Flash Point Testing: A User's Guide

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Flash point testing is an important safety procedure, which every laboratory producing potentially flammable material should consider. Storage and transport methods and potential hazards can be determined using a flash point test. However, many people including those carrying out flash point tests are unaware of the theory involved.

History of Flash Point Testing

Flash point testing was developed in the 19th century as a method of determining the quality of fuels and lubricants.
The methods became standardized by a number of national and international organizations over the years. Closed cup testing was developed in Germany, with the most significant contribution from Berthold Pensky, who modified the British Abel System (the Abel-Pensky) and co-developed the established Pensky-Martens method at the Kaiser-Wilhelm-Institute.
At the same time in the USA, the TAG system and the Cleveland Open Cup method were developed also.

Originally simple gas or electrically heated instruments were only available but since the mid-sixties automatic systems have been available and have become popular.

Fig 1. Petrotest PM4: Pensky-Martens Flash Point Tester
with electric stirring and heating, gas + electric igniter and quick-connection head.
Methods: ASTM D 93 A+B - IP 34 - DIN (EN) 22719 - ISO°2719 - NF M 07-019 - JIS K 2265

Definition of Flash Point

There are many different definitions of what a flash point is. The most common is: The flash point is the lowest temperature at which application of an igniter causes the vapor of a specimen to ignite under the specified test conditions.
A sample flashes when a large flame appears and instantaneously propagates across the surface of the sample.
Note that a blue halo does not constitute a flash point.

Sampling

Correct sampling is essential for consistent flash point results. Standardized procedures exist which must be followed precisely otherwise partial degassing or complete loss of the ignitable vapors will occur by evaporation.
These vapor fractions are the ones with the lowest flash point.

To prevent fractions with low boiling points being lost from large samples, sealed containers and cool storage must be used.

Safety

Safety procedures must be followed when using a flash tester. Fire extinguishers, safety visors and breathing apparatus should all be available.

Draught prevention is important as toxins such as PCBs can be produced during heating. Automated equipment will prevent any potential health risk to the user.

Types of Instrumentation

Four types are available:

- Standard instruments with gas heating and gas ignition
- Electrically heated instruments with gas or electric ignition
- Partially automated instruments with electric heating and automated gradient control
- Fully automatic instruments with automatic flash point detection

Only standard units are accepted by all organizations for referee work. However, they require skill and patience to use and are potentially hazardous to the user. The remaining categories of tester are acceptable to different organizations. DIN does not accept anything other than standard units for referee work whilst ASTM allows fully automatic equipment with the provision that re-checking is carried out from time to time using standard units.

The point is disputed between the various organizations. However, automated equipment guarantees user safety and tests in the USA have shown very little difference between manual and automatic equipment. Differences and non-detection were limited to a very small number of samples that often contained chlorine.

Barometric Pressure

Barometric pressure will have an effect on test results. Calculations in the relevant standards take this into account and must not be left out.

Fig 2. Petrotest CLA 4:
Automatic Cleveland Open Cup
Flash and Fire Point Tester.
Suitable for oils and bitumens,
featuring an automatically moveable test flame.
Methods: ASTM D 92 - IP 36 - ISO 2592

STANDARDIZED SYSTEMS FOR FLASH POINT DETERMINATION

Low Temperatures (-20 ... + 80 °C)

Abel	IP 33, IP 170
TAG	ASTM D 56, IP 304
Rapid	ASTM D 3228, ASTM D 3243, ASTM D 3278, IP 303, ISO 3679, ISO 3680
Pensky-Martens	ASTM D 93

Medium to High Temperatures (+60 ... +360 °C)

Pensky-Martens	ASTM D 93, IP 34, DIN 51 758, ISO 2719
Rapid	ASTM D 3228, ASTM D 3243, ASTM D 3278, IP 303, ISO 3679, ISO 3680

High Temperatures

Cleveland	ASTM D 92, ISO 2592

Highest Temperatures

Auto-ignition	DIN 51 794, ASTM E 659

The Abel, TAG, Pensky-Martens and Cleveland methods determine the point of ignition by increasing the temperature of the sample and applying the igniter.

The Rapid Flash Test can quickly determine if a flash point occurs below or above a specific temperature, but does not find the actual flash point.

The Auto-Ignition System works at extremely high temperatures. The hot surfaces and air inside the container cause the ignition of the sample.

Fig 3. Petrotest TAG 4:
Automatic TAG Closed Cup
Flash and Fire Point Tester
Suitable for fuels and diesel,
featuring an automatic barometric pressure correction and safety shut off.
Methods: ASTM D 56 - IP 304

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Temperature Gradients

As gradients are specified in the standards, fully automatic instruments with automatic gradient control are superior to manual methods.

The gradients are specified as follows:

Instrument	Gradient
Abel	1°C / min.
TAG	1°C / min.
Pensky-Martens	5.5°C / min. *(ASTM method A)* 1.5°C / min. *(ASTM method B)* 3.5°C / min. *(DIN)*
Cleveland	5.5 °C / min.
Rapid test	0 °C / min. (no gradient)

Fig 4. Petrotest ABA 4:
Automatic Abel Flash Point Tester featuring Peltier elements for flash point measurements down to -20°C.
Methods: IP 170 - IP 304 - ISO°1523 - NF M 07-011 - NF T 06-009

Flash Point Detection System

Flash point detection systems operate on the basis of one of the following: pressure deviation; temperature deviation; light effects; ionization effects.
Open cup methods such as the Cleveland use ionization systems for safety.

Closed cup systems such as Abel, TAG and Pensky-Martens detect the significant rise in temperature at the moment of ignition. This has proved reliable in practice.

Open cup methods such as the Cleveland use ionization systems for safety.

Fig 5. Petrotest PMA 4:
Automatic Pensky-Martens Flash Point Tester
featuring search mode for extremely quick determination of provisional flash points.
Methods: ASTM D 93 A+B - IP 34 - NF M 07-019 - JIS K 2265 - DIN (EN) 22719 - ISO°2719

Instrument	Vapor : Liquid Ratio	Opening Time	Surface Area	Filling Depth
Rapid-Test	9.2 : 1	approx. 6.4 %	1940 mm²	1 mm
Pensky-Martens	0.7 : 1	approx. 5.7 %	1120 mm²	34 mm
TAG	1.5 : 1	approx. 6.0 %	2040 mm²	38 mm
Abel	0.5 : 1	approx. 5.4 %	2290 mm²	20 mm
Cleveland	infinite : 1	100 %	3170 mm²	24 mm

Fig 6. Petrotest RT:
Automatic Rapid Closed Cup Flash Point Tester.
Suitable for fuels, diesel and lube oils, featuring the equilibrium yes/no-test method with small-scale cups.
Method: ASTM D 3228 - ASTM°D 3243 - ASTM D 3278 - IP 303 - ISO 3679 - ISO 3680

Location

The flash point tester must be set up in a draught-free location with low ambient lighting and no flammable materials nearby. This is especially important with open cup systems. A fume hood with the fan off is probably the best solution.

Viscosity of Samples

The viscosity of the sample affects the behavior of the substance when heated. In low viscosity samples (<10 cSt) heat is transferred by laminar convection. At higher viscosity ranges (>1,000 cSt) heat transfer occurs by conduction. Both types of heat transfer can be found at viscosity ranges between the two thresholds.

Highly viscous materials may have temperature gradients of up to 10K within them. These problems are eliminated in the Rapid Test System with its small sample volume and in the Pensky-Martens apparatus as it has stirring.

It is impossible to introduce samples with a viscosity of greater than 2,000 cSt using a syringe.

Opening the cover affects flash point determination by creating turbulences that will optimize the vapor concentration for the lowest possible ignition point. In practice this is seen by the fact that ignition can occur at any point on the surface. This is the point of optimum concentration.

The drawback of opening is that ignitable vapor may escape, thus raising the flash point of the sample. Minimized openings plus a large sample volume will reduce problems occurring through vapor loss.

The question may arise that if vapor loss is undesirable why do open cup systems exist? The reason for this is that open cup systems simulate flammability in an open environment whereas closed cup systems simulate an enclosed environment such as a room.

Reference Liquids

Equipment can be re-calibrated against standard reference liquids. Materials that have been officially certified are acceptable according to ISO 9000/BS 5750 but can be expensive. Cheaper solutions for routine re-calibration are materials with works certificates or substances from chemical manufacturers produced in large batches. Flash point values given for chemicals in catalogs are for transport purposes only and should not be taken as the actual value. If these are to be used for re-calibration they should be tested using standard units initially. Samples must not be used twice as ignitable fractions will be lost.

Ignition

Very early systems would use small oil lamps with wicks or a gas flame. Gas is still accepted as the most effective method of ignition. However, several institutions have banned gas ignitions for being potentially hazardous due to the fact that the small ignition flame will go out if there is a draught.

ASTM D 93 accepts gas and electric ignition as equivalent within the 1994 revision. Therefore electric ignition can be used on a day-today basis with gas ignition available for reference.

A criticism of electric ignition is that it leads to elevated results but studies have shown a good relationship between gas and electric ignition. Differences will always exist between samples.

Temperature Sensors

Standardized thermometers such as ASTM 9C and 10C for Method D 93 are available. These are mercury filled but there is a move towards using PT-100 sensors and other non-mercury based thermometers. However, availability is currently poor.

Stirring

Stirring is useful as it prevents temperature differences from being established in the sample. The Pensky-Martens, Abel and Abel-Pensky-SIS Swedish Industrial Standard) specify stirring. Stirring will also agitate the vapor in the cup.

Heating

There is no significant difference in results when electrical or gas heating is used. However, it is doubtful whether precise temperature gradients can be achieved using gas heating, even if very skilled users are operating the equipment.

Barometric Pressure

Barometric pressure will have an effect on test results. Calculations in the relevant standards take this into account and must not be left out.

Conclusion

It is apparent from so many considerations that the true flash point cannot be determined. The standards that apply vary considerably and within each standard there are many possible factors that affect the results.

Results from different methods are not valid unless comparisons are made between a specific material, batch of material or other specific conditions.

Therefore when registering results it is necessary to mention the method used.
However, flash point testing is an important procedure for determining information relevant to safe practice.

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