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Flash Point of 2,2’-Dichloroethyl Sulfide (HD)

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PREFACE

The work described in this report was authorized under Defense Threat Reduction Agency Joint Science and Technology Office (Fort Belvoir, VA) project number CB3662. The work was completed between September and October 2009. At the time this work was performed, the U.S. Army Combat Capabilities Development Command Chemical Biological Center (DEVCOM CBC; Aberdeen Proving Ground, MD) was known as the U.S. Army Edgewood Chemical Biological Center.

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FLASH POINT OF 2,2'-DICHLOROETHYL SULFIDE (HD)

1. INTRODUCTION

The physical properties of the chemical warfare agent (CWA) 2, 2'-dichloroethyl sulfide (HD, also known as mustard) are well documented in the literature[1–13]. These properties help to describe the physical chemical characteristics and behavior of the compound.

One of the properties used to assess the flammability hazard of a material is flash point. Flash point is the lowest temperature at which the vapor above a liquid specimen ignites when an ignition source is applied under specified test conditions.[14,15] It is an empirical property, so the measured value may vary based on a variety of factors such as test method, instrumentation, sample purity, and operational conditions. Therefore, it is important that these testing parameters are identified when a flash point value is reported.

The currently accepted flash point of high purity HD in the literature[2] is 105 °C. However, there is some concern about the reliability of this value because the source provides very little information about the sample purity, test method, and apparatus used to conduct the measurement. To address these uncertainties, the flash point of HD was determined by two different closed cup methods using samples of known purity. The primary purpose of this work was to generate well-documented flash point data for HD, which will help improve agent data verification and validation assessment efforts within the testing community.

2. BACKGROUND

Flash point values can be measured in a variety of different ways using a number of either open cup or closed cup methods. The primary difference between these methods is that with the closed cup procedure, the saturated vapor above the liquid to which the ignition source is applied is confined to a closed space, whereas with open cup methods, the vapor is not confined and is allowed to mix with and be diluted by ambient air. Although both methods provide useful information, the closed cup methods generally give lower values than the open cup[16] ones and are typically preferred because lower values reflect a more conservative assessment of the flammability hazard associated with the material from a safety perspective.

3. EXPERIMENTAL PROCESS

3.1 Materials

HD was synthesized in-house at the Chemical Transfer Facility (CTF; U.S. Army Combat Capabilities Development Command Chemical Biological Center; Aberdeen Proving Ground, MD), and sample purity of this HD lot (HD-U-9084-CTF-N) was determined by freezing point depression.[8] Table 1 provides purity information on the two sample vials from this lot used in this work.

Table 1. HD Flash Point Sample Information

Sample Identification (Lot no. HD-U-9084-CTF-N) (HD15004Dm)	**Purity*** **(mol %)**
Vial no. 6	97.3
Vial no. 5	97.6

*Purity determined by freezing point depression.

3.2 Flash Point Methods

The flash point measurements for this work were conducted using two different ASTM International closed cup methods. Because of the toxic nature of the material being used, all work was performed in a certified laboratory fume hood.

3.2.1 Continuously Closed Cup Tester

Flash point measurements were conducted in accordance with ASTM D 6450.[14] Flash point data were measured using the Grabner flash point high-temperature (FLPH) version FLPH Miniflash tester (Grabner Instruments; Vienna, Austria). Prior to sample measurements, proper instrument operation was validated by determining the flash point of *n*-dodecane (Chem Service Inc., West Chester, PA) (See Section 3.2.3 for instrument validation results). All measurements utilized 1 mL size samples and were based on a constant heating rate of 5.5 °C/min, ignition frequency of 1 °C, and air ventilation of 0.6 s.

In the ASTM D 6450 method, the occurrence of a flash is defined as the temperature at which the hot flame of the ignited vapor causes an instantaneous pressure increase (Δp) of at least 20 kPa inside the closed measuring chamber.[14] The Miniflash tester, however, defines a flash as the temperature at which the pressure exceeds a set threshold (default threshold =20 kPa).[17] This condition is inconsistent with the ASTM $\Delta p \geq 20$ kPa requirement. For example, if a sample has a baseline pressure higher than zero, the sample may exceed the 20 kPa threshold without producing a $\Delta p \geq 20$ kPa. To address this concern, the threshold pressure was set to 50 kPa so that data could be collected over a wider pressure range for determining a flash consistent with ASTM requirements.

Flash point measurements using the continuously closed cup method normally provide stable pressure readings up to the point of the flash, which is denoted by a sharp, well-defined pressure increase for flammable, high purity samples.[14] This is illustrated by the pressure profile for a 99.4 mol % pure sample of *n*-dodecane (Figure 1), which has a literature flash point value of 79 °C (continuously closed cup method).[18]

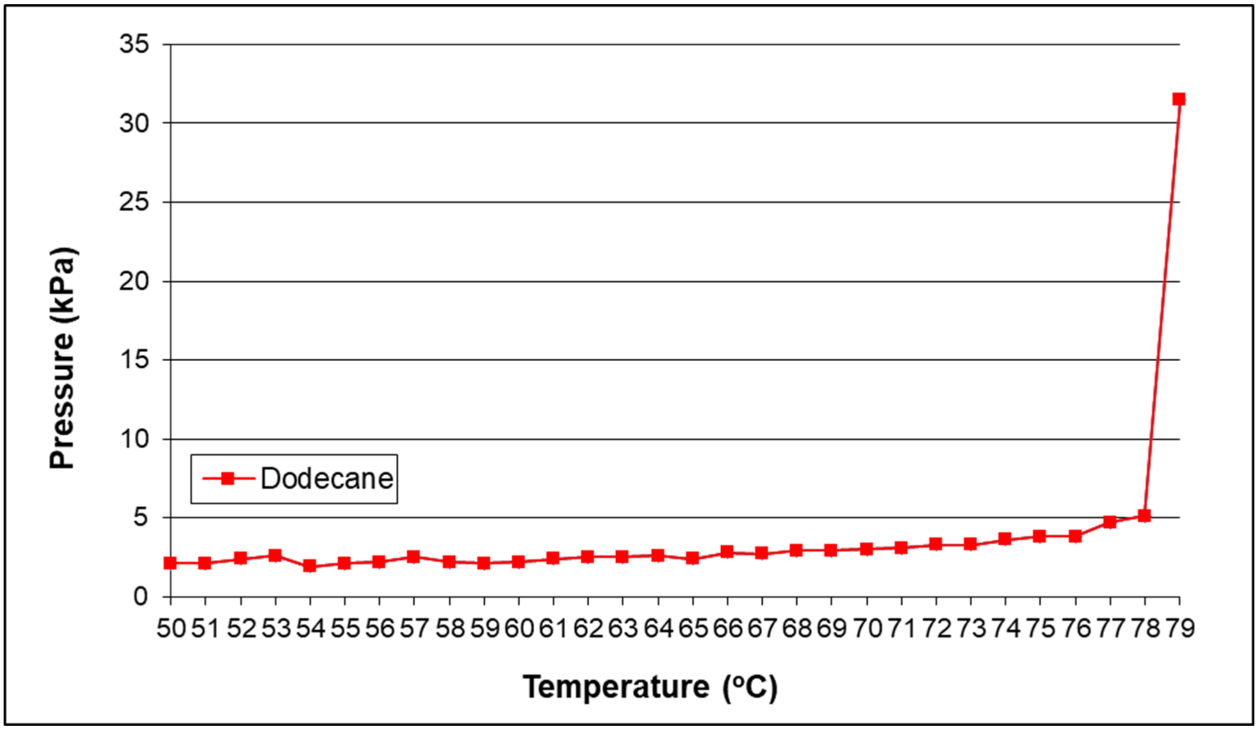

Figure 1. Flash point pressure profile of *n*-dodecane using Miniflash tester.

3.2.2 Small Scale Closed Cup Tester

Flash point measurements were conducted in accordance with a modified version of the ASTM D 3828 method[15] using the Koehler Rapid Flash tester (Koehler Instrument Inc., Bohemia, New York) Model K16502 (ambient to 300 °C). Prior to sample measurements, proper operation of the instrument was validated by determining the flash point of *n*-undecane (Sigma-Aldrich, St. Louis, Missouri).

To provide flash point measurements using the scale closed cup Rapid Flash tester method, the following deviations and modifications were made:

- Because of the hazards associated with this material, measurements were conducted in a fume hood, which required use of a draft shield to prevent extinguishment of the test flame.

- Specimens were loaded through the shutter opening of the tester instead of the filling orifice in order to prevent possible sample contamination.

- During a flash point measurement, the test flame is applied to the vapor space above the specimen. In accordance with the method, a new specimen should be used each time a measurement (i.e., application of the test flame to the vapor space above the specimen) is conducted. To minimize sample volume as the flash point of each sample was being narrowed down, multiple measurements were conducted on the same specimen. Only the results obtained from the first measurement on a given specimen were considered valid for the actual flash point determination.

Flashing, as determined by a small scale closed cup tester, is indicated by an instantaneous propagation of a large test flame over the surface of the specimen. Unlike the continuously closed cup method, which actually collects the temperature and pressure data being generated during measurement, the small scale closed cup method relies solely on the visual observation of the test specimen by the operator, which could introduce a degree of subjectivity. In order to minimize the degree of subjectivity, the method describes certain flashing behaviors that should not be reported as a flash.

One type of flashing behavior, which will be called a "borderline" flash, occasionally occurs near the actual flash point. It is indicated by a blue halo or an enlarged flame, which appears during the application of the test flame.[15] Although the behavior exhibited by borderline flashing may be an indication that the specimen temperature is near the flash point, this particular behavior is not reported as a flash because there is no propagation of the test flame over the specimen.

Another type of flashing behavior, which should not be mistaken for a flash, is what will be termed "enhanced" flashing. This enhanced flashing generally occurs when samples containing low-flashing material produce an abnormally strong flash as the test flame is applied and can be an indication that the test temperature is well above the actual flash point of the sample.[15]

3.2.3 Instrument Validation

Before determining the flash points of the test samples, instrument validation tests are performed on standard materials of known flash points (e.g., *n*-dodecane and *n*-undecane). The instrument validation data (experimental vs literature) for the continuously closed cup method using the Miniflash tester is based on the results from four *n*-dodecane test specimens. Although the pressure increase for one of the samples was 18.7 kPa, which did not exceed the $\Delta p \geq 20$ kPa threshold required by the method, all measurements were consistent with the pressure profile of *n*-dodecane provided in Figure 1. The validation data is given in Table 2. The flash point of *n*-dodecane measured in this work is 78 ± 1 ºC using the continuously closed cup Miniflash tester with a difference of –1 ºC from the literature value of 79 ºC.

The instrument validation data for the small scale closed cup method using the Rapid Flash tester is based on the results from five *n*-undecane test specimens (Table 3). The flash point of *n*-undecane measured in this work is 69 ± 1 ºC using the closed cup Rapid Flash tester with a difference of +3.1 ºC from the literature value of 65.9 ºC.

Table 2. Instrument Validation Results (Experimental vs Literature) Using the Miniflash Tester

Compound	Experimental Data		Literature*[18] (uncertainty) (°C)
	Flash Point (ºC)	Mean Flash Point (ºC ± Std dev)	
n-Dodecane Petrolab Lot no. 271-63A Purity: 99.4%	78	78 ± 1	79.0 (±0)
	77†		
	79		
	78		

*This literature value was based on triplicate sample determinations.
†The pressure increase for this flash point measurement is Δp = –18.7 kPa, which does not exceed the Δp ≥ 20 kPa threshold but still produces a pressure profile consistent with a high purity sample of *n*-dodecane.

Table 3. Instrument Validation Results (Experimental vs Literature) Using the Rapid Flash Tester

Compound	Experimental Data		Literature[19] (uncertainty) (°C)
	Temperature (°C)	Flash/No Flash	
n-Undecane Aldrich Lot no. 02316AB Purity: 99+%	65	No Flash	65.9 (±1.6)
	67	No Flash	
	68	No Flash	
	68	No Flash	
	69*	Flash	

*Measured flash point value.

4. FLASH POINT RESULTS

4.1 Continuously Closed Cup Testing Using Miniflash Tester

Initial flash point measurements were conducted on two HD specimens from sample lot number HD-U-9084-CTF-N (Vial number 6) using the continuously closed cup Miniflash tester. Both of these measurements provided very stable pressure readings from 80 to 104 °C. At 104 °C, a flash occurred. It was indicated by a sharp and well defined pressure increase of ≥20 kPa. This behavior is consistent with the results obtained with the standard (See Figure 1). The results from these measurements produced a flash point equal to 104 °C using the continuously closed cup Miniflash tester. A summary of the results is provided in Table 4, and the HD flash point pressure profile is shown in Figure 2.

Table 4. Summary of HD Flash Point Using Continuously Closed Cup Miniflash Tester

Compound	Flash Point* (°C)	Mean Flash Point (°C)
HD Lot no. HD-U-9084-CTF-N (Vial no. 6)	104	104
	104	

*The uncertainty of this value, based on the results from the dodecane standard measured by the same method, is ±1 °C

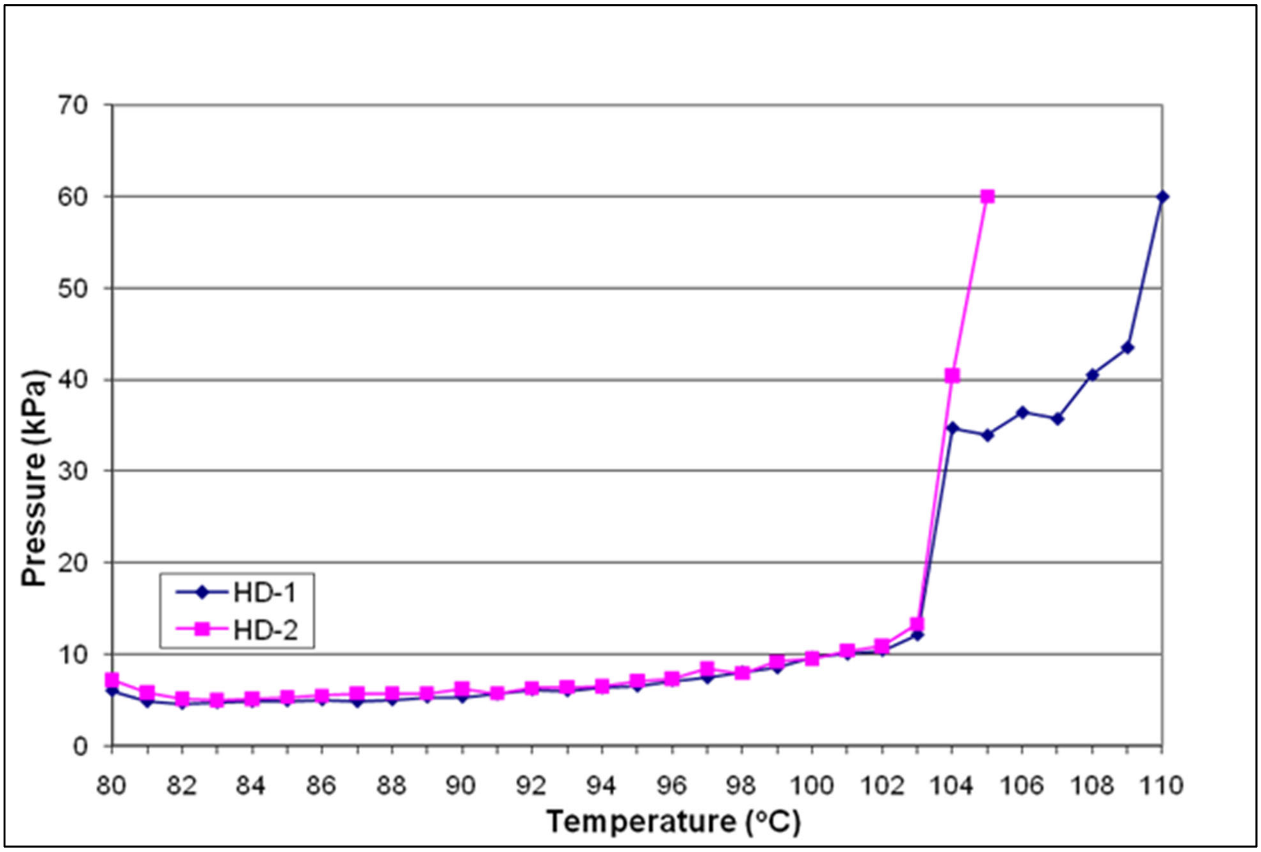

Figure 2. Flash Point pressure profile of HD using continuously closed cup Miniflash tester.

4.2 Small Scale Closed Cup Testing Using Rapid Flash Tester

To determine if similar results could be achieved for HD using a different closed cup method, flash point measurements were also conducted on eight HD specimens from two different samples using the small scale closed cup Rapid Flash tester. These measurements showed signs of borderline flashing at 109 °C, but the actual flash point was observed to be 110 °C. These results are summarized in Table 5.

Table 5. Summary of HD Flash Point Results
Using Small Scale Closed Cup Rapid Flash Tester

Compound	Temperature (°C)	Flash/No Flash
HD Lot no. HD-U-9084-CTF-N (Vial no. 6)	100	No Flash
	110	Flash
	107*	Flash
	107	No Flash
	109	Borderline Flash
HD Lot no. HD-U-9084-CTF-N (Vial no. 5)	109	No Flash
	110†	Flash
	109	No Flash

*Invalid test due to interruption of gas supply.
†Measured flash point value based on this work. The uncertainty of this value, based on the results from the undecane standard measured by the same method, is ±3.1 °C.

5. DISCUSSION

Because flash point values are a function of the instrumental design, sample purity and test conditions,[14,15] comparison of the values generated using different methods should be performed with caution, especially when open cup and closed cup results are considered. In this work, two closed cup methods were used: the Rapid Flash and Miniflash testers. The Rapid Flash tester relies on visual observation and thus, may be considered a more subjective type of method than the Miniflash tester, which relies on a measured pressure increase.

In a case such as the use of two closed cup methods resulting in two different flash point values, it is prudent from a hazard assessment perspective to recommend using the lower of the two values (104 °C). This is consistent with reflecting the “worst-case” scenario from a safety standpoint. It is also important to note that this value is in good agreement with the currently accepted but insufficiently documented literature value of 105 °C.[2]

6. CONCLUSION

The currently accepted flash point of high purity HD in the literature is 105 °C. There were some concerns about the reliability of this value because the source provides very little information about the sample purity, test method, and apparatus used to conduct the measurement. To address these uncertainties, the flash point of high-purity HD was determined by two different closed cup methods using samples of known purity. The following results provide well-documented flash point data for HD, which will help improve agent data verification and validation assessment efforts within the testing community:

- HD flash point — 104 °C (continuously closed cup method)[14] using the Miniflash tester
- HD flash point — 110 °C (closed cup method)[15] using the Rapid Flash tester.

The HD flash points determined in the current study using two different closed cup methods are in reasonable agreement with each other. However, from a hazard assessment perspective, use of the lower of the two values (104 °C) is recommended. This value is also consistent with the currently accepted but insufficiently documented literature value of 105 °C.

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