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Petroleum products and other liquids — Guidance for flash point testing

Produits pétroliers et autres liquides — Lignes directrices pour la détermination du point d'éclair

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ISO copyright office
Case postale 56 • CH-1211 Geneva 20
Tel. + 41 22 749 01 11
Fax + 41 22 749 09 47
E-mail copyright@iso.org
Web www.iso.org

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Foreword

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The main task of technical committees is to prepare International Standards. Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

In exceptional circumstances, when a technical committee has collected data of a different kind from that which is normally published as an International Standard ("state of the art", for example), it may decide by a simple majority vote of its participating members to publish a Technical Report. A Technical Report is entirely informative in nature and does not have to be reviewed until the data it provides are considered to be no longer valid or useful.

Attention is drawn to the possibility that some of the elements of this document may be the subject of patent rights. ISO shall not be held responsible for identifying any or all such patent rights.

ISO/TR 29662 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

Introduction

This Technical Report was written under the guidance and with the assistance of the ISO/TC 28/TC 35 (CEN/TC 19/TC 139) joint working group for flash point methods and the Energy Institute flammability panel ST B 4 with the aim of assisting laboratory managers and technicians, regulators, specification writers and industry in the use, specification and application of flash-point tests for liquids and semi-solids. It is technically identical to CEN/TR 15138:2005, prepared by Technical Committee CEN/TC 19.

The work is based on standards produced by the following organizations:

— ISO/TC 28, *Petroleum products and lubricants*;

— ISO/TC 35, *Paints and varnishes*;

— CEN/TC 19, *Gaseous and liquid fuels, lubricants and related products of petroleum, synthetic and biological origin*;

— CEN/TC 139, *Paints and varnishes*;

— ASTM D01.22, *Health and Safety*;

— ASTM D02.08 B, *Flammability Section*;

— DIN, *Deutsches Institut für Normung*;

— EI ST B 4, *Flammability Panel.*

Petroleum products and other liquids — Guidance for flash point testing

WARNING — The use of this International Standard can involve hazardous materials, operations and equipment. This International Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this International Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This Technical Report is not intended to be a comprehensive manual on flash point tests and the interpretation of test results; nevertheless, it covers the key aspects of these subjects.

The flash point test can be summarized as a procedure where a test portion is introduced into a temperature-controlled test cup and an ignition source is applied to the vapours produced by the test portion to determine if the vapour/air mixture is flammable and, if so, at what temperature.

2 Outline

There are many, slightly different definitions of flash point, however the following definition is widely used in standard test methods:

> The lowest temperature of the test portion, corrected to a barometric pressure of 101,3 kPa, at which the application of an ignition source causes the vapour of the test portion to ignite momentarily and the flame to propagate across the surface of the liquid under the specified conditions of test.

It is important to realize that the value of the flash point is not a physical constant but it is the result of a flash-point test and is dependent on the apparatus and procedure used. This fact is so important that a general statement similar to the following is incorporated into all the main flash-point methods:

> Flash-point values are not a constant physical-chemical property of the materials tested. They are a function of the apparatus design, the condition of the apparatus used and the operational procedure carried out. Flash point can, therefore, be defined only in terms of a standard test method, and no general valid correlation or lack of a fixed bias can be guaranteed between results obtained by different test methods or with test apparatus different from that specified.

Due to the importance of flash-point test results for both safety and regulatory purposes, an identification of the test method should always be included with the test result.

In general, specific products specifications indicate which standard test method should be employed.

3 Brief history

The discovery of petroleum and the increased use of flammable distillates in the 19th century for lighting and heating in place of animal and vegetable oils led to a large number of explosions and other fire-related accidents.

Legislation, such as the UK Petroleum Act in 1862 and the German Petroleum Regulations in 1882, quickly spread around the world and led to the development of many types of test instruments. The following list shows the dates when the major surviving instruments were in a form more or less recognizable today:

1870 – 1880: Abel closed cup, Pensky-Martens closed cup;

1910 – 1920: Tag closed cup, Cleveland open cup.

4 Flash and fire point, and sustained combustion and burning

The flash point is essentially the lowest temperature of the liquid or semi-solid at which vapours from a test portion combine with air to give a flammable mixture and “flash” when an ignition source is applied. Fire point, combustibility and sustained burning tests all use open-cup instruments.

Fire point can be considered as the lowest temperature of the test portion at which vapour combustion and burning commence when an ignition source is applied and, thereafter, is continuous and where the heat produced is self-sustaining and supplies enough vapours to combine with air and burn even after the removal of the ignition source.

Sustained combustion and burning tests are usually carried out with the test portion at a fixed temperature. These test whether vapour combustion and burning commence when an ignition source is applied and, whether, thereafter, they are continuous. If the heat produced is self-sustaining and supplies enough vapours to combine with air, the sample continues to burn even after the removal of the ignition source.

5 Why flash point tests are required

The fundamental reason for the requirement of flash-point measurements is to assess the safety hazard of a liquid or semi-solid with regard to its flammability, and then classify the liquid into a group. The lower the flash point temperature, the greater the risk. This classification is then used to warn of the risk and to enable taking the correct precautions when using, storing or transporting the liquid.

Specifications quote flash-point values for quality-control purposes as well as for controlling the flammability risk.

A change in flash point can indicate the presence of potentially dangerous, volatile contaminants or the adulteration of one product by another.

6 Which flash point method should be used

6.1 First considerations

Firstly, if a flash point method has been specified in a product specification or regulation, then that method should be the first choice. If a number of alternative methods are specified, then the choice is influenced by availability and other factors, such as sample size requirements, speed of testing or precision. In certain circumstances, the choice of the stated referee method can be of special importance. Annex A gives an overview of the most common methods and their use in specifications and regulations.

When testing specifically for contamination or contaminants, certain test methods and procedures are more appropriate than others. In general, an equilibrium test method is recommended for testing samples that can contain traces of volatile contaminants.

When selecting a flash-point method for incorporation into a product specification or regulation, it is important that the product type be included in the scope of the test method and that the temperature range of the product be covered by the test method. If the product is not included in the scope, then the test and the quoted precision do not apply. Where the scope of a test method is general or not suitable, it is recommended to contact an appropriate standardization body for advice.

When testing chemicals, mineral products or corrosive materials, it is recommended to check that the test cup material is suitable and does not produce flammable gases or is not damaged by any possible chemical reaction.

6.2 Open or closed cup

There are two general classes of flash-point tests: open cup and closed cup:

The open cup was initially developed to assess the potential hazards of liquid spillage. In this test, a test portion is introduced into a cup that is open at the top. An ignition source is passed horizontally over the surface of the liquid while the cup and liquid are being heated to test whether the vapours "flash". If the test is repeated at increasing test-portion temperatures, a point can be reached where the test portion continues to burn without further application of the ignition source: this is the fire point. The precision of open-cup tests is somewhat poorer than that of closed-cup tests as the vapours produced by heating the test portion are free to escape to the atmosphere and are more affected by local conditions in the laboratory. When open-cup tests are made at temperatures above ambient, the result is usually higher than that from a closed-cup test due to the reduced concentration of vapours.

The closed-cup test contains any vapours produced and essentially simulates the situation where a potential source of ignition is accidentally introduced into a container. In this test, a test portion is introduced into a cup and a close-fitting lid is fitted to the top of the cup. The cup and test portion are heated and apertures are then opened in the lid to allow air into the cup and the ignition source to be dipped into the vapours to test for a flash.

The closed-cup test predominates in specifications and regulations due to its greater precision and its ability to detect contaminants.

6.3 Non-equilibrium, equilibrium and rapid equilibrium tests

These three types of tests and associated instruments are characterized by the level of temperature stabilization of the test portion and resultant vapours, and by the test portion size and test time.

Test methods such as Pensky-Martens, Tag, Abel and Cleveland are referred to as non-equilibrium tests, as the test temperature of the test portion is increased during the test and the temperature of the vapours is not the same as (not in equilibrium with) the test-portion temperature when the ignition source is dipped at regular intervals into the cup. This type of test has the advantage that it produces a definitive flash-point result. Under normal circumstances, the increasing temperature is not a problem, but when volatile contaminants or components are present, the short time between each dip of the ignition source, combined with the rate of temperature increase, does not allow enough time for flammable vapours to evolve and this can cause unreliable results. For this reason, non-equilibrium tests with lower rates of heating usually perform better than those using higher rates of heating, when volatile contaminants or components are present in the test portion.

Equilibrium tests are preferred for liquids and semi-solids containing volatile components or contaminants and for confirmatory purposes in regulations as the sample temperature is constant or is increased at a very slow rate. This allows enough time for vapours to build up and to reach equilibrium with the test portion before the ignition source is dipped into the cup. The ignition source is dipped in the cup at different test-portion temperatures, thus resulting in a measurement of a flash point, or the ignition source is dipped only once to carry out a "flash - no flash" test to check conformity with specifications and flammability criteria. These equilibrium tests use any type of closed cup in a liquid bath and limit the difference of temperature between the test portion and the liquid bath. The liquid bath is specified because it gives a very even temperature distribution on the outside of the test cup, thus ensuring that there are no hot spots on the cup surface that can cause a localized increase of flammable vapours and a low flash point. Unfortunately, these procedures take a long time to complete.

Rapid-equilibrium (small-scale) tests are not designed primarily to give the actual flash point of a test portion. The test is a “flash - no flash” test to determine whether the test portion's vapours flash at the test temperature. This is useful for checking conformance against specifications and flammability criteria. The test cup is heated to the test temperature, a small test portion is introduced into the cup and, when the test portion is deemed to be at the test temperature, the ignition source is used to test for a “flash”. The actual flash-point temperature is determined by repeating the “flash - no flash” test at different temperatures with a new test portion. The constant temperature of the test cup ensures that the test portion cannot be overheated and that there is a reasonable time for vapours to build up before the ignition source is applied.

6.4 Flash-point automation

For a manual flash-point test, the operator is in control throughout the test and ensures that the temperature, stirring and ignition requirements are met throughout the test and determines when and if a flash occurs. Some semi-auto instruments can assist the operator in detecting a flash or controlling the temperature, but the operator is in control. This is why manual tests are the reference methods in cases of dispute.

Automated flash-point testers conform to all the specified requirements of the manual test method, such as dimensions, heating rate and flash detection, however the electronics, software and mechanics mimic the manual operations. This can significantly reduce operator time but has the disadvantage that more frequent validation of tester operation is required as the instrument operates mainly unattended and is more complex.

Automatic flash-point testers are not based on a manual test and often only key dimensions and parameters are defined in a test method written just for this instrument type. A unique type of test can be advantageous to the user but the complexity of the tester makes it difficult to measure the conformance with the test method. More frequent validation of the tester parameters and operation is required.

Some automated and automatic instruments are available with carousels that allow carrying out a number of tests unattended. This is particularly advantageous where large numbers of samples are tested. However, accurate and reliable measurements can be compromised if the sample temperature does not meet the recommendations stated in the test method. This is especially relevant to samples that are volatile or contain volatile contaminants.

In general, automated instruments are accepted in test methods provided that the instrument shows conformity with the method requirements, including those pertaining to precision.

6.5 Correlation between methods

It is well known that open-cup tests usually give higher flash point results than closed-cup tests for test temperatures above ambient. Some specifications list equivalent flash point methods and sometimes relative bias information for specific products. However, flash point methods employ different apparatus, heating and stirring rates, procedures and sample handling which have an effect on relative biases, especially when the liquid is volatile, or volatile contaminants or components are present. It is therefore not possible and not correct to claim correlation or a fixed relative bias between different test methods for all test samples.

6.6 Precision

The precision of a flash point method is defined by repeatability, r, and reproducibility, R, at a 95 % confidence level such that only 1 test in 20 would be expected to exceed the quoted figure.

The definitions for precision shown below are typical of those used in flash point test methods and are based on the following definitions from ISO 4259[1].

— Repeatability, r, is the difference between two test results obtained by the same operator with the same apparatus under constant operating conditions, on identical test material that would, in the long run, in the normal and correct operation of the test method, exceed the given value in only one case in 20.

— Reproducibility, R, is the difference between two single and independent test results obtained by different operators in different laboratories on identical test material that would, in the long run, in the normal and correct operation of the test method, exceed the given value in only one case in 20.

The precision of the test method is important for assessing the correct operation of flash point instruments and controlling quality in manufacturing and custody transfer of products.

When selecting a flash-point test method or testing a new product, it is important to check that the product type is covered by the scope of the test method and that the expected flash-point temperature is covered by the precision statement.

6.7 Valid temperature ranges

Flash-point instruments often have a wider temperature range than the temperatures covered by the precision of the test method. Temperatures outside those covered by the precision can result in different precision or give unpredictable results. The temperature ranges covered by the precision are shown in the test method; otherwise, it can be necessary to consult the relevant standardization body for advice.

Test-method procedures include information on the required temperature of the test portion when the flash-point test commences and usually define a temperature band over which a result is valid. It is important to follow the specified procedure as failure to do so can result in an incorrect measurement.

7 Testing environment

The flash-point instrument should be located on a flat and stable platform.

It is important to carry out flash-point tests in a draught-free area, as draughts can affect the evolution of flammable vapours as well as cool or extinguish the ignition source. If there are draughts, then a draught screen is recommended.

It is good practice to carry out flash-point tests under a fume hood; in these circumstances, the air flow should be kept to a minimum.

Visual identification of a flash point can be enhanced by carrying out the test in subdued lighting.

8 Safety

The handling of samples for flash-point determinations should be in accordance with local health and safety practices, as the sample can be flammable or toxic.

When handling samples close to a flash-point instrument, it should be remembered that the flash-point apparatus uses a heated hotplate and an ignition source.

Due to the nature of the test, the use of safety glasses and the provision of a suitable local fire extinguisher are strongly advised.

Provision (such as a fume hood) should be made to minimize the effects of any toxic or objectionable vapours.

Where the product type is not known, it is safer to test with a procedure that uses a smaller volume test portion, such as the rapid-equilibrium test.

9 Calibration and verification

9.1 General

In general, a calibration process leads to either an adjustment of the apparatus or the identification of a correction that is applied to a result.

In general, a verification process checks that the apparatus and test procedure give a result that is within the expected tolerances but no adjustment or corrections are made.

9.2 Calibration

The flash-point instrument and its sensors are required to work in accordance with the tolerances stated in the standard method of test. If a sensor, such as the thermometer, is within the requirement for accuracy, then calibration to a higher level of accuracy is not required. If the sensor is outside the specification, it shall either be replaced or be calibrated.

Reference materials with a certified flash point are for verification purposes only; they shall not be used to establish an offset, bias or any other form of correction.

9.3 Verification

Verification that an instrument conforms to a standard method of test is implemented by checking that all the physical parameters are within allowable tolerances, by ensuring that all key parts are clean and function correctly and by carrying out tests using a reference material.

Incorrect dimensions, faulty igniters and the use of incorrect heating media and incorrect heating rates or stirring speeds can affect test results.

Using instruments that are damaged, dirty or contaminated with volatile components can affect the test result.

The use of a certified reference material (CRM) that has a certified flash point for the test method being used is the prime verification procedure. This CRM is preferably a pure chemical, but it can be advantageous to use a stable material similar to the product normally tested. Once an instrument has been verified, it can then be used to produce a lower-cost secondary working standard (SWS) from a stable material for more frequent use. The test method may include allowable tolerances to judge whether the instrument meets the requirement. If this information is not available, the maximum variation from the certified figure is $0{,}7 \times R$ where R is the reproducibility of the test method for the type of certified fluid at the flash-point temperature and the factor 0,7 is a statistically derived constant.

10 Test samples

10.1 Sample handling

All flash-point methods give rules for the handling of samples and the preparation of test portions before testing. These rules are mainly intended to help avoid losing any volatile components that are present. Failure to follow these rules results in an incorrect and high flash-point measurement that does not correctly define the flammability of the product being tested. Contaminated vessels, beakers or other glassware can also affect the result.

Free water in samples is a problem. If the test method does not give any guidance, then this free water should be decanted off.

Samples that contain water as a component, such as water-borne or water-based paints, shall be tested without any pre-treatment with respect to the water content.

10.2 Samples containing volatile components

Flash-point test results are affected by the presence of volatile contaminants. However, the scale of the effect on the result is different depending on the sample handling, test method and procedure, and the amount and type of volatile contaminant present.

The suitability of a test method for detecting the presence of volatile contaminants may be described in the test method. In general, the presence of volatile contaminants results in a flash point at a lower temperature; however, the use of an equilibrium test method is recommended if very low levels of contamination are present.

10.3 Viscous and semi-solid samples

Not all flash-point test methods are suitable for viscous and semi-solid samples. It is, therefore, important to use a test method that includes such samples in its scope or procedure.

In this context, a viscous sample is one that is difficult to pour or to stir.

In general, test methods allow the heating of viscous test samples before the test to make them less viscous, provided that the sample temperature is significantly below the expected flash point. Refer to the sample preparation and procedure sections of the test method for detailed requirements.

11 Instrumentation

11.1 Ignition sources

The flash point is dependent on the position and size of the ignition source and the temperature of the ignition source until it is above about 1 300 °C.

The most proven and accepted ignition source is the gas flame, which burns at a sufficiently high temperature to give reliable results when using natural gases or coal gases. The gas flame does have the following disadvantages: it is necessary to light it, it is necessary to set the size of the flame, it can be blown out by draughts and, of course, a gas supply is required. These disadvantages should be overcome mainly by using a gas or electric pilot light, an efficient draught screen and a rechargeable gas tank.

A widely used alternative is the hot wire igniter, which can be turned on and off automatically as required and is not be “blown out” by a strong flash. This approach is not allowed in a number of test methods as difficulties have been encountered when testing products containing traces of volatile contaminants. At present, all open-cup tests mandate gas-flame igniters. Other disadvantages of hot wire igniters are the possible change in igniter temperature over a period of time and the lifespan of the device.

NOTE Under certain circumstances, the use of electric ignition sources can give results different from those obtained using a flame ignition source.

Another approach is the use of an electric spark as the ignition source. This has been successfully adopted in one test instrument and test method.

11.2 Flash detection

The traditional reference method for observing a flash is by the human eye. However, for automated and automatic instruments or for some products where the flash is not visible, this is not possible. The following two flash detectors are most commonly utilized.

— The ionizing ring detector operates as organic compounds burn by collecting positive ions and turning them into an electrical current to detect a flash. This type of detector is mechanically robust and is mainly used with open-cup instruments as it covers a relatively large area of the test portion’s surface. Water vapour can be a problem with this type of detector and, hence, thermal detectors are becoming more popular for closed-cup applications.

— The thermal detector measures the increase in temperature caused by a flash. The detector is fragile as it is necessary that it have a small mass to ensure response to the fast increase in temperature caused when the vapours ignite. This detector type is very reliable and is less affected by the presence of water vapour.

The use of a pressure sensor to detect the flash point has been successfully adopted in one closed-cup test method.

11.3 Stirring

Stirring of the test portion during the test is specified in many test methods to keep the whole of the test portion at the same temperature and, thus, avoid incorrect flash points caused by vaporization at the hotter surface of the cup or poor heat transfer through the liquid. It also assists the electronics or the operator in heating the test portion at the specified rate or to the required temperature.

Stirring shall be stopped before testing for a flash to allow the vapour space to stabilize.

11.4 Temperature measurement

Some test methods still mandate the use of prescribed mercury-in-glass thermometers; however, most test methods now allow alternative temperature-measuring devices provided that their performance is at least equal to that of the mercury thermometer. The use of mercury thermometers is being phased out in some countries due to safety concerns and alternative liquids are being proposed.

As alternative electronic temperature-measuring devices are not specified in detail in test methods, this can lead to measurement problems, even though the accuracy requirement is met. This is caused by the differing dynamic performance of the device or the immersion depth being incorrect.

Calibrated thermometers are often used in flash-point instruments, but the requirement is that the thermometer conform to the test-method requirement. To reach this requirement, calibration can be required.

11.5 Care of the instrument

Manual instruments are very robust while automated and automatic instruments can be more fragile; but all require careful treatment and servicing to ensure correct operation.

Traces of a material from a previous test on the test-cup lid or in the test cup can affect the next test result.

Spilt samples and other debris around the test cup can cause the incorrect opening and closing of lids and shutters as well as be a potential fire or health hazard.

11.6 Sub-ambient testing

Samples containing volatile contaminants can have very low flash points. Besides cooling the sample to avoid the loss of these volatile contaminants, it is necessary that the instrument be capable of controlling the test portion at these low temperatures and in conformance with the test method procedure.

Uncontrolled warming of a test portion from a sub-ambient temperature during a test gives an indication of the flash point. However, this is unreliable and not in conformance with the test method. In this instance, the precision quoted in the test method does not apply.

Many instruments are now available that use an external cryostat or have integral electronic “Peltier” cooling to enable the correct controlled heating rates.

12 Flash point testing effects

The following are the most common effects noticed during flash point testing.

- A halo is seen around the ignition source; this is not a flash point but indicates that a flash point will be detected at the next dip.
- A "popping" sound is heard; this is a flash point only if a flash is detected. If a flash is not detected, then it indicates that a flash point will probably be detected at the next dip.
- The igniter (flame) is blown out during dipping; this is a flash point only if a flash is detected. If a flash is not detected, then it indicates that a flash point will probably be detected at the next dip.
- The sample burns instead of flashing when the igniter is dipped; this indicates that the flash point is probably at a temperature significantly lower than the current test temperature.
- The measured flash point is much higher than expected; this can be due to the presence of excess volatile components that do not flash due to the lack of enough air (oxygen) in the test cup. A test at a much lower temperature can give a flash point.
- The measured flash point is much lower than expected; this can be due to the presence of volatile components in the test sample or to solvents used to clean the test-cup assembly.
- Some halogenated compounds extinguish an ignition flame.
- Non-flammable vapours, such as water vapour, extinguish an ignition flame or do not allow the mixture to ignite.

13 Test results

13.1 Barometric pressure correction

When the test portion is heated, molecules evaporate to form a vapour. This vapour exerts a pressure, which increases with temperature and depends on the volatility of the components in the test portion.

If atmospheric pressure is low, then the temperature to which it is necessary to heat the test portion to produce a vapour pressure high enough to form a flammable mixture with air is reduced.

If atmospheric pressure is high, then it is necessary that the test portion be at a higher temperature to produce a vapour pressure high enough to form a flammable mixture with air.

In order to correct for the effects of atmospheric pressure, the standard equation for the corrected flash point temperature, T_{c}, expressed in degrees Celsius, as given in Equation (1), is applied to all flash point results:

$$T_{\mathrm{c}} = T_{\mathrm{o}} + 0{,}25(101{,}3 - p) \quad (1)$$

where

T_{o} is the observed flash point temperature, expressed in degrees Celsius;

p is the measured atmospheric pressure, expressed in kilopascals.

In the vast majority of instances, the correction makes very little difference to the result; however, locations at high altitude can cause corrections as large as 4 °C, while severe weather conditions or locations below normal sea level can also cause significant deviations.

13.2 Expression and reporting of results

All flash-point methods include instructions on how the test result should be reported. It is important to follow the instructions given in the test method regarding the rounding of decimals following measurement or barometric corrections. Incorrect use of the rules leads to an incorrect assessment of a test sample's suitability in meeting regulations or specifications.

The requirements to report further details of the test sample, test parameters and any non-conformance with the test method are included to enable documentation of the history of the test for traceability or in the case of a dispute or a request for a repeat test. The reporting of any unusual occurrences during the test provides further useful information.