GUIDANCE ON ASSESSMENT OF FLASH POINT

1.0 INTRODUCTION

Flash point is the minimum temperature at which a liquid or volatile solid gives off sufficient vapor to form an ignitable mixture with air. The sample is deemed to have flashed when the flame appears and instantaneously propagates itself over the entire surface of the fluid.

The flash point is not an intrinsic property of a material. Its value will depend on the apparatus design, condition of the apparatus used and the test procedure used.
As such, the reference method is very prescriptive and must be followed closely.

In practice, a single compound reference standard will be assigned multiple flash points depending on the reference method.

Common uses of the flash point tests:

- Assess flammability for shipping and safety regulations.
- Detect presence of contamination of material by volatiles (e.g., gasoline in diesel).
- Determine if a product meets specifications (e.g., fuels, cosmetics).

2.0 REFERENCE TEST METHODS

Below is a list of flash point reference methods grouped by the apparatus design category. This list is not exhaustive. New reference methods are actively being developed.

1. **Pensky-Martens –** ASTM D93
2. **Tag Cup –** ASTM D56
3. **Rapid Equilibrium –** ASTM D3828, ASTM D3278, ASTM D3941
4. **Cleveland Open Cup –** ASTM D92
5. **Abel Closed Cup –** IP 170
6. **Continuously Closed Cup –** ASTM D6450

Some reference methods have multiple procedures that have to be followed based on the sample type. For example, ASTM D93 has three procedures (Procedure A for homogenous petroleum liquids; Procedure B for residual fuel oils, used lubricating oils, mixtures of petroleum liquids with solids, and petroleum liquids that tend to form a surface film under test conditions; and Procedure C for biodiesel).

As stated in ASTM D93, “no general valid correlation can be guaranteed between results obtained by different test methods, or with test apparatus different from that specified”. As such, the concept of method bias does not exist.

Many regulatory agencies require testing of wastes (solids, liquids, or mixtures) for compliance purposes, solely to confirm that flash point is below a specified regulatory limit (e.g. for TDG or landfill disposal applications). For such compliance testing purposes, it is acceptable to stop the analysis above the applicable regulatory limit (it is not necessary to continue the flash point test to the upper temperature limit of the reference method if no flash is observed). Such decisions need to be agreed upon by the customer as per ISO/IEC 17025, Clause 4.4.2. Some ASTM flash point methods do have an option for reporting flash/no flash instead of a numerical value.

3.0 COMMENTS FOR SECTIONS OF THE RATING GUIDE APPENDIX WHICH MAY BE UNIQUE TO FLASH POINT

3.1 Test Method Validation (02.01)

3.1.1 Accuracy

Accuracy is determined by the analysis of single compound certified reference materials (CRM) as well as multi-compound mixtures (e.g., diesel) over the anticipated working range.

Single compound CRMs are available from NIST as well as many commercial vendors. They are assigned a method-specific flash point value and will come with a certificate specifying the reference method, certified value, traceability and uncertainty. Single compound CRMs will confirm that an unmodified reference method is functioning properly.

As stated in Section 1.0, because of the nature of flash point, the reference method must be followed and not modified. Laboratories that try to make a modification often validate this modification using a single compound CRM, but this is not valid. A single compound flash point value may not change as a result of a modification to the method but when the laboratory is analyzing real samples with multi-components (e.g., fuels, wastes), there could be a large change in flash point values. Previous diesel PT study samples (which would have a method-specific consensus flash point) would provide a more realistic indication of the validity of the change. For solids, a clean sand matrix spiked with a multi-component liquid PT sample would provide more useful information. That being said, it is recognized that reference materials and/or PT samples that contain multi-components with a certified or consensus method-specific value are difficult to source.

It is recognized that sometimes reference methods are applied to samples for which they were not developed or intended; for example, most reference methods deal with liquid or semi-viscous samples and some regulatory bodies specify the use of some of these methods with solid samples. The most common method reference for solid samples is ASTM D93. In this case, it's logical that the sample cup stirrer cannot be used but aside from that, all other test settings must be followed.

3.1.2 Precision

Each time a sample bottle is opened to remove a sample aliquot for testing, there could be a loss of volatile compounds. The magnitude of this effect on the flash point will depend on the contribution of the specific compounds to the sample flash point as well as the number of times a sample bottle has been opened and the amount of sample remaining. As a guideline, ASTM D93 states that minimum sample bottle volume should be fifty percent.

As volatile compounds are lost, there is a tendency for the flash point to increase over time as the sample volume decreases. A common practice to alleviate this situation is to buy liquids in bulk and then transfer them to a series of smaller containers, which are used in validation experiments or for routine QC.

3.1.3 Fitness For Use

To determine if the flash point method is fit for use, the laboratory's test method performance must be compared with the performance requirements in the reference method. Since test results are method dependent, it is important that the laboratory supports its selection of a specific reference method based on customer or regulatory body requirements. It may also be possible that the customer or regulatory body may specify several reference methods based on the viscosity of the sample.

3.1.4 Manual Testing

Accuracy and precision can be analyst dependent when manual test equipment is used. Separate statistics should be calculated for each analyst in this case.

3.2 Test Procedure (03.01)

Procedure must exactly follow the referenced ASTM method specified (the ASTM methods are very prescriptive).

As an example, the requirements and settings from the ASTM D93 reference method are summarized below. If another reference method is used, ensure that all it's prescriptive elements are being followed.

3.2.1 Ignition Source

- Gas flame or electric ignitors are acceptable.
- Gas pressure supplied to the apparatus should < 3 kPa.
- Flame diameter - 3.2 to 4.8 mm (0.126 to 0.189 in.).
- Electric ignitors shall be of the hot-wire type and adjusted to manufacturer's specifications.

When using a gas flame as the ignition source, meticulous attention needs to be paid to the details relating to the test flame application, test flame size, rate of temperature increase, and rate of passing the test flame over the sample to obtain reliable results.

3.2.2 Heating Rate

- D93 Procedure A: 5 to 6 °C per minute.
- D93 Procedure B: 1.0 to 1.6 °C per minute.
- D93 Procedure C: 2.5 to 3.5 °C per minute.

3.2.3 Stirring Rate

- D93 Procedure A: 90 to 120 rpm, stirring in a downward direction.
- D93 Procedure B: 240 to 260 rpm, stirring in a downward direction.
- D93 Procedure C: 90 to 120 rpm, stirring in a downward direction.

3.2.4 Flash Point Ignition Cycle – D93: 1.5 seconds

- Discontinue the stirring of the test specimen and apply the ignition source.
- Lower the ignitor into the vapor space of the test cup in 0.5 s.
- Leave in its lowered position for 1 s, and quickly raise to its upward position.

3.2.5 Flash Check Start Temperature

- If a sample flash point is unknown, two tests will usually have to be performed. You don't want to start applying the ignition source at a temperature too far away or to close to the flash point.
- When a flash point is detected at a temperature which is > 28°C above the temperature of the first application of the ignition source, or when a flash point is detected at a temperature which is < 18°C above the temperature of the first application of the ignition source, the result shall be considered approximate, and the test repeated with a fresh test specimen.

• Adjust the expected flash point for this next test to the temperature of the approximate result. The first application of the ignition source with the fresh test specimen shall be 23 +/- 5°C below the temperature at which the approximate result was found.

The flash point is considered the stage where a large flame appears and instantaneously propagates itself over the entire surface of the test specimen. Do not confuse the true flash point with a blue halo or an enlarged flame that sometimes occurs, especially with halogenated hydrocarbons and admixtures on application of the flame.

3.3 Sample History (04.01)

Note: These sample history requirements are based on the types of samples addressed in the reference methods listed in Section 2.0 and do not apply to solids.

3.3.1 Sample Containers

• D93 - Do not store samples in gas permeable containers (e.g., plastic containers); use glass or metal containers with caps that have inner seals.
• D93 - The sample container shall be from 85 to 95 % full for liquid and liquid waste samples.
• D93 - Not less than 50% full prior to any sample being taken.
Containers should be capped at all times except when taking a specimen for analysis.

3.3.2 Sample Handling

• When possible, the flash point should be the first analysis made on the sample when received in the lab.
• D93 – No sample transfer can be performed unless the sample temperature is at least 18 °C below the expected flash point or at a temperature of 15 ± 5 °C for samples with no known or expected flash point.
• This precooling applies to any labware or instrument component that touches the sample.

Each reference method identified above in section 2.0 is prescriptive in the sampling requirements of the test method. To avoid erroneously high flash points precautions should be taken to avoid the loss of volatile materials. Do not open containers unnecessarily, to prevent the loss of volatile materials or possible introduction of moisture or both. Erroneous flash points will result if air bubbles or foam collected on the top of the sample are not eliminated.

3.3.3 Storage Location

• D93 - Avoid storage of samples at temperatures in excess of 35°C.

3.3.4 Sample Hold Time

• D93 - None specified.

3.4 Method Calibration (05.01)

3.4.1 Certified Reference Material (CRM)

• D93 states that a CRM be used to verify performance at least annually.
• CRM is a stable, pure (99 + mole % purity) hydrocarbon with a method specific flash point established by a method-specific interlaboratory study.
• D93 Flash Point Values and Limits:

Hydrocarbon	FP °C	Tolerance
n–decane	52.8	±2.3
n–undecane	68.7	±3.0
n–tetradecane	109.3	±4.8
n–hexadecane	33.9	±5.9

3.5 Method QC (06.01)

3.5.1 Secondary Working Standards (Daily QC)

• Once the performance of the apparatus has been verified, the flash point of secondary working standards (SWSs) can be determined along with their control limits. These secondary materials can then be utilized for more frequent performance checks.
• SWS is a stable hydrocarbon or petroleum product whose composition is known to remain appreciably stable.
• PT fuel samples may be used as method QC; these types of samples are more sensitive to method deviations and potential problems.

3.5.2 Duplicates

• As a rule of thumb, liquid hydrocarbon sample duplicates are reproducible if the sample bottle is more than half full. Refer to section 3.1.2 Precision for more details.
• Note that duplicate data will be lost if the test is stopped at the regulatory limit, if there was no flash.

3.5.3 Proficiency Testing Program

As per P02-03 – *Proficiency Testing Policy for Accreditation*, all applicant/accredited laboratories shall demonstrate their technical proficiency by their satisfactory participation in a suitable proficiency testing activity.
PT programs providing PT samples include:
• InnoTech Alberta International Quality Assurance Exchange Program (IQAEP).
• ASTM PT Program.
Although solids flash point PT programs available from Phenova and ERA are typically solvents rather than solvent spiked soils, they are still a good indicator of a laboratory's performance.

3.6 Equipment (09.01)

3.6.1 Ventilation

• Tests are to be performed in a draft-free room or compartment. Tests made in a laboratory hood or in any location where drafts occur are not reliable.
• ASTM D93 allows the apparatus along with a draft shield to be placed in a fume hood.
• Fume hood draw must be turned off during the ignition source application period and then back on to remove objectionable vapours, if present.
Care should be used if performing ASTM D92 during the last 17°C rise in temperature prior to the flashpoint to avoid disturbing the vapors in the test cup.

3.6.2 Thermometer

• Glass thermometers have to conform to the requirements of the specific flash point method.
• Electronic temperature measuring device, such as resistance thermometers or thermocouples, have to exhibit the same temperature response as the mercury thermometers
Thermometers, both glass and electronic require a verification and calibration frequency specified. Traceability records must be maintained.

3.6.3 Barometer

• The barometric pressure used in the flash point test correction calculation is the ambient pressure for the laboratory at the time of the test.
• Barometer has to display the absolute pressure and not one corrected to sea level
• Accuracy of +/- 0.5 kPa is required.
• Traceability records must be maintained.

3.7 Test Report (ISO/IEC 17025, Clause 5.10.3)

3.7.1 Test Report Content

Test results are dependent on the actual reference method used for testing. Therefore, the test report should explicitly state the reference method used, information on any unique test conditions (some reference methods may allow some parameter choices) and any variance from the reference method.