A.2. BOILING TEMPERATURE

1. **METHOD**

The majority of the methods described are based on the OECD Test Guideline (1). The fundamental principles are given in references (2) and (3).

1.1. INTRODUCTION

The methods and devices described here can be applied to liquid and low melting substances, provided that these do not undergo chemical reaction below the boiling temperature (for example: auto-oxidation, rearrangement, degradation, etc.). The methods can be applied to pure and to impure liquid substances.

Emphasis is put on the methods using photocell detection and thermal analysis, because these methods allow the determination of melting as well as boiling temperatures. Moreover, measurements can be performed automatically.

The 'dynamic method' has the advantage that it can also be applied to the determination of the vapour pressure and it is not necessary to correct the boiling temperature to the normal pressure (101,325 kPa) because the normal pressure can be adjusted during the measurement by a manostat.

Remarks:

The influence of impurities on the determination of the boiling temperature depends greatly upon the nature of the impurity .When there are volatile impurities in the sample, which could affect the results, the substance may be purified.

1.2 DEFINITIONS AND UNITS

The normal boiling temperature is defined as the temperature at which the vapour pressure of a liquid is 101,325 kPa.

If the boiling temperature is not measured at normal atmospheric pressure, the temperature dependence of the vapour pressure can be described by the Clausius-Clapeyron equation:

$$\log p = \frac{\Delta H_v}{2,3RT} + const..$$

where:

p = the vapour pressure of the substance in pascals

ΔH_v = its heat of vaporization in J mol^{-1}

R = the universal molar gas constant = 8,314 J mol^{-1} K^{-1}

T = thermodynamic temperature in K

The boiling temperature is stated with regard to the ambient pressure during the measurement.

Conversions

Pressure (units: kPa)

100 kPa = 1 bar = 0,1 MPa
        ('bar' is still permissible but not recommended)

133 Pa = 1 mm Hg = 1 Torr
        (the units 'mm Hg' and 'Torr' are not permitted).

1 atm = standard atmosphere = 101 325 Pa
        (the unit 'atm' is not permitted).

Temperature (units: K)

$t = T - 273,15$

t: Celsius temperature, degree Celsius (°C)

T: thermodynamic temperature, kelvin (K)

1.3. REFERENCE SUBSTANCES

Reference substances do not need to be employed in all cases when investigating a new substance. They should primarily serve to check the performance of the method from time to time and to allow comparison with results from other methods.

Some calibration substances can be found in the methods listed in the Appendix.

1.4. PRINCIPLE OF THE TEST METHOD

Five methods for the determination of the boiling temperature (boiling range) are based on the measurement of the boiling temperature, two others are based on thermal analysis.

1.4.1. Determination by use of the ebulliometer

Ebulliometers were originally developed for the determination of the molecular weight by boiling temperature elevation, but they are also suited for exact boiling temperature measurements. A very simple apparatus is described in ASTM D 1120-72 (see Appendix). The liquid is heated in this apparatus under equilibrium conditions at atmospheric pressure until it is boiling.

1.4.2. Dynamic method

This method involves the measurement of the vapour recondensation temperature by means of an appropriate thermometer in the reflux while boiling. The pressure can be varied in this method.

1.4.3. Distillation method for boiling temperature

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

1.4.4. Method according to Siwoloboff

A sample is heated in a sample tube, which is immersed in a liquid in a heat-bath. A fused capillary, containing an air bubble in the lower part, is dipped in the sample tube.

1.4.5. Photocell detection

Following the principle according to Siwoloboff, automatic photo-electrical measurement is made using rising bubbles.

1.4.6. Differential thermal analysis

This technique records the difference in temperatures between the substance and a reference material as a function of temperature, while the substance and reference material are subjected to the same controlled temperature programme. When the sample undergoes a transition involving a change of enthalpy, that change is indicated by an endothermic departure (boiling) from the base line of the temperature record.

1.4.7. Differential scanning calorimetry

This tecnique records the difference in energy inputs into a substance and a reference material as a function of temperature, while the substance and reference material are subjected to the same controoled temperature programme. This energy is the energy necessary to establish zero temperature difference between the substance and the reference material. When the sample undergoes a transition involving a change of enthalpy, that change is indicated by an endothermic departure (boiling) from the base line of the heat flow record.

1.5. QUALITY CRITERIA

The applicability and accuracy of the different methods used for the determination of the boiling temperature/boiling range are listed in table 1.

TABLE 1: COMPARISON OF THE METHODS

Method of measurement	Estimated accuracy	Existing standard
Ebulliometer	± 1.4 K (up to 373 K) ([1]) ([2]) ± 2.5 K (up to 600 K) ([1]) ([2])	ASTM D 1120-72 ([1])
Dynamic method	± 0,5 K (up to 600 K) ([2])	
Distillation process (boiling range)	± 0,5 K (up to 600 K)	ISO/R 918, DIN 53171, BS 4591/71
According to Siwoloboff	± 2 K (up to 600 K) ([2])	
Photocell detection	± 0,3 K (up to 373 K) ([2])	
Differential thermal calorimetry	± 0,5 K (up to 600 K) ± 2,0 K (up to 1273 K)	ASTM E 537-76
Differential scanning calorimetry	± 0,5 K (up to 600 K) ± 2,0 K (up to1273 K)	ASTM E 537-76

([1]) This accuracy is only valid for the simple device as for example described in ASTM D 1120-72; it can be improved with more sophisticated ebulliometer devices.

([2]) Only valid for pure substances. The use in other circumstances should be justified.

1.6. DESCRIPTION OF THE METHODS

The procedures of some test methods have been described in international and national standards (see Appendix).

1.6.1. Ebulliometer

See Appendix.

1.6.2. Dynamic method

See test method A.4. for the determination of the vapour pressure.

The boiling temperature observed with an applied pressure of 101,325 kPa is recorded.

1.6.3. Distillation process (boiling range)

See Appendix.

1.6.4. Method according to Siwoloboff

The sample is heated in a melting temperature apparatus in a sample tube, with a diameter of approximately 5 mm (figure 1). Figure 1 shows a type of standardized melting and boiling temperature apparatus (JIS K 0064) (made of glass, all specifications in millimetres).

Figure 1
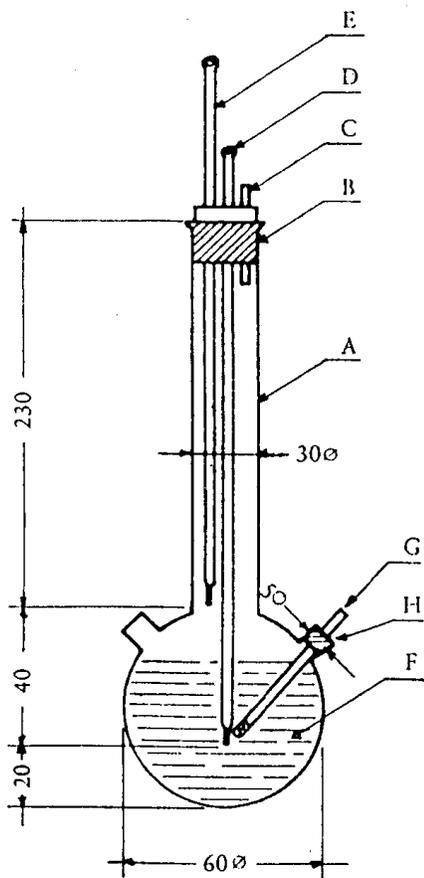
A: Measuring vessel
B: Stopper
C: Vent
D: Thermometer
E: Auxiliary thermometer
F: Bath liquid
G: Sample tube, maximum 5 mm outer diameter; containing a capillary tube, approximately 100 mm long, approximately 1 mm inner diameter and approximately 0,2 to 0,3 mm wall-thickness
H: Side tube

A capillary tube (boiling capillary) which is fused about 1 cm above the lower end is placed in the sample tube. The level to which the test substance is added 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).

Figure 2

Principle according to Siwoloboff
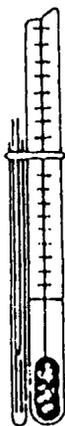
Figure 3

Modified principle

a)   b)   c)
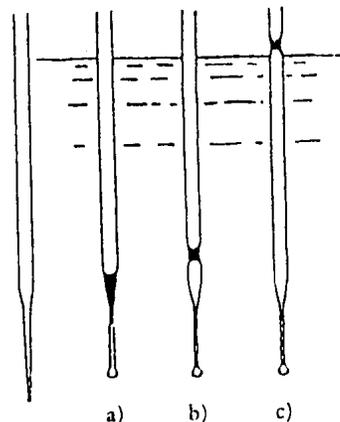
The bath liquid is chosen according to boiling temperature. At temperatures up to 573 K, silicone oil can be used. Liquid paraffin may only be used up to 473 K. The heating of the bath liquid should be adjusted to a temperature rise of 3 K/min at first. The bath liquid must be stirred. At about 10 K below the expected boiling temperature, the heating is reduced so that the rate of temperature rise is less than 1 K/min. Upon approach of the boiling temperature, bubbles begin to emerge rapidly from the boiling capillary.

The boiling temperature is that temperature when, on momentary cooling, the string of bubbles stops and fluid suddenly starts rising in the capillary. The corresponding thermometer reading is the boiling temperature of the substance.

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

1.6.5. Photocell detection

The sample is heated ill a capillary tube inside a heated metal block.

A light beam is directed, via suitable holes in the block, through the substance onto a preciseJy calibrated photocell.

During the increase of the sample temperature, single air bubbles emerge from the boiling capillary.When the boiling temperature is reached the number of bubbles increases greatly. This causes a change in the intensity of light, recorded by a photocell, and gives a stop signal to the 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 down to 253,15 K (-20 °C) without any changes in the apparatus. The instrument merely has to be placed in a cooling bath.

6. Thermal analysis

6.1. Differential thermal analysis

See Appendix.

6.2. Differential scanning calorimetry

See Appendix.

2. DATA

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

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

where:

$\Delta p = (101,325 - p)$ [note sign]

p = pressure measurement in kPa

f_T = rate of change of boiling temperature 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:

TABLE 2: TEMPERATURE -CORRECTIONS FACTORS f_T

Temperature T (K)	Correction factor 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	0,4
548,15	0,45
573,15	0,47

3. REPORTING

The test report shall, if possible, include the following information:

-method used,

-precise specification of the substance (identity and impurities) and preliminary purification step, if any,

-an estimate of the accuracy.

The mean of at least two measurements which are in the range of the estimated accuracy (see table 1) is reported as the boiling temperature.

The measured boiling temperatures and their mean shall be stated and the pressure(s) at which the measurements were made shall be reported in kPa. The pressure should preferably be close to normal atmospheric pressure.

All information and remarks relevant for the interpretation of results have to be reported, especially with regard to impurities and physical state of the substance.

4. **REFERENCES**

(1)   OECD, Paris, 1981, Test Guideline 103, Decision of the Council C (81) 30 final.

(2) IUPAC, B. Le Neindre, B. Vodar, editions. Experimental thermodynamics, Butterworths, London 1975, volume II.

(2)   R. Weissberger edition: Technique of organic chemistry, Physical methods of organic chemistry, Third Edition, Interscience Publications, New York, 1959, volume I, Part I, Chapter VIII.

Appendix

For additional technical details, the following standards may be consulted for example:

1.   Ebulliometer

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

2. Distillation process (boiling range)

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

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

BS 4591/71   Method for the determination of distillation characteristics

DIN 53171   Losungsmittel fur Anstrichstoffe, Bestimmung des Siedeverlaufes

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

3. Differential thermal analysis and differential scanning calorimetry

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

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

ASTM E 472-86   Standard practice for reporting thermoanalytical data

DIN 51005   Thermische Analyse: Begriffe