

# Environmental Protection Agency

## **Method for Distillation of Petroleum Products**

This method is written for the Environmental Protection Agency, National Vehicle and Fuel Emissions Laboratory (NVFEL) internal use. The use of specific brand names by NVFEL in this method are for reference only and are not an endorsement of those products. This document may be used for guidance by other laboratories.

### **NVFEL Reference Number**

126B

### **Implementation Approval**

Original Procedure Authorized by EPCN # 318 on 5-24-2002

### **Revision Description**

- (1) 02-25-2003 The purpose of this change is to revise the procedure as described in EPCN #340.

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## 1.0 Scope

- 1.1 The method is suitable for natural gasoline, motor gasoline, oxygenated gasoline, aviation turbine fuels, special boiling point spirits, naphthas, white spirits, kerosenes, gas oils, distillate fuel oils, and similar petroleum products.

## 2. Summary of Method

A 100 mL sample is distilled using a predetermined program found in Distillation programs in the instrument. The Computer registers the total volume distilled at each prescribed temperature and from these data the results of the test are calculated and reported.

## 3. Significance

This method is the Laboratory Operations Division (LOD) specific version of American Society for Testing and Materials' (ASTM) D 86-01, "The Standard Test Method for the Distillation of Petroleum Products," a method quoted in LOD fuel procurement, federal vehicle emission, and fuels enforcement test programs.

## 4. Applicable Documents

- 4.1 Code of Federal Regulations, Title 40, Part 80, Subpart D, Section 80.46
- 4.2 Code of Federal Regulations, Title 40, Part 86, Subpart D, Section 80.1313, and other applicable sections.
- 4.3 ASTM Standard Method D 86-01 Standard Test Method for the Distillation of Petroleum Products
- 4.4 Herzog Operation Instructions, Electronic, MP 626
- 4.5 Herzog Operation Instructions, Electronic, HAD 627
- 4.6 ISL Operation Instructions, ISL AD86 5G
- 4.7 Attachment A, Thermometer in Distillation Flask
- 4.8 For Enforcement samples, the Chain of Custody Procedure, NVFEL 120.

## 5. Definitions

- 5.1 Final Boiling Point (End Point):  
The maximum thermometer reading obtained during the test.
- 5.2 Initial Boiling Point:  
The thermometer reading that is observed at the instant the first drop falls from the condensate tube.
- 5.5 Percent Recovered:  
The volume, in mL, of condensate observed in the receiving graduate, in connection with a simultaneous thermometer reading
- 5.3 Percent Evaporated:  
The sum of the percent recovered and the percent loss.
- 5.4 Percent Loss:  
100% minus the total percent recovered.
- 5.5 Percent Residue:  
The residue measured in mL measured by 12.14.

## 6. Interferences and/or Limitations

Samples, standards, resistance temperature devices (RTD), flask supports, and glassware must be at the prescribed test temperatures for their fuel group to ensure accuracy.

## 7. Safety

- 7.1 N-pentane, gasoline and toluene are hazardous materials. Specific procedures for handling these materials are listed in their respective Material Safety Data Sheets (MSDS). MSDS's are on file in the Testing Services Group area. The analyst must be familiar with these MSDS procedures prior to performing this procedure.
- 7.2 Automatic distillation apparatuses apply heat to flammable liquids in excess of the flash points of those liquids. The possibility of fire is present when using this test method.
- 7.3 Automatic fire protection equipment must be installed and in working order before use.

- 7.4 Dispose of and do not use any glassware that has cracks in the coke layer or in the glass itself.
- 7.5 Dispose of and do not use any boiling flask that has any brownish residue coating an area greater than 50% of its spherical section.
- 7.6 Flask failure is the chief cause of fires.
- 7.7 In case of a spill of one gallon or more of any of the above reagents or samples, remove all personnel from the area, contact the Emergency Response Team and, if possible, turn the equipment off.
- 7.8 Spills of a gallon or less can be mopped up with spill control pillows or adsorbent found near each distillation instrument.
- 7.9 Contact the Safety Office regarding appropriate disposal of the adsorbent material.
- 7.10 Before analysis, the fire suppression bottle is examined for adequate CO<sub>2</sub> supply pressure (500 psig). The instruments must have CO<sub>2</sub> delivery pressure set between 40 and 60 psig for their respective fire suppression systems.

## 8. Apparatus

- 8.1 Automatic distillation apparatus

Equipment used: Herzog MP 626  
Herzog HAD 627  
ISL AD86 5G

- 8.2 Fume hood

- 8.3 Glassware

Equipment Used: 100-mL receiver specific for each instrument, meeting ASTM specifications, as supplied by the manufacturer.

125-mL side arm boiling flask instrument, meeting ASTM specifications.

- 8.4 Disposable droppers

- 8.5 Rinse bottles for glassware cleaning

- 8.6 Boiling granules, Boileezers or equivalent [CAS# 1344-28-1]
- 8.7 Constant temperature bath
- 8.8 Micro Liquid Laboratory Cleaner, or equivalent

## 9. Reagents and Materials

- 9.1 Petroleum product sample of 100 mL in volume:
  - Toluene [CAS# 108-88-3], bp 228.8 °F (“reagent grade” or better)
  - Neohexane [CAS#75-83-2] bp 122 °F
  - Nonane [CAS#111-84-2] bp 301.3 °F
  - Dodecane [CAS#112-40-3] bp 410.4 °F
  - Tetradecane [CAS#629-59-4] 472 °F
- 9.2 Control Gasoline substantially similar to the emission certification test gasoline specified in 40 CFR 86.113.
- 9.3 Diesel Fuel substantially similar to the emission certification #2 diesel specified in 40 CFR 86.113.

## 10. Sampling

- 10.1 Samples are inspected before analysis for phase separation, leaks, and tampering.
- 10.2 Obtain and inspect samples as described in the NVFEL Enforcement Sample Chain-of-Custody Procedure.

## 11. Calibration

- 11.1 Once a month, check the Celsius temperature settings using the calibrated PT100 Probe Simulator at these target points:

°C  
0.00  
49.99  
100.00  
199.97  
299.98  
399.94.

If the instrument does not have these exact readings, it must be adjusted to these exact values within the reading capability of the instrument, as per the respective instrument manual.

**NOTE:** This does not check the Pt resistor.

- 11.2 Once a month, check liquid level settings in the manufacturer supplied graduated receiver at 0 mL, 5 mL, and 100 mL. If the reading is not correct, see Step 12.3 for corrective action.
- 11.3 Every six months, compare the laboratory electronic barometer with the calibrated mercury barometer, located on the wall in room 407. If the electronic barometer is not reading correctly, call the electronics personnel for service.

## 12. Analytical Procedure

- 12.1 Check and, if necessary, reset the internal clocks on each instrument for the correct date and time.
- 12.2 Verify and, if necessary, readjust the barometers for each instrument per its instruction manual so that they are within 3 mm of Hg of a temperature- and latitude-corrected electronic barometer, which has been verified by a certified mercury barometer.
- 12.3 Verify and, if necessary, readjust the receiver zero volume set points for each instrument, per their respective instruction manuals, once a week or when a new receiver is used.

Receivers are specific to each instrument and can not be used interchangeably.

- 12.4 Using a piece of soft, lint-free absorbent material attached to a cord, swab out the condenser tube on the instrument so that no liquid is visible on its interior surface.

- 12.5 Remove sample from refrigerator or RVP Ice bath and place in  $60 \pm 1$  °F water bath at least one hour before transferring sample to the 100 mL receiver.
- 12.6 Pour the sample into the receiver flask and fill it to the 100 mL mark. Adjust the volume with a disposable pipet.
- 12.7 Add four to ten boiling granules to the boiling flask.
- 12.8 Transfer the contents of the receiver as completely as practical to the boiling flask, taking care not to spill or lose any liquid through the side arm.
- 12.9 Do not dry the receiver flask.
- 12.10 Fit the temperature sensor (RTD) tightly into the neck of the boiling flask with a silicone stopper. Locate the sensor in relationship to the side arm as prescribed by the instrument and RTD manufacturer and shown in Attachment A.
- 12.11 Fit the boiling flask's side arm into the condenser tube with a silicone stopper.
- 12.12 Adjust the flask in a vertical position with the side arm extending 1 to 2 inches into the condenser. Raise and adjust the flask support to fit snugly against the bottom of the flask.
- 12.13 Place the receiver used to measure the sample charge into the receiver compartment under the lower end of the condenser tube. The condenser tube must extend at least 1 inch into the receiver but not below the 100 mL mark. Cover the receiver closely with the gasket found on the instruments.
- 12.14 Using the program appropriate to the instrument and sample, begin the test. The program selected must provide results meeting the analysis conditions outlined in Appendix 1. Perform Steps 12.6 through 12.13 as quickly as possible to minimize changes in starting temperatures and changes in the sample's composition due to evaporation.
- 12.15 After the instrument has measured the end point, the instrument will cool the boiling flask and request the residue of the distillation.

Pour the residue from the boiling flask into a 15 mL centrifuge tube, or other suitable container with graduations less than 1 mL, and estimate the volume. Enter that volume into the instrument as the residue. The instrument will finish the necessary calculations and corrections.



- 12.16 The instruments will automatically sum the times recorded in seconds at the bottom of the column labeled “Dist. Rate” on the output report. Compare the result with the “Time from 5 mL Residue to End Point” specification, found in Appendix 1 for the fuel group analyzed.

If it does not meet the specification, delete the test from the instrument database and discard any hard copy of the test. Reanalyze the sample.

- 12.17 Review the instrument output to verify the remaining acceptance criteria. Repeat any distillation that did not meet the conditions specified in Appendix 1. Multiple analyses are often necessary for gasoline. The analyst initials the output if all the acceptance criteria are met.

**Note:** There should not be any unknowns for enforcement samples. If any enforcement sample is found to be mislabeled or mis-identified, that fact must be noted on the traveler document.

**Note:** Difficulty in achieving a valid test is related to the volatility and composition of the material being tested. Initially the analyst must identify any unknown sample by fuel type and, if it is a gasoline, its expected vapor pressure.

- 12.18 Rinse the boiling flask with sample collected in the receiver. Pour the rinse into an appropriate product drain can. Rinse the flask with gasoline, drain it into a container for gasoline only, and air dry. Do not try to remove the coke from the bottom of the boiling flask.

- 12.19 Rinse the receiver with gasoline and drain it into a container for gasoline only. Air-dry the receiver. If residues are present after drying, clean with a suitable glass cleaning detergent such as Micro Liquid Laboratory Cleaner. Then rinse with hot water and air dry.

- 12.20 Analyze a Certification Diesel Fuel or California Phase II Control Gasoline

The choice of diesel fuel or gasoline is based on a frequency of at least once for every 10 analyses per fuel type. (See Step 14.5)

- 12.21 At least one in ten analyses on each instrument must be run as a laboratory duplicate sample. The duplicate must be run on the same instrument as the initial analysis. (See Steps 14.6, 14.7 and 14.8)

### 13. Calculations and Reporting

- 13.1 Results from each instrument are manually transferred to "Fuel Tests Data Base", "Distillation Table" after the residue has been measured by emptying the contents of the boiling flask into a graduated centrifuge tube, and that volume has been entered into the instrument.
- 13.2 Print out a hard copy of the results from each instrument.
- 13.3 Print out and sign the "Distillation by Date" report from the "Fuel Tests Data Base" file.
- 13.4 Attach the hard copy of results from each instrument to the "Distillation by Date" report and place in the secured file cabinet.

### 14. Performance Criteria

- 14.1 Instrument barometer must be +/- 3 mm of Hg of a temperature and latitude-corrected electronic barometer, corrected by a calibrated mercury barometer every six months.
- 14.2 Two or three of the following must be run once a week or before each series/batch of gasoline samples:

The measured boiling point of Neohexane at 122 °F

The measured boiling point of Toluene at 228.8 °F

The measured boiling point of Nonane at 301.3 °F

These must be within  $\pm 1.8$  °F when analyzed under the conditions described in ASTM D86 (Step 4.3)

- 14.3 Two or three of the following must be run once a week or before each series/batch of diesel samples whichever is less:

The measured boiling point of Tetradecane at 472 °F

The measured boiling point of Nonane at 301.3 °F

The measured boiling point of Dodecane at 410.4 °F

These must be within  $\pm 1.8$  °F when analyzed under the conditions described in ASTM D86 (Step 4.3)

- 14.4 CA Phase II gasoline must be analyzed before each day’s analysis. The 50% and 90% recovered points on each instrument must be within  $\pm 2$  StDev of the last six days results, as recorded in the "Distillation Table" of the Fuel Tests Data Base.
- 14.5 A duplicate sample must be run after every 10 analyzed gasoline and diesel samples on each instrument.
- 14.6 Duplicate sample values must be within  $\pm 1.1$  °F at the 50% evaporation point (See Step 14.8), or an investigation for cause must be performed and reported.
- 14.7 Repeatability for this procedure has been statistically determined using the control gasoline and the certification diesel fuel. The difference between two test results, obtained by the same operator with the same apparatus under constant operating conditions on identical test material, would, in the normal and current operations of the test method, exceed the following values only in one case out of 20:

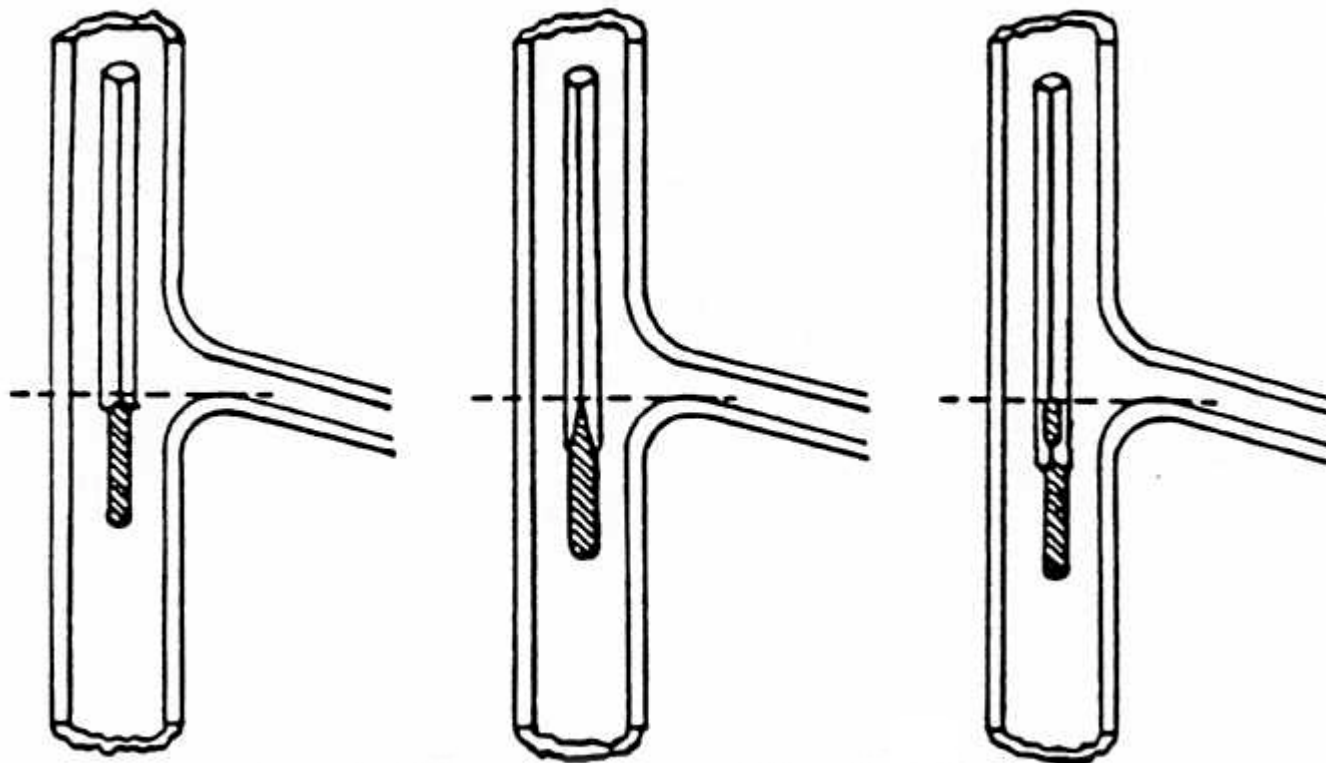
**NOTE:** These are allowed variances from the mean value of the temperature at which the stated percentage has been boiled off.

<u>Gasoline's</u>	<u>Instrument</u>
IBP.....	$\pm 9.2$ °F
10% Evaporated .....	$\pm 4.3$ °F
50% Evaporated .....	$\pm 1.1$ °F
90% Evaporated .....	$\pm 3.5$ °F
End Point.....	$\pm 4.4$ °F

<u>#2 Diesel</u>	<u>Instrument</u>
10 % Recovered .....	$\pm 3.8$ °F
50 % Recovered .....	$\pm 1.8$ °F
90 % Recovered .....	$\pm 1.6$ °F

- 14.8 Record any problems encountered in the analysis of samples in either the Method or Instrument Log Book, as appropriate. If results fall outside of these tolerances, then re-calibrate as in Section 11, obtain a new sample of control fluid, and re-run that sample.
- 14.9 If problems persist, replace the Platinum Resistance Thermometer and return to Section 11 to calibrate the instrument.

Attachment A



Position of Thermometer in Distillation Flask

## Appendix 1.

## Operating and Test Conditions

	<u>Group 1</u>	<u>Group 2</u>	<u>Group 3</u>	<u>Group 4</u>
<b><u>Group Characteristics:</u></b>				
Vapor pressure at 100 °F, psi	9.5	<9.5	<9.5	<9.5
Distillation,	IBP	NA	212 °F	>212 °F
	EP	482 °F	>482 °F	>482 °F
<b><u>Sample Handling:</u></b>				
Temperature of stored sample	32 °F - 50 °F	32 °F - 50 °F	Ambient <sup>(1)</sup>	Ambient <sup>(1)</sup>
If sample is wet:	Resample	Resample	(2)	(2)
<b><u>Apparatus test conditions:</u></b>				
RTD setting	7F	7F	7F	8F
Flask Support hole diameter	1.5 in.	1.5 in.	1.5 in.	2.0 in.
<b><u>Initial test temperatures:</u></b>				
Flask and RTD	55 °F - 65 °F	55 °F - 65 °F	55 °F - 65 °F	Ambient <sup>(1)</sup>
Flask support and shield	Ambient <sup>(1)</sup>	Ambient <sup>(1)</sup>	Ambient <sup>(1)</sup>	NA
Receiver and 100-mL sample	55 °F - 65 °F	55 °F - 65 °F	55 °F - 65 °F	55 °F - Ambient
Condenser temperature	32 °F - 34 °F	32 °F - 40 °F	32 °F - 40 °F	70 °F - 140 °F
Receiver temperature	55 °F - 65 °F	55 °F - 65 °F	55 °F - 65 °F	± 5 °F of charge
<b><u>Times, seconds:</u></b>				
From first heat to initial boiling point	300 - 600	300 - 600	300 - 600	300 - 900
From IBP to 5% recovered	60 - 75	60 - 75	NA	NA
From 5 mL residue to end point	180 - 300	180 - 300	300 max.	300 max.
Uniform average rate of condensation from 5% recovered to 5 mL residue <sup>3</sup> , mL / min	4.0 - 5.0	4.0 - 5.0	4.0 - 5.0	4.0 - 5.0

(1) For this procedure, ambient temperature refers to normal room temperature and may be considered as 68 to 78 °F.

(2) Free water may be removed by shaking the sample with anhydrous sodium sulfate and separating the agent from the sample by decanting.

(3) The rate is calculated and reported for every 10 mL recovered. An acceptable test can have a single 10 mL increment with a condensation rate as low as 3.5 mL/min or as high as 5.5 mL/min. The remainder of the 10 mL increments must each have a condensation rate >4.0 mL/min, but <5.0 mL/min for a valid distillation. .