



OECD GUIDELINE FOR TESTING OF CHEMICALS

"Boiling Point/Boiling Range"
(Ebulliometric Method -
Dynamic Method - Distillation Method -
Siwoloboff Method - Photocell Detection Method)

1. INTRODUCTORY INFORMATION**• Qualifying statement**

The methods and devices described in this Test Guideline can be applied to liquids, provided that these do not undergo chemical reaction at temperatures below the boiling point (for example: autoxidation, rearrangement, degradation, etc.).

• Additional comments

The Dynamic Method was tested in the OECD Laboratory Intercomparison Testing Programme, Part I, 1979, for vapour pressure determination.

• Standard documents

In this Guideline, five methods to determine the boiling point are described. The Ebulliometric Method is based on the ASTM D 1120-72. The Distillation Method is based on the standards ISO R 918 and the draft ISO DIS 4626, BS 4359/68, BS 4591/71, DIN 53171. The Siwoloboff Method is based on JIS K 0064-1966. The Photocell Detection Method is based on the manufacturer's manual (4).

2. METHOD**A. INTRODUCTION, PURPOSE, SCOPE, RELEVANCE,
APPLICATION AND LIMITS OF TEST**

The boiling point of a substance is an environmentally relevant physical chemical property because it is important for identification purposes and is one factor influencing the states in which the substance will exist in the environment.

The emphasis in this Test Guideline has been placed on the description of the method using photocell detection, because this method allows the determination of melting as well as boiling points. Moreover, the measurements can be performed automatically.

The Dynamic Method has the advantage that it can also be applied for the determination of vapour pressure and that it is not necessary to correct the boiling temperature to the normal pressure (101.325 kPa) because the standard pressure can be adjusted during the measurement. However this method is not at present automated. (For a detailed description see Test Guideline 104 for the Vapour Pressure Curve).

Note: In the literature, different boiling points are sometimes quoted for the same substance. These differences are due to such variables as the dimension of the apparatus (for example, the fit of the thermometer), the type of the thermometer, the stem correction, the pressure correction and the accuracy of the pressure measurement. Therefore, the above mentioned international and national standardised methods contain precise requirements for these specified conditions.

The influence of impurities on the determination of the boiling point depends greatly upon the kind of impurity. Thus, the effect can be considered if a highly volatile solvent is present in the sample. Impurities will usually increase/decrease the measured boiling temperature.

• Definitions and units

The standard boiling point is described as the temperature at which the pressure of the saturated vapour of a liquid is the same as the standard pressure.

The measured boiling point is dependent on the atmospheric pressure. This dependence can be described quantitatively by the Clausius-Clapeyron equation as follows:

$$\log p = - \frac{\Delta H_v}{2.3 RT} + \text{constant}$$

(where p is the vapour pressure of the substance, ΔH_v its heat of vaporisation, and R is the universal molar gas constant. $R = 8.31441 \text{ J mol}^{-1} \text{ K}^{-1}$. The temperature T is expressed in K).

The temperature at the boiling point (boiling temperature) is stated in K, with regard to the ambient pressure during the measurement. If no pressure is given, the result refers to a standard pressure of 101.325 kPa.

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Conversions

Pressure (units - kPa)

100 kPa = 1 bar = 0.1 MPa
("bar" units are still permissible but not recommended)

133 Pa = 1 mm Hg = 1 Torr
(the units mm Hg and Torr are no longer permissible)

Temperature (units - K)

$t = T - 273.15$
t in °C, and T in K

At small deviations from the normal pressure (max. ± 5 kPa) the boiling point temperatures are normalised to T_n by means of the following number-value-equation by Sidney-Young:

$$T_n = T + f_T \cdot \Delta p$$

where:

$$\Delta p = (101.325 - p) \text{ note sign}$$

p = barometer measurement in kPa

f_T = rate of change of boiling point with pressure in K/kPa

T = measured boiling temperature in K

T_n = boiling temperature corrected to normal pressure in K

The temperature-correction factors f_T and equations for their approximation are included in the international and national standards mentioned above for many substances. For example, the DIN 53171 method mentions the following rough corrections for solvents included in paints:

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TABLE 1: Temperature-correction-factors f_T

temperature T K	correction factor f_T K/kPa	temperature T K	correction factor f_T K/kPa
323.15	0.26	473.15	0.39
348.15	0.28	498.15	0.41
373.15	0.31	523.15	0.44
398.15	0.33	548.15	0.45
423.15	0.35	573.15	0.47
448.15	0.37		

A table of temperature-correction factors for organic solvents (see ISO/DIS 4626) is included in the Annex.

• Reference substances

The standard methods listed include specifications for calibration and evaluation substances. These compounds need not be employed in all cases when investigating a new substance. They should primarily serve to calibrate the method from time to time and to offer the chance to compare the results when another method is applied.

• Principle of the test methods

All methods for the determination of the boiling point (boiling range) are based on the measurement of the boiling temperature.

Determination by use of the Ebulliometer (1) (5)

Ebullimeters were originally developed for the determination of molecular weight by boiling point elevation, but they are also suited for exact boiling point measurements. A very simple apparatus is described in ASTM D 1120-72. The liquid is heated in this apparatus under equilibrium conditions at atmospheric pressure until it boils. The determined temperature of the liquid, corrected to standard pressure, is the boiling point.

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Dynamic method (2)

This method measures the vapour recondensation temperature by means of a thermocouple in the reflux while boiling. The pressure can be varied in this method.

Distillation method for boiling point (and boiling range)

This method involves distillation of the liquid and measurement of the vapour recondensation temperature and determination of the amount of distillate.

Method according to Siwoloboff (3)

A sample is heated in a sample tube which is immersed in a heat-bath liquid. A fused capillary, containing an air bubble in the lower part, is dipped in the sample tube. The temperature at which a regular string of bubbles escapes from the capillary or the temperature at which the string of bubbles stops and the fluid suddenly starts rising in the capillary (Siwoloboff) is determined.

Photocell detection (4)

Using the principle according to Siwoloboff. Measurements are automatic, the rising bubbles being detected photo-electrically.

• Quality criteria

The different methods for the determination of the boiling point (boiling range) are compared with regard to their use and precision and possibility to standardise/automate in Table 2.

B. DESCRIPTION OF THE TEST PROCEDURES

The procedures of several of the test methods have been established by various international and national standards mentioned above. Reference is made here to those standards which prescribe details of preparations, test conditions and conduct of the test.

• Ebulliometer

See: ASTM D 1120-72, Standard Test Method for Boiling Point of Engine Antifreezes, and reference (5).

"Boiling Point/Boiling Range"**TABLE 2: Comparison of the methods**

Method of measurement	Approximate Accuracy	Ability to Standardise	Automation
Ebulliometer	± 1.4 K (up to 373 K) * ± 2.5 K (above 373 K) *	existing standard ASTM D 1120-72*	difficult as yet
Dynamic method	± 0.5 K	possible	difficult
Distillation process (Boiling range)	± 0.5 K	existing standards e.g. ISO/R 918 DIN 53171 BS 4591/71	difficult as yet
According to Siwoloboff	± 1 K to ± 2 K	possible	automatic method exists see: photocell detection
Photocell detection	± 0.3 K (at 373 K)	possible	measurement process works automatically

- D y n a m i c m e t h o d

See: Test Guideline 104 for Vapour Pressure Curve, Principle of the test methods. The boiling temperature observed with an applied pressure of 101.325 kPa is recorded.

* This accuracy is only valid for pure substances and for the simple device as, for example, described in ASTM D 1120-72; it can be improved with more sophisticated ebulliometer devices.

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- Distillation process (boiling range)

See: ISO/R 918, Test Method for Distillation (Distillation Yield and Distillation Range),

ISO 4626/1980, Volatile Organic Liquids - Determination of Boiling Range of Organic Solvents Used as Raw Materials,

BS 4349/68, Method for Determination of Distillation of Petroleum Products,

BS 4591/71, Method for the Determination of Distillation Characteristics,

DIN 53171, Lösungsmittel für Anstrichstoffe, Bestimmung des Siedeverlaufes,

DIN 51751, Prüfung flüssiger Mineralkohlenwasserstoffe - Bestimmung des Siedeverlaufes.

- Method according to Siwoloboff

The sample is heated in a melting point apparatus in a sample tube, with a diameter of approximately 5 mm (Figure 1).

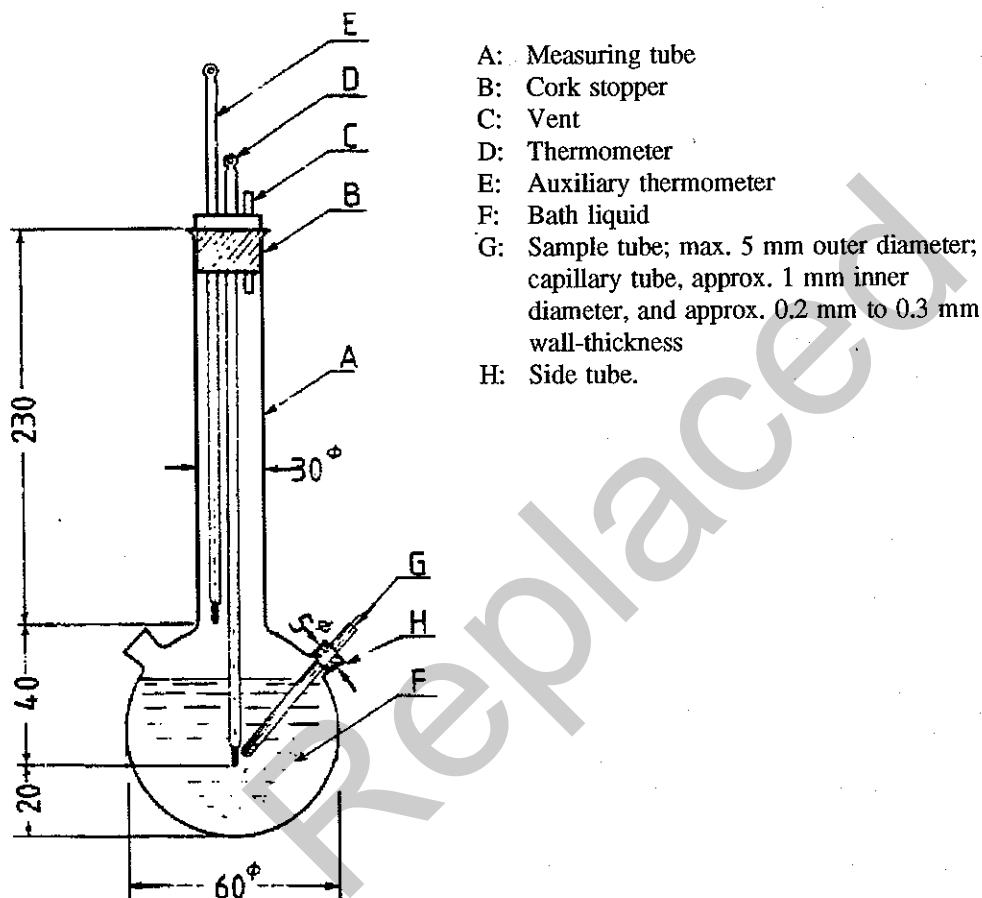
A capillary tube (boiling capillary) fused about 1 cm above the lower end is placed in the sample tube. The level to which the test substance is filled is such that the fused section of the capillary is below the surface of the liquid. The sample tube containing the boiling capillary is fastened either to the thermometer with a rubber-band or is fixed with a support from the side (see Figure 2).

The bath liquid is chosen according to boiling temperature. At temperatures of up to 573 K sulphuric acid or silicon oil can be used. Liquid paraffin may only be used up to 473 K. The heating of the bath liquid should be adjusted to a temperature rise of 3 K/min at first. The bath liquid must be stirred. At about 10 K below the expected boiling point, the heating is reduced so that the rate of temperature rise is less than 1 K/min. When the boiling temperature is approached bubbles begin to emerge from the boiling capillary.

The boiling point is reached when the string of bubbles stops and fluid suddenly starts rising in the capillary. The corresponding thermometer reading is the boiling temperature of the substance.

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Figure 1: Apparatus for the determination of melting and boiling point (JIS K 0064-1966), with specifications in mm.



In the modified principle (Figure 3) the boiling point is determined in the melting point capillary which is stretched to a fine point about 2 cm in length (a) and a small amount of the sample is aspirated. The open end of the fine capillary is closed by melting, so that a small air bubble is located at the end. When heated in the melting point apparatus (b), the air bubble expands. The boiling point corresponds to the temperature at which the substance plug reaches the level of the surface of the bath liquid (c).

• Photocell detection

The sample is heated in a capillary tube inside a heated metal block. A light beam is directed via suitable holes in the block through the substance onto a precisely calibrated photocell. During the increase of the sample temperature, single air bubbles emerge from the boiling capillary. When the boiling temperature is reached the amount of bubbles increases immensely.

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Figure 2:

Principle according to Siwoloboff

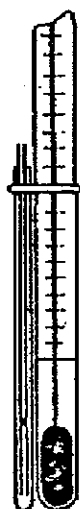


Figure 3:

Modified principle



This causes a change in the intensity of light, which is recorded by a photocell and gives a stop signal to the digital indicator reading out the temperature of a platinum resistance thermometer, located in the block.

This method is especially useful because it allows determinations below room temperature as low as 253.15 K (-20 °C) without any changes in the apparatus. The instrument merely has to be placed in a cold room or cooling bath. The exact execution of the boiling point determination can be obtained from the instrument manual.

• General remarks

The results obtained for mixtures or impure samples are to be interpreted with care. With an impure sample, for instance, the emergence of a low boiling component will be registered as the boiling point. Repeated determinations with the same impure sample can change the composition from measurement to measurement, due to the volatilisation of low boiling components: continuously increasing values are obtained in these circumstances.

Liquids with a tendency to superheat can yield incorrect results. The values obtained are usually too high. This happens more frequently at higher temperatures. Distillation methods or the dynamic vapour pressure method are more suitable for these types of compound.

3. DATA AND REPORTING

• Treatment of results

The boiling point to be determined should be a mean of at least two measurements, which are in the range of approximate accuracy indicated in Table 2. If determinations are not reproducible, other methods should be considered (see General remarks, above).

The measured boiling points and their mean should be stated in K, and the pressure(s) at which the measurement(s) was (were) made should be recorded in kPa. Where a test substance boils over a temperature range, this range should be provided. The measured values should be also corrected to standard pressure. Estimates of accuracy should be provided for all results.

The method used should be indicated, including any deviations from procedures described in this Test Guideline.

4. LITERATURE

1. H. Kienitz in *Methoden der Organischen Chemie* (edited by Houben-Weyl), Vol. 2, pp. 815-821, Georg Thieme Verlag, Stuttgart (1953).
2. *Test Guideline 104 for Vapour Pressure Curve, A 80/5*, Umweltbundesamt, Berlin (1980).
3. A. Siwoloboff, *Ber. d. chem. Ges.* 19, 795 (1886).
4. Manual of Apparatus FP 5 + FP 51, FP 52 and FP 53, Mettler Instrumente AG, CH-8606 Greifensee-Zürich, Switzerland.
5. European Pharmacopoeia, 1, 75 (1974).

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5. ANNEX

TEMPERATURE-CORRECTION FACTORS FOR ORGANIC SOLVENTS (see ISO/DIS 4626)

Product	Thermometer	Boiling point °C at 101.325 kPa	Rate of change of boiling point with pressure	
			K' °C/0.1 kPa (°C/mbar)	K °C/mmHg
Acetone	39 C	56.1	0.029	0.039
Acetonitrile	40 C	81.6	0.032	0.043
Allyl alcohol	40 C	96.9	0.028	0.038
Allyl chloride	38 C	45.1	0.029	0.039
n-Amyl acetate	102 C	149.5	0.036	0.048
n-Amyl alcohol	41 C	138.0	0.031	0.041
Aromatic solvent naphta	42 C	-	0.037	0.049
Benzene	40 C	80.1	0.032	0.042
iso-Butyl acetate	41 C	117.3	0.034	0.045
n-Butyl acetate	41 C	126.1	0.034	0.045
sec-Butyl acetate	40 C	112.4	0.034	0.045
iso-Butyl-alcohol	40 C	107.9	0.027	0.036
n-Butyl-alcohol	40 C	117.7	0.028	0.037
sec-Butyl alcohol	40 C	99.5	0.026	0.035
tert-Butyl alcohol	40 C	82.5	0.025	0.033
p-tert-Butyl toluene	104 C	192.8	0.042	0.056
Cumene	102 C	152.4	0.038	0.051
Cyclohexane	40 C	80.7	0.033	0.044
Cyclohexanone	102 C	155.7	0.038	0.051
Diacetone alcohol	102 C	169.2	0.038	0.050
Di-iso-butyl ketone	103 C	169.3	0.038	0.051
Di-iso-butylene	40 C	101.4	0.034	0.046
1,2-Dichloroethane	40 C	83.5	0.032	0.043
Dichloromethane	38 C	39.8	0.028	0.037
Diethyleneglycol	106 C	245.8	0.038	0.050
Diethylene glycol- mono-n-butyl ether	105 C	230.4	0.038	0.051
Diethylene glycol- monoethyl ether	104 C	201.9	0.036	0.048
Diethylene glycol- monomethyl ether	104 C	193.8	0.035	0.047
Dimethyl formamide	102 C	153.0	0.033	0.044
Dipropylene glycol	106 C	232.8	0.038	0.051
Di-iso-propyl ether	39 C	68.3	0.031	0.041

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Product	Thermometer	Boiling point °C at 101.325-kPa	Rate of change of boiling point with pressure	
			K' °C/0.1 kPa (°C/mbar)	K °C/mmHg
Ethyl acetate	39 C	77.2	0.031	0.041
Ethyl alcohol	39 C	78.3	0.025	0.033
Ethyl benzene	41 C	136.2	0.037	0.049
Ethylene glycol	104 C	197.6	0.032	0.043
Ethylene glycol-mono-n- butyl ether	103 C	171.2	0.035	0.047
Ethylene glycol-monoethyl ether	102 C	135.1	0.033	0.044
Ethylene glycol-monoethyl ether acetate	102 C	156.3	0.035	0.046
Ethylene glycol- monomethyl ether	41 C	124.5	0.031	0.041
Ethylene glycol-mono-iso propyl ether	102 C	142.8	0.033	0.044
2-Ethyl hexanol	104 C	184.8	0.034	0.046
Ethyl-iso-amyl ketone	103 C	158.2	0.037	0.049
n-Hexyl acetate	103 C	171.6	0.038	0.050
Hexylene glycol	104 C	197.1	0.034	0.045
Isophorone	105 C	215.3	0.043	0.057
Mesityloxide	41 C	129.8	0.035	0.047
4-Methoxy-4-methyl-2- pentanone	103 C	160.6	0.037	0.049
Methanol	39 C	64.6	0.025	0.033
Methyl-iso-amyl acetate	102 C	146.2	0.036	0.048
Methyl-iso-amyl ketone	102 C	144.9	0.036	0.048
Methyl-iso-butyl carbinol	41 C	131.8	0.031	0.041
Methyl-iso-butyl ketone	41 C	116.2	0.035	0.046
Mono-ethanol amine	103 C	170.7	0.030	0.040

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Product	Thermometer	Boiling point °C at 101.325 kPa	Rate of change of boiling point with pressure	
			K' °C/0.1 kPa (°C/mbar)	K °C/mmHg
Perchloroethylene	41 C	121.2	0.036	0.048
n-Propyl acetate	40 C	101.6	0.032	0.042
iso-Propyl acetate	40 C	88.5	0.031	0.041
n-Propyl alcohol	40 C	97.2	0.026	0.034
iso-Propyl alcohol	40 C	82.3	0.025	0.033
Propylene glycol	104 C	187.6	0.032	0.043
Propylene oxide	38 C	34.3	0.027	0.036
Pyridine	41 C	115.4	0.035	0.046
Toluene	41 C	110.6	0.035	0.046
Triethylene glycol	107 C	287.6	0.038	0.050
Triethelene glycol- monoethyl ether	106 C	255.4	0.038	0.051
Trichloroethylene	40 C	87.1	0.032	0.043
Vinyl acetate	39 C	72.7	0.030	0.040
White spirit	103 C	-	0.041	0.055
Xylene (isomer mixture)	41 C	-	0.037	0.049
m-Xylene	41 C	139.1	0.037	0.049
o-Xylene	41 C	144.4	0.037	0.050
p-Xylene	41 C	138.3	0.037	0.049

Replaced