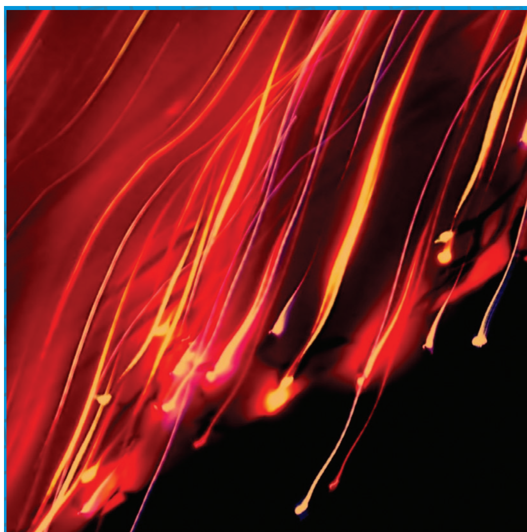

ASTM D7094 - Modified Continuously Closed Cup Flash Point Standard Accepted as a Safe Alternative Method in Various Fuel Specs

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The December 2013 ASTM meeting of the D02 committee marked the turning-point for flash point testing. In this historical meeting, the safer ASTM D7094 flash point standard was officially accepted for the following fuel specifications: Fuel oils (D396), Diesel fuel oils (D975), gas turbine fuel oils (D2880), and kerosene (D3699). From now on, not only the dangerous and outdated ASTM D93 Pensky Martens test is allowed. Instead, you can specify your fuel with this continuously closed cup flash point (CCCFP) method which completely eliminates the risk of fire in your lab. Even if you happen to measure gasoline as a diesel sample by mistake, the small 2ml sample volume and the limited available oxygen make sure that the process remains safe. Using the traditional method, such a mistake would inevitably lead to an explosive flame and 75ml of burning gasoline in a Pensky Martens tester. With a CCCFP tester there are no hazardous consequences at all. The additional benefits of the small sample volume are shorter turnaround times and the fact that this makes flash point testing safer and more economical than ever before.

The History of Flash Point Testing

The flash point defines the lowest temperature at which a liquid forms a vapor / air mixture that can be ignited by an external ignition source. Therefore the flammability of a liquid is categorised by its flash point since the early 19th century. The measurement of the flash point can follow two different basic principles: "open cup" or "closed cup" testers and methods are available. Nowadays the closed cup testers are often preferred since their results are more precise and typically yield lower flash points, which are considered safer, than open cup methods.

Over 100 years ago the two traditional closed cup flash point methods ASTM D56 (TAG method) and D93 (Pensky Martens method) were developed. Both methods require a sample volume of 70-75ml of sample to be heated. At individual temperature steps the closed cup is opened and an open flame or glowing wire ignitor is lowered into the headspace of the sample to ignite the vapor/air mixture. This procedure is repeated until the flash point is reached. A newer method called "small scale closed cup" method shares the same measurement principle but uses a smaller sample volume. However, this ASTM D3828 method is a flash/no-flash method only performing one measurement at a specific temperature and therefore does not give an exact flash point as the result.

In 1999 the ASTM committee published the first continuously closed cup flash point method (ASTM D6450), which uses only 1ml of sample. However, a round robin test (RR-D02-1464) showed that a statistical bias between ASTM D93 and ASTM D6450 exists. This led to the development of the modified continuously closed cup flash point method (MCCCFP) ASTM D7094 which was published in 2004. Currently ASTM D7094 marks the transition of traditional flash point testing towards a faster, more reliable and safer test method.

Continuously Closed Cup Flash Point Methods

These modern flash point methods feature an enclosed sample volume which is not opened during the whole measurement procedure. This is possible since the sample cup, containing only 1 or 2ml of sample, is pressed against the oven plate forming a closed volume. The necessary sample temperature sensor, as well as the ignition electrodes, are incorporated directly into the oven plate. During testing the sample volume is heated by the oven plate transferring its heat onto the sample cup and further on to the sample. At each testing temperature a spark is ignited by the electrodes inflaming the vapors above the sample. A flash point is detected if the pressure increase due to the burning vapors inside the chamber is greater than 20 kPa. Any burning vapors are extinguished automatically just a few milliseconds after their ignition due to the significantly small volume of oxygen inside the measurement volume. Therefore using a CCCFP flash point tester eliminates all safety concerns in modern labs.

The main difference of ASTM D7094 compared to ASTM D6450 is a larger sample volume of 2ml. The second change made to ASTM D6450 is that fresh air is introduced into the sample cup after each ignition depending on the sample temperature. For ASTM D6450 air was introduced independently from the current sample temperature whereas for ASTM D7490 the air volume increases with higher sample temperatures. These two changes resulted in a CCCFP method that was found to have equal results compared to the Pensky Martens technique.

Comparison of ASTM D93 and ASTM D7094

For the comparison of the new MCCCFP method with the ASTM D93 method a large round robin test (RR-D02-1581) was conducted, which results were published in 2004. For this test pure and contaminated diesel fuel and jet fuel samples were measured together with Anisol and Dodecane as pure chemicals. For the higher flash point region lubricating oil samples were selected. All in all the data set realistically represented the current range of flash point samples that most facilities encounter during testing. Each sample was measured by at least eight different labs using ASTM D93 or D7094. Figure one shows selected results of the original data set in the lower flash point range.

Generally speaking both methods exhibited a few outliers throughout the dataset. After eliminating those outliers the results spread is a little smaller for ASTM D7094.

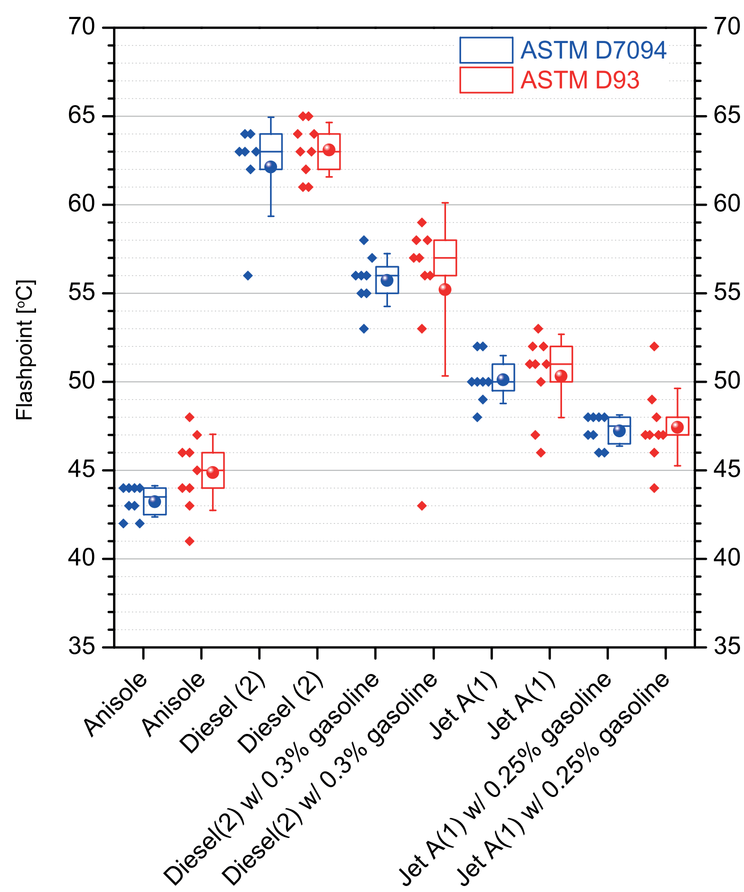

Figure 1: Comparison of the round robin data comparing ASTM D7094 and ASTM D93. Each diamond denotes the result of one lab. The spheres give the average of the according measurements with the standard deviation as the error bars. The boxes show the meridian together with the 25% and 75% percentiles.

The picture, however, changes for the higher temperature range as shown in figure 2. The ASTM D93 method exhibited inconsistent results for lubricant-type samples. The obtained dataset was statistically analysed by ASTM statisticians resulting in the removal of the lubricant samples for the calculation of the repeatability and reproducibility values of the different methods. The obtained precision statements are summarised in table 1 and were published as the official values for the ASTM D7094 standard.

Table 1: Summary of r,R values obtained from the RR-D02-1581 round robin test

	ASTM D93	ASTM D7094
Repeatability (r)	4,1°C	4,1°C
Reproducibility (R)	6,9°C	5,5°C

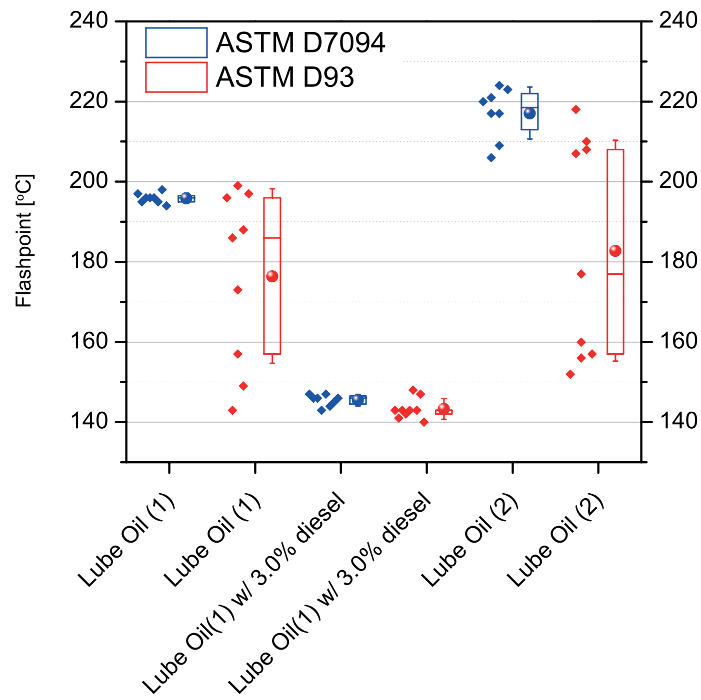

Figure 2: Round robin data for the higher flash point region.

The ASTM statisticians concluded that "a small amount of sample specific bias" was detected "which is random" and does not need to be corrected between the two methods. The second important conclusion from this large round robin test is that the actually stated r,R values of ASTM D93 in the standard itself overestimate the repeatability and reproducibility of samples modern fuel testing labs are facing. Figure 3 summarises all samples evaluated during this round robin test and includes the reproducibility values obtained from the test itself as well as the calculated R values according to the ASTM D93 method. What can clearly be seen is that the new and safe flash point method always falls within the precision statement even for the smaller calculated R values of ASTM D93.

From figure 3 it can be seen that both methods deliver equal results and that there is no statistical bias observed using ASTM D7094. The obtained reproducibility for the new method was actually better than for the Pensky Martens method. This fact is of course important if results from two different labs should be compared in case of a dispute. This favourable outcome was finally recognised at the ASTM meeting in December 2013 by officially accepting ASTM D7094 as an alternative method in the following fuel specifications: Fuel oils (D396), Diesel fuel oils (D975), Gas turbine fuel oils (D2880) and Kerosene (D3699).

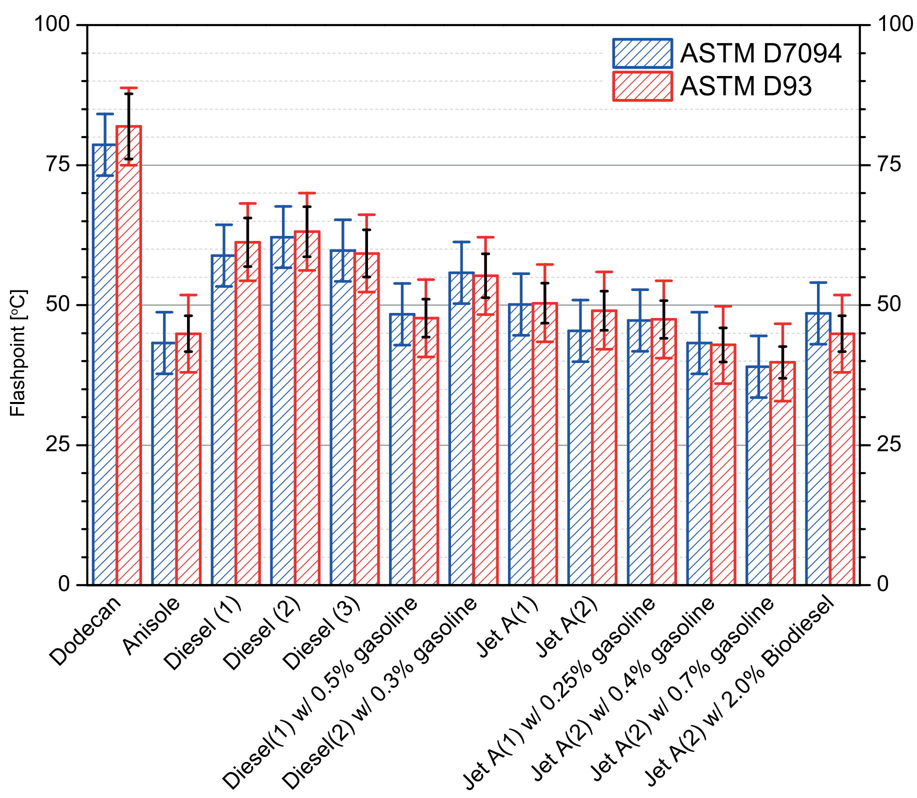

Figure 3: Average values of all participating labs of the round robin test. Colored error bars mark the reproducibility (R) values obtained from the round robin test itself whereas the black error bars show the calculated R value according to ASTM D93.

ERAFLASH - a New Era of Flash Point Testing

ERAFLASH, produced by eralytics, is a continuously closed cup flash point tester that can measure flash points according to ASTM D6450 as well as ASTM D7094. It was developed by Mr. Andreas Schwarzmann and Dr. Roland Aschauer, both long term members of the ASTM 02.08 flammability group. Their combined knowledge led to an industry-leading flash point tester that fully convinced laboratory managers of leading refineries, lube oil manufacturers and independent oil and petroleum testing organisations all over the world.

ERAFLASH uses a patented PBT – Peltier Boost Technology to cover a temperature range of -25 to 420°C (-13 to 788°F) within a single analyser. This innovative technology lifts the Peltier elements from the measurement cell as soon as a potentially harmful temperature for the elements is reached to disconnect them from the oven plate. From there on three powerful heating rods solely take over the heating. During the cool down phase the Peltier elements are pre-cooled and lowered as soon as possible to start actively cooling down the measurement cell and cup. This significantly reduces the turnaround time of ERAFLASH compared to other traditional closed cup testers.

The PBT allows ERAFLASH to cool the sample cell from 200°C to 100°C in less than 80 seconds. Even in the low temperature range, the unit can cool from room temperature to 5°C in around 100 seconds without an external cooling supply.

During heat up the Peltiers support the heating rods to allow unmatched heating rates, which is especially advantageous for high temperature samples. Starting at room temperature, 100°C is reached in less than 50 seconds and for a temperature of 200°C only an additional 70 seconds are needed.

In the past, cleaning flash point testers often took a long time and also involved replacing sensors or other elements of the analyser. With ERAFLASH this is different due to its CPT – Contamination Prevention Technology. This includes sealed ceramics and self-cleaning electrodes which minimises any required cleaning. A well designed oven plate effectively eliminates sample splashing at the moment of ignition further reducing contamination of the oven plate.

These two technologies make ERAFLASH a fast and reliable analyser which requires a minimum of cleaning and maintenance. But ERAFLASH also delivers on-spot measurement results which was proven in a very recent round robin test. Figure 4 combines results from seven different ERAFLASH instruments operated in seven labs with the reference values from ASTM D93 and D3828. The evaluation of these samples gave an excellent repeatability of 2.3°C and a reproducibility of 3.3°C for ERAFLASH.

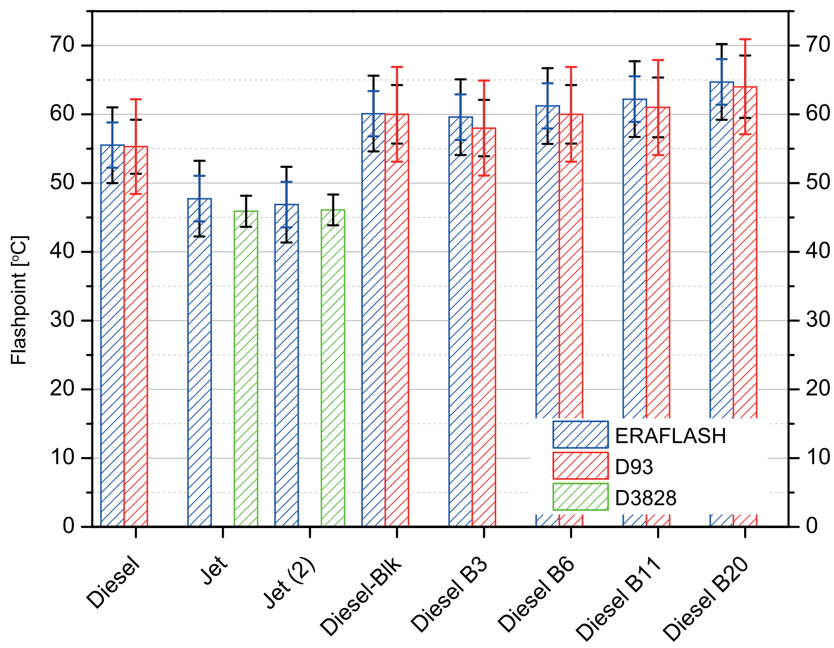

Figure 4: Average flash points of different fuel samples including Diesel/FAME blends from 3 to 20 Vol% measured with ERAFLASH using ASTM D7094 are shown together with the reference values according to ASTM D93 / D3828. The error bars state reproducibilities. For ERAFLASH the obtained values from this round robin test are plotted in blue. The red error bar for D93 is the R value obtained from RR-D02-1581. Black error bars give the published R values from the according standards.

Conclusion

With its move in December 2013 ASTM finally paves the way for a new era of safe flash point testing. Now it is officially possible to specify fuels according to ASTM D7094. This effectively eliminates the need to use large sample volumes in combination with open flames in laboratories with a lot of potentially flammable samples. Not only is ASTM D7094 the safest possible way to measure the flash point of fuel samples, due to the reduced sample volume it is also faster than the Pensky Martens technique. There is no longer a need to stick with a 100 year-old technique and fuel testing laboratories can finally upgrade to the 21st century.

Figure 5: ERAFLASH analyser with the 2ml sample cup for ASTM D7094 compliant measurements

ERAFLASH by eralytics is a state-of-the-art CCCFP flash point tester that fully complies with the latest flash point methods. With its full-colour touch screen operating the analyser is intuitive and easy. In addition to the inherent advantages of CCCFP testers ERAFLASH offers fastest heating and cooling rates and an unmatched temperature range due to the patented PBT design. A fully heat insulated sample cup allows safe sample cup removal moments after the measurement; even if the flash points are above 200°C. In combination with the PBT design this helps to further reduce the turnaround time of ERAFLASH compared to other CCCFP testers significantly. The full aluminum housing and the rugged design of ERAFLASH makes it the ideal choice for stationary as well as mobile laboratories.

For more information please visit our website www.eralytics.com