TECHNICAL REPORT

ISO/TR 29662

Second edition
2020-06

Petroleum products and other liquids — Guidance for flash point and combustibility testing

Produits pétroliers et autres liquides — Lignes directrices pour les essais de combustibilité et de point d'éclair

Reference number
ISO/TR 29662:2020(E)

COPYRIGHT PROTECTED DOCUMENT

ISO copyright office
CP 401 • Ch. de Blandonnet 8
CH-1214 Vernier, Geneva
Phone: +41 22 749 01 11
Email: copyright@iso.org
Website: www.iso.org

Published in Switzerland

Contents

Page

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

The procedures used to develop this document and those intended for its further maintenance are described in the ISO/IEC Directives, Part 1. In particular, the different approval criteria needed for the different types of ISO documents should be noted. This document was drafted in accordance with the editorial rules of the ISO/IEC Directives, Part 2 (see www.iso.org/directives).

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. Details of any patent rights identified during the development of the document will be in the Introduction and/or on the ISO list of patent declarations received (see www.iso.org/patents).

Any trade name used in this document is information given for the convenience of users and does not constitute an endorsement.

For an explanation of the voluntary nature of standards, the meaning of ISO specific terms and expressions related to conformity assessment, as well as information about ISO's adherence to the World Trade Organization (WTO) principles in the Technical Barriers to Trade (TBT) see www.iso.org/iso/foreword.html.

This document was prepared by Technical Committee ISO/TC 28, *Petroleum and related products, fuels and lubricants from natural or synthetic sources*.

This second edition cancels and replaces the first edition (ISO 29662:2009). The main technical changes compared to the previous edition are as follows:

— the title has been changed;

— combustibility test details have been further added;

— a list of examples of regulations have been added;

— test samples, to include biodiesel, mixtures and samples that form a skin during testing have been added;

— the use of low hazard glass thermometers has been added;

— further details regarding the requirements for barometric corrections have been added;

— Annex A has been added to include temperature ranges for each test method.

Any feedback or questions on this document should be directed to the user's national standards body. A complete listing of these bodies can be found at www.iso.org/members.html.

Introduction

This document was written to assist laboratory managers and technicians, regulators, specification writers and industry in the use, specification and application of flash point and combustibility tests for liquids and semi-solids.

The flash point test can be summarised 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 or at what temperature the vapour / air mixture is flammable.

Combustibility tests in this document comprise fire point, sustained combustibility and sustained burning tests. These tests can be summarised 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 catches fire and continues to burn.

This document was developed by the Joint ISO/TC 28 - ISO/TC 35 WG9 on flash point methods.

Petroleum products and other liquids — Guidance for flash point and combustibility testing

1 Scope

This document establishes an overview of test methods in the field to determine flash point and combustibility of petroleum and related products. It presents advice on application and specification development. This document is not intended to be a comprehensive manual on flash point and combustibility tests, and the interpretation of test results, however it covers the key aspects on these subjects.

2 Normative references

The following documents are referred to in the text in such a way that some or all of their content constitutes requirements of this document. For dated references, only the edition cited applies. For undated references, the latest edition of the referenced document (including any amendments) applies.

ISO 1998-1, *Petroleum industry — Terminology — Part 1: Raw materials and products*

ISO 1998-2, *Petroleum industry — Terminology — Part 2: Properties and tests*

3 Terms and definitions

For the purposes of this document, the terms and definitions in ISO 1998-1 and ISO 1998-2 and the following apply.

ISO and IEC maintain terminological databases for use in standardization at the following addresses:

— ISO Online browsing platform: available at https://www.iso.org/obp

— IEC Electropedia: available at http://www.electropedia.org/

3.1
repeatability
r
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 and in the normal operation of the test method, exceed the given value in only one case in 20

Note 1 to entry: The general description deviates from ISO 4259-1 used in many of the standards dealt with in this document.

3.2
reproducibility
R
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 and in the normal operation of the test method, exceed the given value in only one case in 20

Note 1 to entry: The general description deviates from ISO 4259-1 used in many of the standards dealt with in this document.

4 Outline of generic definitions and general statements in test methods

4.1 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, adjusted to account for variations in atmospheric pressure from 101,3 kPa, at which application of an ignition source causes the vapour of the test portion to ignite and the flame to propagate across the surface of the liquid under the specified conditions of test.

4.2 It is important to realise 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 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 only be defined in terms of a standard test method, and no general valid correlation can be guaranteed between results obtained by different test methods or with test apparatus different from that specified.

4.3 Combustibility tests have their own definitions, the following are examples.

— Sustained combustibility: behaviour of a material, under specified test conditions, whereby its vapour can be ignited by an ignition source and, after ignition, sufficient flammable vapour is produced for burning to continue for at least 15 s after the source of ignition has been removed.

— Fire point: lowest temperature of the test portion, adjusted to account for variations in atmospheric pressure from 101,3 kPa, at which application of a test flame causes the vapour of the test portion to ignite and sustain burning for a minimum of 5 s under the specified conditions of test.

— The sustained burning test does not have a formal definition, however, it may be defined as follows: behaviour of a material, under specified test conditions, whereby its vapour can be ignited by an ignition source and, after ignition, sufficient flammable vapour is produced for burning to continue for at least 15 s after the source of ignition has been removed.

NOTE All flash point and combustibility test temperatures are corrected by a formula that compensates if the barometric pressure is not 101,3 kPa.

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

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

5 Brief history

5.1 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 probably recognisable today:

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

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

5.2 Flash point and combustibility tests are key components of transport, safety and health regulations. The examples of such regulations shown below are used in Europe but have numerous equivalents internationally. These regulations have been used in the past to assist in setting specification levels for flash point requirements.

DSD Dangerous substances directive – 2015 replaced by CLP

DPD Dangerous preparations directive – 2015 replaced by CLP

CLP Classification, labelling and packaging

ADR Carriage of dangerous goods by road

GHS Global harmonized system – classification, labelling and packaging

ADN Carriage of dangerous goods by inland waterways

RID Carriage of dangerous goods by rail

6 Flash and fire point, and sustained combustion and burning

6.1 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.

6.2 Fire point can be considered as the lowest temperature of the test portion at which vapour combustion and burning commences 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.

6.3 Sustained combustion and burning tests are usually carried out with the test portion at a fixed temperature and tests whether vapour combustion and burning commences 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.

7 Why are flash point and combustibility tests 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 a risk and to enable the correct precautions to be taken 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.

Test methods that enable the ability of a liquid to support a sustained combustion flame to be assessed, offer a means of further identifying the hazard of liquids under possible fire conditions for use in safety and health regulation classifications.

8 Which test method should be used

8.1 First considerations

Firstly, if a specific test 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 is 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 is included in the scope of the test method and that the temperature range of the product is covered by the test method. If the product is not included in the scope then the test can be unsuitable for the product or the quoted precision does 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 will not produce flammable gases or be damaged by any possible chemical reaction.

The use of the sustained combustibility test is implemented in some safety and health regulations and can be useful for some products to obtain an alternative hazard classification.

8.2 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 of the sample 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 if the vapours ‘flash’. If the test is repeated at increasing test portion temperatures a point can be reached when 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 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 temperature, the result is usually higher than a result 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 is 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 better precision and ability to detect contaminants.

Fire point, sustained combustion and sustained burning tests outlined in this technical report are all open cup type tests.

8.3 Non-equilibrium, equilibrium and rapid equilibrium tests

8.3.1 General

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

8.3.2 Non-equilibrium tests

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 (not in equilibrium) as 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.

8.3.3 Equilibrium tests

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 for the vapours to be in 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 limits 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 hot spots are not present on the cup surface that could cause the localised increase of flammable vapours and thus a low flash point. Unfortunately, these procedures take a long time to complete.

8.3.4 Rapid equilibrium tests

Rapid equilibrium (small scale) tests are not primarily aimed to give the actual flash point of a test portion. The test is a flash no-flash test to determine if 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'. 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.

8.4 Flash point automation

8.4.1 Manual flash point test

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 has occurred. 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 referee in cases of dispute.

8.4.2 Automated flash point testers

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 this does have 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 for conformance to the test method to be measured. More frequent validation of the tester parameters and operation is required.

Some automated and automatic instruments are available with carousels that allow a number of tests to be carried out 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.

When using automated or automatic instruments it is good practice for the operator to monitor the apparatus during the tests. This is especially true if the sample is unknown or contamination is suspected as being present which could cause a fire in the cup. See Clause 10 for further safety advice.

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

8.5 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 temperature. 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.

8.6 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 precision of the test method is important for assessing the correct operation of flash point instruments and for control of 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.

8.7 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 consult the relevant standardisation body for advice.

Test method procedures include information on the required temperature of the test portion when the flash point test commences and usually defines 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.

9 Testing environment

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

It is important to carry flash point tests in a draught free area as draughts can affect the evolution of flammable vapours as well as cooling or extinguishing 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 airflow should be kept to a minimum.

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

10 Safety

The handling of samples for flash point determinations should be in accordance with local health and safety practices, as the sample could 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. Any combustible material, such as test samples, solvents, waste material or paper should not be kept close to the test apparatus.

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

Flash point test safety can be enhanced by the use of devices that automatically dispense an inert gas or vapour over the test cup in the event of a test cup fire. ISO 2719 mandates such a device for new apparatus.

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

Where the product type is not known it is safer to test using a procedure that uses a smaller volume test portion such as the rapid equilibrium test or continuously closed cup.

All flash point methods include a warning or cautionary statement such as the following: “The use of this document can involve hazardous materials, operations and equipment. This document does not purport to address all of the safety problems associated with its use. It is the responsibility of users of this document to take appropriate measures to ensure the safety and health of personnel prior to the application of this document and to determine the applicability of any other restrictions for this purpose.”

11 Calibration and verification

11.1 General

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

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

11.2 Calibration

The test 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 recalibration to a higher level of accuracy is not required. If the sensor is outside the specification it should either be replaced or recalibrated.

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

11.3 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 all key parts are clean and function correctly and by testing using a reference material.

Incorrect dimensions, faulty ignitors, 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.

For flash point tests 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 use a lower cost secondary working standard (SWS) from a stable material for more frequent use.

The test method can 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 $R/\sqrt{2}$ where R is the reproducibility of the test method for the type of certified fluid at the flash point temperature and the factor $\sqrt{2}$ (see ISO 4259-2) is a statistically derived constant.

The sustained combustion test uses prescribed pure chemicals for verification.

12 Test samples

12.1 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, should be tested without any pre-treatment with respect to the water content.

12.2 Samples containing volatile flammable components

Flash point test results are affected by the presence of volatile flammable components. However, the scale of the effect on the result will be 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 to detect the presence of volatile contaminants can 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.

12.3 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 would be 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.

12.4 Biodiesel (B100 FAME- Fatty Acid Methyl Ester)

Biodiesel can be produced from straight vegetable oil, animal oil/fats, tallow and waste cooking oil. The process used to convert these oils to biodiesel is called transesterification. This process is the reaction of a triglyceride (fat/oil) with an alcohol to form esters. The alcohol most commonly used is methanol.

The flash point of biodiesel is usually significantly over 100 °C, however traces of methanol and other alcohols can be still present in the biodiesel and can cause a significant reduction in the flash point.

The presence of these volatile contaminants results in considerably worse precision and a need for the sample to be handled correctly (see 12.1) to ensure the flash point measured is representative of the bulk fuel.

12.5 Mixtures of materials

There are many complex mathematical models for the prediction of flash point when two miscible samples are mixed.

In general the result of a flash point test of a mixture of two components will not be less than the lowest flash point of the two components. However due to azeotropic effects the flash point over a composition range can be less than those of its components. This kind of behaviour is quite dangerous, since the mixture becomes more hazardous than its pure components.

12.6 Samples that form a skin during testing

Certain materials such as paints and asphalts can form a skin during testing. This skin can inhibit the formation of flammable vapours in the test cup and result in an unreliable result.

The formation of a skin can be inhibited by the stirrer prescribed in the test method or the skin can be removed manually.

ISO 2592, the Cleveland open cup test, includes a special procedure to reduce the formation of a skin during testing of asphalt and similar materials. This procedure has been standardized as a separate ASTM test method D8254[22].

13 Instrumentation

13.1 Ignition sources

The flash point is dependent upon 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 gas or coal gas. The gas flame does have the disadvantages that it needs to be lit, the size of the flame needs to be set and it can be blown out by draughts, and of course a gas supply is required. These disadvantages should be mainly overcome by using a gas or electric pilot light, an efficient draught screen and a rechargeable gas tank.

A widely used alternative for closed cup testers is the hot wire ignitor which can be turned on and off automatically as required and is not ‘blown out’ by a strong flash. At present all open cup tests mandate gas flame ignitors although some manufacturers offer hot wire ignitors, however these have not yet been standardized. Disadvantages of hot wire ignitors are the possible change in ignitor temperature over a period of time, and the lifespan of the device.

Under certain circumstances the use of electric ignition sources can give different results to 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 the Modified continuously closed cup test method.

13.2 Flash detection

13.2.1 A flash point is usually defined as the temperature of the test portion when an ignition source causes a flame to propagate over the surface of the test portion. The traditional way of observing a flash is by the human eye. However for automated and automatic instruments or for some products, such as FAME (Biodiesel), where the flash is not visible, this is not possible. The following two flash detectors are most commonly utilised:

13.2.1.1 The ionising 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 usually used for closed cup applications.

13.2.1.2 The thermal detector measures the increase in temperature caused by a flash. The detector is fragile, as it has 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 sensitivity of the detector is set by the manufacturer of the tester so that a localized flash without flame propagation is not identified as a flash point.

13.2.2 The use of a pressure sensor to detect the flash point has been successfully adopted in one closed cup test method[20].

13.3 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 should be stopped before testing for a flash to allow the vapour space to stabilise.

13.4 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 based on more environmentally friendly liquids provided that their performance is at least equal to the mercury thermometer. The availability and use of mercury thermometers is being phased out in most countries due to safety concerns, an international ban on sales of such devices and the availability of alternative low hazard liquid in glass thermometers.

Glass thermometers based on alternative low hazard liquids have a limited temperature range, are slower to respond than mercury thermometers, can have a known bias at elevated temperatures due to stem correction requirements and are prone to liquid column separation. Glass thermometers based on gallium are suitable for higher temperatures and do not suffer from stem correction requirements when used in place of mercury thermometers.

Alternative electronic temperature measuring devices are not specified in detail in most test methods; this can lead to measurement problems even though the reported accuracy meets the requirement. This can be caused by the differing dynamic performance of the device or the immersion depth being incorrect. Alternative devices should therefore conform to the test method performance requirements.

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

13.5 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.

Solvents used to clean apparatus can cause unreliable results when the solvent has not been completely evaporated before the commencement of the preparations for the next test. Significantly lower results can be caused by remaining traces of some solvents especially when tests are at low temperatures such as <40 °C. Follow the advice given in the test method or manufacturer's instructions to clean and dry the apparatus.

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

13.6 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 the instrument should 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 flash point. However, this is unreliable and not in conformance to 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.

14 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 is likely to be detected at the next dip.

— A 'popping' sound is heard – this is only a flash point if a flash is detected. If a flash is not detected, then it indicates that a flash point is likely to be detected at the next dip.

— A violent 'popping' sound is heard and the ignitor (flame) is blown out during dipping - this indicates that the flash point is probably at a slightly lower temperature than the current test temperature

— The ignitor (flame) is blown out during dipping – this is only a flash point if a flash is detected. If a flash is not detected, then it indicates that a flash point will likely be detected at the next dip.

— A flame is seen on the top of the lid – this indicates that the flash point is probably at a lower temperature than the current test temperature, however some sample vapours only burn on the top of the lid and not in the cup due to vapour concentration effects.

— The sample burns instead of flashing when the ignitor is dipped – this indicates that the flash point is probably at a significantly lower temperature than the current test temperature.

— The measured flash point is much higher than expected – this could 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 could give a flash point.

— The measured flash point is much lower than expected – this could 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 a correct flammable mixture evolve.

15 Test results

15.1 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 upon the volatility of the components in the test portion.

If atmospheric pressure is low, then the temperature at which the test portion should be heated to produce a vapour pressure high enough to form a flammable mixture with air will be reduced.

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

In order to neutralise the effects of atmospheric pressure the following standard formula is applied to all flash point results:

$$T_c = T_o + 0{,}25(101{,}3 - p) \quad (1)$$

where

T_c is the corrected flash point temperature in °C;

T_o is the observed flash point temperature in °C;

p is the measured atmospheric pressure in kPa;

0,25 is a constant with dimensions degrees Celsius per kilopascal;

101,3 is used as the standard atmospheric pressure, in kilopascals.

When a flash no-flash test or sustained combustion / burning test is to be conducted at a specification or uncorrected target test temperature, the correction of temperature due to the effects of atmospheric pressure should be made before the test. In this instance use the formula shown in the test method or use Formula (2):

$$t_t = t_s - 0{,}25(101{,}3 - p) \quad (2)$$

where

t_t is the actual test temperature, in degrees Celsius;

t_s is the specification or uncorrected target test temperature, in degrees Celsius.

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 or locations at below normal sea level can also cause significant differences.

Most flash point methods use the Formula (1) which was initially based on experiments carried out on samples and apparatus at different elevations above sea level. The formula was verified by theoretical studies of the vapour pressure of many materials. Various interlaboratory studies (ILS), carried out at a wide range of atmospheric pressures, have shown the formula to be effective. Formulae (1) and (2) have been proven for barometric pressures down to 82,0 kPa and are strictly correct only up to 104,7 kPa.

15.2 Expression and reporting of results

All flash point methods include instructions on how the test result should be reported. It is important to follow these instructions, given in the test method, regarding 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-conformances to the test method are included to enable the history of the test to be documented for traceability or if there should be a dispute or a repeat test requested. The reporting of any unusual occurrences during the test provides further useful information.

Annex A
(informative)

Major test methods used in specifications and regulations

Table A.1 gives an overview of the general use of flash point test methods[1]. Due to the large number of specifications and regulations which call up these test methods it is not possible to list the suitability of each method for different product groups. This information is found in the scope of each of the flash point test methods. Test method precision range is not included as many tests have different precision for different product groups and temperatures. Details of precision can be found in 8.6.

Table A.1 — Overview of test methods

Test method	Test type c/c closed cup, o/c open cup	Test method	Test method range °C
Abel	Flash point c/c	ISO 13736 (IP 170)	−30 to 75
Abel-Pensky	Flash point c/c	DIN 51755[23]	
Cleveland	Flash and fire point o/c	ISO 2592 (IP 36)	79 to 400
	Flash and fire point o/c	ASTM D92[11]	
Pensky-Martens	Flash point c/c	ISO 2719 (IP 34)	40 to 370
	Flash point c/c	ASTM D93[12]	40 to 370
Equilibrium	Flash point c/c	ISO 1516 (IP 491)	−30 to 110
	Flash point c/c	ISO 1523 (IP 492)	−30 to 110
	Flash point c/c	ASTM D3934[15]	0 to 110
	Flash point c/c	ASTM D3941[16]	0 to 110
Rapid equilibrium (small scale)	Flash point c/c	ISO 3679 (IP 523)	−30 to 300
	Flash point c/c	ASTM D3278[13]	0 to 110
	Flash point c/c	ASTM D3828[14]	−30 to 300
	Sustained combustion o/c	ISO 9038	up to 100
	Sustained burning o/c	ASTM D4206[17]	at 49
Small scale ramp	Flash point c/c	ASTM D7236 (IP 534)[21]	−20 to 300
Tag	Flash point c/c	ASTM D56[18]	25 to 93
	Flash and fire point o/c	ASTM D1310[19]	−18 to 165
Modified continuously closed cup	Flash point c/c	ASTM D7094 (IP 620)[20]	<35 to >225

NOTE 1 The following prefixes are used for standards from the following organizations:

ISO International Standardization Organization (ISO)

ASTM ASTM International

DIN Deutsches Institut für Normung

IP Energy Institute

NOTE 2 ISO 3679 and ISO 3680[2] have been combined into a revised ISO 3679.

NOTE 3 Test method ranges are from the actual test method. The range for precision can be less.

1) The list is not intended to infer equivalence between any of the test methods.

Bibliography

[1] ISO 1516, *Determination of flash/no flash — Closed cup equilibrium method*

[2] ISO 1523, *Determination of flash point — Closed cup equilibrium method*

[3] ISO 2592, *Petroleum and related products — Determination of flash and fire points — Cleveland open cup method*

[4] ISO 2719, *Determination of flash point — Pensky-Martens closed cup method*

[5] ISO 3679, *Determination of flash no-flash and flash point — Rapid equilibrium closed cup method*

[6] ISO 3680[2)], *Determination of flash / no flash — Rapid equilibrium closed cup method*

[7] ISO 4259-1, *Petroleum and related products — Precision of measurement methods and results — Part 1: Determination of precision data in relation to methods of test*

[8] ISO 4259-2, *Petroleum and related products — Precision of measurement methods and results — Part 2: Interpretation and application of precision data in relation to methods of test*

[9] ISO 9038, *Test for sustained combustibility of liquids*

[10] ISO 13736, *Determination of flash point — Abel closed-cup method*

[11] ASTM D92, *Standard Test Method for Flash and Fire Points by Cleveland Open Cup Tester*

[12] ASTM D93, *Standard Test Method for Flash point by Pensky-Martens Closed Cup Tester*

[13] ASTM D3278, *Standard Test Methods for Flash Point of Liquids by Small Scale Closed-Cup Apparatus*

[14] ASTM D3828, *Standard Test Methods for Flash Point by Small Scale Closed Cup Tester*

[15] ASTM D3934, *Standard Test Method for Flash/No Flash Test — Equilibrium Method by a Closed-Cup*

[16] ASTM D3941, *Standard Test Method for Flash Point by the Equilibrium Method With a Closed Cup Apparatus*

[17] ASTM D4206, *Standard Test Method for Sustained Burning of Liquid Mixtures Using the Small Scale Open-Cup Apparatus*

[18] ASTM D56, *Standard Test Method for Flash Point by Tag Closed Cup Tester*

[19] ASTM D1310, *Standard Test Method for Flash Point and Fire Point of Liquids by Tag Open-Cup Apparatus*

[20] ASTM D7094, *Standard Test Method for Flash Point by Modified Continuously Closed Cup (MCCCFP) Tester*

[21] ASTM D7236, *Flash Point by Small Scale Closed Cup Tester (Ramp Method)*

[22] ASTM D8254, *Flash and Fire Points of Asphalt by Cleveland Open Cup Tester*

[23] DIN 51755, *Testing of mineral oils and other combustible liquids — Determination of flash point by the closed tester according to Abel-Pensky*

2) Withdrawn.

ICS 75.080
Price based on 15 pages