

# OECD GUIDELINE FOR THE TESTING OF CHEMICALS

Adopted by the Council on 27<sup>th</sup> July 1995

## Boiling Point

### INTRODUCTION

1. This guideline is a revised version of the original Guideline 103 which was adopted in 1981. Two additional methods are contained in the current version. These are the differential thermal analysis and the differential scanning calorimetry. The main change otherwise concerns the format. The revision was based on the EC method "Boiling Temperature", published in 1992 (1).

### INITIAL CONSIDERATIONS

2. Most determinations of the boiling temperature are made at ambient pressure and a calculation is necessary to derive the normal boiling point from the measurement. Measurements at reduced pressure may be appropriate for substances with a high boiling point and substances which decompose at elevated temperatures. The extrapolation over large pressure ranges is prone to errors however. Assuming that the heat of vaporization is constant over a limited temperature range in the vicinity of the normal boiling point, the following form of the Clapeyron - Clausius equation can be applied:

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

where

- p = the vapour pressure of the substance in pascal  
 $\Delta H_v$  = the heat of vaporization in J mol<sup>-1</sup>  
R = the universal gas constant, 8.314 J mol<sup>-1</sup> K<sup>-1</sup>  
T = the thermodynamic temperature in K

3. The influence of impurities on the boiling point depends greatly upon the nature of the impurity. When there are volatile impurities in the sample, the substance may need to be purified.

4. The methods described in this guideline can be applied to liquid and low-melting substances, provided that they do not undergo chemical change, e.g. auto-oxidation, rearrangement, degradation, etc., below the boiling point.

5. The fundamental principles are given in references 2 and 3.

**DEFINITIONS AND UNITS**

6. The normal boiling point of a liquid is defined as the temperature at which the vapour pressure equals the standard atmospheric pressure 101.325 kPa.

7. The temperature at the boiling point 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. The conversion of degrees Celsius to kelvins is according to the formula

$$T = t + 273.15$$

where

T is the Kelvin or thermodynamic temperature, and t is the Celsius temperature.

8. Pressure needs to be expressed in kPa and following conversions apply:

1 bar = 100 kPa,  
1 mm Hg (or Torr) = 0.133 kPa,  
1 atm = 101.325 kPa.

**REFERENCE SUBSTANCES**

9. Reference substances are not needed when investigating a substance. Some substances which may be used for calibration can be found in the standards listed in the appendix.

**DESCRIPTION OF THE METHODS****Ebulliometer****Principle**

10. Ebulliometers were developed for the determination of the molecular weight by boiling point elevation. They are also suited for exact boiling temperature measurements. The liquid is heated under equilibrium conditions at atmospheric pressure until it is boiling.

**Apparatus**

11. A simple apparatus is described in ASTM D 1120-72 (see the appendix).

**Dynamic method****Principle**

12. This method involves the measurement of the vapour recondensation temperature in the reflux while the liquid is boiling. The pressure can be varied and the boiling temperature corresponding to pressure of 101.325 kPa is recorded.

**Apparatus**

13. The apparatus is described in Guideline 104.

### Distillation method

#### Principle

14. The liquid is distilled and the vapour recondensation temperature and the amount of distillate are measured.

#### Apparatus

15. The description of the apparatus is given in standards, e.g. ISO 918-1983 (see the appendix).

### Method according to Siwoloboff

#### Principle

16. A sample is heated gradually in a tube which is immersed in a liquid bath. The sample tube is held in close contact with a thermometer and it contains a boiling capillary which is fused about 1 cm above its lower end (Figure 1). Upon approach of the boiling temperature bubbles emerge rapidly from the lower open end of the capillary. The boiling temperature is that temperature at which, on momentary cooling, the string of bubbles stops and liquid suddenly rises in the capillary.



**Figure 1**  
**Principle according to Siwoloboff**

#### Apparatus

17. The apparatus for the liquid bath is similar to the one which is shown in figure 1 of Guideline 102, apart that at H in the diagram the tube containing the sample and the capillary is inserted. The sample tube has a diameter of approximately 5 mm. The capillary is fused about 1 cm above its lower end. The fused section of the capillary should be below the level of the sample.

#### Procedure

18. The bath liquid is chosen according to the expected boiling temperature of the test substance. Silicone oil can be used for temperatures up to 573 K. Liquid paraffin may only be used for temperatures up to 473 K. At first, the heating of the bath should be adjusted to a temperature rise of 3 K/min. The bath must be stirred. At about 10 K below the expected boiling temperature, the heating is reduced so that the temperature rise is less than 1 K/min. Upon approach of the boiling temperature, bubbles begin to emerge rapidly from the capillary. The boiling temperature is that temperature at which, at momentary cooling, the string of bubbles stops and fluid suddenly rises in the capillary.

### Photocell detection

#### Principle

19. The sample is heated in a capillary inside a heated metal block. A light beam is directed through the sample onto a photocell. When the boiling point is reached, bubbles rising in the capillary give a decrease in the intensity of light received by the photocell. The photocell gives a stop signal to a digital indicator reading out the temperature measured by a resistance thermometer located in the block.

#### Apparatus

20. The apparatus is described in paragraph 13 of Guideline 102.

**Differential thermal analysis****Principle**

21. The difference in temperature between the substance and a reference material, which are both subjected to the same controlled temperature programme, are recorded. When the sample undergoes a transition involving a change in enthalpy (endothermic in the case of boiling), that change is indicated by a departure from the base line of the temperature record.

**Apparatus and procedure**

22. See the standard methods given in the appendix.

**Differential scanning calorimetry****Principle**

23. Samples of the test substance and a reference material are subjected to the same controlled temperature programme. The difference in energy input necessary to maintain identical temperatures in the substance and the reference material is recorded. When the sample undergoes a transition involving a change in enthalpy (endothermic on boiling), that change is indicated by a departure from the base line of the heat flow record.

**Apparatus and procedure**

24. See the standard methods given in the appendix.

**COMPARISON OF THE METHODS**

25. The applicability and estimated accuracy of the various methods are summarized in Table 1. For additional details the standards listed in the appendix should be consulted.

26. The advantage of the methods using photocell detection and thermal analysis is that the same equipment allows the determination of boiling as well as melting temperatures. Moreover, automation is easy. The dynamic method has the advantage that it can also be applied to the determination of the vapour pressure. With the dynamic method moreover it is not necessary to correct the boiling temperature to the normal pressure because this can be set during the measurement by means of a manostat.

**DATA AND REPORTING****Data**

27. At small deviations from the standard atmospheric pressure (maximum  $\pm 5$  kPa) the measured boiling temperatures can be converted to normal boiling points by means of the Sidney Young equation:

$$T_n = T + (f_T \times \Delta p)$$

where

$\Delta p = 101.325 - p$

$p$  = pressure in kPa

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

$T$  = measured boiling temperature in K

$T_n$  = normal boiling point

Correction factors  $f_T$  and equations for their approximation are included in standards listed in the appendix. As an example, the corrections for solvents used in paints given in DIN 53171 are reproduced in Table 2.

Table 1

Method	Estimated accuracy
Ebulliometer	$\pm 1.4$ K (up to 373 K) <sup>(1)</sup> $\pm 2.5$ K (up to 600 K) <sup>(1)</sup>
Dynamic method	$\pm 0.5$ K (up to 600 K)
Distillation method	$\pm 0.5$ K (up to 600 K)
Siwoloboff	$\pm 2.0$ K (up to 600 K)
Photocell detection	$\pm 0.3$ K (at 373 K)
Differential thermal analysis	$\pm 0.5$ K (up to 600 K) $\pm 2.0$ K (up to 1273 K)
Differential scanning calorimetry	$\pm 0.5$ K (up to 600 K) $\pm 2.0$ K (up to 1273 K)

<sup>(1)</sup> This accuracy applies to a simple device such as described in ASTM D 1120-72. More elaborate ebulliometer devices have a higher accuracy.

Table 2

Temperature T (K)	$f_T$ (K/kPa)
323.15	0.26
348.15	0.28
373.15	0.31
398.15	0.33
423.15	0.35
448.15	0.37
473.15	0.39
498.15	0.41
523.15	0.44
548.15	0.45
573.15	0.47

### Test Report

28. The test report shall include the following information;

- method used;
- chemical identity and impurities (preliminary purification step, if any);
- estimated accuracy;
- boiling temperature (the mean of at least two measurements, which are in the range of the estimated accuracy, together with the pressures, preferably close to normal, at which the measurements were made);

- all information and remarks relevant for the interpretation of the results, especially with regards to impurities and physical state of the substance.

### LITERATURE

- (1) Official Journal of the European Communities L 383 A, 15-21 (1992)
- (2) Le Neindre, B. and Vodar B., eds. (1975). IUPAC, Experimental Thermodynamics, Vol. II, Butterworths, London
- (3) Weissberger, R., ed., (1959). Technique of Organic Chemistry, Vol. I, Part I, Chapter VIII, Physical Methods of Organic Chemistry, 3rd ed., Interscience Publ., New York

**APPENDIX****LIST OF STANDARDS****Ebulliometer**

ASTM D 1120-72                      Standard test method for boiling point of engine anti-freezes

**Distillation process (boiling range)**

BS 4349/68                              Method for determination of distillation of petroleum products

BS 4591/71                              Method for the determination of distillation characteristics of organic liquids

DIN 53171                                Lösungsmittel für Anstrichstoffe, Bestimmung des Siedeverhaltens

ISO 918:1983                            Volatile organic liquids for industrial use - Determination of distillation characteristics

JIS K 00-66                              Test method for distillation of chemical products

NF T 20-608                              Distillation: détermination du rendement et de l'intervalle de distillation

**Differential thermal analysis and differential scanning calorimetry**

ASTM E 472-86                         Standard practice for reporting thermoanalytical data

ASTM E 473-85                         Standard definitions of terms relating to thermal analysis

ASTM E 537-76                         Standard method for assessing the thermal stability of chemicals by methods of differential thermal analysis

DIN 51005                                Thermische Analyse (TA)

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1. The first step in the synthesis of the target molecule is the reaction of the starting material with the reagent to form the intermediate. This reaction is carried out in a dry, inert solvent at a temperature of 0°C to room temperature. The reaction mixture is then allowed to warm to room temperature and stirred for a period of 2 hours. The resulting intermediate is then purified by column chromatography using a silica gel column and a gradient of ethyl acetate in hexanes as the eluent. The pure intermediate is then dried under high vacuum and stored in a desiccator until used.

2. The second step in the synthesis is the reaction of the intermediate with the reagent to form the final product. This reaction is carried out in a dry, inert solvent at a temperature of 0°C to room temperature. The reaction mixture is then allowed to warm to room temperature and stirred for a period of 2 hours. The resulting product is then purified by column chromatography using a silica gel column and a gradient of ethyl acetate in hexanes as the eluent. The pure product is then dried under high vacuum and stored in a desiccator until used.

3. The third step in the synthesis is the reaction of the product with the reagent to form the final product. This reaction is carried out in a dry, inert solvent at a temperature of 0°C to room temperature. The reaction mixture is then allowed to warm to room temperature and stirred for a period of 2 hours. The resulting product is then purified by column chromatography using a silica gel column and a gradient of ethyl acetate in hexanes as the eluent. The pure product is then dried under high vacuum and stored in a desiccator until used.

4. The fourth step in the synthesis is the reaction of the product with the reagent to form the final product. This reaction is carried out in a dry, inert solvent at a temperature of 0°C to room temperature. The reaction mixture is then allowed to warm to room temperature and stirred for a period of 2 hours. The resulting product is then purified by column chromatography using a silica gel column and a gradient of ethyl acetate in hexanes as the eluent. The pure product is then dried under high vacuum and stored in a desiccator until used.

5. The fifth step in the synthesis is the reaction of the product with the reagent to form the final product. This reaction is carried out in a dry, inert solvent at a temperature of 0°C to room temperature. The reaction mixture is then allowed to warm to room temperature and stirred for a period of 2 hours. The resulting product is then purified by column chromatography using a silica gel column and a gradient of ethyl acetate in hexanes as the eluent. The pure product is then dried under high vacuum and stored in a desiccator until used.

6. The sixth step in the synthesis is the reaction of the product with the reagent to form the final product. This reaction is carried out in a dry, inert solvent at a temperature of 0°C to room temperature. The reaction mixture is then allowed to warm to room temperature and stirred for a period of 2 hours. The resulting product is then purified by column chromatography using a silica gel column and a gradient of ethyl acetate in hexanes as the eluent. The pure product is then dried under high vacuum and stored in a desiccator until used.

7. The seventh step in the synthesis is the reaction of the product with the reagent to form the final product. This reaction is carried out in a dry, inert solvent at a temperature of 0°C to room temperature. The reaction mixture is then allowed to warm to room temperature and stirred for a period of 2 hours. The resulting product is then purified by column chromatography using a silica gel column and a gradient of ethyl acetate in hexanes as the eluent. The pure product is then dried under high vacuum and stored in a desiccator until used.

8. The eighth step in the synthesis is the reaction of the product with the reagent to form the final product. This reaction is carried out in a dry, inert solvent at a temperature of 0°C to room temperature. The reaction mixture is then allowed to warm to room temperature and stirred for a period of 2 hours. The resulting product is then purified by column chromatography using a silica gel column and a gradient of ethyl acetate in hexanes as the eluent. The pure product is then dried under high vacuum and stored in a desiccator until used.