MINIFLASH TOUCH

BEGINNER

Rev. 3

Contents

1. Objective of this workshop

After this training you will run routine flash point tests, be able to select the correct program for your sample and perform test measurements with reference standards. You will be able to differentiate between the two different continuously closed cup FP methods D6450 and D7094, compare them to the ASTM D93 Pensky Martens method and find out more about the screening program to assess the expected flashpoint. Finally you will explore the results screens and learn about daily maintenance to keep your analyzer clean.

Contents of this workshop are:

1. Introduction and theoretical background to FP testing (by trainer).
2. Installation & Set-up
3. Exercises
    a. How to use the MiniFlash TOUCH
    b. Repeat a CRM measurement
    c. Select and create programs
    d. Screen and measure Diesel
    e. Results Table
    f. Daily Maintenance and cleaning
4. Questions

2. Workshop preparation

Please make sure you have the following items available

1. MINIFLASH FLP (or FLPH) Touch
2. Power cable
3. Protective clothing (Gloves, Safety glasses, Lab coat)
4. Samples (Dodecane, Anisole, Diesel,…)
5. Sample package (sample cup, pipette,…)

3. Introduction and Theory

a. What is the Flash Point?

The flash point of a sample is a measure of the tendency to form a flammable mixture with air. According to ASTM the flash point is the lowest temperature corrected to a pressure of 101.3 kPa (760 mm Hg) at which application of an ignition source causes the vapors of a specimen of the sample to ignite under specified conditions of the test.

More specific the flash point of a substance can be defined as the lowest temperature, at which the substance produces a flammable mixture with air so, that a propagating flame is covering at least 75% of the substance surface.

Flash point tests are required in transport and safety regulations to define flammable and combustible materials. It is required for material safety data sheets for use in the industry to assess the degree of care that must be employed in handling materials like fuels, biofuels, chemicals, solvents, flavors and fragrances, paints, varnish, waste, used oils, bitumen & asphalt and many more.

Flash point tests can also show the presence of highly volatile and flammable materials in a relatively non-volatile and non-flammable liquid (fuel dilution of engine oil).

b. Methods for flash point tests

It is important to know that the flashpoint is not a physical constant, but depends on the method being used. Consequently the flashpoint determination is different from method to method and the definition, when a flashpoint is being reached, has been developed based on empirical evidence.

i. Manual vs. Automatic Methods

There are several standardized methods established: manual methods and automatic flash point testers.

Manual methods represent low cost versions. The user has to observe a possible flash point visually after the ignition with a flame, a glowing wire or an electric arc. The repeatability of this measurement is not very good, since visual observation is always dependent on the individual which is performing the test.

Automatic flash point testers usually consist of a heatable cup, some kind of ignition source like a flame, a glowing wire or an electric arc and an automatic flame detector like a heat sensor or a ionization detector.

The sample is heated to a starting point and afterwards the temperature is increased in a constant rate. In equidistant temperature steps (e.g. every 1°C) the vapor-air mixture in the cup is ignited, the flashpoint is automatically detected.

ii. Open Cup versus Closed Cup Methods

One of the most popular open cup methods is the ASTM D92 Cleveland open Cup method. Today it is used mainly for testing oils and lubricants. Because the cup is not closed, open cup testers suffer from constant evaporation of the flammable components during the test. This makes it slightly more unlikely that flammable vapors are being built above the sample. Tested on the same sample, the flash point measured with an open cup tester may be up to 30°C higher than the flashpoint tested with a closed cup tester. The precision of open cup testers typically is worse than the precision of closed cup testers.

Closed cup testers, like the Pensky Martens (ASTM D93), Abel (IP 170), Tag (ASTM D56) and small scale testers (ASTM D3828) open the cup only for a short time to insert the test flame and close the cup afterwards. Still there remains a risk of fire hazards, because in most closed cup methods 75 mL of sample are ignited.

Continuously closed cup testers, like the MINIFLASH, guarantee that the sample cup is never opened during the test. They use only 1-2 mL of sample.

iii. Recognition of the flash point

Another difference between methods is the different flashpoint determination. The flashpoint can be determined visually. It can be detected by a heat sensor or via a ionization detector. Automated small scale apparatus for example measure the temperature increase: If the temperature increases more than 6°C in 100 ms, then the flashpoint is reached.

The Grabner MINIFLASH method determines the flash point by the pressure increase in the closed chamber. The pressure increase depends strongly on the size of the flame: A flashpoint is reached, once the pressure in the completely closed cup is increasing beyond 20kPa.

iv. Standards for flashpoint testing

Several ASTM standards for the determination of the flash point of petroleum and petroleum products exist. An important method is ASTM D93 Procedure A because it has to be used for the specification of Diesel and aviation turbine fuels.

ASTM D93 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 75 mL of a sample at a predetermined temperature rate.

The sample is heated to a starting point and afterwards the temperature is increased in a constant rate. A specified test flame or a glowing wire is lowered into the vapor space of the briefly opened test cup at regular intervals. The temperature at which a flash is observed is recorded as the so called ‘Closed Cup Flash Point’.

The MINIFLASH method has been introduced to get equivalent results to the Pensky Martens method, but allow higher safety for the operator. The sample size is reduced, no open flame or fumes are generated, hazardous waste is minimized.

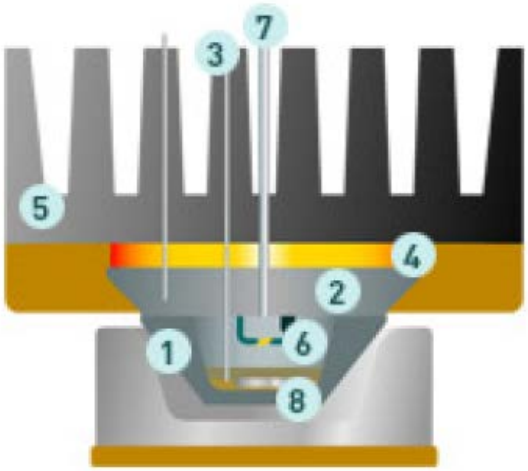
Two methods have been developed:

- ASTM D6450 uses 1 mL of sample and is being used for solvents and clean fuels.
- ASTM D7094 uses 2 mL of sample and is used for contaminated samples and lubricating oil.

After an extensive interlaboratory study the ASTM concluded, that there exists no statistically significant bias between ASTM D7094 and ASTM D93A.

v. Grabner MINIFLASH Measuring method

A Ni-plated aluminum cup (1) with a sample is resting in the sample cup holder. For the test, the sample cup is lifted to the temperature controlled oven (2), forming the test-chamber with a metal to metal seal. A thermocouple (3) is immersed into the sample to measure the temperature. The temperature of the oven is controlled by Peltier elements (4) and an air cooled heat sink (5). The vapor is ignited by a high voltage arc (6) inside the test-chamber. At the flash point, the pressure inside the sealed measuring chamber is increased significantly, which is detected by a built-in pressure transducer (7). A rotating magnet and a small magnet (8) inside the sample cup provides stirring.



4. Setup for first measurements

Preparations

1. Connect the power cable
2. Turn on the MINIFLASH TOUCH (power button on the back side)
3. Prepare the samples (e.g. Anisole, Dodecane)
4. Have 1ml and 2ml sample cups available
5. Use the pipette to fill the sample cup

5. Exercises

We will demonstrate to you how to use the MINIFLASH TOUCH instrument and we will check a CRM (certified reference material) afterwards. Please fill in your measurement results in the results list below each exercise.

a. How to use the MINIFLASH TOUCH

☐ When switched on the first time the screen shows per default two users: “admin” and “service”. Latter is for internal use only.
☐ Press “admin” to log in with administrator rights. For a new instrument there is no password set. Otherwise you are being asked to type in a password.
☐ Explore the different areas of the main screen. Please locate the three buttons (to the left of the “more …” button). These buttons show which measurement programs have been used recently.
☐ Select “Anisol” which is a CRM used for QC. It is one of the most recently used programs on any new instrument.
☐ Tip on the blank area, where you can enter a sample ID. A virtual keyboard will pop up and allows you to enter a sample name (e.g. CRM-Test 1)
☐ Fill 1ml Anisol into the sample cup.

i. Use a cool sample cup (e.g. from the refrigerator)
ii. Put the right cup firmly into the sample cup holder
iii. Take the automatic pipette and equip it with a disposable pipette tip
iv. The handling of the pipette is simple. There are two stopping points when you press down the pipette piston.
v. Try first to get the feeling. For filling with exact 1ml you have to push down to the first stopping point only. Then immerse the tip into the sample and carefully release the piston again.
vi. Push the sample into the cup. You may now you push to the second stopping point to get all sample out

vii. Take a tissue and remove all drops that may have got on the rim of the sample cup.

☐ Place the sample into the instrument. Open the flap by pushing “Press”.
☐ Slide the sample cup holder to the back of the opening until the notch on the bottom of the sample cup holder sits on the little knoll on the lift plate. Make sure not to bend the temperature probe on the top of the measuring chamber.
☐ Once the sample cup holder securely rests on the lift place, turn the holder, until the handle on the sample cup holder points outwards. This is required to make sure the lift does not get stuck when lifting the sample cup to the oven.
☐ Close the lid again.
☐ Press the “RUN” button to start the measurement. The instrument will automatically start the test once initial temperature Ti is reached.
☐ You will hear three test ignitions before the sample cup is lifted inside the instrument.
☐ Observe the temperature bars, for both, oven and sample temperature on the top of the measurement screen.
☐ For each spark (test for flash point) the flash pressure is monitored. Once the flash point is reached, the flash pressure will be suddenly very high (> 20kPa).
☐ The measurement is finished and the result is displayed.
☐ Compare the result with the calibration sheet which comes along with each instrument.
☐ Remove the sample cup. The sample can be disposed of by absorbing the 1ml with a tissue.
☐ Repeat the measurement twice with a new sample. Use a different, cooled sample cup.

	1st result	2nd result	Res. per calib	Offset
Anisol				

b. Repeat a CRM measurement

Please prepare the Dodecane CRM to practice a similar measurement like above.

- ☐ Go back to the main screen and select the Dodecane program, which can be found among the most recent three used.
- ☐ If no longer listed, press “More…” and select the Dodecane program from the program list shown. In cases the program list is longer than the available space on the screen, you can use the finger to scroll down. Use the “Back” button to the top right of the screen to return to the main menu.
- ☐ Run Dodecane twice and compare the results with the values on the instruments calibration sheet. Follow step by step the instructions from the previous example.

	1st result	2nd result	Res. per calib	Offset
Dodecane				

c. Select and create programs

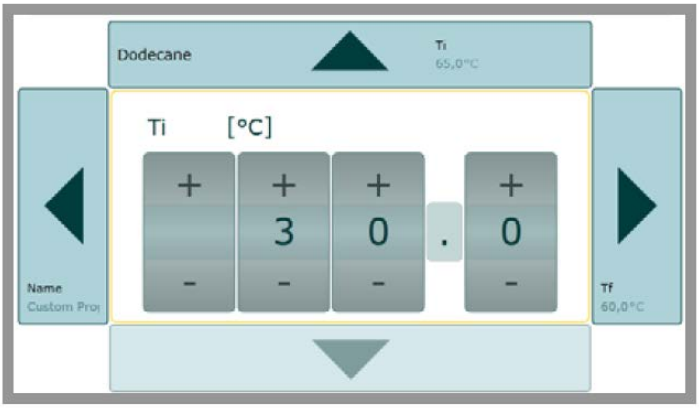
To get a correct flashpoint it is important that samples are being stored cool in a refrigerator, so that no components can vaporize prior to the test. Per standard, the manual mode of ASTM D6450 or D7094 programs should be used. In the manual mode, the oven is already heated to the starting temperature, before the test cup is inserted, which reduces evaporation prior to the test.

The manual mode is not necessary for pure substances: If these substances vaporize, the flash point will not be affected. Also Diesel has almost no volatile components, which could evaporate.

In the following exercise we will have a closer look into the settings of a program and how such settings can be changed and what influence they have on the result.

- ☐ From the main screen select “More…” to enter the program list.
- ☐ The screen is divided in two parts. The lower part gives you a summary table on all previously defined programs and their settings. The upper part allows you to navigate through this table and edit or change program settings.
- ☐ Please use the arrow key at the boarder to move up and down between different programs or left to right between different parameters of the program.
- ☐ Select the Anisol program and press the “Edit” button on the right.

☐ Set the initial temperature: According to the ASTM standard the start temperature must be 18°C below the expected flashpoint.



☐ Anisol flashes around 43°C. Reduce the initial temperature to 25°C
Set the final temperature Tf: The Tf is the temperature after which you would no longer expect a flash point to occur. Or at which you do no longer care, if a flash point is reached. Set the final temperature well above the expected flashpoint. The measurement is automatically stopped when the end temperature Tf is reached. If the end temperature is set too low the measurement can't be finished and stops with the message "no flash".
For Anisol Tf is set to 90°C per default.

☐ Ti-T: Especially for samples where the Ti is set at or ambient temperatures, it is recommended to offset the oven temperature from the initial temperature. For Anisol Ti-T is set to 5°C so the oven or in this case the peltier elements will cool the system down to 5° lower than the Ti. It helps to keep the sample cooled.

☐ In between you can select the Standard. Make sure the Anisol program is set to ASTM D6450. Instead of "automatic", activate "manual".

☐ Finally run another Anisol test. Because you have set the method to manual, you can start ("RUN") the measurement and now use the time until the system cools down to fill your sample in a cooled sample cup. The instrument will ask you to insert the sample cup once Ti is reached. Insert the cup and press "Continue".

☐ Compare the result with the previous runs, observe the different behaviour of the procedure.

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FP Anisol: _____ °C

d. Screen and measure Diesel

- ☐ Navigate back into the “edit” mode of the programs screen.
- ☐ Press the “New…” button and name the new program “Diesel”
- ☐ Diesel has an expected flash point of around 65°C which would require us to set the initial Temperature to Ti=47°C. We assume that we do not know the expected FP and therefore start with Ti=30°C
- ☐ As Tf please set 100°C
- ☐ For the method we are now selecting D6450SCR. This means all parameters are selected as per ASTM standard D6450, but in the screening program the heat rate may be higher than the standard 5.5°C/min.
- ☐ Select the heat rate 10°C/min.
- ☐ Set a Ti-T of 3°C
- ☐ Now run this new program with 1ml of Diesel fuel.
- ☐ Now that you have a rough FP for this Diesel, the expected FP.
- ☐ Modify the program so that Ti is selected 18°C below and change the standard from D6450SCR back to D6450.
- ☐ Repeat the test.
- ☐ Finally, let’s see if there is a difference to D7094.
- ☐ Please modify the “Diesel” program and select D7094 as method.
- ☐ Use the 2mL cup to measure 2ml Diesel according to ASTM D7094.

	D6450 SCR	D6450	D7094
Diesel FP			

e. Explore the results table

In this exercise we will look into the results.

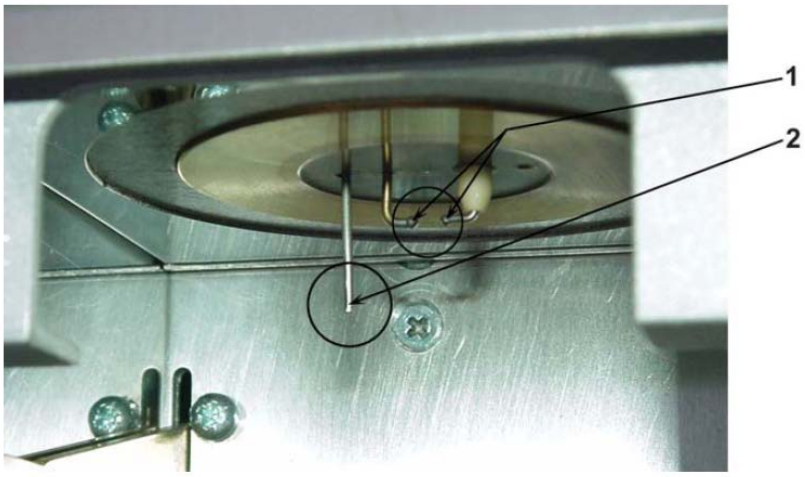
- ☐ From the main menu as well from the measurement menu, you will always see the last two results in the lower part of the screen.
- ☐ You can press the “Show All” button to open the results list screen.
- ☐ If you select a specific result, it will be highlighted and you will be able to see measurement parameters in the window on top of the results list.
- ☐ Select a recent measurement and press detail.
- ☐ In this screen the flash pressure profiles pz-listing and pz-curve illustrate the increase of the flash pressure during the test. You can see that the pz-value increases slowly until the flash point is reached at >20kPa pressure.
- ☐ Next explore the flash pressure profiles for the D6450 Diesel result.
- ☐ With the result highlighted enter the details and select the “Analysis” tab. It will take a while until all the profiles are loaded from the data.
- ☐ Scroll to the very end to check the last profile, when the flash point was reached.
- ☐ For a high quality Diesel this profile must be pointy and narrow, indicating a high ignition quality.
- ☐ Leave the results, press “Back” to return to the main screen.
- ☐ Press on the “Menu”-button on the top right side of the screen.
- ☐ Enter the settings menu. Here you can set your language and different measuring units. You can also select, if the instrument should display the results corrected to the ambient pressure (default).
- ☐ Press on “corrected” to deselect the correction to barometric pressure. The results will automatically be recalculated.
- ☐ Go back to the results screen and observe the difference.
- ☐ Note below for the last result the corrected and uncorrected value. How can you easily differentiate between them?

	Corrected FP	Not corrected	Difference
Diesel FP			

f. Daily Maintenance and Cleaning

Finally, let's perform some simple but important maintenance steps to ensure continuing good results and longer life time and service intervals.

- ☐ Clean the surface of the oven plate well with a tissue
- ☐ **Do not scratch**. The surface must be free of residuals and scratches for good heat contact.
- ☐ Do not bend the temperature sensor (2) and the arc pins (1).
- ☐ Clean the arc pins (1) carefully with the brass brush (cleaning the arc pins is necessary to remove deposits and assure a smooth, repeatable spark).



- ☐ Check also that the little hole on the oven surface, used for the air supply is not blocked by sample. A dental mirror may be useful for this check.
- ☐ Finally for storage and transport, insert some polystyrene into the measuring chamber, to prevent the lift plate from moving.
- ☐ Switch off the instrument. It can now be stored.

ATTENTION: Never switch off the tester when the oven is still hot after a test. Please let the oven and the instrument cool down to room temperature before switching off to prevent overheating of the Peltier elements.

6. Questions

1. ASTM D7094 is equivalent to ASTM D93A Pensky Martens method:
   - ☐ Yes
   - ☐ No

2. Flashpoint is no physical constant. Which parameters affect the flashpoint?
   - ☐ Open or closed cup
   - ☐ Sample type
   - ☐ Flash Detection Method
   - ☐ Automated or manual method
   - ☐ Cooling rate of the analyzer

3. Flashpoint tests are being used for
   - ☐ Air pollution control
   - ☐ Trace analysis
   - ☐ Transportation regulation
   - ☐ Material Safety Data Sheets
   - ☐ Combustion Detection

4. The flashpoint is the lowest temperature, at which
   - ☐ a flame ignites a liquid
   - ☐ a flame covers half of the surface of a liquid
   - ☐ sample vapors form a flammable mixture with air
   - ☐ the sample sustains burning for more than 5 seconds

5. If 50% Diesel is mixed with 50% of a substance of higher volatility
   - ☐ the flashpoint increases
   - ☐ the flashpoint does not change
   - ☐ the flashpoint decreases

6. If 50% Diesel is mixed with 50% of a substance of lower volatility
   - ☐ the flashpoint increases
   - ☐ the flashpoint does not change
   - ☐ the flashpoint decreases

7. With the Grabner Miniflash, the flashpoint is detected
   - ☐ by pressure increase
   - ☐ by temperature change
   - ☐ by ionization
   - ☐ visually

8. Pensky Martens testers require
   - ☐ 1ml of sample
   - ☐ 2ml of sample
   - ☐ 4ml of sample
   - ☐ 75ml of sample
   - ☐ 100ml of sample

9. In general, closed cup testers produce
   - ☐ a lower flashpoint than open cup testers
   - ☐ a similar flashpoint as open cup testers
   - ☐ a higher flashpoint than open cup testers

10. If pure substances are not being cooled properly
   - ☐ their flashpoint will change because volatiles are escaping
   - ☐ their flashpoint will not change