it was measured (14.2).

15.2.2 *Estimated Degree of Thixotropy* (under conditions of shearing-out of structure)—Ratio of the lowest speed viscosities, for both increasing and decreasing speeds, or ratio of the lowest speed viscosities before and after the rest period, and speed at which they were measured (14.3).

16. Precision and Bias

16.1 *Precision*—See Section 23 for precision, including that for measurement of the shear thinning index (ratio of viscosity at 5 r/min to that at 50 r/min). It has not been possible to devise a method for determining precision for viscosities at increasing and decreasing speeds other than as individual measurements. No attempt was made to determine the precision of the measurement of the degree of thixotropy because this parameter is dependent on the material, the time of the test, and other variables.

16.2 *Bias*—No statement of bias is possible with this test method.

TEST METHOD C—VISCOSITY AND SHEAR THINNING OF A SHEARED MATERIAL

17. Apparatus

17.1 High speed laboratory stirrer with speeds of at least 2000 rpm and equipped with a 2-in. (50-mm) diameter circular dispersion blade.[7]

18. Preparation of Specimen

18.1 Insert the 2-in. (50-mm) blade into the center of the can (4.3) so that the blade is about 1 in. (25 mm) from the bottom. Run the mixer at 2000 rpm (Note 8) for 1 min.

NOTE 8—Materials may be sheared at other speeds using other size blades upon agreement between producer and user.

19. Procedure

19.1 Immediately insert the same spindle used in Test Method B into the sheared material in the same manner as in Section 9.

19.2 Start the viscometer and adjust to the highest speed used in Test Method B (13.5). Record the scale reading after ten revolutions (or other agreed-upon number of revolutions).

19.3 Decrease the viscometer speed (Note 7) step-wise and record the scale readings at each speed down to the lowest speed used in Test Method B, recording the scale reading after ten revolutions at each speed (or other agreed-upon number of revolutions).

20. Calculations and Interpretation of Results

20.1 As in Test Method B, calculate the viscosities at each decreasing speed.

20.2 If desired, calculate the degree of shear thinning by the method given in Test Method B, 14.2. The measured viscosity behavior after shearing is essentially that of the paint immediately after application (disregarding changes in solids).

20.3 If desired, estimate the degree of thixotropy (under conditions of *complete* shearing-out of structure) by calculating the ratio of the lowest speed viscosities before and after shear. The lowest speed before-shear viscosity is taken from Test Method B, 14.1, at the lowest increasing speed. The lowest speed after-shear viscosity is taken from 20.1. The higher the ratio, the greater the thixotropy.

[7] Cowles or Shar type mixer/disperser.

21. Report

21.1 Report the following information:

21.1.1 The Brookfield viscometer model and spindle,

21.1.2 The viscosities at decreasing spindle speeds,

21.1.3 The specimen temperature in degrees celsius, and

21.1.4 The speed of the high-speed mixer, size of blade, and time of mixing if different from method.

21.2 *Optional Reporting:*

21.2.1 *Degree of Shear Thinning—Shear thinning index and speed over which it was measured (14.2).*

21.2.2 *Estimated Thixotropy*—Ratio of lowest speed viscosities before and after shear and the speed at which they were measured.

22. Precision and Bias

22.1 *Precision*—The precision for individual viscosity measurements is the same as for Test Method A in Section 23. No attempt has been made to determine the precision of the shear thinning index or degree of thixotropy for Test Method C for the reasons given in 16.1.

22.2 *Bias*—No statement of bias is possible with this test method.

23. Summary of Precision

23.1 In an interlaboratory study of Test Methods A and B, eight operators in six laboratories measured on two days the viscosities of four architectural paints comprising a latex flat, a latex semi-gloss, a water-reducible gloss enamel, and an alkyd semi-gloss, that covered a reasonable range in viscosities and were shear thinning. Measurements at increasing speeds of 5, 10, 20, and 50 r/min (equivalent to eight operators testing 16 samples) were used to obtain the precision of Test Method A. The within-laboratory coefficient of variation for Test Method A (single speed) was found to be 2.49 % with 121 degrees of freedom and for Test Method B (Shear Thinning Index) 3.3 % with 31 degrees of freedom. The corresponding between-laboratories coefficients are 7.68 % with 105 degrees of freedom and 7.63 % with 27 degrees of freedom. Based on these coefficients the following criteria should be used for judging the acceptability of results at the 95 % confidence level:

23.1.1 *Repeatability*—Two results obtained by the same operator at different times should be considered suspect if they differ by more than 7 % relative for single speed viscosity and 9.5 % relative for shear thinning index.

23.1.2 *Reproducibility*—Two results obtained by operators in different laboratories should be considered suspect if they differ by more than 21.6 and 22.1 % relative, respectively, for the same two test methods.

ASTM D 1439-83a

Standard Methods of Testing Sodium Carboxymethylcellulose

Designation: D 1439 – 83a$^{\epsilon 1}$

Standard Methods of Testing Sodium Carboxymethylcellulose[1]

This standard is issued under the fixed designation D 1439; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ϵ) indicates an editorial change since the last revision or reapproval.

$^{\epsilon 1}$ NOTE—Section 39 was revised editorially in April 1985.

1. Scope

1.1 These methods cover the testing of sodium carboxymethylcellulose.

1.2 The test procedures appear in the following order:

	Sections
Moisture	3 to 7
Degree of Etherification:	
Method A—Acid Wash	8, 9 to 14
Method B—Nonaqueous Titration	8, 15 to 20
Viscosity	21 to 26
Purity	27 to 33
Sodium Glycolate	34 to 41
Sodium Chloride	42 to 48
Density	49 to 53

1.3 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Reagents

2.1 *Purity of Reagents*—Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available.[2] Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

2.2 *Purity of Water*—Unless otherwise indicated, references to water shall be understood to mean distilled water.

MOISTURE

3. Scope

3.1 This method covers the determination of the volatile content of sodium carboxymethylcellulose.

3.2 The results of this test are used for calculating the total solids in the sample; and, by common usage, all materials volatile at this test temperature are designated as moisture.

4. Apparatus

4.1 *Oven*—Gravity convection oven, capable of maintaining a temperature of 105 ± 3°C.

4.2 *Weighing Bottles*, low-form, 50-mm inside diameter by 30-mm height, or equivalent.

4.3 *Analytical Balance.*

5. Procedure

5.1 Weigh 3 to 5 g of the sample to the nearest 0.001 g in a tared and covered weighing bottle.

5.2 Place the bottle in an oven at 105°C for 2 h with the cover removed. Cool the bottle in a desiccator, replace the cover, and weigh.

5.3 Replace the sample in the oven for 30 min, cool, and reweigh.

5.4 Continue this procedure to a mass loss of not more than 5 mg for 30 min drying time.

6. Calculation

6.1 Calculate the percentage of moisture as follows.

$$\text{Moisture, \%} = (A/B) \times 100$$

where:

A = mass loss on heating, and

B = grams of sample used.

7. Precision

7.1 Statistical analysis of interlaboratory test results on samples containing 2 to 10 % moisture indicates a precision of ±0.2 % absolute at the 95 % confidence level.

DEGREE OF ETHERIFICATION

8. Scope

8.1 These methods cover the determination of the degree of etherification (D.E.) of sodium carboxymethylcellulose.

8.2 Two methods are included as follows:

8.2.1 *Method A (Acid Wash)*, for crude and purified grades of sodium carboxymethylcellulose with degrees of etherification up to 0.85. Above 0.85 degree of etherification slightly low results may be obtained.

8.2.2 *Method B (Nonaqueous Titration)*, for purified grades of sodium carboxymethylcellulose of all degrees of

[1] These methods are under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials and is the direct responsibility of Subcommittee D01.36 on Cellulosics.

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[2] "Reagent Chemicals, American Chemical Society Specifications," Am. Chemical Soc., Washington, D C For suggestions on the testing of reagents not listed by the American Chemical Society, see "Reagent Chemicals and Standards," by Joseph Rosin, D. Van Nostrand Co., Inc., New York, N.Y., and the "United States Pharmacopeia."

etherification. It is not applicable to the crude grades.

Method A—Acid Wash

9. Summary of Method

9.1 The water-soluble sodium carboxymethylcellulose is converted to the insoluble acid form, purified by washing, dried, and then a weighed sample is reconverted to the sodium salt with a measured excess of sodium hydroxide.

10. Apparatus

10.1 *Stirrer,* air-driven.

10.2 *Buchner Funnel,* 75-mm, fitted with a 70-mm fine-texture, heavy-duty filter paper. A 60-mm medium-porosity, fritted glass funnel may also be used.

10.3 *Drying Oven,* maintained at 105°C.

11. Reagents

11.1 *Diphenylamine Reagent*—Dissolve 0.5 g of diphenylamine in 120 mL of sulfuric acid (H_2SO_4, 9+2). The reagent should be essentially water-white. It will give a deep blue coloration with traces of nitrate or other oxidizing agents.

11.2 *Ethyl Alcohol* (95 volume %)—Denatured ethyl alcohol conforming to either Formula 2B, 3A, or 30 of the U. S. Bureau of Internal Revenue.

11.3 *Ethyl Alcohol* (80 % by volume)—Dilute 840 mL of Formula 2B, 3A, or 30 denatured alcohol to 1 L with water.

11.4 *Hydrochloric Acid, Standard* (HCl, 0.3 to 0.5 *N*).

11.5 *Methanol,* anhydrous.

11.6 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).

11.7 *Sodium Hydroxide, Standard Solution* (0.3 to 0.5 *N*)—Prepare and standardize a 0.3 to 0.5 *N* solution of sodium hydroxide (NaOH).

11.8 *Sulfuric Acid* (9+2)—Carefully mix 9 volumes H_2SO_4 with 2 volumes of water.

12. Procedure

12.1 Weigh approximately 4 g of the sample into a 250-mL beaker and add 75 mL of ethyl alcohol (95 %). Stir the mixture with an air-driven stirrer until a good slurry is obtained. Add 5 mL of HNO_3, while agitating, and continue agitation for 1 to 2 min. Heat the slurry and boil for 5 min. (Caution: Note 1.) Remove the heat and continue agitation for 10 to 15 min.

NOTE 1—Caution—Care should be exercised to avoid fire.

12.2 Decant the supernatant liquid through the filter and transfer the precipitate to the filter with 50 to 100 mL of ethyl alcohol (95 %). Wash the precipitate with ethyl alcohol (80 %) that has been heated to 60°C, until all of the acid has been removed.

12.3 Test for the removal of acid and salts (ash) by mixing a drop of the acid carboxymethylcellulose slurry from the filter with a drop of diphenylamine reagent on a white spot plate. A blue color indicates the presence of nitrate and the necessity for further washing. If the first drop of reagent does not produce a blue color, further drops should be added until an excess of reagent is known to be present, noting the color after each drop. Four to six washings will usually suffice to give a negative test for nitrate.

12.4 Finally, wash the precipitate with a small amount of anhydrous methanol and draw air through it until the alcohol is completely removed. Transfer the precipitate to a glass or aluminum weighing dish provided with a cover. Heat the uncovered dish on a steam bath until the odor of alcohol can no longer be detected (in order to avoid fires due to methanol fumes in the oven), then dry the dish and contents, uncovered for 3 h at 105°C. Place the cover on the dish and cool to room temperature in a desiccator.

12.5 The sulfate ash content of the sample at this point should be less than 0.5 % when determined on 0.5 g of the sample by the procedure given in Section 6 of ASTM Methods D 1347, Testing Methylcellulose.[3] If the ash content is greater than 0.5 %, the sample should be rewashed with ethyl alcohol (80 %). If necessary, the procedure described in 12.1 to 12.4 should be repeated.

12.6 Weigh, to the nearest 0.01 g, about 1 to 1.5 g of the dried acid carboxymethylcellulose (depending on the normality of the acid and base to be used) into a 500-mL Erlenmeyer flask. Add 100 mL of water and 25.00 mL of 0.3 to 0.5 *N* NaOH solution, while stirring. Heat the solution to boiling, and boil for 15 to 30 min.

12.7 Titrate the excess NaOH, while the solution is hot, with the 0.3 to 0.5 *N* HCl to a phenolphthalein end point.

13. Calculation

13.1 Calculate the degree of etherification as follows:

$$A = (BC - DE)/F$$

$$\text{Degree of etherification} = 0.162A/(1 - 0.058A)$$

where:

A = milliequivalents of acid consumed per gram of sample,
B = millilitres of NaOH solution added,
C = normality of the NaOH solution,
D = millilitres of HCl required for titration of the excess NaOH,
E = normality of the HCl,
F = grams of acid carboxymethylcellulose used,
162 = gram molecular mass of the anhydroglucose unit of cellulose, and
58 = net increase in molecular mass of anhydroglucose unit for each carboxymethyl group substituted.

14. Precision

14.1 The precision of this method is estimated to be ±0.03 D.E. units

Method B—Nonaqueous Titration

15. Summary of Method

15.1 This measurement is based upon a nonaqueous acid-base titration. The sample is refluxed with glacial acetic acid, and the resulting sodium acetate is titrated with a standard solution of perchloric acid in dioxane, to a potentiometric end point. Impurities containing alkaline sodium will also be titrated under these conditions. Sodium chloride does not interfere.

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[3] *Annual Book of ASTM Standards,* Vol 15.04.

16. Apparatus

16.1 *pH Meter*, equipped with a standard glass electrode and a calomel electrode modified as follows:

16.1.1 Discard the aqueous potassium chloride solution, then rinse and fill with the calomel electrode solution as described in 17.2.

16.1.2 Add a few crystals of potassium chloride and silver chloride or silver oxide to the electrode.

16.2 *Buret*, micro, 10-mL capacity.

17. Reagents

17.1 *Acetic Acid*, glacial.

17.2 *Calomel Electrode Solution*—Add 2 g of potassium chloride (KCl) and 2 g of silver chloride (AgCl) or silver oxide (Ag_2O) to 100 mL of methanol and shake thoroughly to saturate. Use the supernatant liquid.

17.3 *1,4-Dioxane.*[4]

17.4 *Perchloric Acid* (0.1 *N*)—Add 9 mL of concentrated perchloric acid ($HClO_4$, 70 % to 1 L of dioxane, with stirring (Caution, Note 2). Store in an amber glass bottle. Any slight discoloration that appears on standing may be disregarded.

NOTE 2—Caution—The solution of perchloric acid in dioxane should never be heated or allowed to evaporate.

17.4.1 Standardize the solution as follows: Dry potassium acid phthalate for 2 h at 120°C. Weigh 2.5 g to the nearest 0.0001 g into a 250-mL volumetric flask. Add glacial acetic acid, shake to dissolve, and then make up to volume and mix thoroughly. Pipet 10 mL into a 100-mL beaker and add 50 mL of acetic acid. Place on a magnetic stirrer and insert the electrodes of the pH meter. Add nearly the required amount of $HClO_4$ from a buret, then decrease the increments to 0.05 mL as the end point is approached. Record the millilitres of titrant versus millivolts, and continue the titration a few millilitres beyond the end point. Plot the titration curve and read the volume of titrant at the inflection point. Calculate the normality as follows:

$$\text{Normality} = (A \times 10 \times 1000)/(B \times 204.22 \times 250)$$

where:

A = grams of potassium acid phthalate used,
B = millilitres of $HClO_4$ added,
204.22 = gram molecular mass of potassium acid phthalate,
10 = millilitres of potassium acid phthalate solution added, and
250 = millilitres of glacial acetic acid used to dissolve potassium acid phthalate.

17.5 *Potassium Acid Phthalate*, primary standard, National Bureau of Standards standard sample No. 84.

18. Procedure

18.1 Weigh 0.2 g of the sample, to the nearest 0.0001 g, into a 250-mL Erlenmeyer flask with ground-glass joint. Add 75 mL of acetic acid, connect to a water-cooled condenser, and reflux gently on a hot plate for 2 h.

18.2 Cool, and transfer the solution to a 250-mL beaker with the aid of 50 mL of acetic acid. Place on the magnetic stirrer and titrate to a potentiometric end point with 0.1 *N* $HClO_4$ in accordance with 17.4.

19. Calculation

19.1 Calculate the degree of etherification as follows (Note 3):

$$M = (AN \times 100)/(G \times (100 - B))$$

$$\text{Degree of etherification} = 0.162\,M/(1.000 - (0.080\,M))$$

where:

M = milliequivalents of acid consumed per gram of sample,
A = millilitres of $HClO_4$ added,
N = normality of $HClO_4$,
G = grams of sample used,
B = percent moisture, determined on a separate sample, in accordance with Sections 3 to 6,
162 = gram molecular mass of an anhydroglucose unit of cellulose, and
80 = net increase in molecular mass of an anhydroglucose unit for each sodium carboxymethyl group added.

NOTE 3—The result calculated in accordance with Section 17 includes the alkaline sodium from sodium glycolate; however, if the latter is less than 0.5 %, the interference is negligible.

20. Precision

20.1 Statistical analysis of interlaboratory test results indicates the precision of this method as shown below:

Approximate D.E. Level	Precision, D.E. Units (95 % Confidence Level)
0.40	±0.010
0.80	±0.012
1.35	±0.038

VISCOSITY

21. Scope

21.1 This is an arbitrary method of determining the viscosity of aqueous solutions of sodium carboxymethylcellulose in the viscosity range from 10 to 10 000 cP at 25°C.

21.2 The concentration to be used for the test should be agreed upon between the purchaser and the seller. It should be such that the viscosity of the solution will fall within the range of this test.

21.3 The results for the viscosity of sodium carboxymethylcellulose by this method will not necessarily check with results from other types of instruments used for viscosity measurements.

21.4 The determinations are run on a calculated dry basis that is, the amount of sodium carboxymethylcellulose required for the desired concentration on a dry basis is calculated from the known moisture content.

21.5 This method is intended for referee purposes. The Brookfield spindles and speeds given in Table 1 are recommended for this purpose, but slight derivations from the table may occasionally be found convenient for individual application.

[4] 1,4-Dioxane available as Eastman Kodak Catalog No. 2144 or Mateson, Coleman, and Bell Catalog No. CB 368 has been found satisfactory for this purpose.

TABLE 1 Viscometer Spindles Required for Given Speeds

Viscosity Range, cP	Spindle No.	Speed, rpm	Scale	Factor
10 to 100	1	60	100	1
100 to 200	1	30	100	2
200 to 1000	2	30	100	10
1000 to 4000	3	30	100	40
4000 to 10000	4	30	100	200

22. Apparatus

22.1 *Viscometer,* Brookfield type.[5]

22.2 *Container*—Glass jar, approximately 2⅜-in. (60-mm) in diameter and 5¼ in. (133 mm) deep, unconstricted at the top, capacity 8 oz (2.5 in³).

22.3 *Analytical Balance.*

22.4 *Mechanical Stirrer*—Stirrer constructed of either stainless steel or glass (Fig. 1)[6] attached to a variable speed motor capable of operating at 800 ± 100 rpm under varying load conditions.

22.5 *Water Bath,* constant-temperature, set at 25°C and capable of maintaining that temperature within ±0.2°C.

22.6 *Thermometer*—ASTM Saybolt Viscosity Thermometer having a range from 19 to 27°C and conforming to the requirements for Thermometer 17C, as prescribed in ASTM Specification E 1, for ASTM Thermometers.[7]

23. Procedure

23.1 Determine moisture in accordance with Sections 3 to 6.

23.2 Calculate the dry-basis sample mass necessary to make 240 g of test solution as follows:

$$\text{Mass of sample, g} = 100A/(100 - B)$$

where:

A = desired dry mass of sample, g, and

B = percentage of moisture in the sample as received.

23.3 Calculate the quantity of distilled water required as follows:

$$V = 240 - S$$

where:

V = volume of distilled water, mL, and

S = mass of sample, g.

23.4 Add the calculated quantity of water to the jar. Position the stirrer in the jar allowing minimum clearance between the stirrer and the bottom of the container.

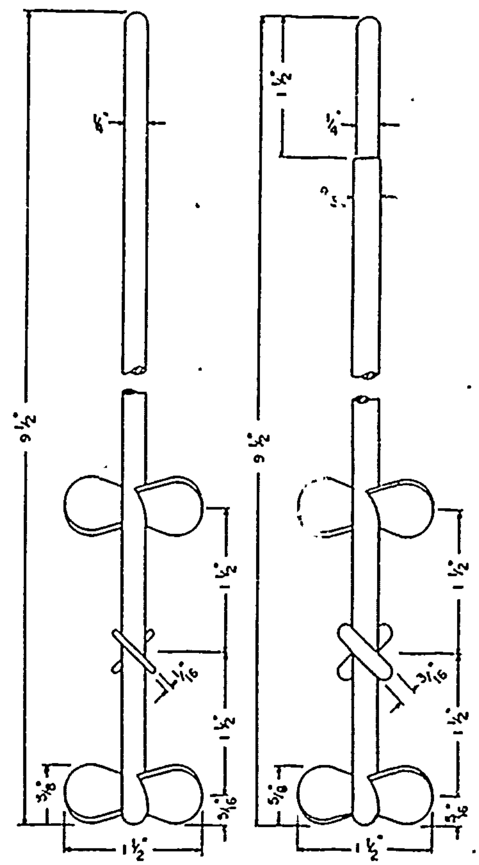
23.5 Begin stirring and slowly add the sodium carboxymethylcellulose sample. Adjust the stirring speed to approximately 800 ± 100 rpm and mix for exactly 2 h. Do not allow the stirring speed to exceed 900 rpm since higher speeds tend to affect viscosity on certain grades of sodium carboxymethylcellulose.

NOTE 4—If the sample is added too rapidly, agglomeration will occur. This may prevent complete dissolution within the required mixing time.

[5] Model LVG, Brookfield Engineering Laboratories, Inc., Stoughton, Mass. or equivalent, has been found satisfactory for this method.

[6] Stirrers made with 1½-in. (38-mm), three-bladed propellers available from A. H Thomas Co., P O. Box 779, Philadelphia, Pa. 19105, Catalog No. 9240K have also been found satisfactory for this purpose.

[7] *Annual Book of ASTM Standards,* Vol 14.01.



in.	mm	in.	mm
1/16	1.5	9/32	7
1/8	3	5/16	7.9
3/16	4.8	5/8	15.8
1/4	6.4	1½	38
		9½	241

FIG. 1 Stirrer Blade

23.6 Remove the stirrer and transfer the sample container to the constant-temperature bath for 1 h. Check the sample temperature with a thermometer at the end of 1 h to ensure that the test temperature has been reached.

23.7 Remove the sample container from the bath and shake vigorously for 10 s. Measure the viscosity with the Brookfield viscometer, selecting the proper spindle and speed from Table 1. Allow the spindle to rotate until a constant reading is obtained.

24. Calculation

24.1 Calculate the viscosity as follows:

$$\text{Viscosity, cP} = \text{reading} \times \text{factor}$$

25. Report

25.1 Report the results as Brookfield viscosity at 25 C, stating the solution concentration and the spindle and speed used.

26. Precision

26.1 The difference between the average of the results obtained by a given operator using a given viscometer and the average of the results obtained by a different operator using a different viscometer should not exceed 10 % of the mean of the averages.

PURITY OF CRUDE SODIUM CARBOXYMETHYLCELLULOSE

27. Scope

27.1 This method covers the determination of purity or percentage of active ingredient in crude sodium carboxymethylcellulose containing no phosphate. The method has been standardized on materials having a degree of etherification of about 0.85 or less.

27.2 For determination of purity of refined sodium carboxymethylcellulose (purity approximately 98 % or higher), analysis for individual or combined impurities and calculation of purity by difference will give more reliable results.

28. Summary of Method

28.1 A 3-g sample is stirred mechanically in a beaker for 15 min with each of two 150-mL portions of ethanol (80 % by volume) at a temperature of 60 to 65°C. The supernatant liquid is decanted through a tared filtering crucible after each treatment. The undissolved matter is transferred quantitatively to the crucible, dried, weighed, and calculated as percentage of sodium carboxymethylcellulose. The temperature of the ethanol during the leaching need not be closely controlled, but the concentration of the ethanol must be closely controlled (sp gr within 0.001).

29. Apparatus

29.1 *Filtering Crucible*, fritted glass, medium-porosity, 50-mL capacity.[8]

29.2 *Mechanical Stirring Motor*, electric or air-driven, with any convenient stirrer of appropriate size.

29.3 *Water Bath*, constant-temperature, maintained at 60 to 65°C.

29.4 *Cover*—A lid to keep a 400-mL beaker substantially covered during mechanical stirring in bath. A flanged lid, preferably of stainless steel, with a slot, wide enough to pass the shaft of the mechanical stirrer, cut from the rim to the center, has been found satisfactory. The center should be cut out somewhat larger than the shaft of the stirrer to permit free rotation of the stirrer. Such a lid serves to weight down the beaker as well as to minimize the evaporation losses during leaching.

30. Reagents

30.1 *Ethanol* (95 volume %)—Undenatured or specially denatured ethanol conforming to Formula 2B (Note 5) of the U. S. Bureau of Internal Revenue.

NOTE 5—Other grades of denatured alcohol, such as Formula 3A, are not satisfactory for this purpose.

30.2 *Ethanol* (80 volume %)—Dilute 840 mL of 95 % ethanol (30.1) to 1 L with water. The specific gravity should be 0.857 ± 0.001 at 25/25°C. If necessary, add water or ethanol until the specific gravity is within the specified limits.

30.3 *Ethyl Ether*, anhydrous, ethanol-free.

31. Procedure

31.1 Weigh 3 to 5 g of the sample into a tared low-form, 65-mm diameter glass weighing dish fitted with a cover. Dry to constant mass at 105 ± 1°C in either a gravity or a mechanical convection oven. Weigh at the end of an initial 2-h heating period, then continue with 30-min heating periods until the change in mass during a 30-min heating period is not more than 0.10 %. If there is an increase in mass of the sample during one or more drying periods, record the lowest mass observed as the mass for use in the calculation of moisture content. Calculate the loss in mass as the percentage of moisture in the sample.

31.2 Weigh 3 ± 0.1 g of the sample, in the "as-received" condition, to the nearest 0.001 g and transfer to a 400-mL beaker.

31.3 Add 150 mL of ethanol (80 %) that has been heated to between 60 and 65°C, and immediately place the beaker in a constant-temperature water bath maintained at 60 to 65°C. The level of the water in the bath should be somewhat higher than the level of the liquid in the beaker. Cover the beaker as completely as possible with a lid that will permit mechanical stirring. Lower a mechanical stirrer almost to the bottom of the beaker, and stir for 10 min at a rate suitable to provide good agitation without spattering material on the walls of the beaker above the liquid level.

31.4 Stop the stirrer. Allow the undissolved matter to settle with the beaker still in the bath, and then decant the hot supernatant liquid as completely as possible through a tared, fritted-glass filtering crucible.

31.5 Add 150 mL of ethanol (80 %), at 60 to 65°C to the beaker and proceed in accordance with 31.3 and 31.4.

31.6 After decanting the supernatant liquid as completely as possible, transfer the insoluble matter to the crucible with the aid of ethanol (80 %) at 60 to 65°C in a wash bottle, being careful to scrape all insoluble matter from the lid, the stirrer, and the beaker. A total of about 250 mL of ethanol (80 %) will normally be required to transfer the insoluble matter to the crucible and to further wash the insoluble matter in the crucible. During the operations prescribed in this paragraph, suction should be applied only while filtration is in progress. Every effort should be made to avoid drying-out of the filter cake. If fines appear to pass through the filter, use only gentle suction.

31.7 Wash the residue in the crucible with 50 mL of ethanol (95 %) at room temperature, and finally with several portions of ether at room temperature (Note 6). Without permitting suction to continue longer than necessary, place the crucible in a beaker or weighing bottle on the steam bath until no odor of ether can be detected.

NOTE 6—Thorough washing with ether is necessary to remove ethanol completely from the insoluble matter. If ethanol is not completely removed before oven drying, it may not be completely removed during the oven drying.

31.8 Place the crucible in an oven at 105 ± 1°C for 1 h. Stir the contents of the crucible with a dissecting needle or thin rod (preferably of smooth-surfaced metal) to break up the cake and facilitate complete drying. Again, dry at 105 ±

[8] Corning No 416120 available from A H Thomas Co., P O Box 779, Philadelphia, Pa. 19105. Catalog No. 4142-C 50 M, has been found satisfactory for this purpose.

1°C for 1 h. Place the crucible in a desiccator. Cover it with a flat glass plate, weighing bottle cover, or other suitable cover to minimize absorption of moisture from the atmosphere in the desiccator; and cool to room temperature (at least 30 min.). Weigh the uncovered crucible as rapidly as possible.

31.9 Dry the crucible for additional 1-h periods until the change in mass during a 1-h drying period does not exceed 0.003 g. If increases in mass are observed after such additional drying periods, record the lowest mass observed as the mass of the crucible plus dry sodium carboxymethylcellulose.

32. Calculation

32.1 Calculate the percentage of sodium carboxymethylcellulose on the dry basis as follows:

Sodium carboxymethylcellulose, % = $(A \times 10,000)/(B\,(100 - C))$

where:

A = mass of dried residue,
B = mass of sample used, and
C = percentage of moisture in the sample as received.

33. Precision

33.1 Statistical analysis of interlaboratory test results indicate a precision of ±0.6 % absolute at the 95 % confidence level.

SODIUM GLYCOLATE

34. Scope

34.1 This method covers the determination of the sodium glycolate content of purified sodium carboxymethylcellulose containing not more than 2.0 % sodium glycolate.

35. Summary of Method

35.1 The sodium carboxymethylcellulose is dissolved in acetic acid (50 %), precipitated with acetone and sodium sulfate and the insoluble material filtered off. The filtrate containing the sodium glycolate (as glycolic acid) is treated to remove the acetone and reacted with 2,7-dihydroxy naphthalene. The resulting color is measured at 540 nm with a spectrophotometer calibrated with known solutions.

36. Apparatus

36.1 *Spectrophotometer or Filter Photometer*, suitable for measuring absorbance at 540 nm.

36.2 *Absorption Cells*, for spectrophotometer, 1-cm light path.

36.3 *Aluminum Foil*—Cut to approximately 2-in. (51-mm) squares.

37. Reagents

37.1 *Acetic Acid*, glacial.

37.2 *Acetone*.

37.3 *Dihydroxy Naphthalene Reagent* (0.100 g/litre)—Dissolve 0.100 g of 2,7-dihydroxy naphthalene in 1 litre of sulfuric acid (H_2SO_4). Before using, allow the solution to stand until the initial yellow color disappears. If the solution is very dark, discard it and prepare a new solution from a different supply of H_2SO_4. This solution is stable for approximately 1 month if stored in a dark bottle.

37.4 *Glycolic Acid, Standard Solution* (1 mg glycolic acid/mL)—Dry several grams of glycolic acid in a desiccator at room temperature overnight. Accurately weigh 0.100 g of the dried material, dissolve in water, and make up to volume in a 100-mL volumetric flask. This solution will contain 1 mg of glycolic acid/mL. The solution is stable for approximately 1 month.

37.5 *Sodium Sulfate* (Na_2SO_4).

37.6 *Sulfuric Acid* (sp gr 1.84)—Concentrated H_2SO_4.

38. Preparation of Calibration Curve

38.1 Into a series of five 100-mL volumetric flasks, accurately introduce 1, 2, 3, and 4-mL aliquots of the standard glycolic acid solution, reserving the fifth flask for a blank. Add sufficient water to each flask to give a total volume of 5 mL. Add 5 mL of glacial acetic acid, make up to volume with acetone and mix. These solutions will contain 0, 1, 2, 3 and 4 mg of glycolic acid, respectively.

38.2 Pipet 2 mL of each of these solutions into individual 25-mL volumetric flasks. Place the uncovered flasks upright in a boiling water bath for exactly 20 min to remove the acetone. Remove the flasks from the bath and cool.

38.3 To each flask, add 20 mL of 2,7-dihydroxy naphthalene reagent as follows. Add 5 mL of reagent initially, mix thoroughly, then add the remaining 15 mL of reagent and mix. Cover the mouth of the flasks with a small piece of aluminum foil and place upright in the boiling water bath for 20 min. Remove from the bath, cool, and make up to volume with H_2SO_4.

38.4 Measure the absorbance of each solution at 540 nm against the blank solution. Plot the milligrams of glycolic acid in the original 100 mL of solution against absorbance to give a calibration curve.

39. Procedure

39.1 Weigh about 0.5 g of the sample (0.2 g for semirefined grades) to the nearest 0.001 g and transfer to a 100-mL beaker. Moisten the sample thoroughly with 5 mL of acetic acid followed by 5 mL of water, and stir with a glass rod until solution is complete (usually about 15 min is required). Slowly add 50 mL of acetone, stirring during addition, followed by approximately 1 g of NaCl. Stir several minutes to ensure complete precipitation of the carboxymethylcellulose.

39.2 Filter through a soft, open-texture paper, previously wetted with a small amount of acetone, and collect the filtrate in a 100-mL volumetric flask. Use an additional 30 mL of acetone to facilitate transfer of the solids and to wash the filter cake. Make up to volume with acetone and mix.

39.3 Prepare a blank solution containing 5 mL of water and 5 mL of glacial acetic acid in another 100-mL volumetric flask. Make up to the mark with acetone and mix.

39.4 Pipet 2 mL of the solution from the sample and 2 mL of the blank solution into separate 25-ml volumetric flasks. Develop the color and measure the absorbance in accordance with 38.2 to 38.4.

39.5 Using the observed absorbance, refer to the calibration curve and read the corresponding milligrams of glycolic acid.

40. Calculation

40.1 Calculate the sodium glycolate content as follows.

$$\text{Sodium glycolate, \%} = (B \times 12.9)/[W \times (100 - A)]$$

where:

B = milligrams of glycolic acid, read from the calibration curve,
W = grams of sample used,
A = percentage of moisture in the sample as received, and
12.9 = (gram molecular mass of sodium glycolate per gram molecular mass of glycolic acid) × 10.

41. Precision

41.1 Statistical analysis of intralaboratory data on material containing less than 0.50 % sodium glycolate indicate a precision of ±0.03 % absolute at the 95 % confidence level.

SODIUM CHLORIDE

42. Scope

42.1 This method covers the determination of the sodium chloride content of purified sodium carboxymethylcellulose.

43. Summary of Method

43.1 The sodium carboxymethylcellulose is dissolved in water and titrated with a standard solution of silver nitrate to a potentiometric end point. Hydrogen peroxide is added to reduce the viscosity of the solution.

44. Apparatus

44.1 *pH Meter,* equipped with a silver electrode and a mercurous sulfate-potassium sulfate electrode.
44.2 *Buret,* micro, 10-mL capacity.

45. Reagents

45.1 *Hydrogen Peroxide* (30 mass %)—Concentrated hydrogen peroxide (H_2O_2).
45.2 *Nitric Acid* (sp gr 1.42)—Concentrated nitric acid (HNO_3).
45.3 *Silver Nitrate, Standard Solution* (0.1 *N*)—Dissolve 17.0 g of silver nitrate ($AgNO_3$) in 1 L of water. Store in an amber glass bottle. Standardize the solution as follows:
45.3.1 Dry the sodium chloride (NaCl) for 2 h at 120°C. Weigh 0.65 g to the nearest 0.0001 g, into a 250-mL beaker and add 100 mL of water. Place on a magnetic stirrer, add 10 mL of HNO_3, and insert the electrodes of the pH meter. Add nearly the required amount of $AgNO_3$ solution from a buret, then decrease the increments to 0.05 mL as the end point is approached. Record the millilitres of titrant versus millivolts, and continue the titration a few millilitres beyond the end point. Plot the titration curve and read the volume of titrant at the inflection point. Calculate the normality as follows:

$$\text{Normality} = (A \times 1000)/(B \times 58.45)$$

where:

A = grams of NaCl used,
B = millilitres of $AgNO_3$ solution added, and
58.45 = gram molecular mass of NaCl.

45.4 *Sodium Chloride* (NaCl).

46. Procedure

46.1 Weigh 5 g of the sample, to the nearest 0.0001 g, into a 250-mL beaker. Add 50 mL of water and 5 mL of H_2O_2 (30 %). Place the beaker on a steam bath, stirring occasionally to achieve a nonviscous solution. If solution is not complete after 20 min, add 5 mL more of H_2O_2 and heat until solution is complete.
46.2 Cool the beaker, add 100 mL of water and 10 mL of HNO_3. Place it on the magnetic stirrer and titrate to the potentiometric end point with 0.1 *N* $AgNO_3$ solution in 45.3.

47. Calculation

47.1 Calculate the sodium chloride content as follows:

$$\text{Sodium chloride, \%} = (AN \times 584.5)/[G \times (100 - B)]$$

where:

A = millilitres of $AgNO_3$ solution added,
N = normality of $AgNO_3$ solution,
G = grams of sample used,
B = percent moisture, determined on a separate sample in accordance with Sections 3 to 6, and
584.5 = gram molecular mass of NaCl × 10.

48. Precision

48.1 The precision of this method is estimated to be ±0.05 % absolute for material containing less than 0.50 % sodium chloride and ±0.10 % absolute for material containing greater than 0.59 % sodium chloride.

DENSITY

49. Scope

49.1 This method covers the determination of the bulk density of sodium carboxymethylcellulose.

50. Summary of Method

50.1 A weighed amount of sodium carboxymethylcellulose is transferred to a 250-mL graduated cylinder and the graduate vibrated to settle the powder.

51. Apparatus

51.1 *Vibrator*—A magnetic-type electric vibrator attached to the vertical support rod of a ring stand approximately 1 ft (0.3 m) above the base. A condenser clamp of sufficient size to hold a 250-mL graduated cylinder also shall be attached to the above rod. The base of the stand should be weighted.

52. Procedure

52.1 Place 50.0 g of sodium carboxymethylcellulose in a 250-mL graduated cylinder and place it in the condenser clamp. Turn on the vibrator and allow the cylinder to vibrate for 3 min. Record the level (in millilitres) to which the sample has compacted.
52.2 Alternatively, the sample may be compacted manually. Tap it on a hard surface by dropping the cylinder repeatedly from a height of about 1 in. (25 mm) until the volume of the sample remains constant. In order to prevent cylinder breakage, cover the tapping surface with a ⅛ to ¼-in. (3 to 6-mm) thick rubber sheet or use a plastic graduated cylinder.

53. Calculation

53.1 Calculate the density as follows:

$$\text{Density, g/mL} = 50/\text{observed reading, mL}$$

The American Society for Testing and Materials takes no position respecting the validity of any patent rights asserted in connection with any item mentioned in this standard. Users of this standard are expressly advised that determination of the validity of any such patent rights, and the risk of infringement of such rights, are entirely their own responsibility.

This standard is subject to revision at any time by the responsible technical committee and must be reviewed every five years and if not revised, either reapproved or withdrawn. Your comments are invited either for revision of this standard or for additional standards and should be addressed to ASTM Headquarters. Your comments will receive careful consideration at a meeting of the responsible technical committee, which you may attend. If you feel that your comments have not received a fair hearing you should make your views known to the ASTM Committee on Standards, 1916 Race St., Philadelphia, PA 19103.

ASTM D 4380-84

Standard Test Method for
Density of Bentonitic Slurries

Standard Test Method for Density of Bentonitic Slurries[1]

This standard is issued under the fixed designation D 4380, the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the determination of the density of slurries used in slurry construction techniques, such as are used for barriers to control the horizontal movement of liquids. This test method is modified from API Recommended Practice 13B.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 653 Terminology Relating to Soil, Rock, and Contained Fluids[2]

2.2 *American Petroleum Institute (API) Standard:*

API RP 13B Recommended Practice Standard Procedure for Testing Drilling Fluids (Section 1)[3]

3. Terminology

3.1 For definitions of terms relating to this test method, refer to Terminology D 653.

4. Summary of Method

4.1 The mud balance is the instrument generally used for this test method. The weight of a fixed volume of the slurry is measured by moving a rider counterweight along a graduated scale. The density of the slurry is then read directly off the graduated scale after the instrument is balanced.

5. Significance and Use

5.1 This test method provides for the determination of the density of bentonitic slurries in the laboratory and field. For freshly mixed slurry, this test method may be used as an indicator of mix proportions. For in-trench slurry, a certain value may be specified for maintaining trench stability.

6. Apparatus

6.1 *Mud Balance*—Any instrument of sufficient accuracy to permit measurement within ±0.01 g/cm³ may be used, however, the mud balance is the instrument generally used (see Fig. 1). The mud balance consists of a mud cup attached to one end of a beam which is balanced on the other end by a fixed counterweight and a rider free to move along a graduated scale. A level bubble is mounted on the beam. Attachments for extending the range of the balance may be used.

7. Calibration

7.1 The instrument should be calibrated frequently with fresh water. Fresh water should give a reading of 1.00 g/cm³ at 70°F (21.1°C). If it does not, adjust the balancing screw or the amount of lead shot in the well at the end of the graduated arm as required.

8. Procedure

8.1 Set up the instrument base approximately level.

8.2 Fill the clean, dry cup with slurry to be tested, place the cap on the cup, and rotate the cap until firmly seated. Make sure some of the slurry is expelled through the hole in the cap to free trapped air or gas.

8.3 Wash or wipe the excess slurry from the outside of the cup.

8.4 Place the beam on the support and balance it by moving the rider along the graduated scale. The beam is horizontal when the leveling bubble is on the center line.

8.5 Read the density at the side of the rider toward the knife edge. Make appropriate corrections when a range extender is used.

8.6 Clean and dry the instrument thoroughly after each use.

9. Calculations

9.1 To convert the density to other units, use the following relationships:

$$\rho \text{ in g/cm}^3 = \text{specific gravity (numerically), or}$$

$$\rho \text{ in lb/ft}^3 = (\rho \text{ in g/cm}^3)\ 62.43, \text{ or}$$

$$\rho \text{ in lb/gal} = (\rho \text{ in g/cm}^3)\ 8.35$$

10. Report

10.1 Record the density to the nearest 0.01 g/cm³.

11. Precision and Bias

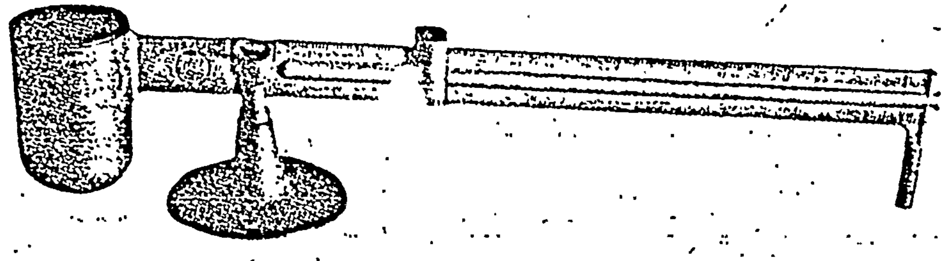
11.1 The precision and bias of this test method have not been established. Data are being sought that will be suitable for developing a precision and bias statement.

[1] This test method is under the jurisdiction of ASTM Committee D-18 on Soil and Rock and is the direct responsibility of Subcommittee D18.20 on Impermeable Barriers.

Current edition approved June 29, 1984. Published September 1984.

[2] *Annual Book of ASTM Standards*, Vol 04.08.

[3] Available from the American Petroleum Institute, 2101 L St., NW, Washington, DC 20037.



NOTE—Photo courtesy of N. L. Baroid-N. L. Industries, Inc., Houston TX.

FIG. 1 Mud Balance

ASTM D 1343-86

Standard Test Method for Viscosity of Cellulose Derivatives by Ball-Drop Method

Designation: D 1343 – 86

Standard Test Method for Viscosity of Cellulose Derivatives by Ball-Drop Method[1]

This standard is issued under the fixed designation D 1343; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This method has been approved for use by agencies of the Department of Defense to replace Method 4272-1 of Federal Test Method Standard No. 141A and for listing in the DoD Index of Specifications and Standards.

1. Scope

1.1 This test method describes the apparatus and general procedure for making ball-drop viscosity measurements on solutions of various cellulose derivatives. Instructions for sample preparation, solution concentration, and other details are discussed in the ASTM methods for the respective cellulose derivatives.

1.2 This test method is applicable to solutions of various cellulose derivatives having viscosities greater than 10 P, by using balls of various diameters and densities. Viscosity results are expressed preferably in poises.

1.3 In commercial practice, viscosities are often expressed in seconds using 3/32-in. (2.38-mm) stainless steel balls.[2] When the viscosity is outside the practical range for these balls (75 to 300 P), the measurement can be made using a calibrated pipet viscometer or a different ball and calculating the observed viscosity to the corresponding time for a 3/32-in. ball, even though it is a small fraction of a second.

1.4 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 301 Methods of Testing Soluble Cellulose Nitrate[3]

D 445 Test Method for Kinematic Viscosity of Transparent and Opaque Liquids (and the Calculation of Dynamic Viscosity)[4]

D 817 Methods of Testing Cellulose Acetate Propionate and Cellulose Acetate Butyrate[3]

D 871 Methods of Testing Cellulose Acetate[3]

3. Summary of Method

3.1 A solution of the cellulose derivative is made in a suitable solvent and allowed to equilibrate at a chosen temperature. A stainless steel or aluminum ball is dropped into the solution, and the time required for it to cover a measured distance in its fall is recorded. The viscosity of the solution can then be calculated in poise or recorded in seconds.

4. Significance and Use

4.1 This test provides an easy method of determining the viscosity of cellulose derivatives in a given solvent. The answers are in units commonly used in industrial practice. Such information is needed for cellulose derivatives that are to be extruded, molded, sprayed, or brushed as is or in solution.

5. Apparatus

5.1 *Constant-Temperature Water Bath*, glass-walled.

5.2 *Bottles and Caps:*

5.2.1 Bottles, round or square, conforming to the dimensional requirements shown in Table 1, shall be used. Screw caps of metal or phenolic plastic in sizes to fit the bottles and having aluminum foil or cardboard and cellophane liners may be used to close the bottles. Alternatively, rubber stoppers covered with aluminum or tin foil, may also be used as closures. In this latter case, solvent loss during measurement of viscosity can be minimized by removing the stopper, leaving the foil in place, and making a small hole in the center of the foil through which the balls may be dropped.

5.2.2 Timing marks shall be provided around each bottle or on the front and back of the glass-walled constant-temperature water bath, to avoid parallax errors. The lower timing mark shall be approximately 1.25 in. (32 mm) above the base of the bottle, and the upper mark shall be 2.00 ± 0.02 in. (50.8 ± 0.5 mm) above the lower mark. A practical means of marking consists of wrapping a 2-in. strip of transparent sheeting around the water bath at the proper location. The edges of the sheeting may be darkened with crayon. A light located back of the water bath aids in observing the ball during its fall.

5.3 *Balls*—Unless specifically directed otherwise, balls of varying size and density shall be used, depending on the viscosity of the solution. Table 2 gives the useful ranges, approximate apparatus constants, and dimensions of several such balls. The exact diameter, weight, and density shall be determined accurately for each lot of balls used.

5.4 *Graduate*—A 50 or 100-ml graduated cylinder, having a round top opening that can be tightly stoppered, shall be used for determining the density of the solution in grams per millilitre.

5.5 *Stop Watch*—A stop watch reading to 0.2 s.

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[1] This test method is under the jurisdiction of ASTM Committee D-1 on Paint and Related Coatings and Materials and is the direct responsibility of Subcommittee D01.36 on Cellulosics.

Current edition approved July 25, 1986. Published September 1986. Originally published as D 1343 – 54. Last previous edition D 1343 – 69 (85).

[2] When a 3/32-in. stainless steel ball is used, the viscosities in seconds should be practically the same as those obtained using the apparatus described in Section 11 of Methods D 871 – 48, and in Section 10 of Specifications D 301 – [illegible], which last appeared in the 1952 *Annual Book of ASTM Standards*, Part 4.

[3] *Annual Book of ASTM Standards*, Vol 06.02.

[4] *Annual Book of ASTM Standards*, Vol 05.01.

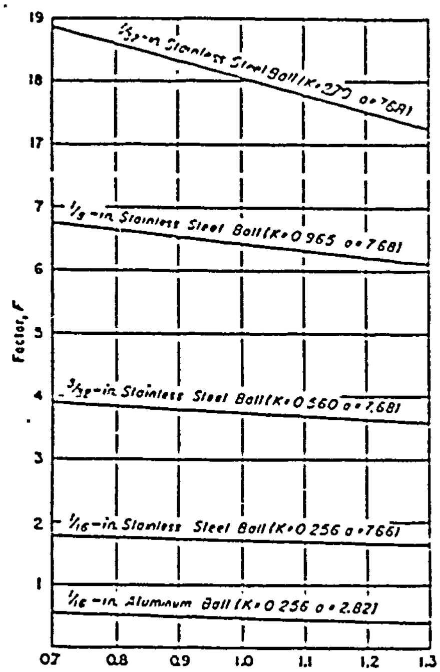

FIG. 1 Factors for Converting Viscosities in Seconds to Poises
$\eta = F \times t$

TABLE 1 Bottles[A]

Bottle	Round	Square
Capacity, oz	16	16
Weight, oz	12	12
Height, in.	6.7	7
Inside diameter, cm	6.4	
Side to side, cm	...	6.0
Corner to corner, cm	...	7.2

[A] Approximate sizes. Bottles satisfactory for this purpose may be obtained from the Owens Illinois Glass Co., Ohio Illinois Bldg., Toledo, Ohio, 43601, as follows: round bottle No. C-3145 with cap 63-400, French square bottle A-6732 with cap 48-400.

6. Calibration

6.1 Calculate the apparatus constant, K, using the following equation and exact dimensions of the bottle and balls used:

$$K = 2gr^2[1 - 2.104(d/D) + 2.09(d/D)^3]/9L$$

where:

g = acceleration of gravity in cgs units
r = ball radius, cm,
d = ball diameter, cm,
D = bottle diameter, cm (in the case of square bottles the average of the side to side and corner to corner diameters shall be used), and
L = distance of ball drop, cm.

7. Procedure

7.1 *Preparation of Solution*—Dry the sample and prepare a solution as specified for the particular material. Such instructions are given in the viscosity sections of Methods D 301, D 871, and Methods D 817. Weigh into the bottle an appropriate amount of dry sample and specified solvent accurate to 0.1 g, to make about 350 ml of solution. Close the bottle tightly. Allow to stand a short time for the solvent to penetrate the sample. Then tumble or shake until a uniform solution is obtained. Transfer to the water bath at 25 ± 0.1 C, and allow the solution to come to temperature.

7.2 *Viscosity Determination*—Drop a 3/32-in. (2.38-mm) stainless steel ball through the center of the column of solution and time its fall through the marked 2-in. (50.8 mm) distance, using a stop watch and taking precautions to avoid parallax errors. If the observed time is less than 20 s or greater than 100 s repeat the measurement, unless directed otherwise, using a different ball (see Table 2) which has a time of fall within these limits. If the solution is known to be thixotropic in nature or if the times of fall for successive balls vary significantly, use freshly prepared solutions for duplicate measurements or measurements with balls of other sizes.

7.3 *Determination of Lower Viscosities*—If the viscosity of the solution is too low to measure satisfactorily using one of the balls, use a calibrated pipet as described in Test Method D 445, or other instrument of suitable range. Calculate the result in poises. Convert poises to equivalent ball-drop seconds as shown in 8.2.

7.4 *Density Determination*—Determine the density of the solution in grams per cubic centimetre by measuring the volume at 25 ± 0.1 C of a known weight of the solution contained in a suitable tightly stoppered graduated cylinder.

8. Calculation

8.1 *Ball-Drop Viscosities*—Calculate the viscosity in poises as follows:

$$\eta = K(a - b)t$$

where:

η = viscosity at the specified temperature, P,
K = apparatus constant,[5]

[5] See Table 2 for approximate values.

TABLE 2 Balls

Ball	Viscosity Range, P	Typical Data: Apparatus Constant K	Diameter, cm	Weight, g	Density, g/cm³, ρ
1/16-in. (1.59-mm) (aluminum)	10 to 50	0.256	0.1588	0.00591	2.82
1/16-in. (1.59-mm) (stainless steel)	25 to 150	0.256	0.1588	0.01605	7.66
3/32-in. (2.38-mm)	75 to 300	0.560	0.2380	0.0542	7.68
1/8-in. (3.18-mm)	125 to 600	0.965	0.3170	0.1277	7.68
7/32-in. (5.56-mm)	250 to 1800	2.70	0.5555	0.6897	7.68

= ball density[5], in g/cm^3,
= solution density, g/cm^3, and
= time of fall, s.

n the case of a ball of stated diameter and density, this calculation can be simplified to:

$$\eta = F \times t,$$

here:

$F = K(a - b)$.

This factor varies with solution density, b. Approximate factors for the various balls can be read from Fig. 1. Exact factors can be calculated from the exact measurements of the viscometer and balls.

8.2 *Poises to Seconds*—Poises may be converted to equivalent ball-drop seconds, t, as follows:

$$t(\text{for } 3/32\text{-in. ball}) = \eta / K(a - b)$$

here:

= observed viscosity, P,
K = apparatus constant for the 3/32 in. stainless steel ball,
= ball density for the 3/32-in. stainless steel ball, and
= solution density for the solution being tested.

9. Report

9.1 Results shall be reported in poises, or in seconds, for a 3/32-in. stainless steel ball.

10. Precision and Bias

10.1 The within-laboratory precision of the test was determined by submitting 25 pairs of replicate samples to be run by any one of several operators. Each sample in a specific pair was submitted within 3 to 5 days. Each pair consisted of one sample at the 20-second viscosity level and one at the 60-second viscosity level. The data below shows the 95 % confidence limits (two sigma) for the two levels.

Viscosity Level	95 % Confidence Limits
60 sec	±3.83 sec
20 sec	±1.00 sec

Data are not available at this time to show interlaboratory precision.

10.2 Since there is no accepted reference material suitable for determining the bias for the procedure in this test method for measuring ball-drop viscosity, no statement on bias can be made.

ASTM D 92-85

Standard Test Method for
Flash and Fire Points by Cleveland Open Cup

Designation: D 92 – 85

Designation: 36/84

An American National Standard
American Association State
Highway and Transportation Officials Standard
AASHTO No.: T48
DIN 51 376

Standard Test Method for Flash and Fire Points by Cleveland Open Cup[1]

This standard is issued under the fixed designation D 94, the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This test method was adopted as a joint ASTM-IP standard in 1965.

This test method has been adopted for use by government agencies to replace Method 1103.7 of Federal Test Method Standard No. 791b, and Method 4294 of Federal Test Method Standard No. 141A.

1. Scope

1.1 This test method covers determination of the flash and fire points of all petroleum products except fuel oils and those having an open cup flash below 175°F (79°C).

1.2 The values stated in inch-pound units are to be regarded as the standard.

NOTE 1—It is the practice in the United Kingdom and in many other countries to use IP Method 35, unless Test Method D 93 - IP 34 is specified. This test method may occasionally be specified for the determination of the fire point of a fuel oil. For the determination of the flash points of fuel oils, use Test Method D 93 - IP 34. Test Method D 93 - IP 34 should also be used when it is desired to determine the possible presence of small but significant concentrations of lower flash point substances which may escape detection by Test Method D 92. Test Method D 1310 may be employed if the flash point is below 175°F (79°C); as determined by Test Method D 92 - IP 36.

1.3 *This standard should be used to measure and describe the properties of materials, products, or assemblies in response to heat and flame under controlled laboratory conditions and should not be used to describe or appraise the fire hazard or fire risk of materials, products, or assemblies under actual fire conditions. However, results of this test may be used as elements of a fire risk assessment which takes into account all of the factors which are pertinent to an assessment of the fire hazard of a particular end use.*

1.4 *This standard may involve hazardous materials, operations and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of whoever uses this standard to consult and establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

D 93 Test Method for Flash Point by Pensky-Martens Closed Tester[2]

D 1310 Test Method for Flash Point and Fire Point of Liquids by Tag Open-Cup Apparatus[2]

E 1 Specification for ASTM Thermometers[3]

2.2 *Other Method:*

IP Method 35 Flash Point (Open) and Fire Point by Means of the Pensky-Martens Apparatus[4]

3. Definitions

3.1 *flash*—point the lowest temperature corrected to a barometric pressure of 101.3 kPa (760 mm Hg), at which application of a test flame causes the vapor of a specimen to ignite under specified conditions of test.

NOTE 2—The material is deemed to have flashed when a large flame appears and instantaneously propagates itself over the surface of the specimen.

Occasionally, particularly near the actual flash point, the application of the test flame will cause a blue halo or an enlarged flame, this is not a flash and should be ignored.

3.2 *fire point*—the lowest temperature at which a specimen will sustain burning for 5 s.

4. Summary of Method

4.1 The test cup is filled to a specified level with the sample. The temperature of the sample is increased rapidly at first and then at a slow constant rate as the flash point is approached. At specified intervals a small test flame is passed across the cup. The lowest temperature at which application of the test flame causes the vapors above the surface of the liquid to ignite is taken as the flash point. To determine the fire point, the test is continued until the application of the test flame causes the oil to ignite and burn for at least 5 s.

5. Significance and Use

5.1 Flash point measures the tendency of the sample to form a flammable mixture with air under controlled laboratory conditions. It is only one of a number of properties that must be considered in assessing the overall flammability hazard of a material.

5.2 Flash point is used in shipping and safety regulations to define "flammable" and "combustible" materials. One

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.08 on Volatility.

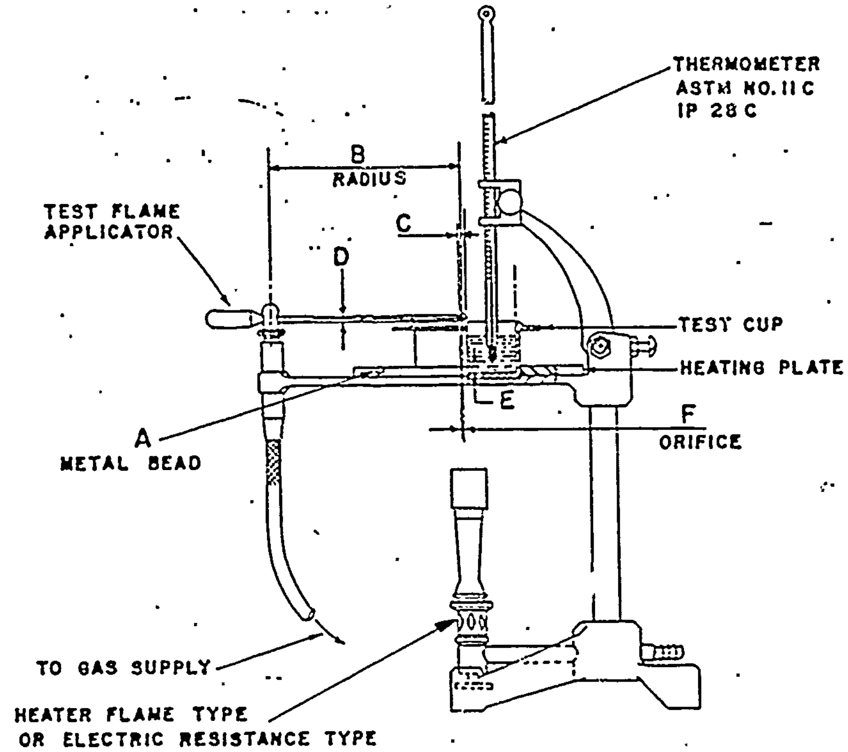
Current edition approved Oct. 25, 1985. Published December 1985. Originally published as D 92 – 21. Last previous edition D 92 – 78ε1.

In the IP, this test method is under the jurisdiction of the Standardization Committee.

[2] *Annual Book of ASTM Standards*, Vol 05.01.

[3] *Annual Book of ASTM Standards*, Vols 05.03 and 14.01.

[4] Available from the Institute of Petroleum, 61 New Cavendish St., London, W.1., England.



	inches min	inches max	millimetres min	millimetres max
A—Diameter	0.126	0.189	3.2	4.8
B—Radius	6	nominal	152	nominal
C—Diameter	0.063	nominal	1.6	nominal
D		0.078		2
E	0.236	0.276	6	7
F—Diameter	0.031	nominal	0.8	nominal

FIG. 1 Cleveland Open Cup Apparatus

should consult the particular regulation involved for precise definitions of these classes.

5.3 Flash point can indicate the possible presence of highly volatile and flammable materials in a relatively nonvolatile or nonflammable material.

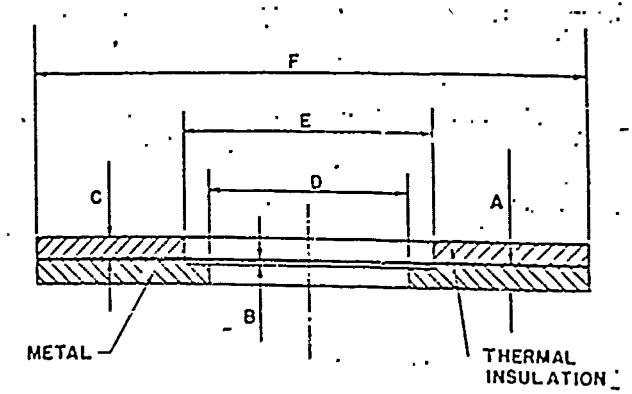
5.4 Fire point measures the characteristics of the sample to support combustion.

6. Apparatus

6.1 *Cleveland Open Cup Apparatus*—This apparatus consists of the test cup, heating plate, test flame applicator, heater, and supports described in detail in the annex. The assembled apparatus, heating plate, and cup are illustrated in Figs. 1, 2, and 3, respectively. Dimensions are listed in Tables 1, 2, and 3, respectively.

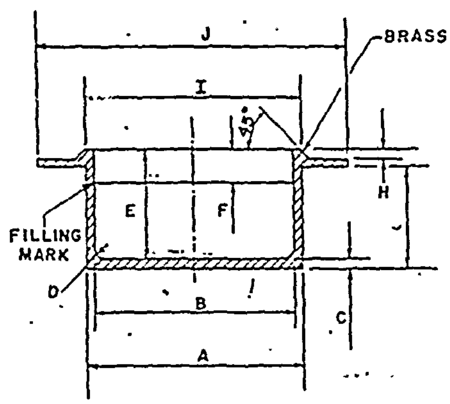
6.2 *Shield*—A shield 18 in. (460 mm) square and 24 in. (610 mm) high and having an open front is recommended.

6.3 *Thermometer*—A thermometer having a range as shown below and conforming to the requirements prescribed in Specification E 1 or in the Specifications for IP Standard Thermometers:



	inches min	inches max	millimetres min	millimetres max
A	0.26	0.276	6	7
B	0.020	0.039	0.5	1.0
C	0.236	2.276	6	7
D—Diameter	2.165	2.205	55	56
E—Diameter	2.736	2.776	69.5	70.5
F—Diameter	5.748	6.260	146	159

FIG. 2 Heating Plate



	inches min	inches max	millimetres min	millimetres max
A	2.658	2.717	67.5	69
B	2.480	2.520	63	64
C	0.110	0.138	2.8	3.5
D—Radius	0.157	nominal	4	nominal
E	1.280	1.339	32.5	34
F	0.354	0.394	9	10
G	1.221	1.280	31	32.5
H	0.110	0.138	2.8	3.5
I	2.638	2.756	67	70
J	3.819	3.937	97	100

FIG. 3 Cleveland Open Cup

Temperature Range	Thermometer Number ASTM	IP
20 to 760°F	11F	28F
−6 to +400°C	11C	28C

NOTE 3—There are automatic flash point testers available and in use which may be advantageous in the saving of testing time, permit the use of smaller samples, and have other factors which may merit their use. If automatic testers are used, the user must be sure that all of the manufacturer's instructions for calibrating, adjusting, and operating the instrument are followed. In any cases of dispute, the flash point as determined manually shall be considered the referee test.

7. Safety Precautions

7.1 The operator must exercise and take appropriate safety precautions during the initial application of the test flame, since samples containing low-flash material may give an abnormally strong flash when the test flame is first applied.

8. Sampling

8.1 Erroneously high flash points may be obtained if precautions are not taken to avoid the loss of volatile material. Do not open containers unnecessarily and make a transfer unless the sample temperature is at least the equivalent of 18°F (10°C) below the expected flash point. Do not use samples from leaky containers for this test.

8.2 Do not store samples in plastic (polyethylene, polypropylene, etc.) containers, since volatile material may diffuse through the walls of the enclosure.

8.3 Light hydrocarbons may be present in the form of gases, such as propane or butane and may not be detected by testing because of losses during sampling and loading of the test apparatus. This is especially evident on heavy residums or asphalts from solvent extraction processes.

9. Preparation of Apparatus

9.1 Support the apparatus on a level steady table in a draft-free room or compartment. Shield the top of the apparatus from strong light by any suitable means to permit ready detection of the flash point. Tests made in a laboratory hood (Note 4) or in any location where drafts occur are not to be relied upon. During the last 30°F (17°C) rise in temperature prior to the flash point, care must be taken to avoid disturbing the vapors in the test cup by careless movements or breathing near the cup.

NOTE 4—With some samples whose vapors or products of pyrolysis are objectionable, it is permissible to place the apparatus with shield in a hood, the draft of which is adjustable so that vapors may be withdrawn without causing air currents over the test cup during the final 100°F (56°C) rise in temperature prior to the flash point.

9.2 Wash the test cup with an appropriate solvent to remove any oil or traces of gum or residue remaining from a previous test. If any deposits of carbon are present, they should be removed with steel wool. Flush the cup with cold water and dry for a few minutes over an open flame or a hot plate to remove the last traces of solvent and water. Cool the cup to at least 100°F (56°C) below the expected flash point before using.

9.3 Support the thermometer in a vertical position with the bottom of the bulb ¼ in. (6.4 mm) from the bottom of the cup and locate at a point halfway between the center and side of the cup on a diameter perpendicular to the arc (or line) of the sweep of the test flame and on the side opposite to the test flame burner arm.

NOTE 5—The immersion line engraved on the thermometer will be 5/64 in. (2 mm) below the level of the rim of the cup when the thermometer is properly positioned.

10. Procedure

10.1 Fill the cup at any convenient temperature (Note 6) so that the top of the meniscus is exactly at the filling line. If too much sample has been added to the cup, remove the excess, using a medicine dropper; however, if there is sample on the outside of the apparatus, empty, clean, and refill it. Destroy any air bubbles on the surface of the sample.

NOTE 6—Viscous samples should be heated until they are reasonably fluid before being poured into the cup; however, the temperature during heating must not exceed 100°F (56°C) below the probable flash point.

10.2 Light the test flame and adjust it to a diameter of ⅛ to 3/16 in. (3.2 to 4.8 mm), the size of the comparison bead if one is mounted on the apparatus.

10.3 Apply heat initially so that the rate of temperature rise of the sample is 25 to 30°F (14 to 17°C)/min. When the sample temperature is approximately 100°F (56°C) below the anticipated flash point, decrease the heat so that the rate of temperature rise of the last 50°F (28°C) before the flash point is 9 to 11°F (5 to 6°C)/min.

10.4 Starting at least 50°F (28°C) below the flash point, apply the test flame when the temperature read on the thermometer reaches each successive 5°F (2°C) mark. Pass the test flame across the center of the cup, at right angles to the diameter which passes through the thermometer. With a smooth, continuous motion apply the flame either in a straight line or along the circumference of a circle having a radius of at least 6 in. (150 mm). The center of the test flame must move in a horizontal plane not more than 5/64 in. (2 mm) above the plane of the upper edge of the cup and passing in one direction only. At the time of the next test flame application, pass the flame in the opposite direction. The time consumed in passing the test flame across the cup in each case shall be about 1 s.

NOTE 7: Caution—Meticulous attention to all details relating to the test flame applicator, size of the test flame, rate of temperature increase, and rate of passing the test flame over the sample is necessary for good results.

10.5 Record as the observed flash point the temperature read on the thermometer when a flash appears at any point on the surface of the oil, but do not confuse the true flash with the bluish halo that sometimes surrounds the test flame.

10.6 To determine the fire point, continue heating so that the sample temperature increases at a rate of 9 to 11°F (5 to 6°C)/min. Continue the application of the test flame at 5°F (2°C) intervals until the oil ignites and continues to burn for at least 5 s. Record the temperature at this point as the observed fire point of the oil.

11. Calculation and Report

11.1 Observe and record the barometric pressure at the time of the test. When the pressure differs from 760 mm Hg, correct the flash or fire point, or both, by means of the following equations:

$$\text{Corrected flash or fire point, or both} = F + 0.06\,(760 - P)$$

$$\text{or Corrected flash or fire point, or both} = C + 0.03\,(760 - P)$$

where:

F = observed flash or fire point, or both, to the nearest 5°F,
C = observed flash or fire point, or both, to the nearest 2°C, and
P = barometric pressure, mm Hg.

11.2 Record the corrected flash or fire point, or both, to the nearest 5°F or 2°C.

11.3 Report the recorded flash or fire point value, or both, as the COC flash or fire point, or both, ASTM D 92 – IP 36 of the sample tested.

12. Precision and Bias

12.1 The following data should be used judging the acceptability of results (95 % confidence).

12.1.1 Duplicate results by the same operator should be considered suspect if they differ by more than the following amounts:

	Repeatability
Flash point	15°F (8°C)
Fire point	15°F (8°C)

12.1.2 The result submitted by each of two laboratories should be considered suspect if the results differ by more than the following amounts:

	Reproducibility
Flash point	30°F (17°C)
Fire point	25°F (14°C)

12.2 *Bias*—The bias statement is being developed for this test method.

ANNEX

(Mandatory Information)

A1. APPARATUS FOR THE CLEVELAND OPEN TESTER

A1.1 *Test Cup*, conforming to Fig. 3 with dimensions as shown in Table 3. The cup shall be made of brass or other non-rusting metal of equivalent heat conductivity. The cup may be equipped with a handle.

A1.2 *Heating Plate*—A brass, cast iron, wrought iron, or steel plate with a center hole surrounded by an area of plane depression, and a sheet of hard asbestos board which covers the metal plate except over the area of plane depression in which the test cup is supported. The essential dimensions of the heating plate are shown in Fig. 2; however, it may be square instead of round, and the metal plate may have suitable extensions for mounting the test flame applicator device and the thermometer support. Also, a metal bead, as mentioned in A1.3, may be mounted on the plate so that it extends through and slightly above a suitable small hole in the asbestos board.

A1.3 *Test Flame Applicator*—The device for applying the flame may be of any suitable type, but it is suggested that the tip be approximately $\frac{1}{16}$ in. (1.6 mm) in diameter at the end, and that the orifice be $\frac{1}{32}$ in. (0.8 mm) in diameter. The device for operating the test flame may be mounted in such a manner as to permit automatic duplication of the sweep of the test flame, the radius of swing being not less than 6 in. (150 mm) and the center of the orifice being supported so that it swings in a plane not greater than $\frac{5}{64}$ in. (2 mm) above the plane of the rim of the cup. It is desired that a bead, having a diameter of $\frac{1}{8}$ to $\frac{3}{16}$ in. (3.2 to 4.8 mm) be mounted in a convenient position on the apparatus so that the size of the test flame can be compared to it.

A1.4 *Heater*—Heat may be supplied from any convenient source. The use of a gas burner of alcohol lamp is permitted, but under no circumstances are products of combustion or free flame to be allowed to come up around the cup. An electric heater controlled by a variable voltage transformer is preferred. The source of heat shall be centered under the opening of the heating plate with no local superheating. Flame-type heaters may be protected from drafts or excessive radiation by any suitable type of shield that does not project above the level of the upper surface of the asbestos board.

A1.5 *Thermometer Support*—Any convenient device may be used which will hold the thermometer in the specified position during a test and which will permit easy removal of the thermometer from the test cup upon completion of a test.

A1.6 *Heating Plate Support*—Any convenient support which will hold the heating plate level and steady may be employed.

ASTM D 240-87

Standard Test Method for Heat of Combustion
of Liquid Hydrocarbon Fuels by Bomb Calorimeter

Standard Test Method for Heat of Combustion of Liquid Hydrocarbon Fuels by Bomb Calorimeter[1]

This standard is issued under the fixed designation D 240; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

This test method has been adopted for use by government agencies to replace Method 2502 of Federal Test Method Standard No. 791b.

$^{\epsilon 1}$ NOTE—An editorial correction was made in Section 10.2 in November 1988.

1. Scope

1.1 This test method[2] covers the determination of the heat of combustion of liquid hydrocarbon fuels ranging in volatility from that of light distillates to that of residual fuels.

1.2 Under normal conditions, this test method is directly applicable to such fuels as gasolines, kerosines, Nos. 1 and 2 fuel oil, Nos. 1-D and 2-D diesel fuel and Nos. 0-CT, 1-CT, and 2-CT gas turbine fuels.

1.3 The values stated in SI units are to be regarded as the standard.

1.4 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific hazard statements, see 7.5, 7.7, 7.8 and 9.3.

2. Referenced Documents

2.1 *ASTM Standards:*

D 129 Test Method for Sulfur in Petroleum Products (General Bomb Method)[3]

D 2382 Test Method for Heat of Combustion of Hydrocarbon Fuels by Bomb Calorimeter (High-Precision Method)[4]

E 1 Specification for ASTM Thermometers[5]

E 200 Practice for Preparation, Standardization, and Storage of Standard Solutions for Chemical Analyses[6]

3. Terminology

3.1 *Definitions:*

3.1.1 *Gross Heat of Combustion*, expressed as megajoules per kilogram. The gross heat of combustion at constant volume of a liquid or solid fuel containing only the elements carbon, hydrogen, oxygen, nitrogen, and sulfur is the quan tity of heat liberated when a unit mass of the fuel is burned i oxygen in an enclosure of constant volume, the products c combustion being gaseous carbon dioxide, nitrogen, sulfu dioxide, and liquid water, with the initial temperature of th fuel and the oxygen and the final temperature of th products at 25°C.

3.1.2 *Net Heat of Combustion*, expressed as megajoule per kilogram. The net heat of combustion at constar pressure of a liquid or a solid fuel containing only th elements carbon, hydrogen, oxygen, nitrogen, and sulfur . the quantity of heat liberated when a unit mass of the fuel . burned in oxygen at a constant pressure of 0.101 MPa (atm), the products of combustion being carbon dioxid nitrogen, sulfur dioxide, and water, all in the gaseous stat with the initial temperature of the fuel and the oxygen an the final temperature of the products of combustion at 25°C

3.1.3 The following relationships may be used for cor verting to other units:

1 cal (International Table calorie) = 4.1868 J [A]
1 Btu (British thermal unit) = 1055.06 J
1 cal (I.T.)/g = 0.0041868 MJ/kg [A]
1 Btu/lb = 0.002326 MJ/kg [A]

[A] Conversion factor is exact.

3.2 *Energy Equivalent* (effective heat capacity or wate equivalent) of the calorimeter is the energy required to rais the temperature 1° expressed as MJ/°C.

3.2.1 *Description of Term Specific to This Standard*—Th energy unit of measurement employed in this test method i the joule with the heat of combustion reported in megajoule per kilogram (Note 1).

$$1\ MJ/kg = 1000\ J/g$$

NOTE 1—In SI the unit of heat of combustion has the dimensio J/kg but for practical use a multiple is more convenient. The MJ/kg customarily used for the representation of heats of combustion c petroleum fuels.

3.3 *Symbols*

3.3.1 The net heat of combustion is represented by th symbol Q_n and is related to the gross heat of combustion b the following equation:

$$Q_n\ (\text{net, } 25°C) = Q_g\ (\text{gross, } 25°C) - 0.2122 \times H$$

[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.05 on Properties of Fuels, Petroleum, Coke and Oil Shale.

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[2] A more precise method designed specifically for use with aviation turbine fuels, although it can be used for a wide range of volatile and nonvolatile fuels is described in Test Method D 2382. *Annual Book of ASTM Standards*, Vol 05.02.

[3] *Annual Book of ASTM Standards*, Vol 05.01.

[4] *Annual Book of ASTM Standards*, Vol 05.02.

[5] *Annual Book of ASTM Standards*, Vols 05.03 and 14.03.

[6] *Annual Book of ASTM Standards*, Vol 15.05.

where:

Q_n (net, 25°C) = net heat of combustion at constant pressure, MJ/kg

Q_g (gross, 25°C) = gross heat of combustion at constant volume, MJ/kg

H = mass % of hydrogen in the sample.

3.3.2 *Temperatures* may be measured in Celsius degrees.

NOTE 2—Temperatures may be recorded in either Fahrenheit degrees or ohms or other units when using electric thermometers. The same units must then be used in all calculations, including standardization.

3.3.3 *Time* is expressed in calculations in minutes and decimal fractions thereof. It may be measured in minutes and seconds.

3.3.4 *Weights* are measured in grams.

4. Summary of Test Method

4.1 Heat of combustion is determined in this test method by burning a weighed sample in an oxygen bomb calorimeter under controlled conditions. The heat of combustion is computed from temperature observations before, during, and after combustion, with proper allowance for thermochemical and heat transfer corrections. Either isothermal or adiabatic calorimeter jackets may be used.

5. Significance and Use

5.1 The heat of combustion is a measure of the energy available from a fuel. A knowledge of this value is essential when considering the thermal efficiency of equipment for producing either power or heat.

5.2 The heat of combustion as determined by this test method is designated as one of the chemical and physical requirements of both commercial and military turbine fuels and aviation gasolines.

5.3 The mass heat of combustion, the heat of combustion per unit mass of fuel, is a critical property of fuels intended for use in weight-limited craft such as airplanes, surface effect vehicles, and hydrofoils. The range of such craft between refueling is a direct function of the heat of combustion and density of the fuel.

6. Apparatus

6.1 *Test Room, Bomb, Calorimeter, Jacket, Thermometers, and Accessories,* as described in Annex A1.

7. Reagents

7.1 *Benzoic Acid, Standard*[7]—Benzoic acid powder must be compressed into a tablet or pellet before weighing. Benzoic acid pellets for which the heat of combustion has been determined by comparison with the National Bureau of Standards sample are obtainable commercially for those laboratories not equipped to pellet benzoic acid.

7.2 *Gelatin Capsules.*

7.3 *Methyl Orange or Methyl Red Indicator.*

7.4 *Mineral Oil.*

7.5 *Oxygen*—Commercial oxygen produced from liquid air can be used without purification. If purification is necessary see Annex A1.11.

NOTE 3: Warning—Oxygen vigorously accelerates combustion. See Annex A3.2.

7.6 *Pressure-Sensitive Tape*[8]—Cellophane tape 38 mm (1½ in.) wide, free of chlorine and sulfur.

7.7 *Alkali, Standard Solution:*

7.7.1 *Sodium Hydroxide Solution* (0.0866 N)—Dissolve 3.5 g of sodium hydroxide (NaOH) in water and dilute to 1 L. Standardize with potassium acid phthalate and adjust to 0.0866 N as described in Method E 200.

NOTE 4: Warning—Corrosive. Can cause severe burns or blindness. Evolution of heat produces a violent reaction or eruption upon too rapid mixture with water. See Annex A3.1.

7.7.2 *Sodium Carbonate Solution* (0.0725 N)—Dissolve 3.84 g of Na_2CO_3 in water and dilute to 1 L. Standardize with potassium acid phthalate and adjust to 0.0725 N as described in Method E 200.

7.8 *2,2,4-Trimethylpentane* (isooctane), *Standard.*[9]

NOTE 5: Warning—Extremely flammable. Harmful if inhaled. Vapors may cause flash fire. See Annex A3.3.

8. Standardization

8.1 Determine the energy equivalent of the calorimeter as the average of not less than six tests using standard benzoic acid.[10] These tests should be spaced over a period of not less than three days. Use not less than 0.9 g nor more than 1.1 g of standard benzoic acid (C_4H_4COOH). Make each determination according to the procedure described in Section 9 and compute the corrected temperature rise, t, as described in 10.1 or 10.2. Determine the corrections for nitric acid (HNO_3) and firing wire as described in 10.3 and substitute in the following equation:

$$W = (Q \times g + e_1 + e_2)/t \qquad (1)$$

where:

W = energy equivalent of calorimeter, MJ/°C,

Q = heat of combustion of standard benzoic acid, MJ/g, calculated from the certified value,

g = weight of standard benzoic acid sample, g,

t = corrected temperature rise, as calculated in 10.1 or 10.2, °C,

e_1 = correction for heat of formation of nitric acid, MJ, and

e_2 = correction for heat of combustion of firing wire, MJ.

8.1.1 Standardization tests should be repeated after changing any part of the calorimeter and occasionally as a check on both calorimeter and operating technique.

8.2 *Checking the Calorimeter for Use with Volatile Fuels*—Use *2,2,4-trimethylpentane* to determine whether the results obtained agree with the certified value (47.788 MJ/kg, weight in air) within the repeatability of the test method. If results do not come within this range, the method of

[7] Obtainable from the National Bureau Standards, Washington, DC 20234, as standard sample No. 39i.

[8] Cellophane tape Scotch Brand No. 600 or 610 available from the Minnesota Mining and Manufacturing Company meets the specification requirements.

[9] Obtainable from the National Bureau Standards, Washington, DC 20234, as standard sample No. 217b.

[10] See Jessup, R. S., "Precise Measurement of Heat of Combustion with a Bomb Calorimeter," *NBS Monograph 7*, U. S. Government Printing Office

handling the sample may have to be changed (Annex A1.8). If this is not possible or does not correct the error, run a series of tests using *2,2,4-trimethylpentane* to establish the energy equivalent for use with volatile fuels.

8.3 *Heat of Combustion of Pressure-Sensitive Tape or Gelatin/Mineral Oil*—Determine the heat of combustion of either the pressure-sensitive tape or 0.5 g gelatin capsule/mineral oil in accordance with Section 9 using about 1.2 g of tape or 0.5 g gelatin capsule/mineral oil and omitting the sample. Make at least three determinations and calculate the heat of combustion as follows:

$$Q_{pst} = (\Delta t \times W - e_1)/1000\,a \qquad (2)$$

where:

Q_{pst} = heat of combustion of the pressure-sensitive tape or mineral oil, MJ/kg,
Δt = corrected temperature rise, as calculated in accordance with 10.1 or 10.2, °C,
W = energy equivalent of the calorimeter, MJ/°C,
e_1 = correction for the heat of formation of HNO_3, MJ, and
a = mass of the pressure-sensitive tape or gelatin capsule/mineral oil, g.

Average the determinations, and redetermine the heat of combustion of the tape or gelatin capsule/mineral oil whenever a new roll or batch is started.

9. Procedure

9.1 *Weight of Sample*—Control the weight of sample (including any auxiliary fuel) so that the temperature rise produced by its combustion will be equal to that of 0.9 to 1.1 g of benzoic acid (Note 6). Weigh the sample to the nearest 0.1 mg.

NOTE 6—If the approximate heat of combustion of the sample is known, the required weight can be estimated as follows.

$$g = 26.454/Q_s \qquad (3)$$

where:

g = weight of sample, g, and
Q_s = MJ/kg.

NOTE 7—Some fuels may contain water and particulate matter (ash) that will degrade calorimetric values. If the heat of combustion is required on a clean fuel, filter the sample to remove free water and insoluble ash before testing.

9.1.1 For highly volatile fluids, reduce loss with use of tape[11] or gelatin capsule mineral oil.

9.1.2 *Tape*—Place a piece of pressure-sensitive tape across the top of the cup, trim around the edge with a razor blade, and seal tightly. Place 3 by 12-mm strip of tape creased in the middle and sealed by one edge in the center of the tape disk to give a flap arrangement. Weigh the cup and tape. Remove from the balance with forceps. Fill a hypodermic syringe with the sample. The volume of sample can be estimated as follows:

$$V = (W \times 0.00032)/(Q \times D)$$

where:

V = volume of sample to be used, mL,
W = energy equivalent of calorimeter, J/°C,
Q = approximate heat of combustion of the sample, MJ/kg, and
D = density, kg/m^3, of the sample.

9.1.2.1 Add the sample to the cup by inserting the tip of the needle through the tape disk at a point so that the flap of tape will cover the puncture upon removal of the needle. Seal down the flap by pressing lightly with a metal spatula. Reweigh the cup with the tape and sample. Take care throughout the weighing and filling operation to avoid contacting the tape or cup with bare fingers. Place the cup in the curved electrode and arrange the fuse wire so that the central portion of the loop presses down on the center of the tape disk.

9.1.3 *Gelatin/Mineral Oil*—Weigh the cup and gelatin capsule. The capsule should only be handled with forceps. Add the sample to the capsule. Reweigh the cup with capsule and sample. If poor combustion is expected with the capsule, add several drops of mineral oil on the capsule and reweigh the cup and contents. Place the cup in the curved electrode and arrange the fuse wire so that the central portion of the loop contacts the capsule and oil.

9.2 *Water in Bomb*—Add 1.0 mL of water to the bomb from a pipet.

9.3 *Oxygen*—With the test sample and fuse in place, slowly charge the bomb with oxygen to 30-atm (3.0-MPa) gage pressure at room temperature (Note 9). Do *not* purge the bomb to remove entrapped air.

NOTE 8: Caution—Be careful not to overcharge the bomb. If, by accident, the oxygen introduced into the bomb should exceed 4.0 MPa, *do not* proceed with the combustion. An explosion might occur with possible violent rupture of the bomb. Detach the filling connection and exhaust the bomb in the usual manner. Discard the sample, unless it has lost no weight, as shown by reweighing.

NOTE 9—Lower or higher initial oxygen pressures may be used within the range from 2.5 to 3.5 MPa, provided the same pressure is used for all tests, including standardization.

9.4 *Calorimeter Water*—Adjust the calorimeter water temperature before weighing as follows:

Isothermal jacket method	1.6 to 2.0°C below jacket temperature
Adiabatic jacket method is (9.6)	1.0 to 1.4°C below room temperature.

NOTE 10—This initial adjustment will ensure a final temperature slightly above that of the jacket for calorimeters having an energy equivalent of approximately 10.2 kJ/°C. Some operators prefer a lower initial temperature so that the final temperature is slightly below that of the jacket. This procedure is acceptable, provided it is used in all tests, including standardization.

9.4.1 Use the same amount (±0.5 g) of distilled or deionized water in the calorimeter vessel for each test. The amount of water (2000 g is usual) can be most satisfactorily determined by weighing the calorimeter vessel and water together on a balance. The water may be measured volumetrically if it is measured always at the same temperature.

9.5 *Observations, Isothermal Jacket Method*—Assemble the calorimeter in the jacket and start the stirrer. Allow 5 min for attainment of equilibrium, then record the calorimeter temperatures (Note 11) at 1-min intervals for 5 min. Fire

[11] Acceptable procedures for handling volatile liquids include those described in the reports referenced at the end of this test method. References (1) to (6) describe glass sample holders, (7) describes a metal sample holder, (8) describes a gelatin sample holder.

the charge at the start of the sixth minute and record the time and temperature, t_a. Add to this temperature 60 % of the expected temperature rise, and record the time at which the 60 % point is reached (Note 12). After the rapid rise period (about 4 to 5 min), record temperatures at 1-min intervals on the minute until the *difference* between successive readings has been constant for 5 min.

NOTE 11—Use a magnifier and estimate all readings (except those during the rapid rise period) to the nearest 0.002°C when using ASTM Bomb Calorimeter Thermometer 56C. Estimate Beckmann thermometer readings to the nearest 0.001°C and 25-Ω resistance thermometer readings to the nearest 0.0001 Ω. Tap mercurial thermometers with a pencil just before reading to avoid errors caused by mercury sticking to the walls of the capillary.

NOTE 12—When the approximate expected rise is unknown, the time at which the temperature reaches 60 % of the total can be determined by recording temperatures at 45, 60, 75, 90, and 105 s after firing and interpolating.

9.6 *Observations, Adiabatic Jacket Method* (NOTE 13)—Assemble the calorimeter in the jacket and start the stirrers. Adjust the jacket temperature to be equal to or slightly lower than the calorimeter, and run for 5 min to obtain equilibrium. Adjust the jacket temperature to match the calorimeter within ±0.01°C and hold for 3 min. Record the initial temperature (Note 6) and fire the charge. Adjust the jacket temperature to match that of the calorimeter during the period of rise, keeping the two temperatures as nearly equal as possible during the rapid rise, and adjusting to within ±0.01°C when approaching the final equilibrium temperature. Take calorimeter readings at 1-min intervals until the *same* temperature is observed in three successive readings. Record this as the final temperature. Time intervals are not recorded as they are not critical in the adiabatic method.

NOTE 13—These instructions supersede the instructions given in 9.5 when using jackets equipped for adiabatic temperature control.

9.7 *Analysis of Bomb Contents*—Remove the bomb and release the pressure at a uniform rate such that the operation will require not less than 1 min. Examine the bomb interior for evidence of incomplete combustion. Discard the test if unburned sample or sooty deposits are found.

9.7.1 Wash the interior of the bomb, including the electrodes and sample holder, with a fine jet of water and quantitatively collect the washings in a beaker. Use a minimum of wash water, preferably less than 350 mL. Titrate the washings with standard alkali solution, using methyl orange or methyl red indicator.

9.7.2 Remove and measure the combined pieces of unburned firing wire, and subtract from the original length. Record the difference as "wire consumed."

9.7.3 Determine the sulfur content of the sample if it exceeds 0.1 %. Determine sulfur by analyzing the bomb washings remaining after the acid titration, using the procedure described in Test Method D 129.

10. Calculation

10.1 *Temperature Rise in Isothermal Jacket Calorimeter*—Using data obtained as prescribed in 9.5, compute the temperature rise, t, in an isothermal jacket calorimeter as follows:

$$t = t_c - t_a - r_1(b - a) - r_2(c - b) \tag{4}$$

where:

t = corrected temperature rise,
a = time of firing,
b = time (to nearest 0.1 min) when the temperature rise reaches 60 % of total,
c = time at beginning of period in which the rate of temperature change with time has become constant (after combustion),
t_a = temperature at time of firing, corrected for thermometer error (Note 14),
t_c = temperature at time, c, corrected for thermometer error (Note 14),
r_1 = rate (temperature units per minute) at which temperature was rising during 5-min period before firing, and
r_2 = rate (temperature units per minute) at which temperature was rising during the 5-min period after time c. If the temperature is falling, r_2 is negative and the quantity $-r_2(c - b)$ is positive.

NOTE 14—All mercury-in-glass thermometers must be corrected for scale error, using data from the thermometer certificate prescribed in Annex A1, A1.5.1, or A1.5.2. Beckmann thermometers also require a setting correction and an emergent stem correction (Annex A2, A2.1.2). Solid-stem ASTM Thermometers 56F and 56C do not require emergent stem corrections if all tests, including standardization are performed within the same 5.5°C interval. If operating temperatures exceed this limit, a differential emergent stem correction (Annex A2, A2.1.1) must be applied to the correct temperature rise, t, in all tests, including standardization.

10.2 *Temperature Rise in Adiabatic Jacket Calorimeter*—Using data obtained as prescribed in 9.6, compute the temperature rise, t, in an adiabatic jacket calorimeter as follows:

$$t = t_f - t_a \tag{5}$$

where:

t = corrected temperature rise,
t_a = temperature when charge was fired, corrected for thermometer error (Note 14, and
t_f = final equilibrium temperature, corrected for the thermometer error (Note 14).

10.3 *Thermochemical Corrections* (Annex A2)—Compute the following for each test:

e_1 = correction for heat of formation of nitric acid (HNO_3), MJ = cm^3 of standard (0.0866 *N*) NaOH solution used in titration × 5/10^6,
e_2 = correction for heat of formation of sulfuric acid (H_2SO_4). MJ = 58.6 × percentage of sulfur in sample × mass of sample/10^6,
e_3 = correction for heat of combustion of firing wire, MJ,
= 1.13 × millimetres of iron wire consumed/10^6,
= 0.96 × millimetres of Chromel C wire consumed/10^6, and
e_4 = correction for heat of combustion of pressure-sensitive tape or gelatin capsule and mineral oil, MJ = mass of tape or capsule oil, g × heat of combustion of tape or capsule/oil, MJ/kg/10^6.

10.4 *Gross Heat of Combustion*—Compute the gross heat of combustion by substituting in the following equation:

$$Q_g = (tW - e_1 - e_2 - e_3 - e_4)/1000\ g \tag{6}$$

where:

Q_g = gross heat of combustion, at constant volume expressed as MJ/kg (Note 10),

t = corrected temperature rise as calculated in 10.1 or 10.2, °C,

W = energy equivalent of calorimeter, MJ/°C (Section 8),

e_1, e_2, e_3, e_4 = corrections as prescribed in 10.3, and

g = weight of sample, g.

NOTE 15—The gross heat of combustion at constant pressure may be calculated as follows:

$$Q_{gp} = Q_g + 0.006145H$$

where:

Q_{gp} = gross heat of combustion at constant pressure, $\frac{MJ}{kg}$, and

H = hydrogen content, mass %.

10.5 *Net Heat of Combustion:*

10.5.1 If the percentage of hydrogen, H, in the sample is known, the net heat of combustion may be calculated as follows:

$$Q_n = Q_g - 0.2122 \times H \quad (7)$$

where:

Q_n = net heat of combustion at constant pressure, MJ/kg,

Q_g = gross heat of combustion at constant volume, MJ/kg, and

H = mass percent of hydrogen in the sample.

10.5.2 If the percentage of hydrogen in aviation gasoline and turbine fuel samples is not known, the net heat of combustion may be calculated as follows:[12]

$$Q_n = 10.025 + (0.7195)Q_g \quad (8)$$

where:

Q_n = net heat of combustion at constant pressure, MJ/kg,

Q_g = gross heat of combustion at constant volume, MJ/kg.

11. Report

11.1 Net heat of combustion is the quantity required in practical applications. The net heat should be reported to the nearest 0.005 MJ/kg.

NOTE 16—Usually the gross heat of combustion is reported for fuel oils in preference to net heat of combustion.

11.2 To obtain the gross or net heat of combustion in cal (I.T.)/g or Btu/lb divide by the appropriate factor reporting to the nearest 0.5 cal/g or 1 Btu/lb.

$$Q_{Btu}/lb = (Q, MJ/kg)/0.002326$$

$$Q_{cal}/lb = (Q, MJ/kg)/0.0041868$$

12. Precision and Bias[13]

12.1 *Precision*—The precision of this test method as obtained by statistical examination of interlaboratory test results is as follows:

12.1.1 *Repeatability*—The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in the following table only in one case in twenty.

Repeatability	0.13 MJ/kg

12.1.2 *Reproducibility*—The difference between two single and independent results, obtained by different operators working in different laboratories on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in the following table only in one case in twenty.

Reproducibility	0.40 MJ/kg

12.2 *Bias*—No general statement is made on bias for the standard since comparison with accepted reference materials (covering the range of values expected when the method is used) is not available.

[12] Equation 8 is recommended only if the percentage of hydrogen is not known. It is based in Eq 7 and an empirical relation between H and the percentage of hydrogen in aviation gasolines and turbine fuels, developed from data by R. S. Jessup and C. S. Cragos, "Net Heat of Combustion of AN-F-28 Aviation Gasolines," Nat. Advisory Committee for Aeronautics, *Technical Note No 996*, June 1945, and Joseph A. Cogliano and Ralph S. Jessup, "Relation Between Net Heat of Combustion and Aniline-Gravity Product of Aircraft Fuels," Nat Bureau of Standards *Report 2348*, March 1953.

[13] The summary of cooperative test data from which these repeatability and reproducibility values were calculated was published for information as Appendix XII to the 1957 Report of Committee D-2 on Petroleum Products and Lubricants. The summary of test data was also published from 1958 to 1966, inclusive, as Appendix III to ASTM Method D 240. The data are now filed at ASTM Headquarters as Research Report No. RR D-2-38.

ANNEXES

(Mandatory Information)

A1. APPARATUS FOR HEAT OF COMBUSTION TEST

A1.1 *Test Room*—The room in which the calorimeter is operated must be free from drafts and not subject to sudden temperature changes. The direct rays of the sun shall not strike the jacket or thermometers. Adequate facilities for lighting, heating, and ventilating shall be provided. Thermostatic control of room temperature, and controlled relative humidity are desirable.

A1.2 *Oxygen Bomb*—The oxygen bomb shall have an internal volume of 350 ± 50 mL. All parts shall be constructed of materials which are not affected by the combustion process or products sufficiently to introduce measurable heat input or alteration of end products. If the bomb is lined with platinum or gold, all openings shall be sealed to prevent combustion products from reaching the base metal. The bomb must be designed so that all liquid combustion products can be completely recovered by washing the inner surfaces. There must be no gas leakage during a test. The bomb must be capable of withstanding a hydrostatic pressure test to a gage pressure of 3000 psi (20 MPa) at room temperature, without stressing any part beyond its elastic limit.[14]

A1.3 *Calorimeter*—The calorimeter (Note A1.1) vessel shall be made of metal (preferably copper or brass) with a tarnish-resistant coating, and with all outer surfaces highly polished. Its size shall be such that the bomb will be completely immersed in water when the calorimeter is assembled. It shall have a device for stirring the water thoroughly and at a uniform rate, but with minimum heat input. Continuous stirring for 10 min shall not raise the calorimeter temperature more than 0.01°C starting with identical temperatures in the calorimeter, room, and jacket. The immersed portion of the stirrer shall be coupled to the outside through a material of low heat conductivity.

NOTE A1.1—As used in this test method, the term "calorimeter" designates the bomb, the vessel with stirrer, and the water in which the bomb is immersed.

A1.4 *Jacket*—The calorimeter shall be completely enclosed within a stirred water jacket and supported so that its sides, top, and bottom are approximately 10 mm from the jacket wall. The jacket may be arranged so as to remain at substantially constant temperature, or with provision for rapidly adjusting the jacket temperature to equal that of the calorimeter for adiabatic operation. It must be constructed so that any water evaporating from the jacket will not condense on the calorimeter.[14]

A1.4.1 A double-walled jacket with a dead-air insulation space may be substituted for the constant-temperature water jacket if the calorimeter is operated in a constant-temperature (±2°F) (±1°C) room. The same ambient conditions must be maintained for all experiments, including standardization.

A1.5 *Thermometers*—Temperatures in the calorimeter and jacket shall be measured with the following thermometers or combinations thereof:

A1.5.1 *Etched Stem, Mercury-in-Glass, ASTM Bomb Calorimeter Thermometer* having a range from 66 to 95°F or 19 to 35°C, 18.9 to 25.1°C, or 23.9 to 30.1°C, as specified, and conforming to the requirements for Thermometer 56F, 56C, 116C, or 117C, respectively, as prescribed in Specification E 1. Each of these thermometers shall have been tested for accuracy at intervals no larger than 2.5°F or 2.0°C over the entire graduated scale. Corrections shall be reported to 0.005°F or 0.002°C, respectively, for each test point.

A1.5.2 *Beckmann Differential Thermometer*, range 6°C reading upward as specified and conforming to the requirements for Thermometer 115C as prescribed in Specification E 1. Each of these thermometers shall be tested for accuracy at intervals no larger than 1°C over the entire graduated scale and corrections reported to 0.001°C for each test point.

A1.5.3 *Calorimetric Type Platinum Resistance Thermometer*, 25-Ω.

A1.6 *Thermometer Accessories*—A magnifier is required for reading mercury-in-glass thermometers to one tenth of the smallest scale division. This shall have a lens and holder designed so as not to introduce significant errors due to parallax.

A1.6.1 A Wheatstone bridge and galvanometer capable of measuring resistance of 0.0001 Ω are necessary for use with resistance thermometers.

A1.7 *Timing Device*—A watch or other timing device capable of measuring time to 1 s is required for use with the isothermal jacket calorimeter.

A1.8 *Sample Holder*—Nonvolatile samples shall be burned in an open crucible of platinum (preferred), quartz or acceptable base metal alloy. Base metal alloy crucibles are acceptable if after a few preliminary firings the weight does not change significantly between tests.

A1.9 *Firing Wire*—Use a 100-mm length of No. 34 B & S gage iron wire or Chromel C resistance wire. Shorter lengths may be used if the same length is employed in all tests, including standardization tests. Platinum wire may be used if the ignition energy is small and reproducible.

A1.10 *Firing Circuit*—A 6 to 16-V alternating or direct current is required for ignition purposes with an ammeter or pilot light in the circuit to indicate when current is flowing. A step-down transformer connected to a 115-V 50/60 Hz lighting circuit of storage batteries may be used.

A1.2 Caution—The ignition circuit switch shall be of the momentary contact type, normally open, except when held closed by the operator.

A1.11 *Oxygen Purifying Device*—Commercial oxygen produced from liquid air can generally be used without

[14] The apparatus available from Parr Instrument Co., 211 Fifty-Third St., Moline, IL 61265 has been satisfactory for this purpose.

purification. Oxygen prepared by electrolysis of water should not be used without purification, as it may contain enough hydrogen to affect results by 1 % or more. Combustible impurities may be removed from oxygen by passing it over copper oxide (CuO) at about 500°C.

A2. CORRECTIONS

A2.1 THERMOMETER CORRECTIONS[15]

A2.1.1 The differential emergent stem correction for solid stem calorimetric thermometers (56F and 56C) may be computed from the following equation:

$$\text{Differential stem correction} = K(t_c - t_a)(t_a + t_c - L - T) \quad \text{(A2.1)}$$

where:

K = differential expansion coefficient of mercury in glass = 0.00016 for Celsius thermometers or 0.00009 for Fahrenheit thermometers.
L = scale reading to which the thermometer was immersed,
T = mean temperature of emergent stem,
t_a = initial temperature reading, and
t_c = final temperature reading.

A2.1.2 Differential emergent stem correction for a Beckmann thermometer immersed to the zero of the scale may be computed as follows:

$$\text{Differential stem correction} = K(t_c - t_a)(S + t_c + t_a - T) \quad \text{(A2.2)}$$

where:

S = "setting" (temperature at zero reading) of the thermometer.
K, T, t_c and t_a as defined in A2.1.1.

A2.1.3 "Setting" correction for a Beckmann thermometer may be computed as follows:

$$\text{"Setting" correction} = \text{factor} \times (t_c - t_a)$$

where:

Factor is obtained from Table A2.1 and
t_c and t_a as defined in A2.1.1.

TABLE A2.1 Correction Factors

Setting	Factor
15	−0.0015
20	0.0000
25	+0.0015
30	+0.0029
35	+0.0043
40	+0.0056

A2.2 THERMOCHEMICAL CORRECTIONS

A2.2.1 *Heat of Formation of Nitric Acid*—A correction of 5 J is applied for each cubic centimetre of standard (0.0866 N) or standard (0.0725 N) NaOH solution used in the acid titration. This is based on the assumption that (1) all of the acid titrated is HNO_3 and (2) the heat of formation of 0.1 N HNO_3 under the test conditions is 57.8 kJ/mole. When H_2SO_4 is also present, part of the correction for H_2SO_4 is contained in the e_1 correction, and the remainder in the e_2 correction.

A2.2.2 *Heat of Formation of Sulfuric Acid*—A correction of 5.86 kJ is applied to each gram of sulfur in the sample. This is based upon the heat of formation of 0.17 N H_2SO_4, which is −301.4 kJ/mole. But, a correction equal to 2 × 57.8 kJ/mole of sulfur was applied for H_2SO_4 in the e_1 correction. Thus, the additional correction necessary is 301.4 − (2 × 57.8) = 185.8 kJ/mole or 5.86 kJ/g of sulfur.

A2.2.2.1 The value of 5.86 kJ/g of sulfur is based on a fuel oil containing a relatively large amount of sulfur since as the percentage of sulfur decreases, the correction decreases and consequently a larger error can be tolerated. For this calculation 0.8 % S, 99.2 % CH_2 was taken as the empirical composition of fuel oil. If a 0.6-g sample of such a fuel oil is burned in a bomb containing 1 cm^3 of water, the H_2SO_4 formed will be approximately 0.17 N.

A2.2.2.2 Using data from National Bureau of Standards *Circular No. 500*, the heat of reaction SO_2 (g) + ½ O_2 (g) + 651 H_2O (l) − $H_2SO_4 \cdot 650\,H_2O$ (l) at constant volume and 3 MPa is −301.4 kg/mole.

A2.2.3 *Heat of Combustion of Fuse Wire*—The following heats of combustion are accepted:

Iron wire, No. 34 B & S gage	=	1.13 J/mm
Chromel C wire No. 34 B & S gage	=	0.96 J/mm

A2.2.4 *Heat of Combustion of Pressure-Sensitive Tape*—The correction for the heat of combustion of the tape (as determined in accordance with 8.3) assumes complete combustion of the tape.

[15] For a complete discussion of those corrections see the American Institute of Physics Symposium, *Temperature, Its Measurement and Control in Science and Industry*, Reinhold Publishing Corp., New York, NY 1941.

A3. PRECAUTIONARY STATEMENTS

A3.1 Sodium Hydroxide

Warning—Corrosive. Can cause severe burns or blindness. Evolution of heat produces a violent reaction or eruption upon too rapid mixture with water.

Before using, secure information on procedures and protective measures for safe handling.

Do not get in eyes, on skin, on clothing.

Avoid breathing dusts or mists.

Do not take internally.

When handling, use chemical safety goggles or face shield, protective gloves, boots and clothing.

When mixing with water, add slowly to surface of solution to avoid violent spattering. In the preparation of solutions do not use hot water, limit temperature rise, with agitation, to 10°C/min or limit solution temperature to a maximum of 90°C. No single addition should cause a concentration increase greater than 5 %.

A3.2 Oxygen

Warning—Oxygen vigorously accelerates combustion.

Do not exceed the sample size limits.

Do not use oil or grease on regulators, gages, or control equipment.

Use only with equipment conditioned for oxygen service by carefully cleaning to remove oil, grease, and other combustibles.

Keep combustibles away from oxygen and eliminate ignition sources.

Keep surfaces clean to prevent ignition or explosion, or both, on contact with oxygen.

Always use a pressure regulator. Release regulator tension before opening cylinder valve.

All equipment and containers used must be suitable and recommended for oxygen service.

Never attempt to transfer oxygen from cylinder in which it is received to any other cylinder.

Do not mix gases in cylinders.

Do not drop cylinder. Make sure cylinder is secured at all times.

Keep cylinder valve closed when not in use.

Stand away from outlet when opening cylinder valve.

Keep cylinder out of sun and away from heat.

Keep cylinder from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinders.

For technical use only. Do not use for inhalation purposes.

Use only in well-ventilated area.

See compressed gas association booklets G-4 and G-4.1 for details of safe practice in the use of oxygen.

A3.3 2,2,4-Trimethylpentane

Warning—Extremely flammable. Harmful if inhaled.

Vapors may cause flash fire.

Keep away from heat, sparks, and open flame.

Keep container closed.

Use with adequate ventilation.

Avoid buildup of vapors and eliminate all sources of ignition, especially nonexplosion-proof electrical apparatus and heaters.

Avoid prolonged breathing of vapor or spray mist.

Avoid prolonged or repeated skin contact.

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ASTM D 2650-88

Standard Test Method for
Chemical Composition of Gases by Mass Spectrometry

Designation: D 2650 – 88

An American National Standard

Standard Test Method for Chemical Composition of Gases By Mass Spectrometry[1]

This standard is issued under the fixed designation D 2650; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This test method covers the quantitative analysis of gases containing specific combinations of the following components: hydrogen; hydrocarbons with up to six carbon atoms per molecule; carbon monoxide; carbon dioxide; mercaptans with one or two carbon atoms per molecule; hydrogen sulfide, and air (nitrogen, oxygen, and argon). This test method cannot be used for the determination of constituents present in amounts less than 0.1 mole %. Dimethylbutanes are assumed absent unless specifically sought.

NOTE 1—Although experimental procedures described herein are uniform, calculation procedures vary with application. The following influences guide the selection of a particular calculation: qualitative mixture composition; minimum error due to components presumed absent, minimum cross interference between known components, maximum sensitivity to known components, low frequency and complexity of calibration; and type of computing machinery.

Because of these influences, a tabulation of calculation procedures recommended for stated applications is presented in Section 12 (Table 1).

NOTE 2—This test method was developed on Consolidated Electrodynamics Corporation Type 103 Mass Spectrometers. Users of other instruments may have to modify operating parameters and the calibration procedure.

1.2 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* For specific precautionary statements, see Note 6 and Annex A1.

2. Referenced Documents

2.1 *ASTM Standards:*

D 1137 Method for Analysis of Natural Gases and Related Types of Gaseous Mixtures by the Mass Spectrometer[2]

D 1145 Method of Sampling Natural Gas[3]

D 1247 Method of Sampling Manufactured Gas[3]

D 1265 Practice for Sampling Liquefied Petroleum (LP) Gases[4]

D 1302 Method for Analysis of Carbureted Water Gas by the Mass Spectrometer[5]

E 137 Practice for Evaluation of Mass Spectrometers for Quantitative Analysis from a Batch Inlet[6]

3. Terminology

3.1 *Definitions:*

3.1.1 *mass number or m/e value of an ion*—the quotient of the mass of that ion (given in atomic mass units) and its positive charge (number of electrons lost during ionization).

3.1.2 *parent peak of a compound*—the peak at which the *m/e* is equal to the sum of the atomic mass values for that compound. This peak is sometimes used as 100 % in computing the cracking pattern coefficients.

3.1.3 *base peak of a compound*—the peak used as 100 % in computing the cracking pattern coefficient.

3.1.4 *cracking pattern coefficient*—the ratio of a peak at any *m/e* relative to its parent peak (or in some cases its base peak).

3.1.5 *sensitivity*—the height of any peak in the spectrum of the pure compound divided by the pressure prevailing in the inlet system of the mass spectrometer immediately before opening the expansion bottle to leak.

3.1.6 *partial pressure*—the pressure of any component in the inlet system before opening the expansion bottle to leak.

3.1.7 *cracked gases*—hydrocarbon gases that contain unsaturates.

3.1.8 *straight-run gases*—hydrocarbon gases that do not contain unsaturates.

3.1.9 *GLC*—a gas-liquid chromatographic column that is capable of separating the isomers of butenes, pentenes, hexanes, and hexenes.

3.1.10 *IR*—infrared equipment capable of analyzing gases for the butene isomers.

4. Summary of Test Method

4.1 The molecular species which make up a gaseous mixture are dissociated and ionized by electron bombardment. The positive ions of the different masses thus formed are accelerated in an electrostatic field and separated in a magnetic field. The abundance of each mass present is recorded. The mixture spectrum obtained is resolved into individual constituents by means of simultaneous equations derived from the mass spectra of the pure compounds.

5. Significance and Use

5.1 A knowledge of the composition of refinery gases is useful in diagnosing the source of plant upsets, in determining the suitability of certain gas streams for use as fuel, or as feedstocks for polymerization and alkylation, and for

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[1] This test method is under the jurisdiction of ASTM Committee D-2 on Petroleum Products and Lubricants and is the direct responsibility of Subcommittee D02.04 on Hydrocarbon Analyses.

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[2] Discontinued: see *1980 Annual Book of ASTM Standards*, Part 26.

[3] Discontinued: see *1986 Annual Book of ASTM Standards*, Vol 05.05.

[4] *Annual Book of ASTM Standards*, Vol 05.01.

[5] Discontinued, see *1968 Annual Book of ASTM Standards*, Part 19.

[6] *Annual Book of ASTM Standards*, Vol 14.01.

monitoring the quality of commercial gases.

6. Interferences

6.1 In setting up an analysis, it is possible that a constituent was ignored. Also, an impure calibration may have been used. The spectrum calculated from the composition found is to, therefore, be compared with the observed spectrum of the mixture at masses independent of the original calculation. Differences so computed, called residuals, should as a general rule be less than 1 % of the original mixture peak for an acceptable analysis. Masses suitable for this calculation are tabulated with each calculation procedure.

NOTE 3—Another strategy employed to reduce interferences and increase accuracy consists of using spectra which have been corrected for contributions caused by the rare isotopes of carbon and hydrogen.

7. Apparatus

7.1 *Mass Spectrometer*—Any mass spectrometer can be used with this test method that shall be proven by performance tests described herein and in Practice E 137.

8. Reference Standards

8.1 The mass spectrometer must be calibrated with each of the components constituting the unknown mixture to be analyzed. The calibrating compounds must be of the highest possible purity.[7] Calibrants may be prepared in the laboratory doing the analysis or purchased ready for use. In general, the mass spectrometer is capable of detecting impurities in calibrants and the contribution of such impurities to the calibration spectrum can be removed.

NOTE 4—Some of the calculation procedures require the use of combined spectra, for example, air and butylenes. Three frequently used possibilities for producing combined spectra are as follows:

(*1*) Representative fraction from a specific source,

(*2*) Multiplication factors to convert the spectrum of a pure constituent to a simulated spectrum of the mixture, and

(*3*) Proportionality factors for combining actual calibrations.

A recommended concentration limit for combined mixtures is given. At the level recommended, the residual spectrum contribute less than 0.1 % error in any one result when the concentration of any constituent in the combined mixture is doubled.

9. Sampling

9.1 Samples shall be collected by methods known to provide a representative mixture of the material to be analyzed. Samples can be collected in accordance with Method D 1145 or Methods D 1247 or D 1265.

10. Calibration and Standardization

10.1 *Apparatus*—Determine whether operating conditions remain normal by making certain tests periodically, following instructions furnished by the manufacturer of the apparatus. Include in these tests rate of leak, ion-beam control settings, pattern reproducibility, and galvanometer calibrations.

10.1.1 To ascertain pattern stability, the following schedule is provided both for laboratories that have mass spectrometers with conventional temperature control and for laboratories that vary the temperature of the ionization chamber to obtain constant patterns:

Run Number	Compound
1	*n*-butane
2	*n*-butane
3	hydrogen
4	*n*-butane
5	hydrogen

10.1.2 If the 43/58 and 43/29 ratios of the first two runs do not agree with 0.8 %, further runs must be made until agreement is attained, either by adjusting the temperature of the ionization chamber or by other techniques commonly used by the laboratory. In any case, the three 43/58 and 43/29 ratios must agree within 0.8 % and the three butane sensitivities within 1 %. The two hydrogen sensitivities must agree within 1.5 %. A standard gas sample can also be used as an additional check.

10.2 *Reference Standards*—Check the entire range with the spectrometer evacuated. This check provides a blank or background spectrum. If the approximate composition of the mixture is not known, make a preliminary run over the entire operating mass range. If the composition is known, the necessary calibrating gases should have been run recently enough before the mixture to preclude pattern changes. The calibrating gases should be run in order of decreasing molecular weight. If isomers are present, do not run them in succession. Introduce the calibrating gases through the inlet system at a pressure closely approximating that used for the mixture spectrum. It is important that the recordings of the mass spectra of the calibrants and the gas mixture begin at the same ion accelerating voltage, the same magnetic field, and at the same interval after opening the sample volume to the leak manifold.

10.2.1 Run the hydrocarbon calibration gases as follows: introduce sufficient sample into the evacuated inlet system to give 30 to 60 mtorr (4 to 6.7 Pa) pressure in the expansion reservoir of the instrument (Note 6). Adjust the magnetic field and the ion-accelerating voltage for the range m/e 2 to 4 on the collector. Open the valve between the expansion reservoir and the leak manifold. One minute later, start the recorder and sweep. After sweeping over the above range, stop the sweep and recorder and quickly adjust the magnetic field and ion-accelerating voltage for the range m/e 12 to 100. Two minutes after admission of sample to the leak, start the recorder and sweep. After sweeping $m/e = 100$, pump out the reservoir and leak manifold. At least 5 min of pumping time should be allowed between each run.

NOTE 6—Warning: Samples and reference mixtures are extremely flammable. Keep away from heat, sparks, and open flames. Use with adequate ventilation, see Annex A1.1 through A1.5. Cylinders shall be supported at all times. Hydrocarbon vapors that may be vented shall be controlled to assure compliance with applicable safety and environmental regulations.

10.3 *Calibration Data*—After the peaks of the calibration spectrogram have been measured, recorded, and corrected for background, transform them into a state appropriate for further computation. Obtain the sensitivities if desired by dividing the number of divisions of the base peak by the recorded sample pressure in the expansion reservoir of the

[7] Research grade hydrocarbons from either Phillips Petroleum Co., Bartlesville, OK, or American Petroleum Institute Standards Reference Office, Carnegie Mellon University, Pittsburgh, PA, have been found satisfactory.

mass spectrometer. Repeat the procedure for each calibrant.

11. Procedure

11.1 Introduce the sample without fractionation (see Section 9). Obtain the mass spectrum of the mixture under the same conditions as the calibration spectra (see Section 10). List the peak heights of the spectrum along with the appropriate m/e value.

12. Calculation

12.1 Schemes for calculating specific mass spectrometer gas analyses are shown in Table 1. Each results in a report of analysis on the samples as received in mole (gas-volume) percent unless otherwise noted. These schemes are possible procedures from which the user can make a choice on the basis of his particular problem.

The calculation basic to all mass spectrometric gas analysis is the solution of simultaneous equations. These are constructed in accordance with Eq 1:

$$m_i = \Sigma a_{ij} \times x_j \quad (1)$$

where:

m_i = mixture peak height at the ith m/e used,

a_{ij} = pattern coefficient for the jth component on the ith peak, and

x_j = corrected base peak height of component j.

These equations will be solved, where indicated by the Unicomponent Peak Method:

$$x_j = (m_j - \Sigma_{k=1}^{k=j-1} a_{jk} \times x_k)/a_{jj} \quad (2)$$

where $k = 1$ refers to the heaviest component.

Where simultaneous solution is indicated, a variety of direct arithmetic procedures may be used interchangeably.[8] Where increased precision or error control has been specified in this test method, more complex calculations must be used.[9]

In each of the above calculations, the xj's must be divided by the sensitivity for j to get partial pressure. Sensitivity coefficients may be used instead of the a_{ij} in which case this step is not applicable.

The sum of the partial pressures should agree within 1 % with the pressure measured in the expansion reservoir of the mass spectrometer unless water vapor is present in the sample. Divide each partial pressure by the total calculated pressure and multiply by 100 to obtain mole percentages.

13. Report

13.1 Results shall be reported in mole (gas-volume) percent correct to one decimal place. Comments shall appear on the form in the event the sample is not reported on an "as received" basis. In any event the serial number of the calculation procedure shall appear on a report of analysis.

14. Precision and Bias

14.1 The precision of this test method as determined by statistical examination of interlaboratory results is as follows:

14.1.1 *Repeatability*—The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would in the long run, in the normal and correct operation of the test method, exceed the values shown in Tables 2 and 3 only in one case in twenty.

14.1.2 *Reproducibility*—The difference between two single and independent results obtained by different operators working in different laboratories on identical test material would, in the long run, in the normal and correct operation of the test method, exceed the values as shown in Tables 2 and 3 only in one case in twenty.

NOTE 7—The precision for this test method was not obtained in accordance with RR:D02-1007.

14.2 *Bias*—A bias statement cannot be determined because there is no acceptable reference material suitable for determining the bias for the procedure in this test method.

[8] Crout, P. D., "A Short Method for Evaluating Determinants and Solving Systems of Linear Equations with Real or Complex Coefficients," Marchant Calculating Machine Co., *Bulletins MM-182* and *183*, ASTBA, September 1941. Dwyer, P. S., *Psychometrika*, Vol 6, 1941, p. 101. Hotelling, H., *Am. Math. Stat.*, Vol 14, 1943, p. 1.

[9] "Triangular Inverse Method," *Analytical Chemistry*, ANCHA, Vol 30, 1959, p. 877.

TABLE 1 Calculation Procedures for Mass Spectrometer Gas Analysis

NOTE—Coding of calculation procedures is as follows:
O = Order peaks are used in the calculation expressed serially from 1 to *n*, *n* being the total number of components.
P = *m/e* of peak used and prefix, *M*, if monoisotopic.
M = Method of computation
U = Unicomponent Peak Method
M_a = Simultaneous equations where "a" identifies the particular set of equations if more than one is used.
C = Chemically removed.
Residual = *m/e* of peak suitable as an independent check on the method.

Serial No.	1			2			3			4			5			6		
Name or Application	D 1137[A] Natural Gas			D 1302[B] Carbureted Water Gas			H_2-C_6			Reformer Gas			C_3,C_4			*i*C_4		
Component	O	P	M	O	P	M	O[C]	P[C]	M	O	P	M	O[C]	P[C]	M	O	P	M
Hydrogen	...	...	...	6	2	M	16	2	U	17	2	M	0	...	...	...	...	...
Methane	15	16	U	7	15/16	M	15	16	U	16	16	M	0	...	...	...	...	...
Ethylene	13	27	M2	12	27	M	13	26	U	15	26	M	0	...	...	...	...	...
Ethane	12	30	M2	8	30	M	12	30	U	13	30	M	0	...	...	...	...	...
Propene	10	42	M2	11	42	M	8	42	M2	12	42	M	6	42	M	...	...	M
Propane	9	29	M2	9	29	M	3	44	M1	14	29	M	9	29	M	3	29	M
Butadiene	...	...	...	9	...	...	3	...	...	10	54	M	9	...	M	...	...	M
Butene-1	8	56	M2	5	56	U	9	41	M2	8	56	M	8	41	M	...	...	M
Butene-2	8	56	M2	5	56	U	10	55	M2	8	56	M	4	55	M	...	...	M
Isobutene	8	56	M2	5	56	U	11	56	M2	8	56	M	5	39	M	...	...	M
Isobutane	7	43	M2	5	...	...	4	M43	M1	11	43	M	7	43	M	2	43	M
n-Butane	6	58	M2	4	58	U	5	58	M1	6	58	M	2	58	M	1	58	M
Pentenes	...	...	...	3	70	U	2	70	U	9	55	M	3	70	M	...	...	M
Isopentane	...	...	...	3	...	...	6	M57	M1	7	57	M	1	72	M	...	...	...
n-Pentane	4	72	M2	2	72	U	7	72	M2	5	72	M	...	...	...	...	...	...
Benzene	...	...	...	2	...	...	7	...	...	4	78	M	...	...	...	...	...	...
Hexanes	...	...	...	2	...	...	7	...	...	...	...	M	...	...	...	...	...	...
C_6 cyclic paraffins	...	...	...	2	...	...	7	...	...	3	84	M	...	...	...	...	...	...
Hexanes	5	57	M2	2	...	...	1	71	U	2	86	M	...	...	...	...	...	...
Toluene	...	...	...	2	...	...	1	...	...	1	92	M	...	...	...	...	...	...
Hydrogen sulfide	2	34	M1	2	...	...	1	...	...	21	34	M	...	...	...	...	...	...
Carbon dioxide	11	44	M2	10	44	M	1	...	C	20	44	M	...	...	...	...	...	...
Carbon monoxide	...	...	...	13	12	M	1	...	C	18	28	M	...	...	...	...	...	...
Nitrogen	14	28	M2	14	14	M	14	28	U	19	14	M	...	...	...	...	...	...
Air	3	32	M1	1	32	U	14	...	...	22	32	M	1	32	U	...	...	...
Helium	1	4	U	1	...	...	14	...	...	[D]	[D]	...	...	...	...	...	...	...

Serial No.	7			8			9			10			11			12			13		
Name or Application	Commercial Propane			Commercial Butane			BB Stream (Cracked Butanes)			Dry Gas Cracked Fuel Gas			Mixed Iso and Normal Butanes			Reformer Make-Up Gas			Unstabilized Fuel Gas		
Component	O	P	M	O	P	M	O[C]	P[C]	M	O	P	M	O	P	M	O	P	M	O[C]	P[C]	M
Hydrogen	...	...	...	...	...	...	...	...	...	15	2	M	...	...	...	10	2	M	16	2	M
Methane	...	...	...	...	...	...	...	...	...	14	16	M	...	...	...	9	16	M	15	16	M
Ethylene[F]	7	26	M	...	...	...	...	...	...	12	26	M	...	...	...	...	...	...	13	26	M
Ethane	6	30	M	...	...	...	...	...	...	11	30	M	...	...	...	7	30	M	12	30	M
Propene	5	42	M	7	42	M	6	42	M	10	42	M	...	...	...	...	...	...	8	42	M
Propane	3	44	M	4	44	M	4	44	M	7	44	M	3	44	M	5	44	M	6	44	M
Butadiene	...	...	...	...	...	...	1	54	M	3	54	M	...	...	...	...	...	...	2	54	M
Butene-1	1	56	M	1	56	M	7	41	M	1	...	...	...	...	...	...	...	...	9	41	M
Butene-2	1	56	M	1	56	M	8	56	M	1	56	M	...	...	...	...	...	...	10	56	M
Isobutene	1[E]	[E]	M	1	[E]	[E]	9	39	M	1	[E]	...	4	43	M	...	...	...	11	39	M
Isobutane	4	43	M	5	43	M	5	43	M	8	43	M	1	58	M	6	43	M	7	43	M
n-Butane	2	58	M	2	58	M	2	58	M	4	58	M	...	...	...	2	58	M	3	58	M
Pentenes	...	...	...	6	70	M	[F]	70	U	9	70	M	...	...	...	3	57	M	...	70	U
Isopentane	...	...	...	3	57	M	3	57	M	5	57	M	2	57	M	4	72	M	4	57	M
n-Pentane	...	...	...	...	...	...	...	...	...	6	72	M	...	...	...	...	...	...	5	72	M
Benzene	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	[H]	[H]	D

TABLE 1 *Continued*

Serial No.	7			8			9			10			11			12			13		
Name or Application	Commercial Propane			Commercial Butane			BB Stream (Cracked Butanes)			Dry Gas Cracked Fuel Gas			Mixed Iso and Normal Butanes			Reformer Make-Up Gas			Unstabilized Fuel Gas		
Component	O	P	M	O	P	M	O[C]	P[C]	M	O	P	M	O	P	M	O	P	M	O[C]	P[C]	M
Hexenes	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	H	H	D
C_6 cyclic paraffins	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	H	H	D
Hexanes	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	H	H	D
Toluene	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	H	H	D
Hydrogen sulfide	...	...	...	...	...	...	...	...	...	G	...	C	...	...	...	G	G	C	G	G	C
Carbon dioxide	...	...	...	...	...	...	...	...	...	G	...	C	...	...	...	G	G	C	G	G	C
Carbon monoxide	...	...	...	...	...	...	...	...	...	13	28	M	...	...	...	8	28	M	14	28	M
Nitrogen	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...	...
Air	...	...	...	...	...	...	...	...	...	2	32	M	...	...	...	1	32	M	1	32	M
Acid Gases	...	...	...	...	...	...	...	...	...	G	...	C	...	...	...	G	G	C	G	G	C
Residual[I]	8	27	M	8	27	M	10	27	M	16	14	M	5	27	M	11	14	M	17	14	M
Residual[I]	9	29	M	9	29	M	11	29	M	17	15	M	6	29	M	12	15	M	18	15	M
Residual[I]	...	...	...	...	...	...	...	...	...	18	27	M	...	...	...	13	27	M	19	27	M
Residual[I]	...	...	...	...	...	...	...	...	...	19	29	M	...	...	...	14	29	M	20	29	M

Serial No.	14			15			16		
Name or Application	H_2-C_6 Cracked Gas			H_2-C_6 Straight Run Gas			Light Refinery Gas		
Component	O	P	M	O	P	M	O	P	M
Hydrogen	1	2	M	1	2	M	20	2	U
Methane	2	16	M	2	16	M	17	16	M
Ethylene	4	26	M	...	...	...	14	26	M
Ethane	7	30	M	5	30	M	13	30	M
Propene	11	42	M	...	...	...	12	42	M
Propane	6	29	M	4	29	M	10	29	M
Butadiene	15	54	M	...	...	...	...	...	...
Butene-1	...	...	...	...	...	...	11	56	M
Butene-2	16	56	M	...	...	...	...	...	...
Isobutene	...	...	...	...	...	...	...	...	...
Isobutane	12	43	M	9	43	M	9	43	M
n-Butane	18	58	M	14	58	M	8	58	M
Pentenes	21	70	M	...	...	...	15	70	M
Isopentane	17	57	M	13	57	M	7	57	M
n-Pentane	22	72	M	18	72	M	6	72	M
Benzene	...	...	...	19	78	M	5	78	U
Hexenes	23	84	M	...	...	...	4	84	U
C_6 cyclic paraffins	...	...	...	20	84	M	...	...	...
Hexanes	...	...	...	17	71	M	3	86	U
Toluene	...	...	...	21	92	M	...	...	...
Hydrogen sulfide	9	34	M	7	34	M	1	34	U
Carbon dioxide	13	44	M	10	44	M	16	44	U
Carbon monoxide	...	...	...	...	...	...	18	12	U
Nitrogen	5	28	M	...	...	...	19	28	U
Air	8	32	M	6	32	M	2	32	U
Water	3	18	M	3	18	M	...	...	...
Cyclobutane	...	...	...	12	56	M	...	...	...
Cyclopentene	20	67	M	...	...	...	...	...	...
Pentadienes	20	67	M	...	...	...	...	...	...
Cyclopentane	...	...	...	16	70	M	...	...	...
Methylmercaptan	14	48	M	11	48	M	...	...	...
Ethylmercaptan	19	62	M	15	62	M	...	...	...
Residual 41	10	41	M	8	41	M	...	...	...
Residual 14	24	14	M	22	14	M	...	...	...

[A] Method D 1137.

[B] Method D 1302.

[C] The mass spectrometer analysis for isomeric butenes is far less accurate than for the other hydrocarbon components. The inaccuracies involved in the isomeric butene analysis by mass spectrometer range from 1.0 to 4.0 mole % depending upon the concentration, ranges, and extent of drifts in instrument calibrations. These inaccuracies will range still higher when pentenes are present in larger than 0.5 % concentrations. See *Analytical Chemistry*, Vol 22, 1950, p. 991, *Ibid*, Vol 21, 1949, p. 547, and *Ibid*, Vol 21, 1949, p. 572.

[D] In Method 4, butylenes and pentenes spectra are composites based on typical GLC analyses. Hexene and hexane spectra are from appropriately corrected spectra of representative fractions.

[E] Butenes are grouped if they are less than 5 %.

[F] If pentenes exceed 1 %, they are determined by other means and the spectrum removed from the poly spectrum.

[G] Chemically removed.

[H] Removed from sample by distillation.

[I] Residuals Groups A: *m/e* 72, 58, 57, 44, 43. Group B *m/e* 56, 42, 30, 29, 14. All Group A residual shall be 0.2 division or less with the residual of the largest peak also being less than 0.3 % of its total peak height. All Group B residuals shall be less than 1 % of the peak height or 0.2 division, whichever is greater.

TABLE 2 Summary of Results of Sample Calculated by Scheme 16

Component	Mole percent, Average	σ_r[A]	σ_R[B]
Hydrogen	20.6	0.2	2.2
Methane	34.1	0.4	1.4
Ethylene	5.4	0.1	0.2
Ethane	12.4	0.1	0.9
Propylene	7.9	0.1	0.6
Propane	5.8	0.3	0.3
Butylenes	2.6	0.1	0.2
Isobutane	2.5	0.1	0.4
Normal butane	1.2	0.1	0.2
Pentenes	0.4	0.1	0.1
Isopentane	0.5	0.1	0.2
Normal pentane	0.1	0.0	0.2
Nitrogen/carbon monoxide	0.5	0.1	0.5
Carbon dioxide	0.2	0.0	0.2
Hydrogen sulfide	5.8	0.1	0.9
Number of laboratories	14	6	14
Number of analyses	23	15	23

[A] σ_r repeatability standard deviation.
[B] σ_R reproducibility standard deviation.

TABLE 3 Precision of Procedures for Mass Spectrometer Analysis

Serial No.	1		14	
Name	D 1137 Natural Gas[A]		H_2-C_6 Cracked Gas	
Component	Repeatability	Reproducibility	Composition	Repeatability
Hydrogen	...	...	12.581	0.14
Methane	0.2	0.5	16.333	0.20
Ethylene	...	...	2.116	0.03
Ethane	0.1	0.3	7.357	0.10
Propene	0.02	0.04	7.883	0.16
Propane	0.02	0.05	6.601	0.12
Butene-1	...	...	...	...
Butene-2	...	...	5.333	0.19
Isobutene	...	...	...	...
Isobutane	...	...	5.528	0.18
n-Butane	...	...	1.484	0.09
Pentenes	...	...	1.015	0.10
Isopentane	...	...	1.270	0.11
n-Pentane	...	...	0.116	0.05
Hexanes	...	...	0.123	0.02
Carbon dioxide	0.02	0.03	...	...
Nitrogen	0.2	0.3	32.146	0.53
Cyclopentene	...	...	0.038	0.01
Degrees of Freedom	50 Laboratories	...	...	

[A] Method D 1137.

ANNEX

(Mandatory Information)

A1. PRECAUTIONARY STATEMENTS

A1.1 Hydrogen

Keep away from heat, sparks, and open flame and non-explosion proof electrical devices.

Use with adequate ventilation.

Never drop cylinder. Make sure cylinder is supported at all times.

Keep cylinder out of sun and away from heat.

Always use a pressure regulator.

Release regulator tension before opening cylinder.

Do not transfer cylinder contents to another cylinder. Do not mix gases in cylinder.

Keep cylinder valve closed when not in use.

Do not inhale.

Do not enter storage areas unless adequately ventilated.

Stand away from cylinder outlet when opening cylinder valve.

Keep cylinder from corrosive environment.

A1.2 Flammable Gas

Keep away from heat, sparks, and open flame, and non-explosion proof electrical devices.

Use with adequate ventilation.

Never drop cylinder. Make sure cylinder is supported at all times.

Keep cylinder out of sun and away from heat.

Always use a pressure regulator. Release regulator tension before opening cylinder.

Do not transfer cylinder contents to another cylinder. Do not mix gases in cylinder.

Keep cylinder valve closed when not in use.

Do not inhale.

Do not enter storage areas unless adequately ventilated.

Stand away from cylinder outlet when opening cylinder valve.

Keep cylinder from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinder.

For technical use only. Do not inhale.

A1.3 Flammable Liquefied Gas

Keep away from heat, sparks, and open flame and non-explosion proof electrical devices.

Use with adequate ventilation.

Never drop cylinder. Make sure cylinder is supported at all times.

Keep cylinder out of sun and away from heat.

Always use a pressure regulator. Release regulator tension before opening cylinder.

Do not transfer cylinder contents to another cylinder. Do not mix gases in cylinder.

Keep cylinder valve closed when not in use.

Do not inhale.

Do not enter storage areas unless adequately ventilated.

Stand away from cylinder when opening cylinder valve.

Keep cylinder from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinder.

For technical use only. Do not inhale.

A1.4 Flammable Liquid (general)

Keep away from heat, sparks and open flame.

Keep container closed.

Use only with adequate ventilation.

Avoid prolonged breathing of vapor or spray mist.

Avoid prolonged or repeated contact with skin.

A1.5 Pressurized Gas (general)

Keep container closed.

Use with adequate ventilation.

Do not enter storage area unless adequately ventilated.

Always use a pressure regulator. Release regulator tension before opening cylinder.

Do not transfer cylinder contents to another cylinder. Do not mix gases in cylinder.

Do not drop cylinder. Make sure cylinder is supported at all times.

Stay away from cylinder outlet when opening cylinder valve.

Keep cylinder out of sun and away from heat.

Keep cylinder from corrosive environment.

Do not use cylinder without label.

Do not use dented or damaged cylinder.

For technical use only. Do not use for inhalation purposes.

APPENDIX

(Nonmandatory Information)

X1. REFERENCE STANDARDS FOR PROCEDURES 14 AND 15

X1.1 *Butenes*—Butene-1, butene-2, and isobutene may be averaged ⅓, ⅓, ⅓. However, when a straight average is applied, limit the butenes total to 10 to 15 mole % to hold maximum error of lighter components to ±0.5 mole % and limited to 5 mole % to keep maximum error of lighter components to ±0.1 mole %. For a more accurate determination of lighter components, for example, ethylene, nitrogen, propylene, and propane—gases from representative refinery streams, are to be run by a GLC or IR method to obtain ratios of the butenes present. Weighted sensitivity coefficients allow accurate analyses for lighter components plus accurate total butene content through a 0 to 100 % butene range. The continued accuracy obtained depends upon the stability of the refinery operation units, therefore, checks from time to time by an independent method (GLC or IR) enable mass spectrometric data processing groups to know the margins of error or to obtain new weighted sensitivity coefficients to maintain low deviations.

X1.2 *Pentenes*—Utilize weighted sensitivity coefficients at all times when pentenes content is likely to be above 1 mole %, due primarily to error caused in propane and propylene analysis.

X1.2.1 Gases from representative refinery streams can be run by a GLC method to obtain pentene ratios which then can be used to calculate weighted sensitivity coefficients. Alternatively, a C_5 cut could be obtained from a low-temperature fractional distillation of a sample of the type to be analyzed. The mass spectrum of this cut is recorded and the contributions of the normal and isopentane and normal butane present removed from the spectrum. The residual spectrum is typical of the pentenes present in samples of this type.

X1.2.2 Obtain checks from time to time on the pentene ratios to maintain low deviation.

X1.3 *Hexenes*—Obtain weighted sensitivity coefficients as explained in X1.2 for pentenes. However, a C_6 fraction from low-temperature distillation will be difficult to correct for pentenes present and if this approach is utilized it is suggested that a total C_6's residual spectrum be calculated rather than attempting to correct out the C_6 saturates. If a C_6 fraction is used, regard samples with more than 1 mole % of C_6's as inaccurate due to errors possible in incorrectly removing C_6 contributions to lighter components.

X1.3.1 If weighted sensitivities are employed, regard samples with over 2 mole % of C_6 as inaccurate due to probable variations in refinery units operation, since most operation units try to keep C_6's to a minimum in gas streams.

X1.4 *Hexanes*—Obtain weighted sensitivity coefficients as described in X1.3. The amount of hexanes present in a gas sample are not to exceed 1 mole %, otherwise regard the analysis as inaccurate as described in X1.3.

ASTM E 537-86

Standard Test Method for Assessing the Thermal Stability of Chemicals by Methods of Differential Thermal Analysis

Designation: E 537 – 86

Standard Test Method for Assessing The Thermal Stability Of Chemicals By Methods Of Differential Thermal Analysis[1]

This standard is issued under the fixed designation E 537; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

INTRODUCTION

Committee E-27 is currently engaged in developing methods to determine the hazard potential of chemicals. An estimate of this potential may usually be obtained by using program CHETAH (*ASTM DS 51*) to compute the maximum energy of reaction of the chemical or mixture of chemicals.[2]

The expression "hazard potential" as used by this committee is defined as the degree of susceptibility of material to ignition or release of energy under varying environmental conditions.

The primary purpose of this test method is to detect enthalpic changes and to approximate the temperature of initiation of these events. Thermal analysis techniques including differential thermal analysis (DTA) and differential scanning calorimetry (DSC) offer the advantage of using very small samples on the order of a few milligrams. Revision of this test method has been undertaken to extend the assessment of thermal stability of chemicals through use of atmospheres at elevated pressure.

1. Scope

1.1 This test method covers the ascertainment of the presence of enthalpic changes, using a minimum quantity of sample, normally in the milligram range, and approximates the temperature at which these enthalpic changes occur.

1.2 This test method utilizes techniques of differential thermal analysis (DTA) and differential scanning calorimetry (DSC); it may be performed on solids, liquids, or slurries.

1.3 This test method may be carried out in an inert or a reactive atmosphere with an absolute pressure range from 100 Pa through 7 MPa and over a temperature range from −150°C to above 1000°C.

1.4 *This standard may involve hazardous materials, operations, and equipment. This standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.* Specific safety precautions are given in Section 8.

2. Referenced Documents

2.1 *ASTM Standards:*

E 472 Practice for Reporting Thermoanalytical Data[3]

E 473 Definitions of Terms Relating to Thermal Analysis[3]

E 967 Practice for Temperature Calibration of Differential Scanning Calorimeters and Differential Thermal Analyzers[3]

3. Terminology

3.1 *Definitions:*

3.1.1 *differential thermal analysis (DTA)*—a technique in which the temperature difference between the substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program (ITCA, 1980) (see Definitions E 473).

3.1.2 *differential scanning calorimetry (DSC)*—a technique in which the difference in energy inputs into a substance and a reference material is measured as a function of temperature while the substance and reference material are subjected to a controlled temperature program (ITCA, 1980) (see Definitions E 473).

3.2 *Descriptions of Terms Specific to This Standard:*

3.2.1 *DTA (DSC) curve*—a record of a thermal analysis where the temperature difference (ΔT) or the energy change (Δq) is plotted on the ordinate and temperature or time is plotted on the abscissa (see Figs. 1 and 2 and Definitions E 473).

3.2.2 *peak*—that portion of a heating curve which is attributable to the occurrence of a single process. It is normally characterized by a deviation from the established baseline, a maximum deflection, and a reestablishment of a baseline not necessarily identical to that before the peak (see Fig. 1).

NOTE 1—There will be instances when upon scanning in temperature an endotherm will be observed that is immediately followed by or is

[1] This test method is under the jurisdiction of ASTM Committee E-27 on Hazard Potential of Chemicals and is the direct responsibility of Subcommittee E27.02 on Thermal Stability.

Current edition approved July 25, 1986. Published September 1986. Originally published as E 537 – 76. Last previous edition E 537 – 84.

[2] A complete assessment of the hazard potential of chemicals must take into account a number of realistic factors not considered in this test method or the CHETAH program.

[3] *Annual Book of ASTM Standards*, Vol 14.02.

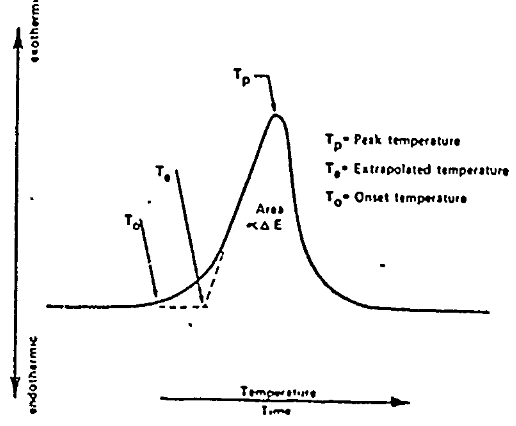

FIG. 1 Typical DTA—DSC Curve with Exotherm

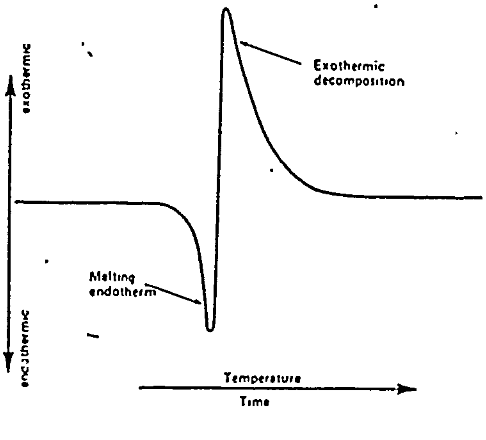

FIG. 2 Thermogram Illustrating a Melting Process Immediately Followed by an Exothermic Decomposition

in conjunction with an exotherm as shown in Fig. 2. This type of competing reactions makes it difficult and at times impossible to locate the true peak and onset temperatures.

3.2.3 *peak temperature*—the temperature corresponding to the maximum deflection of the DTA or DSC curve.

3.2.4 *onset temperature*—the temperature at which a deflection from the established baseline is first observed.

3.2.5 *extrapolated onset temperature*—empirically, the temperature found by extrapolating the baseline (prior to the peak) and the leading side of the peak to their intersection (see Fig. 1).

3.2.6 *reaction*—any transformation of material accompanied by a change of enthalpy which may be endothermic or exothermic.

3.2.7 *thermal stability*—the absence of a reaction (for the purposes of this test method only, see 3.2.6).

4. Summary of Method

4.1 In DTA, thermocouples for both the sample and reference material are connected in series-opposition so as to measure a temperature difference (ΔT). An additional thermocouple is provided to measure the absolute temperature (T) of the sample or reference.

4.2 In DSC, a measurement is made of the energy change (Δq) associated with the observed change of enthalpy. Provisions are made to measure the absolute temperature (T) of the sample or reference or the average temperature of both.

4.3 A sample of the material to be examined and of a thermally inert reference material are placed in separate holders.

4.4 The sample and reference materials are simultaneously heated at a controlled rate of up to 30°C/min under an equilibrated atmosphere. A record of ΔT or Δq is made as a function of temperature (T). Alternatively, the temperature of the sample and reference may be increased to a fixed and predetermined value and a record of ΔT or Δq made as a function of time (t).

4.5 When the sample undergoes a transition involving a change of enthalpy, that change is indicated by a departure from the initially established baseline of the temperature record.

5. Significance and Use

5.1 This test method is useful in detecting potentially hazardous reactions including those from volatile chemicals and in estimating the temperatures at which these reactions occur. This test method is recommended as an early test for detecting the reactive hazards of an uncharacterized chemical substance or mixture (note Section 8).

5.2 The magnitude of change of enthalpy may not necessarily denote the relative hazard. For example, certain exothermic reactions are often accompanied by gas evolution which increases the potential hazard. Alternatively, the extent of energy release for certain exothermic reactions may differ widely with the extent of confinement of volatile products. Thus, the presence of an exotherm or of an endotherm and its approximate temperature are the most significant criteria in this test method (see Section 3 and Fig. 1).

5.3 When volatile substances are being studied, it is important to perform this test with a confining pressurized atmosphere so thattwchanges of enthalpy which can occur above normal boiling or sublimation points may be detected. As an example, an absolute pressure of 1.14 MPa (150 psig) will generally elevate the boiling point of a volatile organic substance 100°C. Under these conditions exothermic decomposition is often observed.

5.4 For some substances the rate of enthalpy change during an exothermic reaction may be small at normal atmospheric pressure, making an assessment of the temperature of instability difficult. Generally a repeated analysis at an elevated pressure will improve the assessment by increasing the rate of change of enthalpy.

5.5 Although certain types of thermal analysis instrumentation offer the additional advantage of measuring the magnitude of the change in enthalpy, such measurements are beyond the scope of this test method. The three significant criteria of this test method are, the detection of a change of enthalpy; the approximate temperature at which the event occurs, and the observance of effects due to the cell atmosphere and pressure.

6. Limitations

6.1 A host of environmental factors affect the existence, magnitude, and temperature of an exothermic reaction. Some, including heating rate, instrument sensitivity, degree of confinement, and atmosphere reactivity will affect the detectability of an exothermic reaction using this procedure. Therefore, it is imperative that the qualitative results obtained from the application of this test method be viewed only as an indication of the thermal stability of a chemical.

7. Apparatus

7.1 The equipment used in this test method shall be capable of displaying changes of enthalpy as a function of either time (t) or temperature (T), and shall have the capability of subjecting the sample cell to different atmospheres of equilibrated pressures.

7.2 The differential thermal analytical instrument (DTA or DSC) may be purchased or custom built to various degrees of refinement and sophistication. The basic components of an apparatus satisfactory for this test method include:

7.2.1 Sample containers,

7.2.2 Measuring cell capable of containing a pressure of 7 MPa,

7.2.3 Heating unit,

7.2.4 Programmable temperature controller,

7.2.5 Continuous temperature measuring and recording equipment, and

7.2.6 Stable, adjustable pressure supply.

7.3 Analysis may be initiated at a temperature below ambient by providing a means of cooling the sample and reference, their respective containers, and the heating unit to the same initial temperature.

8. Safety Precautions

8.1 The use of this test method as an initial test for material whose potential hazards are unknown requires that precautions be taken during the sample preparation and testing.

8.2 Where particle size reduction by grinding is necessary, the user of the test method should presume that the material is dangerous.

8.3 The use of this test method may require operation at elevated temperatures and pressures. All precautions associated with such temperatures and pressures should be observed.

9. Calibration

9.1 For purposes of this test method, calibrate the the absolute temperature scale within ±2°C in accordance with Practice E 967.

10. Sample and Reference Materials

10.1 The selection of an adequate sample size will depend upon the availability of the material, the degree of dilution required, the sensitivity of the instrument, the magnitude of the change of enthalpy, and the heating rate. Additionally, sample size must be compatible with the potential for a sudden large energy release. This test method should, therefore, be carried out on as small a quantity of material as possible, typically 1 to 50 mg.

10.2 Samples should be representative of the material being studied including particle size and purity.

10.3 The reference material must not undergo any thermal transformation over the temperature range under study. Typical reference materials include calcined aluminum oxide, glass beads, silicone oil, or an empty container.

10.4 Samples shall be prepared to achieve good thermal contact between them and their containers. For liquid samples it is recommended that approximately 20 % by weight of an inert material like aluminum oxide be added to the sample.

11. Recommended Conditions of Tests

11.1 *Sample Size*—A 5-mg sample is generally considered adequate. Decrease the sample size if the response is too energetic.

11.2 *Heating Rate*—A rate of 10 to 30°C/min is considered normal. If an endothermic response is immediately followed by an exotherm (Note 1, Fig. 2), then lower heating rates of 2 to 10°C/min are recommended.

11.3 *Temperature Range*—The temperature shall range from room temperature to 500°C.

11.4 *Pressure Range*—An equilibrated absolute pressure of 1.14 MPa (150 psig) is adequate for most elevated pressure tests.

11.5 *Y-Axis Sensitivity*—The equivalence of 1 mW/cm is usually sufficient to record the entire exotherm. Decreases in y-axis sensitivity may be necessary if the reaction is too energetic.

12. Procedure

12.1 Prepare a sample of the material to be examined and of the reference material in respective containers and place into the measuring cell. Be certain intimate thermal contact with the sensors is achieved. (See 10.1 for appropriate sample size.)

NOTE 2—For volatile materials it is often of interest to examine thermal stability at temperatures beyond the normal boiling or sublimation point. Additionally, samples suspect of being potentially energetic may exhibit nondescript exothermic activity at ambient pressure. In either situation a repeat analysis in an atmosphere of elevated pressure using either sealed sample containers or a pressurized measuring cell is recommended.

12.2 For equipment that includes a pressurizable measuring cell, seal and adjust the measuring cell atmosphere to the desired equilibrium pressure. An absolute pressure of 1.14 MPa is recommended for an elevated pressure thermal analysis of organic substances using this test method.

NOTE 3—When sealed containers are used, they should be provided with a vent (pinhole) to ensure that the internal pressure is in equilibrium with the applied pressure.

12.3 For equipment that cannot maintain an elevated pressure within its measuring cell, place the sample and reference materials in hermetically sealed containers with an appropriate atmosphere.

NOTE 4—Hermetically sealed containers will self pressurize due to increased partial pressures with increasing temperature. For most samples, however, this internal pressure will not be known but is typically less than 300 kPa. This approach is, therefore, a less satisfactory alternative for elevated pressure thermal analysis than a pressurized cell.

12.4 Heat the measuring cell at a controlled rate of up co 30°C/min and record the DTA or DSC curve. Continue heating until the highest temperature of interest is recorded or until the sample is destroyed or is lost by volatilization. For most organic compounds the normal temperature range is from 20 to 500°C.

NOTE 5—Any increase in heating rate may accentuate the recorder response for the ordinate but will also increase the measured onset temperature of an exothermic reaction.

12.5 Restore the measuring cell to ambient temperature and pressure upon completion of the analysis.

12.6 It may be informative to repeat the analysis at a slower heating rate (2°C/min to 10°C/min) when a complex change of enthalpy is encountered (see Fig. 2 and Note 1).

13. Report

13.1 Reporting of thermal data generated with this test method should comply with that outlined in Practice E 472 including a complete description of:

13.1.1 Sample and reference by name, composition, combination thereof, or formula, or

13.1.2 Apparatus and sample containers,

13.1.3 Composition and pressure of the sample atmosphere,

13.1.4 Heating rate and temperature range, and

13.1.5 *Y*-axis sensitivity.

13.2 Determine the onset, extrapolated onset, and peak temperatures of all reactions recorded from the DTA (DSC) curve.

13.3 When a thermal analysis is repeated using a different atmospheric composition or pressure or a different heating rate, note any significant changes in the DTA (DSC) curves resulting from the different experimental conditions. The magnitude of the recorded change of enthalpy, if measurable, may be significant but is beyond the scope of this test method.

14. Precision and Bias

14.1 The object of this test method is to ascertain the presence or absence of an exotherm and the approximate temperature of onset. Neither the magnitude of the exotherm nor the absolute value of the onset temperature are critical to the test method.