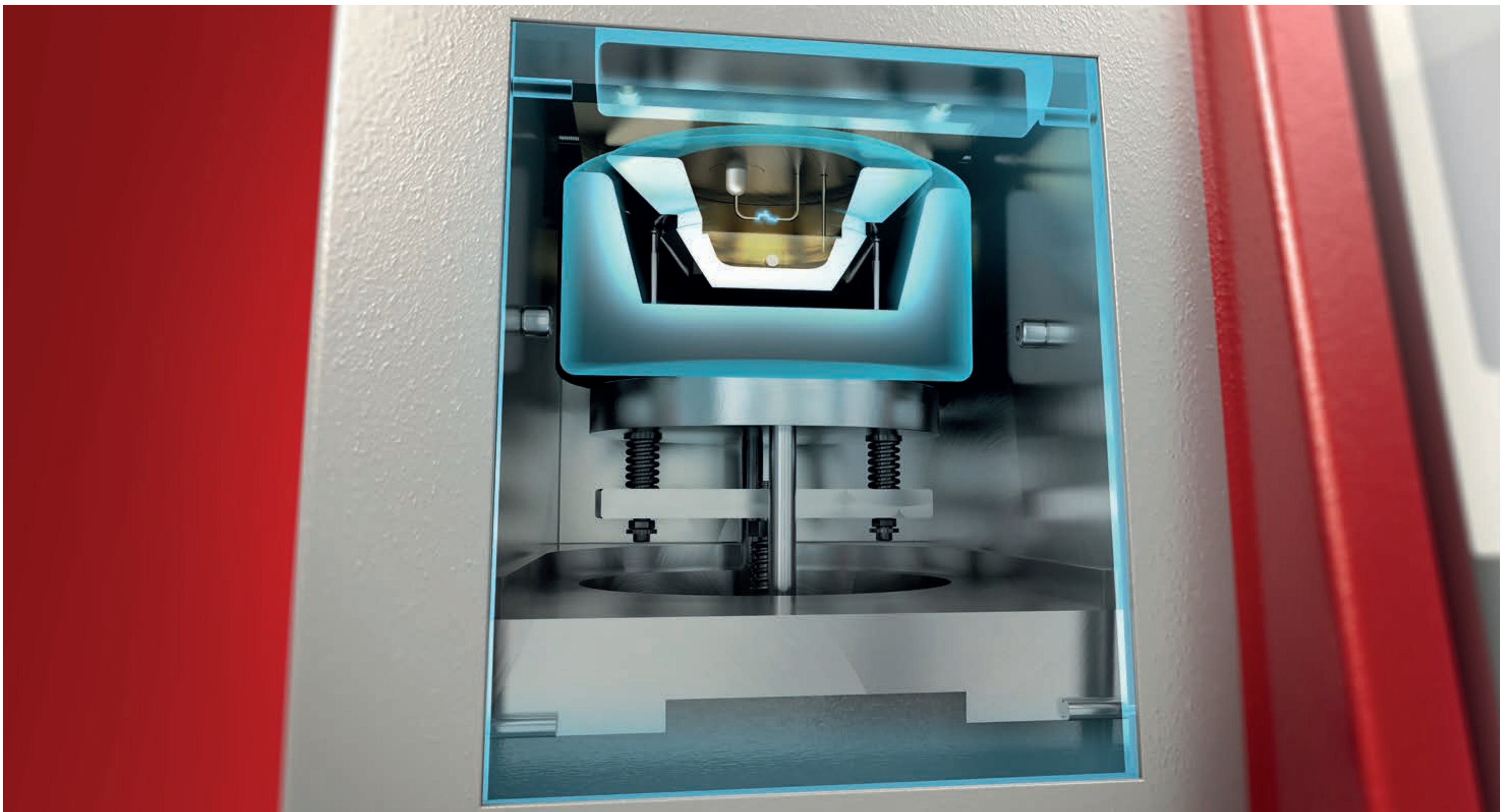

# ASTM D7094 – THE MOST PRECISE METHOD FOR CLOSED CUP FLASH POINT TESTING

## Introduction

**The flash point of a compound is regarded as the prime safety parameter for a flammable material and is used for the classification of hazardous material in shipping and safety regulations. The lower the flash point, the more ignitable a compound. This parameter describes the dangers associated with the storage, transport and the general use of flammable materials, like fuels, oils, chemicals, fragrances, paints, and waste. For diesel and aviation turbine fuels, the flash point is considered a key quality parameter, and for used oils, the flash point is an easy and accurate way to measure fuel dilution.**

**Due to its importance, a wide variety of flash point methods have been developed over the years. Recently, the newest flash point method, ASTM D7094, underwent a large interlaboratory study (ILS) to determine the precision for contemporary fuels and blends as well as chemicals. The results presented in the research report RR-D02-2086 showed that ASTM D7094 has the best precision of all available flash point methods.**

## Development of modern flash point methods

By definition, the flash point is "the lowest temperature at which vapors of a material will ignite, when given an external ignition source."

The simplest technical implementation of this definition lead to the invention of the Pensky-Martens flash point tester over 150 years ago. In this method, a large amount of sample (75 mL) is kept in a container, where the temperature is ramped from ambient towards the flash point. In regular temperature intervals, a lid is opened, and the vapors of the sample are exposed to an open flame. If the sample ignites, as visually detected by the eruption of a flame, the flash point has been reached at the current temperature. If no flame is detected, the lid is closed, and the sample is heated until the next ignition.

The Pensky-Martens method was later made into a standard test method known as ASTM D93 (equivalent to EN ISO 2719) and this method is known as a closed cup flash point method. Note that the "closed cup" only refers to the state of the cup between the ignitions (in contrast to the "open cup" like ASTM D92); during the ignition the sample is exposed to an ignition source like an open flame. With time, various other flash point methods based on the closed cup design were developed like ASTM D56 (TAG), EN ISO 13736 (Abel) and ASTM D3828.

The combination of hot flammable materials and open flames makes closed cup flash point methods like ASTM D93 one of the prime fire hazards in petroleum testing laboratories. Well aware of these dangers, the US Navy commissioned the development of an inherently safe flash point testing method in the 1990s to be used on its fleet. The aim was to develop a superior flash point method to overcome the deficiencies of available methods, which meant no open flame, a minimum sample size and a significantly shorter measuring time than the existing methods.

Based on this premise, the modified continuously closed cup flash point method (MCCCFP), ASTM D7094, was developed with safety and efficiency in mind. In this newer method, 2 mL, rather than 75 mL of sample is kept in a temperature-controlled chamber where two electrodes initiate an electric arc at regular temperature intervals to attempt to ignite the sample's vapors. When ignited, the flash point is detected via a sudden rise in chamber pressure. Due to the internal electrodes, the entirety of the test remains continuously closed, eliminating the possibility of an open flame. The small sample volume reduces cleaning efforts, waste, and the thermal management, makes ASTM D7094 twice as fast as the ASTM D93 method[1].

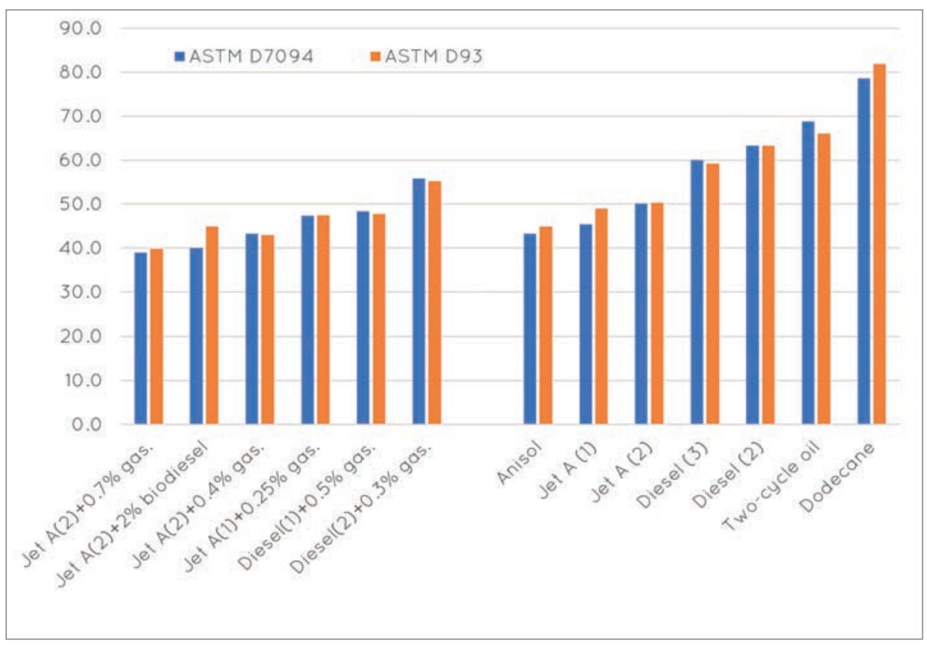


*Figure 1: Average reported flash points for ASTM D7094 and ASTM D93 from RR-D02-1581.*

## Precision of flash point methods

The flash point is a critical property of a material, but is not a static constant, meaning that the results change based on the conditions present. The dynamic nature of flash points means that it is a method defined parameter. For such method defined parameters, adherence to a standardized test method is required to ensure consistent results and the accuracy of the reported values.

International standardization organizations, like ASTM or ISO, publish standardized test methods for a variety of flash point testing. Today a wide range of flash point methods are available ranging from the traditional closed cup flash point methods, like ASTM D93 (Pensky Martens, EN ISO 2719) and ASTM D56 (TAG) to the more modern, inherently safe ASTM D7094 (MCCCFP), published first in 2003.

When new methods are developed, standardization organizations arrange interlaboratory studies (ILS) to gauge the precision of a method, and the relative bias the new method has to other methods when measuring the same parameter. While the traditional methods often have poorly documented precision, modern methods are heavily scrutinized before publication and adaptation into product specifications.

Shortly after its creation, an ILS was conducted in 2004[2] to establish the precision of ASTM D7094 and to determine the relative bias to ASTM D93. This program investigated both pure and contaminated fuel and oil samples and a summary of the reported results is shown in Figure 1. Based on statistical evaluation according to ASTM D6708 of the two methods, it was concluded that "there is no statistically significant bias between these two methods". Unlike other flash point ILSs, half of the samples in RR-D02-1581 were neat samples spiked with either gasoline or biodiesel (i.e. contaminated samples). Even though the data clearly showed that the precision for the contaminated samples was worse than for the neat samples (~30%), a pooled precision statement for all types of samples was developed and published.

Further ASTM ILS programs using ASTM D7094 were carried out in 2013 for Diesel and Diesel/Biodiesel blends[3] and in 2020 for aviation turbine fuel[4]. The latter was a Multi Method Study (MMS), where several flash point methods were compared on a sample set of aviation turbine fuels.

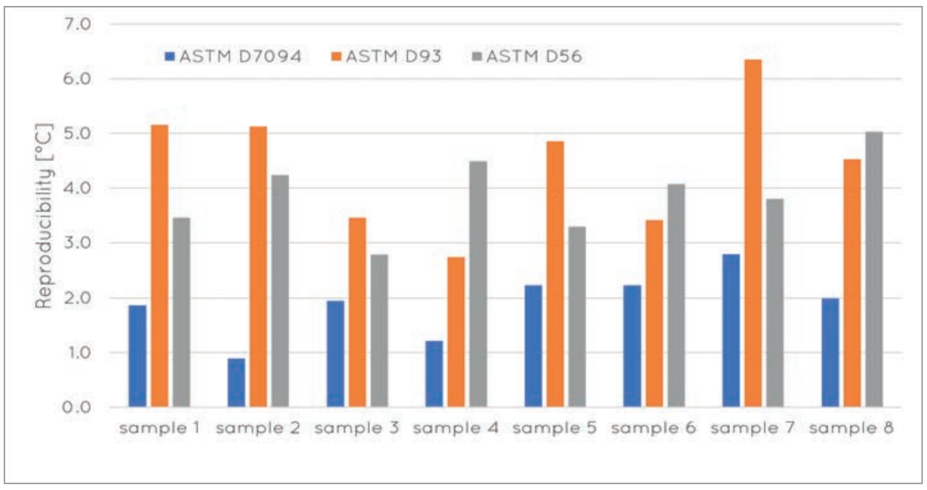


*Figure 2: Reproducibility for jet fuels as reported in research report D02: 2020 for ASTM D56, ASTM D93 and ASTM D7094. The reproducibility was calculated as 2.82 times the sample reproducibility standard deviation.*

Figure 2 shows the reproducibility for ASTM D56, ASTM D93 and ASTM D7094. In this study ASTM D7094 demonstrated a factor of 2 better precision as compared to the other flash point methods. It is worth noting that in this study, ASTM D93 produced precision data that was significantly worse than the values in the published method by about 50%.

In 2022, the most extensive ILS program of any flash point method to date was carried out with commercial fuels, involving 20 laboratories and 25 different liquids according to ASTM D6300. This resulted in a total of around 1000 measurements being taken to establish new precision data for ASTM D7094. A detailed research report is available from ASTM under RR-D02-2086[5]. RR-D02-2086 represents the most comprehensive flash point ILS covering all temperatures and materials encountered in flash point testing including aviation turbine fuels, diesels, renewable diesels, diesel-biodiesel blends, synthetic aviation turbine fuel, lubricating and turbine oils as well as off spec products and chemicals.

Figure 3 shows the flash point temperature ranges of each fuel specification and the corresponding reproducibility of the new D7094 (MCCCFP) and the historical D93 (PM)[6] methods. The better reproducibility of ASTM D7094 is clearly visible over the entire temperature range and especially at higher temperatures, where lubricants are typically measured. The difference in precision at these higher temperatures is more than a factor 2.

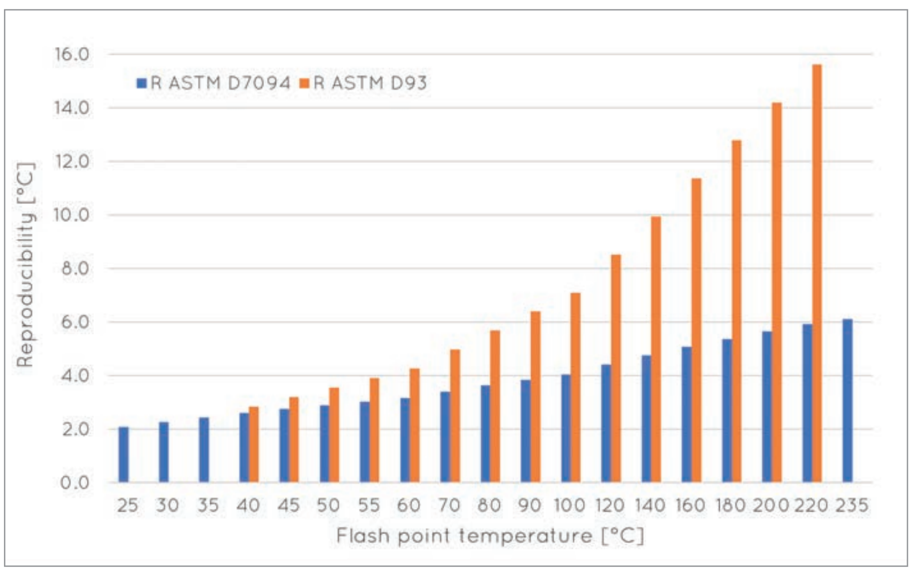


*Figure 3: Reproducibility for ASTM D7094 as reported in research report RR-D02-2086. The corresponding values for ASTM D93 were obtained from ASTM D93-20.*

Figure 4 shows the comparison of ASTM D7094 to ASTM D56[7] in the relevant temperature range. Also here, the published reproducibility is significantly better over the entire temperature range.

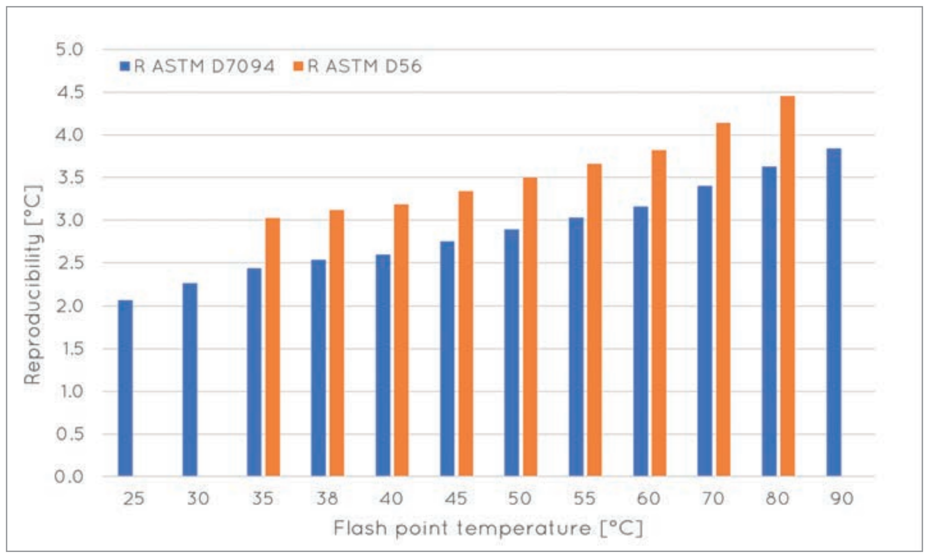


*Figure 4: Reproducibility for ASTM D7094 as reported in research report RR-D02-2086. The corresponding values for ASTM D56 were obtained from ASTM D56-22.*

Over the course of about twenty years since ASTM D7094 was introduced, four major ILSs have corroborated the findings that D7094 is the more precise and reproducible flash point test method. The superior reproducibility of ASTM D7094 compared to other flash point methods is summarized in figure 5, which compares the precision of various flash point methods for typical product types including fragrances, aviation turbine and diesel fuel as well as lubricants. As the traditional close cup methods generally are not able to cool the sample below ambient, it is not able to measure the very low flash point of the fragrances.

| Material | Flash Point (°C) | ASTM D7094 R (°C) | ASTM D93 R (°C) | ASTM D56 R (°C) |
|---|---|---|---|---|
| Flavors & Fragrances | 23 | 2.0 | N/A | N/A |
| Jet Fuels | 40 | 2.6 | 2.8 | 3.1 |
| Diesel Fuels | 60 | 3.2 | 4.3 | 3.8 |
| Oil | 200 | 5.6 | 14.2 | N/A |

*Figure 5: Reproducibility for selected flash point methods. For ASTM D7094 the values were obtained from research report RR-D02-2086. The corresponding values were obtained from ASTM D93-20 and ASTM D56-22 respectively.*

The vast amount of published precision data from various ILSs confirms the reliability of ASTM D7094 compared to other flash point methods. As a relatively new method, it is listed in many, but not all, relevant product specifications largely due to the corporate lean towards traditional methods despite a plethora of evidence supporting the adoption of newer, safer methods. However, it is important to note that in most product specifications, the obsolete and dangerous, open-flame manual method still persists as the referee method. In these cases, an automatic D93 test with glowing wire ignition and secondary safety features is no more a referee method than the safer and faster ASTM D7094 alternative.

## Summary

The ASTM D7094 flash point standard was developed to overcome the deficiencies of traditional flash point methods and has established itself as the most advanced standard with the best benefits on the market. Its superior precision has been consistently proven since its introduction, and its safety features surpass all other conventional flash point methods.

eralytics eraflash flash point testers fully comply with ASTM D7094 and offer exceptional accuracy over a wide temperature range, even when analyzing contaminated samples. Their inherently safe design with no open ignition source eliminates the risk of fire hazards in the laboratory environment. Thanks to the PBT® (Peltier Boost Technology), these analyzers work twice as fast as conventional methods, e.g. ASTM D93. In addition, eralytics' flash point testers require only 2 mL of sample, which minimizes waste and significantly speeds up both cleaning procedures and thermal regulation.

[1] *https://eralytics.com/wp-content/uploads/ERAFLASH-Efficiency-through-maximum-safety-and-measuring-speed.pdf*

[2] *The research report RR-D02-1581 can be requested via service@astm.org*

[3] *The research report RR-D02-1880 can be requested via service@astm.org.*

[4] *The research report RR-D02-2020 can be requested via service@astm.org.*

[5] *The research report RR-D02-2086 can be requested via service@astm.org.*

[6] *https://store.astm.org/d0093-20.html*

[7] *https://store.astm.org/d0056-22.html*

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