The New Safety Standard
For Flash Point Testing: ASTM D 7094

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Several ASTM standards cover the determination of the flash point of petroleum and petroleum products. ASTM D 93A is an important method for the specification of Diesel and aviation turbine fuels. 70 mL of a sample are heated in a closed cup with a predetermined temperature rate. A test flame is lowered into the vapor space at regular intervals to observe a flash, the so called 'Closed Cup Flash Point'.

Strict safety regulations in refinery laboratories speak against using open flames close to highly flammable liquids. The quest for a safer flashpoint method was a challenging task for instruments manufacturers.

This new method operates with a small continuously closed cup, an electric arc and smaller sample size, reducing waste and turnaround time. Now there is a portable, rugged and fully automated apparatus on the market. And even for contaminated samples there is no bias between the new ASTM D 7094 and D 93A.

Several ASTM standards for the determination of the flash point of petroleum and petroleum products exist. An important method is ASTM D 93 Procedure A because it has to be used for the specification of Diesel and aviation turbine fuels.

ASTM D 93 is called 'Pensky-Martens Method', after the two German chemists who developed this flash point method and apparatus in the 19th century. This traditional closed cup method requires heating of 70 mL of a sample at a predetermined temperature rate. A specified test flame or a glowing wire is lowered into the vapor space of the briefly opened test cup at regular intervals. Then the temperature at which a flash is observed is recorded as the so called 'Closed Cup Flash Point'.

Because of the strict safety regulations in refinery laboratories, the use of an open flame in combination with highly flammable liquids is a major safety issue for the petroleum industry. The request for a safer flashpoint method was a difficult challenge for petroleum instruments manufacturers. It took until 1999, when a new method was published under the designation ASTM D 6450-99.

This new method uses only 1 mL sample in a continuously closed sample cup. It uses an electric arc ignition instead of an open flame, introduces air into the closed test chamber by means of a pump. The flash point is detected by an increase in pressure in the test chamber. The heating rate is the same as in D 93A. ASTM D 6450 is also known as the Continuously Closed Cup Flash Point method (CCCFP). This method offers other significant improvements: the much smaller sample size leads to less waste, cleaning is easier, the turnaround time is reduced significantly and that together offers the possibility to manufacture a portable, rugged and fully automated apparatus.

An interlaboratory study was conducted in 1997 (RR:D02-1464). The sample set consisted of three pure chemicals, one pure hydrocarbon, three fuels, and three lubricating oils. The samples were tested according to method D 93A as well as according to the proposed new method that later became D 6450.

This study showed a fair agreement between ASTM D 93A and the proposed method. The repeatability and reproducibility of D 93A in this study was significantly worse than the published values. Based on the results of this study, the repeatability and reproducibility of the new CCCFP method were derived, and the method was later accepted and published as ASTM D 6450-99.

It later turned out that for samples that were contaminated with small concentrations of material with a much lower flash point (e.g. diesel with small amounts of gasoline or lubricating oil containing diesel fuel), D 6450 results were higher than results obtained by test method D 93A. The observed differences were, depending on the nature and concentration of the contaminant, up to 8°C.

The manufacturer of the D 6450 apparatus informed ASTM about this offset in 2000. They reported on research to find modifications to the D 6450 method in order to reduce the bias between D 6450 and D 93A even for such contaminated samples.

Above - Continuously Closed Cup Flash Point Tester MINIFLASH FLP (ASTM D 7094 & D 6450) from the Austrian manufacturer of automatic petroleum testing equipment GRABNER INSTRUMENTS (www.grabner-instruments.com)

The Task Group on CCCFP was therefore not disbanded.

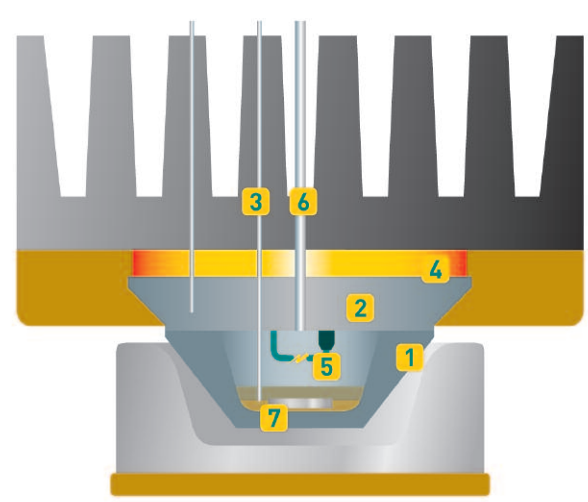
In December 2000, data were presented that suggested that with a change of some parameters in D 6450, the difference to D 93 results for contaminated samples could be eliminated.

Based on the results of a preliminary study, the ASTM Flash Point Task Group decided to conduct an interlaboratory study to generate data that would serve as a basis to decide if D 6450 should be modified. It was agreed that the sample set shall include contaminated fuels and lubricating oils and that the samples shall be tested using D 6450-99, D 93A, and the proposed modified CCCFP method, later published as ASTM D 7094.

SAMPLE SET DESIGN

The sample set consisted of 15 samples:
Jet A(1)
Jet A(2)
Diesel(1)
Diesel(2)
Diesel(3)
Lubricating Oil (1)
Lubricating Oil (2)
2-Stroke Oil
Anisole
Jet A(1) w/ 0.25 V% gasoline
Jet A(2) w/ 0.4 V% gasoline
Jet A(2) w/ 2.0 V% biodiesel
Diesel(2) w/ 0.3 V% gasoline
Diesel(1) w/ 0.5 V% gasoline
Lube Oil(1) w/ 3 V% diesel

TABLE 1 Sample Set



Above - ASTM D 7094 MEASURING PRINCIPLE
The Ni-plated aluminum cup (1) with a capacity of 7 mL containing the 2 mL sample in the temperature controlled oven (2), test-chamber closed with a metal to metal seal. Thermocouple (3) is immersed to measure temperature of the sample. The oven temperature is set with Peltier elements (4) and air cooled heat sink. The vapor is ignited by a controlled arc (5). At the flashpoint, the spontaneous pressure increase inside the chamber is detected by a pressure transducer (6). A rotating magnet and a small magnet (7) in the sample provide proper stirring.

The contaminated samples were prepared by adding the respective percentages of the contaminant volumetrically to the pure samples contained in large drums.

The samples were homogenized by rolling the sample containers. After that, samples were filled in 250 mL glass bottles.

Each of the 9 participating laboratories received three 250 mL bottles of each sample, one for each method so that each method could be run on a fresh sample.

PRECISION

The precision data were calculated by Richard M. Stanley, Chevron Information Tech Co.

Precision for ASTM D 93A Pensky-Martens method:

The distributions of results for both lubricating oils and for the jet A with biodiesel were distinctively bimodal. Hence these samples were considered to be outliers and have been eliminated.

The precision estimates from the remaining sample set are:

Repeatability r = 4.1 °C

Reproducibility R = 6.9 °C

Compared to the published reproducibility of 0.078 times the flash point in °C, the precision for D 93A estimated from this test program is larger for all samples except one (Lube oil 2).

Precision for the modified CCCFP method ASTM D 7094:

Repeatability r = 4.1 °C

Reproducibility R = 5.5 °C

If the two lube oil samples are eliminated form the analysis, as was the case for the precision estimate of D 93A, the precision becomes better: r = 3.8°C and R = 5.4°C.

Repeatability r = 3.8 °C

Reproducibility R = 5.4 °C

Comparison to ASTM D 93A

The comparison between the different flash point methods used in this test program was performed by Richard M. Stanley, Chevron Information Tech Co., according to ASTM D6708, "Standard Practice for Statistical Assessment and Improvement of the Expected Agreement Between Two Methods that Purport to Measure the Same Property of a Material".

The range for these comparisons is restricted from about 40°C to about 145°C because the two samples with a higher flash point, the two lubricating oils, had to be removed from the ASTM D 93A data set (see above).

ASTM D 7094 and ASTM D 93A Comparison

There is a small amount of sample specific bias which is random. **Based on the analysis according to ASTM D6078, no bias correction is needed.**

For the existing ASTM method D 93, the repeatability r and the reproducibility R estimated from this test program are significantly worse than the published values. This is, at least partly, explained by the large fraction of contaminated samples used in this study. It is a well known fact that samples of comparatively high flash point that are contaminated with a small amount of material of a much lower flash point are among the most difficult samples in the field of flash point testing.

For D 93A, however, the two samples with a high flash point of 200°C and above had to be eliminated from the data analysis because of a bimodal distribution of the results. Since these samples were pure lubricating oils, contamination cannot account for this behaviour.

SUMMARY

The data from the interlaboratory study group indicate that for pure fuels, oils, and chemicals, method D 6450-99 show results that are very close to the results obtained by method D 93A. For the test samples that are contaminated with small amounts of material of significantly lower flash point (diesel with gasoline, jet with gasoline, lubricating oil with diesel), the results obtained by method D 6450 are higher than the D 93A results.

The modified CCCFP method ASTM D 7094 that is similar to D 6450 but uses different test parameters gives results in close agreement to D 93A for pure fuels, oils, and chemicals, like D 6450. But also for the contaminated samples, the results obtained by D 7094 show no bias to D 93A.

In fact, the analysis according to practice D 6708 showed that, on the basis of the sample set used in the interlaboratory study, no statistically significant bias is observed between the methods ASTM D 7094 and D 93A.