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Proposal for a

REGULATION OF THE EUROPEAN PARLIAMENT AND OF THE COUNCIL

concerning the Registration, Evaluation, Authorisation and Restrictions of Chemicals (REACH)

ORIGINAL: EN

(presented by the Commission)

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ANNEX X

INTRODUCTION

The Annex sets out test methods for the determination of physicochemical, toxicological and ecotoxicological properties listed in Annexes A-D to this Regulation. The methods are based on those recognised and recommended by competent international bodies (in particular OECD).

When such methods were not available, national standards or scientific consensus methods have been adopted. Generally, tests should be performed with the substance as defined by the Regulation. Attention should be given to the possible influence of impurities on the test results.

When the methods of this Annex are inappropriate for the investigation of a certain property, the notifier must justify the alternate method used.

PART A: METHODS FOR THE DETERMINATION OF PHYSICO-CHEMICAL PROPERTIES

A.1. MELTING/FREEZING 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 are to be applied for the determination of the melting temperature of substances, without any restriction in respect to their degree of purity .

The selection of the method is dependent on the nature of the substance to be tested. In consequence the limiting factor will be according to, whether or not the substance can be pulverized easily, with difficulty, or not at all.

For some substances, the determination of the freezing or solidification temperature is more appropriate and the standards for these determinations have also been included in this method.

Where, due to the particular properties of the substance, none of the above parameters can be conveniently measured, a pour point may be appropriate.

1.2. DEFINITIONS AND UNITS

The melting temperature is defined as the temperature at which the phase transition from solid to liquid state occurs at atmospheric pressure and this temperature ideally corresponds to the freezing temperature.

As the phase transition of many substances takes place over a temperature range, it is often described as the melting range.

Conversion of units (K to °C)

$t = T - 273{,}15$

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 are listed in the references (4).

1.4. PRINCIPLE OF THE TEST METHOD

The temperature (temperature range) of the phase transition from the solid to the liquid state or from the liquid to the solid state is determined. In practice while heating/cooling a sample of the test substance at atmospheric pressure the temperatures of the initial melting/freezing and the final stage of melting/freezing are determined. Five types of methods are described, namely capillary method, hot stage methods, freezing temperature determinations, methods of thermal analysis, and determination of the pour point (as developed for petroleum oils).

In certain cases, it may be convenient to measure the freezing temperature in place of the melting temperature.

1.4.1. Capillary method

1.4.1.1. Melting temperature devices with liquid bath

A small amount of the finely ground substance is placed in a capillary tube and packed tightly. The tube is heated, together with a thermometer, and the temperature rise is adjusted to less than about 1 K/min during the actual melting. The initial and final melting temperatures are determined.

1.4.1.2. Melting temperature devices with metal block

As described under 1.4.1.1., except that the capillary tube and the thermometer are situated in a heated metal block, and can be observed through holes in the block.

1.4.1.3. Photocell detection

The sample in the capillary tube is heated automatically in a metal cylinder. A beam of light is directed through the substance, by way of a hole in the cylinder, to a precisely calibrated photocell. The optical properties of most substances change from opaque to transparent when they are melting. The intensity of light reaching the photocell increases and sends a stop signal to the digital indicator reading out the temperature of a platinum resistance thermometer located in the heating chamber. This method is not suitable for some highly coloured substances.

1.4.2. Hot Stages

1.4.2.1. Kofler hot bar

The Kofler hot bar uses two pieces of metal of different thermal conductivity, heated electrically, with the bar designed so that the temperature gradient is almost linear along its length. The temperature of the hot bar can range from 283 to 573 K with a special temperature-reading device including a runner with a pointer and tab designed for the specific bar. In order to determine a melting temperature, the substance is laid, in a thin layer, directly on the surface of the hot bar. In a few seconds a sharp dividing line between the fluid and solid phase develops. The temperature at the dividing line is read by adjusting the pointer to rest at the line.

1.4.2.2. Melt microscope

Several microscope hot stages are in use for the determination of melting temperatures with very small quantities of material. In most of the hot stages the temperature is measured with a sensitive thermocouple but sometimes mercury thermometers are used. A typical microscope hot stage melting temperature apparatus has a heating chamber which contains a metal plate upon which the sample is placed on a slide. The centre of the metal plate contains a hole permitting the entrance of light from the illuminating mirror of the microscope. When in use, the chamber is closed by a glass plate to exclude air from the sample area.

The heating of the sample is regulated by a rheostat. For very precise measurements on optically anisotropic substances, polarized light may be used.

1.4.2.3. Meniscus method

This method is specifically used for polyamides.

The temperature at which the displacement of a meniscus of silicone oil, enclosed between a hot stage and a cover-glass supported by the polyamide test specimen, is determined visually.

1.4.3. Method to determine the freezing temperature

The sample is placed in a special test tube and placed in an apparatus for the determination of the freezing temperature. The sample is stirred gently and continuously during cooling and the temperature is measured at suitable intervals. As soon as the temperature remains constant for a few readings this temperature (corrected for thermometer error) is recorded as the freezing temperature.

Supercooling must be avoided by maintaining equilibrium between the solid and the liquid phases.

1.4.4. Thermal analysis

1.4.4.1 Differential thermal analysis (DTA)

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 (melting) or exothermic (freezing) departure from the base line of the temperature record.

1.4.4.2 Differential scanning calorimetry (DSC)

This technique 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 controlled 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 (melting) or exothermic (freezing) departure from the base line of the heat flow record.

1.4.5. Pour point

This method was developed for use with petroleum oils and is suitable for use with oily substances with low melting temperatures.

After preliminary heating, the sample is cooled at a specific rate and examined at intervals of 3 K for flow characteristics. The lowest temperature at which movement of the substance is observed is recorded as the pour point.

1.5. QUALITY CRITERIA

The applicability and accuracy of the different methods used for the determination of the melting temperature/melting range are listed in the following table:

TABLE: APPLICABILITY OF THE METHODS

A. Capillary methods

Method of measurement	**Substances which can be pulverized**	**Substances which are not readily pulverized**	**Temperature range**	**Estimated accuracy ([1])**	**Existing standards**
Melting temperature devices with liquid bath	yes	only to a few	273 to 573 K	± 0,3 K	JIS K 0064
Melting temperature with metal block	yes	only to a few	293 to >573 K	± 0,5 K	ISO 1218 (E)
Photocell detection	yes	Several with appliance devices	253 to 573 K	± 0,5 K	

([1]) Dependent on type of instrument and on degree of purity of the substance

B. Hot stages and freezing methods

Method of measurement	**Substances which can be pulverized**	**Substances which are not readily pulverized**	**Temperature range**	**Estimated accuracy (1)**	**Existing standards**
Kofler hot bar	yes	no	283 to >573 K	± 1K	ANSI/ASTM D 3451-76
Melt microscope	yes	only to a few	273 to >573 K	± 0,5 K	DIN 53736
Meniscus method	no	Specifically for polyamides	293 to >573 K	± 0,5 K	ISO 1218 (E)
Freezing temperature	yes	yes	223 to 573 K	± 0,5 K	e.g. BS 4695
(1) Dependent on type of instrument and on degree of purity of the substance					

C. Thermal analysis

Method of measurement	**Substances which can be pulverized**	**Substances which are not readily pulverized**	**Temperature range**	**Estimated accuracy (1)**	**Existing standards**
Differential Thermal Analysis	yes	Yes	173 to 1273 K	up to 600K ± 0,5K up to 1273K ± 2,0K	ASTM E 537-76
Differential Scanning Calorimetry	yes	yes	173 to 1273 K	up to 600K ± 0,5K up to 1273K ± 2,0K	ASTM E 537-76
(1) Dependent on type of instrument and on degree of purity of the substance					

D. Pour point

Method of measurement	**Substances which can be pulverized**	**Substances which are not readily pulverized**	**Temperature range**	**Estimated accuracy (1)**	**Existing standards**
Pour Point	for petroleum oils and oily substances	for petroleum oils and oily substances	223 to 323 K	± 0,3 K	ASTM D 97-66
(1) Dependent on type of instrument and on degree of purity of the substance					

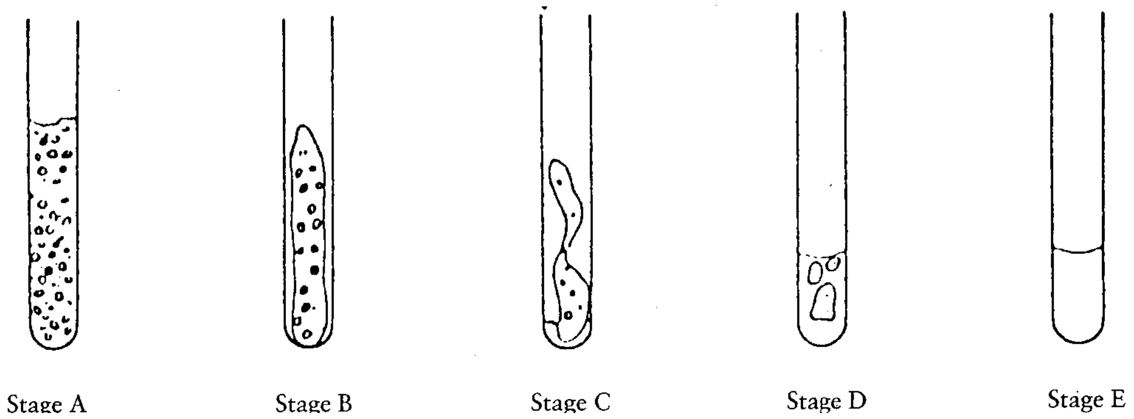
1.6. DESCRIPTION OF THE METHODS

The procedures of nearly all the test methods have been described in international and national standards (see Appendix 1).

1.6.1. Methods with capillary tube

When subjected to a slow temperature rise, finely pulverised substances usually show the stages of melting shown in figure 1.

Figure 1



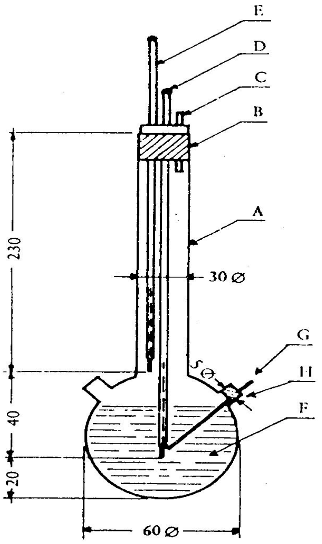
Stage A	(Beginning of melting): fine droplets adhere uniformly to the inside wall of the capillary tube
Stage B	a clearance appears between the sample and the inside wall due to shrinkage of the melt
Stage C	the shrunken sample begins to collapse downwards and liquefies
Stage D	a complete meniscus is formed at the surface but an appreciate amount of the sample remains solid
Stage E	(Final stage melting): there are no solid particles

During the determination of the melting temperature, the temperatures are recorded at the beginning of the melting and at the final stage.

1.6.1.1. Melting temperature devices with liquid bath apparatus

Figure 2 shows a type of standardized melting temperature apparatus made of glass (JIS K 0064); all specifications are in millimeters.

Figure 2



A: Measurement vessel
B: Stopper
C: Vent
D: Thermometer
E: Auxiliary thermometer
F: Bath liquid
G: Capillary tube made of glass, 80 to 100 mm in length, 1,0 ± 0,2 mm inner diameter, 0,2 to 0,3 mm wall thickness
H: Side tube

Bath liquid:

A suitable liquid should be chosen. The choice of the liquid depends upon the melting temperature to be determined, e.g. liquid paraffin for melting temperatures no higher than 473 K, silicone oil for melting temperatures no higher than 573 K.

For melting temperatures above 523 K, a mixture consisting of three parts sulphuric acid and two parts potassium sulphate (in mass ratio) can be used. Suitable precautions should be taken if a mixture such as this is used.

Thermometer:

Only those thermometers should be used which fulfill the requirements of the following or equivalent standards:

ASTM E 1-71, DIN 12770, JIS K 8001.

Procedure:

The dry substance is finely pulverized in a mortar and is put into the capillary tube, fused at one end, so that the filling level is approximately 3 mm after being tightly packed. To obtain a uniform packed sample, the capillary tube should be dropped from a height of approximately 700 mm through a glass tube vertically onto a watch glass.

The filled capillary tube is placed in the bath so that the middle part of the mercury bulb of the thermometer touches the capillary tube at the part where the sample is located. Usually the capillary tube is introduced into the apparatus about 10 K below the melting temperature.

The bath liquid is heated so that the temperature rise is approximately 3 K/min. The liquid should be stirred. At about 10 K below the expected melting temperature the rate of temperature rise is adjusted to a maximum of 1 K/min.

Calculation:

The calculation of the melting temperature is as follows:

$T = T_D + 0{,}00016\ (T_D - T_E)\ n$

where:

T = corrected melting temperature in K

T_D = temperature reading of thermometer D in K

T_E = temperature reading of thermometer E in K

n = number of graduations of mercury thread on thermometer D at emergent stem.

1.6.1.2 Melting temperature devices with metal block

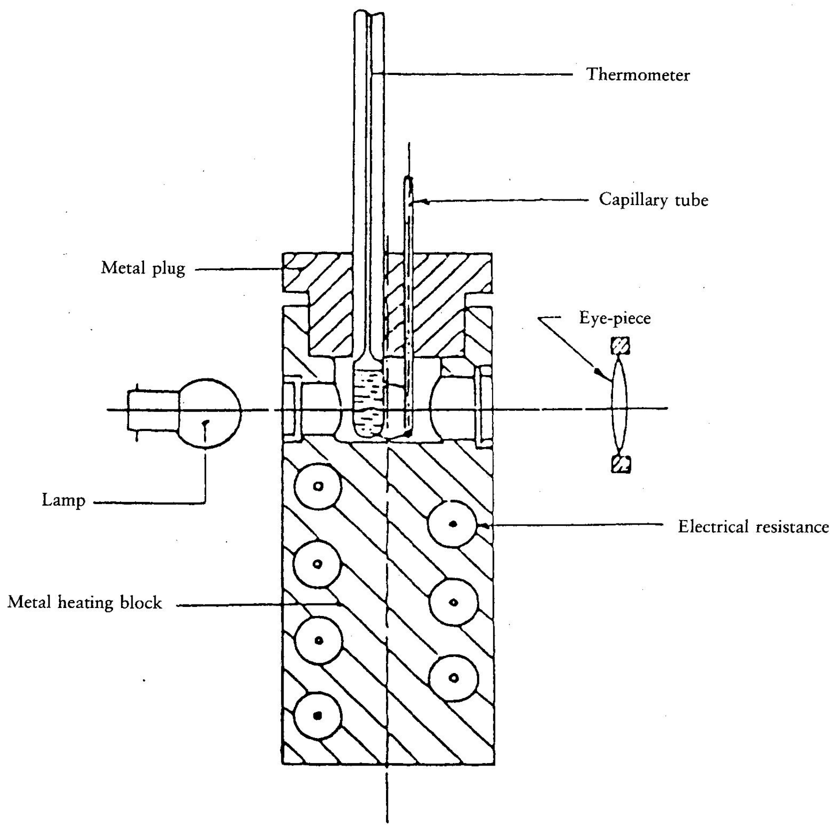
Apparatus:

This consists of:

- a cylindrical metal block, the upper part of which is hollow and forms a chamber (see figure 3),
- a metal plug, with two or more holes, allowing tubes to be mounted into the metal block,
- a heating system, for the metal block, provided for example by an electrical resistance enclosed in the block,
- a rheostat for regulation of power input, if electric heating is used,
- four windows of heat-resistant glass on the lateral walls of the chamber, diametrically disposed at right-angles to each other. In front of one of these windows is mounted an eye-piece for observing the capillary tube. The other three windows are used for illuminating the inside of the enclosure by means of lamps,
- a capillary tube of heat-resistant glass closed at one end (see 1.6.1.1).

See standards mentioned in 1.6.1.1. Thermoelectrical measuring devices with comparable accuracy are also applicable.

Figure 3



1.6.1.3. Photocell detection

Apparatus and procedure:

The apparatus consists of a metal chamber with automated heating system. Three capillary are filled accordingly to 1.6.1.1 and placed in the oven.

Several linear increases of temperature are available for calibrating the apparatus and the suitable temperature rise is electrically adjusted at a pre-selected constant and linear rate. recorders show the actual oven temperature and the temperature of the substance in the capillary tubes.

1.6.2. Hot stages

1.6.2.1. Kofler hot bar

See Appendix.

1.6.2.2. Melt microscope

See Appendix.

1.6.2.3. Meniscus method (polyamides)

See Appendix.

The heating rate through the melting temperature should be less than 1 K/min.

1.6.3. Methods for the determination of the freezing temperature

See Appendix.

1.6.4. Thermal analysis

1.6.4.1. Differential thermal analysis

See Appendix.

1.6.4.2. Differential scanning calorimetry

See Appendix.

1.6.5. Determination of the pour point

See Appendix.

2. DATA

A thermometer correction is necessary in some cases.

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 tables) is reported as the melting temperature.

If the difference between the temperature at the beginning and at the final stage of melting is within the limits of the accuracy of the method, the temperature at the final stage of melting is taken as the melting temperature; otherwise the two temperatures are reported.

If the substance decomposes or sublimes before the melting temperature is reached, the temperature at which the effect is observed shall be reported.

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 102, Decision of the Council C(81) 30 final.

(2) IUPAC, B. Le Neindre, B. Vodar, eds. Experimental thermodynamics, Butterworths, London 1975, vol. II, 803-834.

(3) R. Weissberger ed.: Technique of organic Chemistry, Physical Methods of Organic Chemistry, 3rd ed., Interscience Publ., New York, 1959, vol. I, Part I, Chapter VII.

(4) IUPAC, Physicochemical measurements: Catalogue of reference materials from national laboratories, Pure and applied chemistry, 1976, vol. 48, 505-515.

APPENDIX

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

1. Capillary methods

1.1. Melting temperature devices with liquid bath

ASTM E 324-69	Standard test method for relative initial and final melting points and the melting range of organic chemicals
BS 4634	Method for the determination of melting point and/or melting range
DIN 53181	Bestimmung des Schmelzintervalles von Harzen nach Kapilarverfarehn
JIS K 00-64	Testing methods for melting point of chemical products.

1.2 Melting temperature devices with metal block

DIN 53736	Visuelle Bestimmung der Schmelztemperatur von teilkristallinen Kunststoffen
ISO 1218 (E)	Plastics- polyamides -determination of 'melting point'

2. Hot stages

2.1. Kofler hot bar

ANSI/ ASTM D 3451-76	Standard recommended practices for testing polymeric powder coatings

2.2. Melt microscope

DIN 53736	Visuelle Bestimmung der Schmelztemperatur von teilkristallinen Kunststoffen.

2.3. Meniscus method (polyamides)

ISO 1218 (E)	Plastics -poly ami des -determination of 'melting point'
ANSI/ ASTM D 2133-66	Standard specification for acetal resin injection moulding and extrusion materials

NF T 51-050	Resines de polyamides. Determination du 'point de fusion' methode du menisque

3. Methods for the determination of the freezing temperature

BS 4633	Method for the determination of crystallizing point
BS 4695	Method for Determination of Melting Point of petroleum wax (Cooling Curve)
DIN 51421	Bestimmung des Gefrierpunktes von Flugkraftstoffen, Ottokraftstoffen und Motorenbenzolen
ISO 2207	Cires de petrole: determination de la temperature de figeage
DIN 53175	Bestimmung des Erstarrungspunktes von Fettsiiuren
NF T 60-114	Point de fusion des paraffines
NF T 20-051	Methode de determination du point de cristallisation (point de Congelation
ISO 1392	Method for the determination of the freezing point

4. Thermal analysis

4.1. Differential thermal analysis

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

4.2. 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

5. Determination of the pour point

NBN 52014	Echantillonnage et analyse des produits du petrole: Point de trouble et point d'ecoulement limite -Monsterneming en ontleding van aardolieproducten: Troebelingspunt en vloeipunt

ASTM D 97-66	Standard test method for pour point of petroleum oils
ISO 3016	Petroleum oils –Determination of pour point

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 technique 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 controlled 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.

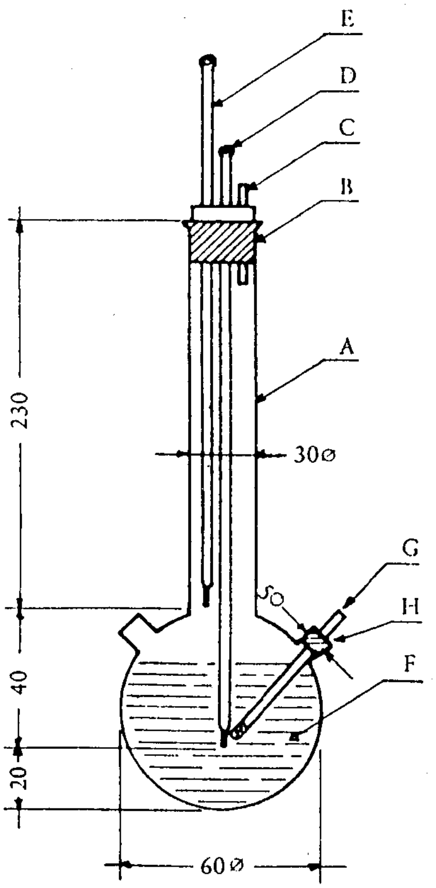
1.6.3. Distillation process (boiling range)

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

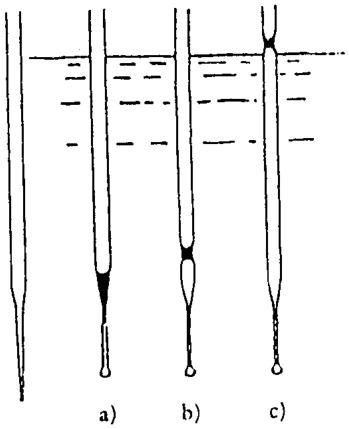
A capillary tube (boiling capillary) which is fused about 1 cm above the lower end is placed in the sample tube. The level to which the test substance is added is such that the fused section of the capillary is below the surface of the liquid. The sample tube containing the boiling capillary is fastened 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



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 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 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.

1.6.6. Thermal analysis

1.6.6.1. Differential thermal analysis

See Appendix.

1.6.6.2. 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:

$$T_n = T + (f_T \text{ x } \Delta p)$$

where:

Δp	= (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.

(3) 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

1.1 Melting temperature devices with liquid bath

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

A.3 RELATIVE DENSITY

1. METHOD

The methods described are based on the OECD Test Guideline (1). The fundamental principles are given in reference (2).

1.1. INTRODUCTION

The methods for determining relative density described are applicable to solid and to liquid substances, without any restriction in respect to their degree of purity. The various methods to be used are listed in table 1.

1.2. DEFINITIONS AND UNITS

The relative density D_4^{20} of solids or liquids is the ratio between the mass of a volume of substance to be examined, determined at 20 °C, and the mass of the same volume of water, determined at 4 °C. The relative density has no dimension.

The density, ρ, of a substance is the quotient of the mass, m, and its volume, v.

The density, ρ, is given, in SI units, in kg/m3.

1.3. REFERENCE SUBSTANCES (1) (3)

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.

1.4. PRINCIPLE OF THE METHODS

Four classes of methods are used.

1.4.1. Buoyancy methods

1.4.1.1. Hydrometer (for liquid substances)

Sufficiently accurate and quick determinations of density may be obtained by the floating hydrometers, which allow the density of a liquid to be deduced from the depth of immersion by reading a graduated scale.

1.4.1.2. Hydrostatic balance (for liquid and solid substances)

The difference between the weight of a test sample measured in air and in a suitable liquid (e.g. water) can be employed to determine its density.

For solids, the measured density is only representative of the particular sample employed. For the determination of density of liquids, a body of known volume, v, is weighed first in air and then in the liquid.

1.4.1.3. Immersed body method (for liquid substances) (4)

In this method, the density of a liquid is determined from the difference between the results of weighing the liquid before and after immersing a body of known volume in the test liquid.

1.4.2. Pycnometer methods

For solids or liquids, pycnometers of various shapes and with known volumes may be employed. The density is calculated from the difference in weight between the full and empty pycnometer and its known volume.

1.4.3. Air comparison pycnometer (for solids)

The density of a solid in any form can be measured at room temperature with the gas comparison pycnometer. The volume of a substance is measured in air or in an inert gas in a cylinder of variable calibrated volume. For the calculation of density one mass measurement is taken after concluding the volume measurement.

1.4.4. Oscillating densitimeter (5) (6) (7)

The density of a liquid can be measured by an oscillating densitimeter. A mechanical oscillator constructed in the form of a U-tube is vibrated at the resonance frequency of the oscillator which depends on its mass. Introducing a sample changes the resonance frequency of the oscillator. The apparatus has to be calibrated by two liquid substances of known densities. These substances should preferably be chosen such that their densities span the range to be measured.

1.5. QUALITY CRITERIA

The applicability of the different methods used for the determination of the relative density is listed in the table.

1.6. DESCRIPTION OF THE METHODS

The standards given as examples, which are to be consulted for additional technical details, are attached in the Appendix.

The tests have to be run at 20 °C, and at least two measurements performed.

2. DATA

See standards.

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.

The relative density, D_4^{20}, shall be reported as defined in 1.2, along with the physical state of the measured substance.

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.

TABLE: APPLICABILITY OF METHODS

Method of measurement	Density		Maximum possible dynamic viscosity	Existing Standards
	solid	liquid		
1.4.1.1. Hydrometer		yes	5 Pa s	ISO 387, ISO 649-2, NF T 20-050
1.4.1.2. Hydrostatic balance				
(a) solids	yes			ISO 1183 (A)
(b) liquids		yes	5 Pa s	ISO 901 and 758
1.4.1.3. Immersed body method		yes	20 Pa s	DIN 53217
1.4.2. Pycnometer				ISO 3507
(a) solids	yes			ISO 1183(B), NF T 20-053
(b) liquids		yes	500 Pa s	ISO 758
1.4.3. Air comparison pycnometer	yes			DIN 55990 Teil 3, DIN 53243
1.4.4. Oscillating densitimer		yes	5 Pa s	

4. REFERENCES

(1) OECD, Paris, 1981, Test Guideline 109, Decision of the Council C(81) 30 final.

(2) R. Weissberger ed., Technique of Organic Chemistry, Physical Methods of Organic Chemistry, 3rd ed., Chapter IV, Interscience Publ. , New York, 1959, vol. I, Part 1.

(3) IUPAC, Recommended reference materials for realization of physico-chemical properties, Pure and applied chemistry, 1976, vol. 48, 508.

(4) Wagenbreth, H., Die Tauchkugel zur Bestimmung der Dichte von Flüssigkeiten, Technisches Messen tm, 1979, vol.ll, 427-430.

(5) Leopold, H., Die digitale Messung von Flüssigkeiten, Elektronik, 1970, vol. 19,297-302.

(6) Baumgarten, D., Füllmengenkontrolle bei vorgepackten Erzeugnissen -Verfahren zur Dichtebestimmung bei flüssigen Produkten und ihre praktische Anwendung, Die Pharmazeutische Industrie, 1975, vol. 37,717 -726.

(7) Riemann, J., Der Einsatz der digital en Dichtemessung im Brauereilaboratorium, Brauwissenschaft, 1976, vol. 9,253-255.

APPENDIX

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

1. Buoyancy Methods

1.1 Hydrometer

DIN 12790, ISO 387	Hydrometer; general instructions
DIN 12791	Part I: Density hydrometers; construction, adjustment and use
	Part II: Density hydrometers; standardized sizes, designation
	Part III: Use and test
ISO 649-2	Laboratory glassware: Density hydrometers for general purpose
NF T 20-050	Chemical products for industrial use - Determination of density of liquids - Areometric method
DIN 12793	Laboratory glassware: range find hydrometers

1.2 Hydrostatic balance

For solid substances

ISO 1183	Method A: Methods for determining the density and relative density of plastics excluding cellular plastics
NF T 20-049	Chemical products for industrial use - Determination of the density of solids other than powders and cellular products - Hydrostatic balance method
ASTM-D-792	Specific gravity and density of plastics by displacement
DIN 53479	Testing of plastics and elastomers; determination of density

For liquid substances

ISO 901	ISO 758
DIN 51757	Testing of mineral oils and related materials; determination of density
ASTM D 941-55, ASTM D 1296-67 and ASTM D 1481-62	
ASTM D 1298	Density, specific gravity or API gravity of crude petroleum and liquid petroleum products by hydrometer method
BS 4714	Density, specific gravity or API gravity of crude petroleum and liquid petroleum products by hydrometer method

1.3 Immersed body method

DIN 53217	Testing of paints, varnishes and similar coating materials; determination of density; immersed body method

2. Pycnometer Methods

2.1. For liquid substances

ISO 3507	Pycnometers
ISO 758	Liquid chemical products; determination of density at 20 °C
DIN 12797	Gay-Lussac pycnometer (for non-volatile liquids which are not too viscous)
DIN 12798	Lipkin pycnometer (for liquids with a kinematic viscosity of less than l00 . 10-6 m2 s-1 at 15 °C)
DIN 12800	Sprengel pycnometer (for liquids as DIN 12798)
DIN 12801	Reischauer pycnometer (for liquids with a kinematic viscosity of less than l00 . 10-6 m2 s-1 at 20 °C, applicable in particular also to hydrocarbons and aqueous solutions as well as to liquids with higher vapour pressure, approximately 1 bar at 90 °C)
DIN 12806	Hubbard pycnometer (for viscous liquids of all types which do not have too high a vapour pressure, in particular also for paints, varnishes and bitumen)
DIN 12807	Bingham pycnometer (for liquids, as in DIN 12801)
DIN 12808	Jaulmes pycnometer (in particular for ethanol - water mixture)
DIN 12809	Pycnometer with ground-in thermometer and capillary side tube (for liquids which are not too viscous)
DIN 53217	Testing of paints, varnishes and similar products; determination of

	density by pycnometer
DIN 51757	Point 7: Testing of mineral oils and related materials; determination of density
ASTM D 297	Section 15: Rubber products - chemical analysis
ASTM D 2111	Method C: Halogenated organic compounds
BS 4699	Method for determination of specific gravity and density of petroleum products (graduated bicapillary pycnometer method)
BS 5903	Method for determination of relative density and density of petroleum products by the capillary- stoppered pycnometer method
NF T 20-053	Chemical products for industrial use - Determination of density of solids in powder and liquids - Pyknometric method

2.2. For solid substances

ISO 1183	Method B: Methods for determining the density and relative density of plastics excluding cellular plastics
NF T 20-053	Chemical products for industrial use -Determination of density of solids in powder and liquids -Pyknometric method
DIN 19683	Determination of the density of soils

3. Air Comparison Pycnometer

DIN 55990	Part 3: Prüfung von Anstrichstoffen und ähnlichen Beschichrungsstoffen; Pulverlack; Bestimmung der Dichte
DIN 53243	Anstrichstoffe; Chlorhaltige Polymere; Prüfung

A.4. VAPOUR PRESSURE

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

It is useful to have preliminary information on the structure, the melting temperature and the boiling temperature of the substance to perform this test.

There is no single measurement procedure applicable to the entire range of vapour pressures. Therefore, several methods are recommended to be used for the measurement of vapour pressure from $< 10^{-4}$ to 10^{5} Pa.

Impurities will usually affect the vapour pressure, and to an extent which depends greatly upon the kind of impurity.

Where there are volatile impurities in the sample, which could affect the result, the substance may be purified. It may also be appropriate to quote the vapour pressure for the technical material.

Some methods described here use apparatus with metallic parts; this should be considered when testing corrosive substances.

1.2. DEFINITIONS AND UNITS

The vapour pressure of a substance is defined as the saturation pressure above a solid or liquid substance. At the thermodynamic equilibrium, the vapour pressure of a pure substance is a function of temperature only.

The SI unit of pressure which should be used is the pascal (Pa).

Units which have been employed historically, together with their conversion factors, are:

1 Torr (≡ 1 mm Hg) = $1{,}333 \times 10^{2}$ Pa

1 atmosphere = $1{,}013 \times 10^{5}$ Pa

1 bar = 10^{5} Pa

The SI unit of temperature is the kelvin (K).

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

The temperature dependence of the vapour pressure is 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 $\mathrm{Jmol^{-1}}$

R = the universal molar gas constant in $\mathrm{Jmol^{-1}\,K^{-1}}$

T = thermodynamic temperature in 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.

1.4. PRINCIPLE OF THE TEST METHODS

For determining the vapour pressure, seven methods are proposed which can be applied in different vapour pressure ranges. For each method, the vapour pressure is determined at various temperatures. In a limited temperature range, the logarithm of the vapour pressure of a pure substance is a linear function of the inverse of the temperature.

1.4.1. Dynamic method

In the dynamic method, the boiling temperature which pertains to a specified pressure is measured.

Recommended range:

10^3 up to 10^5 Pa.

This method has also been recommended for the determination of normal boiling temperature and is useful for that purpose up to 600 K.

1.4.2. Static method

In the static process, at thermodynamic equilibrium, the vapour pressure established in a closed system is determined at a specified temperature. This method is suitable for one component and multicomponent solids and liquids.

Recommended range:

10 up to 10^5 Pa.

This method can also be used in the range 1 to 10 Pa, providing care is taken.

1.4.3. Isoteniscope

This standardized method is also a static method but is usually not suitable for multicomponent systems. Additional information is available in ASTM method D-2879-86.

Recommended range:

from 100 up to 10^5 Pa.

1.4.4. Effusion method: Vapour pressure balance

The quantity of substance leaving a cell per unit time through an aperture of known size is determined under vacuum conditions such that return of substance into the cell is negligible (e.g. by measurement of the pulse generated on a sensitive balance by a vapour jet or by measuring the weight loss).

Recommended range:

10^{-3} to 1 Pa.

1.4.5. Effusion method: By loss of weight or by trapping vaporisate

The method is based on the estimation of the mass of test substance flowing out per unit of time of a Knudsen cell (4) in the form of vapour, through a micro-orifice under ultra-vacuum conditions. The mass of effused vapour can be obtained either by determining the loss of mass of the cell or by condensing the vapour at low temperature and determining the amount of volatilized substance using chromatographic analysis. The vapour pressure is calculated by applying the Hertz-Knudsen relation.

Recommended range:

10^{-3} to 1 Pa.

1.4.6. Gas saturation method

A stream of inert carrier gas is passed over the substance in such a way that it becomes saturated with its vapour. The amount of material transported by a known amount of carrier gas is measurable either by collection in a suitable trap or by an intrain analytical technique. This is then used to calculate the vapour pressure at a given temperature.

Recommended range:

10^{-4} to 1 Pa.

This method can also be used in the range 1 to 10 Pa providing care is taken.

1.4.7. Spinning rotor

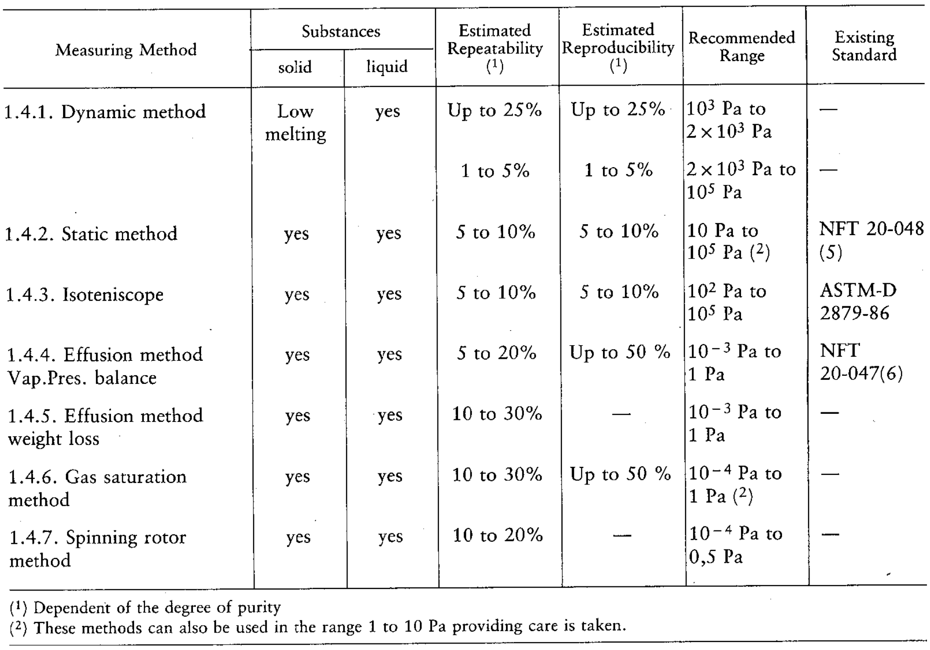
In the spinning rotor gauge, the actual measuring element is a small steel ball which is suspended in a magnetic field and rotates with high speed. The gas pressure is deduced from the pressure-dependent slow-down of the steel ball.

Recommended range:

10^{-4} to 0,5 Pa.

1.5. QUALITY CRITERIA

The various methods of determining the vapour pressure are compared as to application, repeatability , reproducibility , measuring range, existing standard. This is done in the following table.



Measuring Method	Substances		Estimated Repeatability (1)	Estimated Reproducibility (1)	Recommended Range	Existing Standard
	solid	liquid				
1.4.1. Dynamic method	Low melting	yes	Up to 25%	Up to 25%	10^3 Pa to 2×10^3 Pa	—
			1 to 5%	1 to 5%	2×10^3 Pa to 10^5 Pa	—
1.4.2. Static method	yes	yes	5 to 10%	5 to 10%	10 Pa to 10^5 Pa (2)	NFT 20-048 (5)
1.4.3. Isoteniscope	yes	yes	5 to 10%	5 to 10%	10^2 Pa to 10^5 Pa	ASTM-D 2879-86
1.4.4. Effusion method Vap.Pres. balance	yes	yes	5 to 20%	Up to 50 %	10^{-3} Pa to 1 Pa	NFT 20-047(6)
1.4.5. Effusion method weight loss	yes	yes	10 to 30%	—	10^{-3} Pa to 1 Pa	—
1.4.6. Gas saturation method	yes	yes	10 to 30%	Up to 50 %	10^{-4} Pa to 1 Pa (2)	—
1.4.7. Spinning rotor method	yes	yes	10 to 20%	—	10^{-4} Pa to 0,5 Pa	—

(1) Dependent of the degree of purity

(2) These methods can also be used in the range 1 to 10 Pa providing care is taken.

1.6. DESCRIPTION OF THE METHODS

1.6.1. Dynamic measurement

1.6.1.1. Apparatus

The measuring apparatus typically consists of a boiling vessel with attached cooler made of glass or metal (figure 1), equipment for measuring the temperature, and equipment for regulating and measuring the pressure. A typical measuring apparatus shown in the drawing is made from heat-resistant glass and is composed of five parts:

The large, partially double-walled tube consists of a ground jacket joint, a cooler, a cooling vessel and an inlet.

The glass cylinder, with a Cottrell 'pump', is mounted in the boiling section of the tube and has a rough surface of crushed glass to avoid 'bumping' in the boiling process.

The temperature is measured with a suitable temperature sensor (e.g. resistance thermometer, jacket thermocouple) immersed in the apparatus to the point of measurement (No.5, figure 1) through a suitable inlet (e.g. male ground joint).

The necessary connections are made to the pressure regulation and measuring equipment.

The bulb, which acts as a buffer volume, is connected with the measuring apparatus by means of a capillary tube.

The boiling vessel is heated by a heating element (e.g. cartridge heater) inserted into the glass apparatus from below. The heating current required is set and regulated via a thermocouple.

The necessary vacuum of between 10^2 Pa and approximately 10^5 Pa is produced with a vacuum pump.

A suitable valve is used to meter air or nitrogen for pressure regulation (measuring range approximately 10^2 to 10^5 Pa) and ventilation.

Pressure is measured with a manometer.

1.6.1.2. Measurement procedure

The vapour pressure is measured by determining the boiling temperature of the sample at various specified pressures between roughly 10^3 and 10^5 Pa. A steady temperature under constant pressure indicates that the boiling temperature has been reached. Frothing substances cannot be measured using this method.

The substance is placed in the clean, dry sample vessel. Problems may be encountered with non-powder solids but these can sometimes be solved by heating the cooling jacket. Once the vessel has been filled the apparatus is sealed at the flange and the substance degassed. The lowest desired pressure is then set and the heating is switched on. At the same time, the temperature sensor is connected to a recorder.

Equilibrium is reached when a constant boiling temperature is recorded at constant pressure. Particular care must be taken to avoid bumping during boiling. In addition, complete condensation must occur on the cooler. When determining the vapour pressure of low melting solids, care should be taken to avoid the condenser blocking.

After recording this equilibrium point, a higher pressure is set. The process is continued in this manner until 10^5 Pa has been reached (approximately 5 to 10 measuring points in all). As a check, equilibrium points must be repeated at decreasing pressures.

1.6.2. Static measurement

1.6.2.1. Apparatus

The apparatus comprises a container for the sample, a heating and cooling system to regulate the temperature of the sample and measure the temperature. The apparatus also includes instruments to set and measure the pressure. Figures 2a and 2b illustrate the basic principles involved.

The sample chamber (figure 2a) is bounded on one side by a suitable high-vacuum valve. A U-tube containing a suitable manometer fluid is attached to the other side. One end of the U-tube branches off to the vacuum pump, the nitrogen cylinder or ventilation valve, and a manometer.

A pressure gauge with a pressure indicator can be used instead of a U-tube (figure 2b).

In order to regulate the temperature of the sample, the sample vessel together with valve and U-tube or pressure gauge is placed in a bath which is kept at a constant temperature of ± 0,2 K. The temperature measurements are taken on the outside wall of the vessel containing the sample or in the vessel itself.

A vacuum pump with an upstream cooling trap is used to evacuate the apparatus.

In method 2a the vapour pressure of the substance is measured indirectly using a zero indicator. This takes into account the fact that the density of the fluid in the U-tube alters if the temperature changes greatly.

The following fluids are suitable for use as zero indicators for the U-tube, depending on the pressure range and the chemical behaviour of the test substance: silicone fluids, phthalates. The test substance must not dissolve noticeably in or react with the U-tube fluid.

For the manometer, mercury can be used in the range of normal air pressure to 10^2 Pa, while silicone fluids and phthalates are suitable for use below 10^2 Pa down to 10 Pa. Heatable membrane capacity manometers can even be used at below 10^{-1} Pa. There are also other pressure gauges which can be used below 10^2 Pa.

1.6.2.2. Measurement procedure

Before measuring, all components of the apparatus shown in figure 2 must be cleaned and dried thoroughly.

For method 2a, fill the U-tube with the chosen liquid, which must be degassed at an elevated temperature before readings are taken.

The test substance is placed in the apparatus, which is then closed and the temperature is reduced sufficiently for degassing. The temperature must be low enough to ensure that the air is sucked out, but -in the case of multiple component system- it must not alter the composition of the material. If required, equilibrium can be established more quickly by stirring.

The sample can be supercooled with e.g. liquid nitrogen (taking care to avoid condensation of air or pump fluid) or a mixture of ethanol and dry ice. For low-temperature measurements use a temperature-regulated bath connected to an ultra-cryomat.

With the valve over the sample vessel open, suction is applied for several minutes to remove the air. The valve is then closed and the temperature of the sample reduced to the lowest level desired. If necessary, the degassing operation must be repeated several times.

When the sample is heated the vapour pressure increases. This alters the equilibrium of the fluid in the U-tube. To compensate for this, nitrogen or air is admitted to the apparatus via a valve until the pressure indicator fluid is at zero again. The pressure required for this can be read off a precision manometer at room temperature. This pressure corresponds to the vapour pressure of the substance at that particular measuring temperature.

Method 2b is similar but the vapour pressure is read off directly.

The temperature-dependence of vapour pressure is determined at suitably small intervals (approximately 5 to 10 measuring points in all) up to the desired maximum. Low-temperature readings must be repeated as a check.

If the values obtained from the repeated readings do not coincide with the curve obtained for increasing temperature, this may be due to one of the following:

The sample still contains air (e.g. high-viscosity materials) or low-boiling substances, which is/ are released during heating and can be removed by suction following further supercooling.

The cooling temperature is not low enough. In this case liquid nitrogen is used as the cooling agent.

If either l or 2 is the case, the measurements must be repeated.

The substance undergoes a chemical reaction in the temperature range investigated (e.g. decomposition, polymerization).

1.6.3. Isoteniscope

A complete description of this method can be found in reference 7. The principle of the measuring device is shown in figure 3. Similarly to the static method described in 1.6.2, the isoteniscope is appropriate for the investigation of solids or liquids.

In the case of liquids, the substance itself serves as the fluid in the auxiliary manometer. A quantity of the liquid, sufficient to fill the bulb and the short leg of the manometer section, is put in the isoteniscope. The isoteniscope is attached to a vacuum system and evacuated, then filled by nitrogen. The evacuation and purge of the system is repeated twice to remove residual oxygen. The filled isoteniscope is placed in an horizontal position so that the sample spreads out into a thin layer in the sample bulb and manometer section (U-part). The pressure of the system is reduced to 133 Pa and the sample gently warmed until it just boils (removal of dissolved fixed gases). The isoteniscope is then placed so that the sample returns to the bulb and short leg of the manometer, so that both are entirely filled with liquid. The pressure is maintained as for degassing; the drawn-out tip of the sample bulb is heated with a small flame until sample vapour released expands sufficiently to displace part of the sample from the upper part of the bulb and manometer arm into the manometer section of the isoteniscope, creating a vapour-filled, nitrogen-free space.

The isoteniscope is then placed in a constant temperature bath, and the pressure of nitrogen is adjusted until its pressure equals that of the sample. Pressure balance is indicated by the manometer section of the isoteniscope. At the equilibrium, the vapour pressure of nitrogen equals the vapour pressure of the substance.

In the case of solids, depending on the pressure and temperature range, the manometer liquids listed in 1.6.2.1 are used. The degassed manometer liquid is filled into a bulge on the long arm of the isoteniscope. Then the solid to be investigated is placed in the bulb and is degassed at elevated temperature. After that the isoteniscope is inclined so that the manometer liguid can flow into the U-tube. The measurement of vapour pressure as a function of temperature is done according to 1.6.2.

1.6.4. Effusion method: Vapour pressure balance

1.6.4.1. Apparatus

Various versions of the apparatus are described in the literature (1). The apparatus described here illustrates the general principle involved (figure 4). Figure 4 shows the main components of the apparatus, comprising a high-vacuum stainless steel or glass container, equipment to produce and measure a vacuum and built-in components to measure the vapour pressure on a balance. The following built-in components are included in the apparatus:

- an evaporator furnace with flange and rotary inlet. The evaporator furnace is a cylindrical vessel, made of e.g. copper or a chemically resistant alloy with good thermal conductivity. A glass vessel with a copper wall can also be used. The furnace has a diameter of approximately 3 to 5 cm and is 2 to 5 cm high. There are between one and three openings of different sizes for the vapour stream. The furnace is heated either by a heating spiral around the outside. To prevent heat being dissipated to the base plate, the heater is attached to the base plate by a metal with low thermal conductivity (nickel-silver or chromium-nickel steel), e.g. a nickel-silver pipe attached to a rotary inlet if using a furnace with several openings. This arrangement has the advantage of allowing the introduction of a copper bar. This allows cooling from the outside using a cooling bath,

- if the copper furnace lid has three openings of different diameters at 900 to each other, various vapour pressure ranges within the overall measuring range can be covered (openings between approximately 0,30 and 4,50 mm diameter). Large openings are used for low vapour pressure and vice versa. By rotating the furnace the desired opening or an intermediate position in the vapour stream (furnace opening - shield - balance pan) can be set and the stream of molecules is released or deflected through the furnace opening onto the scale pan. In order to measure the temperature of the substance, a thermocouple or resistance thermometer is placed at a suitable point,

- above the shield is a balance pan belonging to a highly sensitive microbalance (see below). The balance pan is approximately 30 mm in diameter. Gold-plated aluminium is a suitable material,

- the balance pan is surrounded by a cylindrical brass or copper refrigeration box. Depending on the type of balance, it has openings for the balance beam and a shield opening for the stream of molecules and should guarantee complete condensation of the vapour on the balance pan. Heat dissipation to the outside is ensured e.g. by a copper bar connected to the refrigeration box. The bar is routed through the base plate and thermally insulated from it, e.g. with a chromium-nickel steel tube. The bar is immersed in a Dewar flask containing liquid nitrogen under the base plate or liquid nitrogen is circulated through the bar. The refrigeration box is thus kept at approximately -120 °C. The balance pan is cooled exclusively by radiation and is satisfactory for the pressure range under investigation (cooling approximately 1 hour before the start of measurement),

- the balance is positioned above the refrigeration box. Suitable balances are e.g. a highly sensitive 2-arm electronic microbalance (8) or a highly sensitive moving coil instrument (see OECD Test Guideline 104, Edition 12.05.81),

- the base plate also incorporates electrical connections for thermocouples (or resistance thermometers) and heating coils,

- a vacuum is produced in the vessel using a partial vacuum pump or high-vacuum pump (required vacuum approximately 1 to 2 $.10^{-3}$ Pa, obtained after 2 h pumping). The pressure is regulated with a suitable ionisation manometer.

1.6.4.2. Measurement procedure

The vessel is filled with the test substance and the lid is closed. The shield and refrigeration box are slid across the furnace. The apparatus is closed and the vacuum pumps are switched on. The final pressure before starting to take measurements should be approximately 10^{-4} Pa. Cooling of the refrigeration box starts at 10^{-2} Pa.

Once the required vacuum has been obtained, start the calibration series at the lowest temperature required. The corresponding opening in the lid is set, the vapour stream passes through the shield directly above the opening and strikes the cooled balance pan. The balance pan must be big enough to ensure that the entire stream guided through the shield strikes it. The momentum of the vapour stream acts as a force against the balance pan and the molecules condense on its cool surface.

The momentum and simultaneous condensation produce a signal on the recorder. Evaluation of the signals provides two pieces of information:

1. In the apparatus described here the vapour pressure is determined directly from the momentum on the balance pan (it is not necessary to know the molecular weight for this (2)). Geometrical factors such as the furnace opening and the angle of the molecular stream must be taken into account when evaluating the readings.

2. The mass of the condensate can be measured at the same time and the rate of evaporation can be calculated from this. The vapour pressure can also be calculated from the rate of evaporation and molecular weight using the Hertz equation (2).

$$p = G\sqrt{\frac{2\pi RT\times 10^{3}}{M}}$$

where

G = evaporation rate ($\mathrm{kg\ s^{-1}\ m^{-2}}$)

M = molar mass ($\mathrm{g\ mol^{-1}}$)

T = temperature (K)

R = universal molar gas constant ($\mathrm{J mol^{-1}\ K^{-1}}$)

p = vapour pressure (Pa)

After the necessary vacuum is reached, the series of measurements is commenced at the lowest desired measuring temperature.

For further measurements, the temperature is increased by small intervals until the maximum desired temperature value is reached. The sample is then cooled again and a second curve of the vapour pressure may be recorded. If the second run fails to confirm the results of the first run, then it is possible that the substance may be decomposing in the temperature range being measured.

1.6.5. Effusion method -by loss of weight

1.6.5.1. Apparatus

The effusion apparatus consists of the following basic parts:

- a tank that can be thermostated and evacuated and in which the effusion cells are located,
- a high vacuum pump (e.g. diffusion pump or turbomolecular pump) with vacuum gauge,
- a trap, using liquefied nitrogen or dry ice.

An electrically heated, aluminium vacuum tank with 4 stainless steel effusion cells is shown in figure 5 for example. The stainless steel foil of about 0,3 mm thickness has an effusion orifice of 0,2 to 1,0 mm diameter and is attached to the effusion cell by a threaded lid.

1.6.5.2. Measurement procedure

The reference and test substances are filled into each effusion cell, the metal diaphragm with the orifice is secured by the threaded lid, and each cell is weighed to within an accuracy of 0,1 mg. The cell is placed in the thermostated apparatus, which is then evacuated to below one tenth of the expected pressure. At defined intervals of time ranging from 5 to 30 hours, air is admitted into the apparatus, and the loss in mass of the effusion cell is determined by reweighing.

In order to ensure that the results are not influenced by volatile impurities, the cell is reweighed at defined time intervals to check that the evaporation rate is constant over at least two such intervals of time.

The vapour pressure p in the effusion cell is given by:

$$p = \frac{m}{KAt}\sqrt{\frac{2\pi RT}{M}}$$

where

p	= vapour pressure (Pa)
m	= mass of the substance leaving the cell during time t (kg)
t	= time (s)
A	= area of the hole (m^2)
K	= correction factor
R	= universal gas constant ($Jmol^{-1}$ K^{-1})
T	= temperature (K)
M	= molecular mass (kg mol^{-1})

The correction factor K depends on the ratio of length to radius of the cylindrical orifice:

ratio	0,1	0,2	0,6	1,0	2,0
K	0,952	0,909	0,771	0,672	0,514

The above equation may be written:

$$p = E\frac{m}{t}\sqrt{\frac{T}{M}}$$

where $E = \frac{1}{KA}\sqrt{2\pi R}$ and is the effusion cell constant.

This effusion cell constant E may be determined with reference substances (2,9), using the following equation:

$$E = \frac{p(r)t}{m}\sqrt{\frac{M(r)}{T}}$$

where

p(r) = vapour pressure of the reference substance (Pa)

M(r) = molecular mass of the reference substance (kg.mol^{-l})

1.6.6. Gas saturation method

1.6.6.1. Apparatus

A typical apparatus used to perform this test comprises a number of components given in figure 6a and described below (1).

Inert gas:

The carrier gas must not react chemically with the test substance. Nitrogen is usually sufficient for this purpose but occasionally other gases may be required (10). The gas employed must be dry (see figure 6a, key 4: relative humidity sensor).

Flow control:

A suitable gas-control system is required to ensure a constant and selected flow through the saturator column.

Traps to collect vapour:

These are dependent on the particular sample characteristics and the chosen method of analysis. The vapour should be trapped quantitatively and in a form which permits subsequent analysis. For some test substances, traps containing liquids such as hexane or ethylene glycol will be suitable. For others, solid absorbents may be applicable.

As an alternative to vapour trapping and subsequent analysis, in-train analytical techniques, like chromatography, may be used to determine quantitatively the amount of material transported by a known amount of carrier gas. Furthermore, the loss of mass of the sample can be measured.

Heat exchanger:

For measurements at different temperatures it may be necessary to include a heat-exchanger in the assembly.

Saturator column:

The test substance is deposited from a solution onto a suitable inert support. The coated support is packed into the saturator column, the dimensions of which and the flow rate should be such that complete saturation of the carrier gas is ensured. The saturator column must be thermostated. For measurements above room temperature, the region between the saturator column and the traps should be heated to prevent condensation of the test substance.

In order to lower the mass transport occurring by diffusion, a capillary may be placed after the saturator column (figure 6b).

1.6.6.2. Measurement procedure

Preparation of the saturator column:

A solution of the test substance in a highly volatile solvent is added to a suitable amount of support. Sufficient test substance should be added to maintain saturation for the duration of the test. The solvent is totally evaporated in air or in a rotary evaporator, and the thoroughly mixed material is added to the saturator column. After thermostating the sample, dry nitrogen is passed through the apparatus.

Measurement:

The traps or in-train detector are connected to the column effluent line and the time recorded. The flow rate is checked at the beginning and at regular intervals during the experiment, using a bubble meter (or continuously with a mass flow-meter).

The pressure at the outlet to the saturator must be measured. This may be done either:

(a) by including a pressure gauge between the saturator and traps (this may not be satisfactory because this increases the dead space and the adsorptive surface); or

(b) by determining the pressure drops across the particular trapping system used as a function of flow rate in a separate experiment (this may be not very satisfactory for liquid traps).

The time required for collecting the quantity of test substance that is necessary for the different methods of analysis is determined in preliminary runs or by estimates. As an alternative to collecting the substance for further analysis, in-train quantitative analytical technique may be used (e.g. chromatography). Before calculating the vapour pressure at a given temperature, preliminary runs are to be carried out to determine the maximum flow rate that will completely saturate the carrier gas with substance vapour. This is guaranteed if the carrier gas is passed through the saturator sufficiently slowly so that a lower rate gives no greater calculated vapour pressure.

The specific analytical method will be determined by the nature of the substance being tested (e.g. gas chromatography or gravimetry).

The quantity of substance transported by a known volume of carrier gas is determined.

1.6.6.3. Calculation of vapour pressure

Vapour pressure is calculated from the vapour density , W/V, through the equation:

$$p = \frac{W}{V} x \frac{RT}{M}$$

where:

p = vapour pressure (Pa)

W = mass of evaporated test substance (g)

V = volume of satUrated gas (m^3)

R = universal molar gas constant ($Jmol^{-l}\ K^{-1}$)

T = temperature (K)

M = molar mass of test substance ($g\ mol^{-l}$)

Measured volumes must be corrected for pressure and temperature differences between the flow meter and the thermostated saturator. If the flow meter is located downstream from the vapour trap, corrections may be necessary to account for any vaporized trap ingredients (1).

1.6.7. Spinning rotor (8, 11, 13)

1.6.7.1. Apparatus

The spinning rotor technique can be carried out using a spinning rotor viscosity gauge as shown in figure 8. A schematic drawing of the experimental set-up is shown in figure 7.

The measuring apparatus typically consists of a spinning rotor measuring head, placed in a thermostated enclosure (regulated within 0,1 °C). The sample container is placed in a thermostat ted enclosure (regulated within 0,01 °C), and all other parts of the set-up are kept at a higher temperature to prevent condensation. A high-vacuum pump device is connected to the system by means of high-vacuum valves.

The spinning rotor measuring head consists of a steel ball (4 to 5 mm diameter) in a tube. The ball is suspended and stabilized in a magnetic field, generally using a combination of permanent magnets and control coils.

The ball is made to spin by rotating fields produced by coils. Pick-up coils, measuring the always present low lateral magnetization of the ball, allow its spinning rate to be measured.

1.6.7.2 Measurement procedure

When the ball has reached a given rotational speed v(o) (usually about 400 revolutions per second), further energizing is stopped and deceleration takes place, due to gas friction.

The drop of rotational speed is measured as a function of time. As the friction caused by the magnetic suspension is negligible as compared with the gas friction, the gas pressure p is given by:

$$p = \frac{\pi \bar{c} r \rho}{\sigma 10 t} x \ln \frac{v(t)}{v(0)}$$

where

$\bar{c}$ = average speed of the gas molecules

r = radius of the ball

ρ = mass density of the ball

σ = coefficient of tangential momentum transfer (ε = 1 for an ideal spherical surface of the ball)

t = time

v(t) = rotational speed after time t

v(o) = initial rotational speed

This equation may also be written:

$$p = \frac{\pi \bar{c} r \rho}{10 \sigma} x \frac{t_n - t_{n-1}}{t_n x t_{n-1}}$$

where t_n, t_{n-1} are the times required for a given number N of revolutions. These time intervals t_n and t_{n-1} succeed one another, and $t_n > t_{n-1}$.

The average speed of the gas molecule c is given by:

$$\bar{c} = \left(\frac{8RT}{\pi M}\right)^{\frac{1}{2}}$$

where:

T = temperature

T = temperature (K)

M = molar mass

2. DATA

The vapour pressure from any of the preceding methods should be determined for at least two temperatures. Three or more are preferred in the range 0 to 50 °C, in order to check the linearity of the vapour pressure curve.

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,
- at least two vapour pressure and temperature values, preferably in the range 0 to 50 °C,
- all of the raw data,
- a log p versus 1/ T curve,
- an estimate of the vapour pressure at 20 or 25 °C.

If a transition (change of state, decomposition) is observed, the following information should be noted:

- nature of the change,
- temperature at which the change occurs at atmospheric pressure,
- vapour pressure at 10 and 20 °C below the transition temperature and 10 and 20 °C above this temperature (unless the transition is from solid to gas).

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 104, Decision of the Council C(81) 30 final.

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(6) NF T 20-047 AFNOR (Sept. 85). Chemical products for industrial use - Determination of vapour pressure of solids and liquids within range from 10-3 to 1 Pa -Vapour pressure balance method.

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APPENDIX 1 - ESTIMATION METHOD

INTRODUCTION

Calculated values of the vapour pressure can be used:

– for deciding which of the experimental methods is appropriate,

– for providing an estimate or limit value in cases where the experimental method cannot be applied due to technical reasons (including where the vapour pressure is very low),

– to help identify those cases where omitting experimental measurement is justified because the vapour pressure is likely to be < 10 $^{-5}$ Pa at ambient temperature.

ESTIMATION METHOD

The vapour pressure of liquids and solids can be estimated by use of the modified Watson Correlation (a). The only experimental data required is the normal boiling point. The method is applicable over the pressure range from 10^5 Pa to 10^{-5} Pa.

Detailed information on the method is given in 'Handbook of Chemical Property Estimation Methods' (b).

CALCULATION PROCEDURE

According to (b) the vapour pressure is calculated as follows:

$$\ln P_{vp} \approx \frac{\Delta H_{vb}}{\Delta Z_b R T_b}\left[1 - \frac{\left(3 - 2\frac{T}{T_b}\right)^m}{\frac{T}{T_b}} - 2m\left(3 - 2\frac{T}{T_b}\right)^{m-1} \ln \frac{T}{T_b}\right]$$

where:

T = temperature of interest

T_b = normal boiling point

P_{vp} = vapour pressure at temperature T

ΔH_{vb} = heat of vaporization

ΔZ_b = compressibility factor (estimated at 0,97)

m = empirical factor depending on the physical state at the temperature of interest

Further

$$\frac{\Delta H_{vb}}{T_b} = K_F(8{,}75 + R \ln T_b)$$

where K_F is an empirical factor considering the polarity of the substance. For several compound types, K_F factors are listed in reference (b).

Quite often, data are available in which a boiling point at reduced pressure is given. In such a case, according to (b), the vapour pressure is calculated as follows:

$$\ln P_{vp} \approx \ln P_1 + \frac{\Delta H_{v1}}{\Delta Z_b R T_1}\left[1 - (3 - 2\frac{T}{T_1})m\frac{T_1}{T} - 2m(3 - 2\frac{T}{T_1})^{m-1} \ln \frac{T}{T_1}\right]$$

where T_1 is the boiling point at the reduced pressure P_1.

REPORT

When using the estimation method, the report shall include a comprehensive documentation of the calculation.

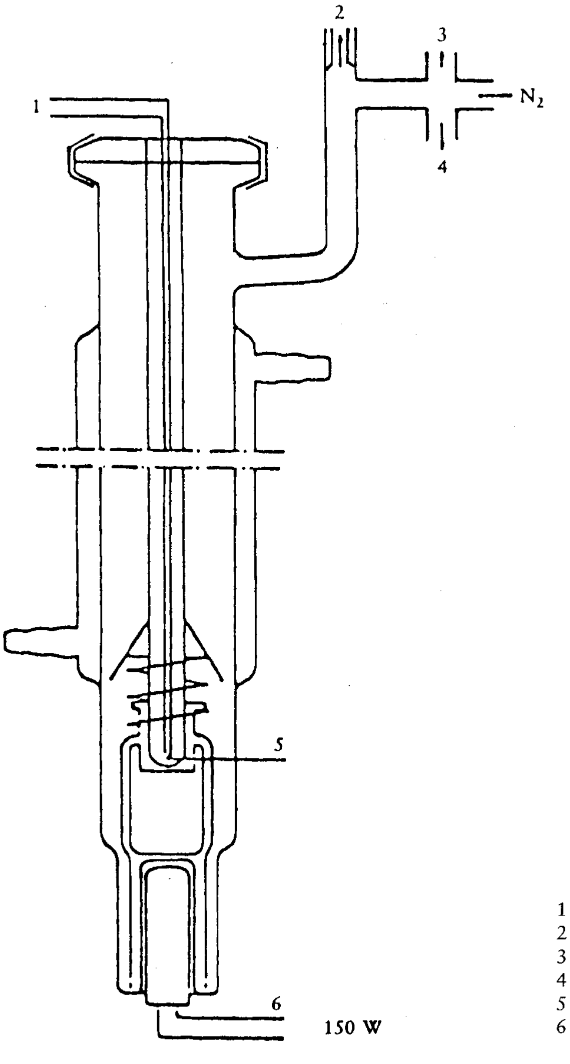
LITERATURE

(a) K.M. Watson, Ind. Eng. Chem; 1943, vol. 35,398.

(b) W.J. Lyman, W.F. Reehl, D.H. Rosenblatt. Handbook of Chemical Property Estimation Methods, Mc Graw-Hill, 1982.

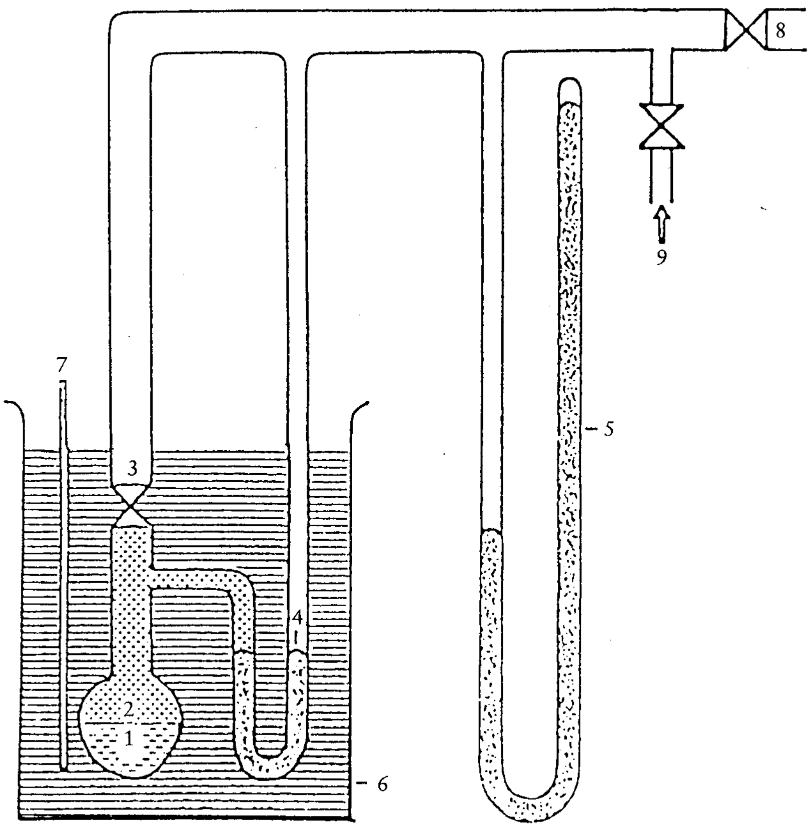
APPENDIX 2

Figure 1
Apparatus for determining the vapour pressure curve according to the dynamic method.



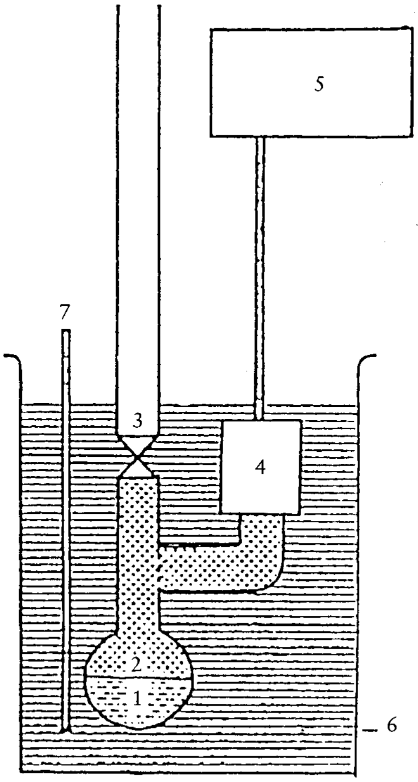
1 = Thermocouple
2 = Vacuum buffer volume
3 = Pressure gauge
4 = Vacuum
5 = Measuring point
6 = Heating element *circa* 150 W

Figure 2a
Apparatus for determining the vapour pressure curve according to the static method (using a U-tube manometer)



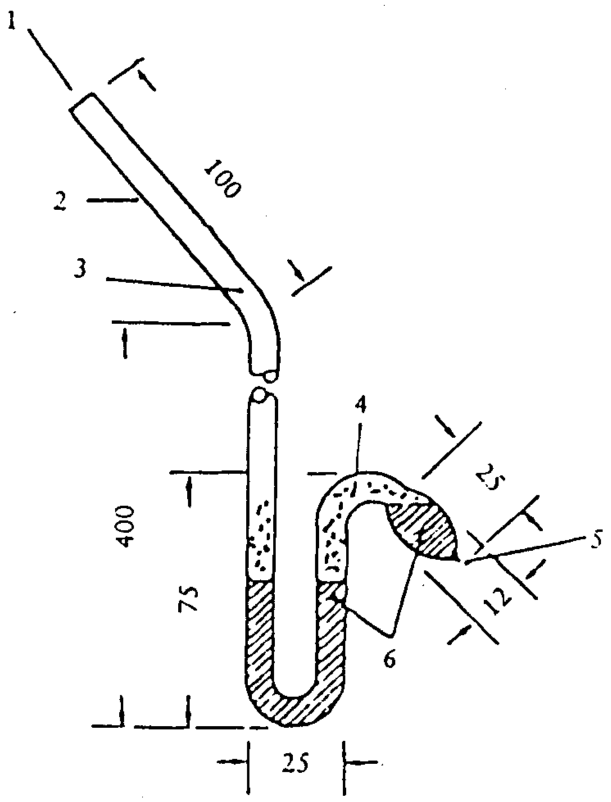
1. Test substance
2. Vapour phase
3. High vacuum valve
4. U-tube (auxiliary manometer)
5. Manometer
6. Temperature bath
7. Temperature measuring device
8. To vacuum pump
9. Ventilation

Figure 2b
Apparatus for determining the vapour
pressure curve according to the static method (using a pressure indicator)



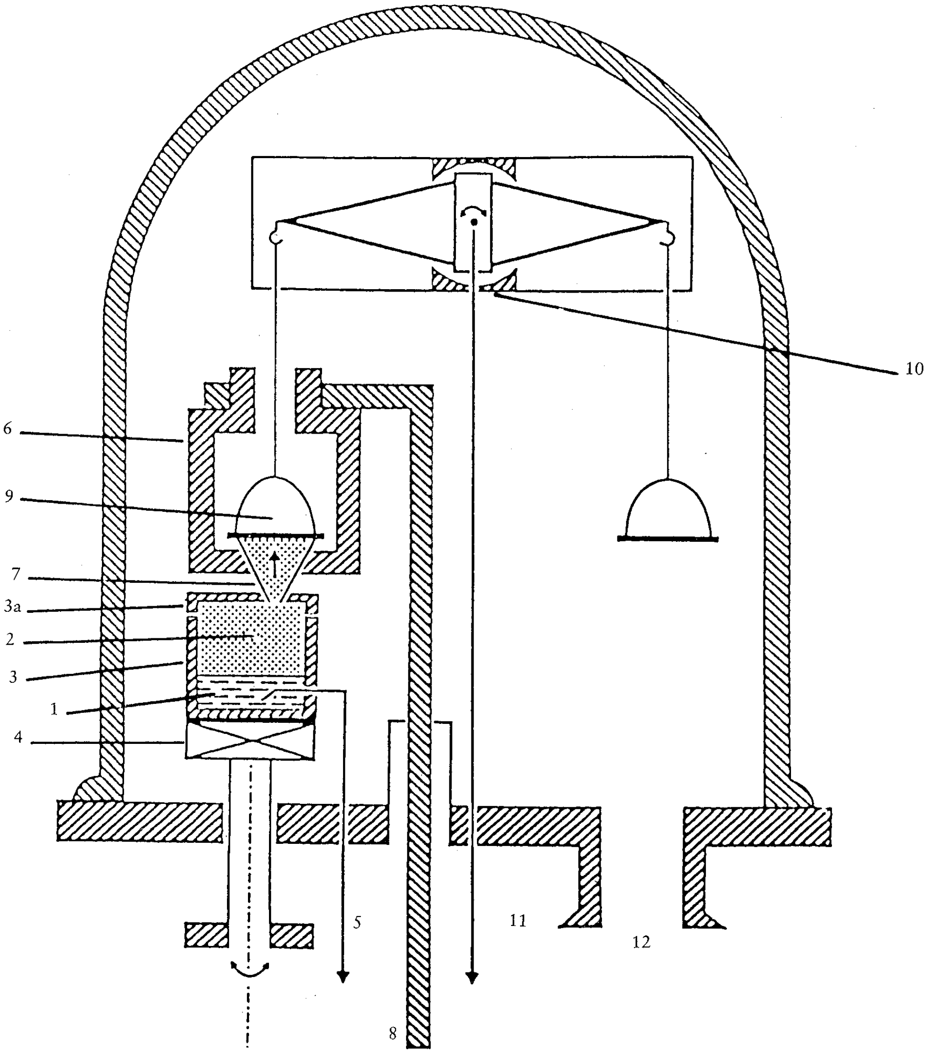
1. Test substance
2. Vapour phase
3. High vacuum valve
4. Pressure gauge
5. Pressure indicator
6. Temperature bath
7. Temperature measuring device

Figure 3
Isoteniscope (see reference 7)



1. To pressure control and measurement system
2. 8 mm OD tube
3. Dry nitrogen in pressure system
4. Sample vapour
5. Small tip
6. Liquid sample

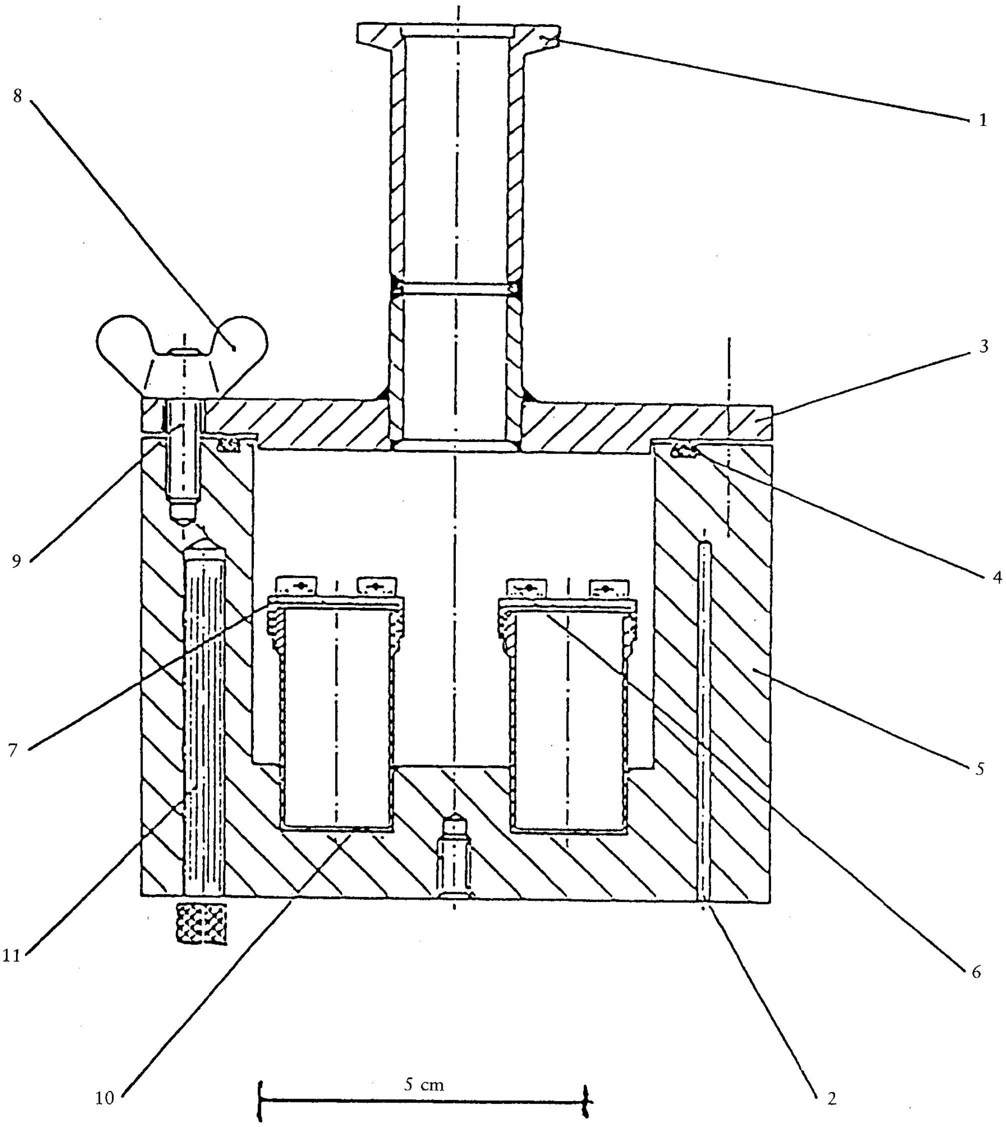
Figure 4
Apparatus for determining the vapour pressure curve according to the vapour pressure balance method



1. Test substance
2. Vapour phase with vapour stream
3. Evaporation furnace with rotary inlet
3a. Furnace lid with opening
4. Furnace heating (refrigeration)
5. Measurement of temperature of sample
6. Refrigeration box
7. Shield
8. Refrigeration bar for refrigeration box
9. Balance pan
10. Microbalance
11. To recorder
12. To high-vacuum pump

Figure 5

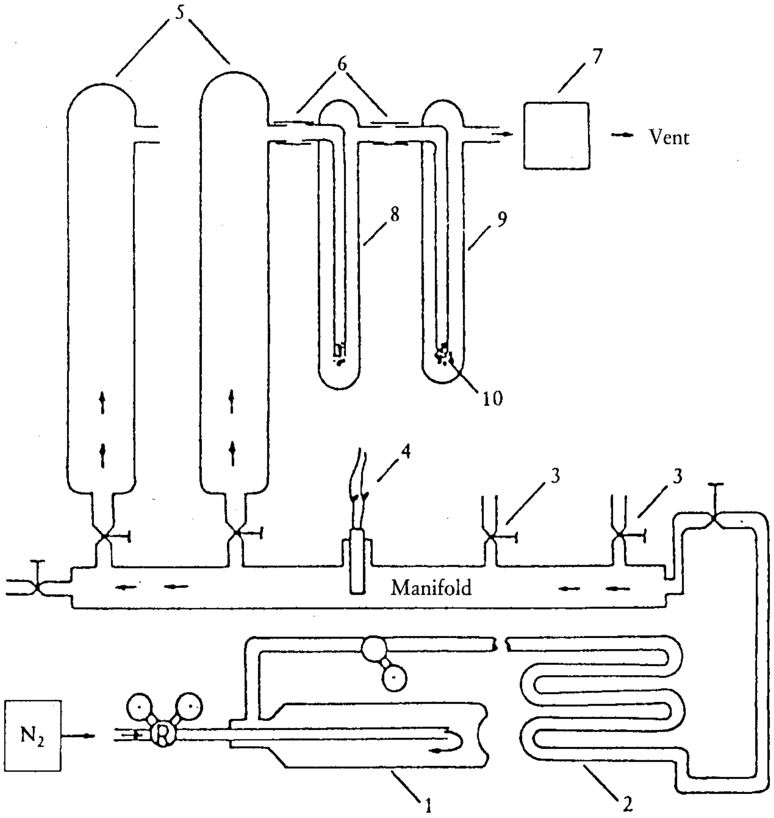
Example of apparatus for evaporation at low pressure by effusion methode, with an effusion cell volume of 8 cm^3



1 Connection to vacuum
2 Wells for platinum resistance thermometer or temperature measurement and control (2)
3 Lid for vacuum tank
4 O-ring
5 Aluminium vacuum tank
6 Device for installing and removing the effusion cells
7 Threaded lid
8 Butterfly nuts (6)
9 Bolts (6)
10 Stainless steel effusion cells
11 Heater cartridges (6)

Figure 6a

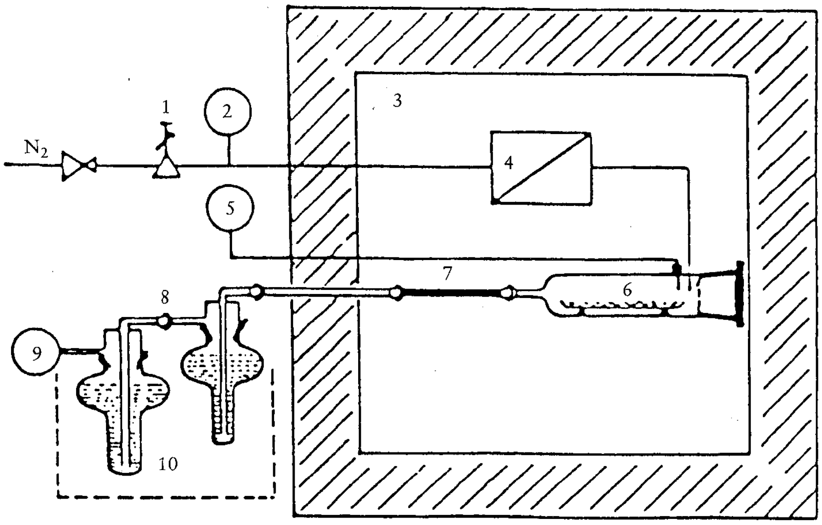
An example of a flow system for the determination of vapour pressure by the gas saturation method



1 = Flow regulator
2 = Heat exchanger
3 = Needle valves
4 = Relative humidity sensor
5 = Saturation columns
6 = PTFE joints
7 = Flow meter
8 = Trap (absorber)
9 = Oil trap
10 = Fritted bubbler

Figure 6b

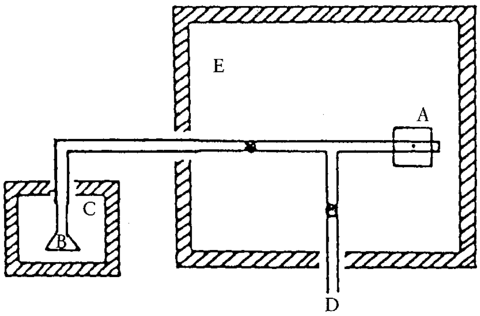
An example of a system for the determination of vapour pressure by the gas saturation method, with a capillary placed after the saturation chamber



1. Thermal mass flowmeter
2. Manometer
3. Temperature-controlled chamber
4. Thermostating coil for carrier gas
5. Thermometer (Pt 100)
6. Gas saturation chamber
7. Capillary
8. Absorption vessels
9. Gas meter
10. Cold trap

Figure 7

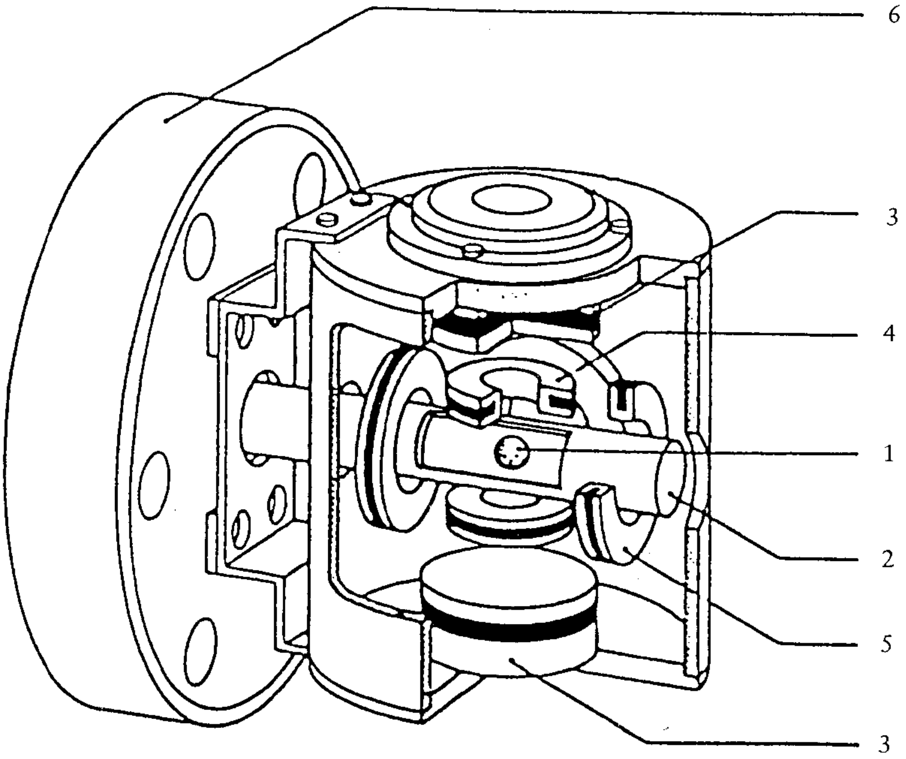
Example of the experimental set-up for spinning rotor method



Vapour pressure apparatus
A. spinning rotor sensor head;
B. sample cell;
C. thermostat
D. vacuum line (turbo pump);
E. air thermostat.

Figure 8

Example of spinning rotor measuring head



1. Ball;
2. Evacuated tubular extension of 6
3. Permanent magnets (2);
4. Coils (2) for vertical stabilization;
5. Driving coils (4)
6. Connection flange.

A.5. SURFACE TENSION

1. METHOD

The methods described are based on the OECD Test Guideline (1). The fundamental principles are given in reference (2).

1.1. INTRODUCTION

The described methods are to be applied to the measurement of the surface tension of aqueous solutions.

It is useful to have preliminary information on the water solubility, the structure, the hydrolysis properties and the critical concentration for micelles formation of the substance before performing these tests.

The following methods are applicable to most chemical substances, without any restriction in respect to their degree of purity.

The measurement of the surface tension by the ring tensiometer method is restricted to aqueous solutions with a dynamic viscosity of less than approximately 200 mPa s.

1.2. DEFINITIONS AND UNITS

The free surface enthalpy per unit of surface area is referred to as surface tension.

The surface tension is given as:

N/m (SI unit) or

mN/m (SI sub-unit)

1 N/m = 103 dynes/cm

1 mN/m = 1 dyne/cm in the obsolete cgs system

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.

Reference substances which cover a wide range of surface tensions are given in references 1 and 3.

1.4. PRINCIPLE OF THE METHODS

The methods are based on the measurement of the maximum force which it is necessary to exert vertically, on a stirrup or a ring in contact with the surface of the liquid being examined placed in a measuring cup, in order to separate it from this surface, or on a plate, with an edge in contact with the surface, in order to draw up the film that has formed.

Substances which are soluble in water at least at a concentration of 1 mg/l are tested in aqueous solution at a single concentration.

1.5. QUALITY CRITERIA

These methods are capable of greater precision than is likely to be required for environmental assessment.

1.6. DESCRIPTION OF THE METHODS

A solution of the substance is prepared in distilled water. The concentration of this solution should be 90% of the saturation solubility of the substance in water; when this concentration exceeds 1 g/l, a concentration of 1 g/l is used for testing. Substances with a water solubility lower than 1 mg/l need not be tested.

1.6.1. Plate method

See ISO 304 and NF T 73-060 (Surface active agents -determination of surface tension by drawing up liquid films).

1.6.2. Stirrup method

See ISO 304 and NF T 73-060 (Surface active agents -determination of surface tension by drawing up liquid films).

1.6.3. Ring method

See ISO 304 and NF T 73-060 (Surface active agents - determination of surface tension by drawing up liquid films).

1.6.4. OECD harmonized ring method

1.6.4.1. Apparatus

Commercially available tensiometers are adequate for this measurement. They consist of the following elements:

- mobile sample table,
- force measuring system,

1.6.4.1.1. Mobile sample table

The mobile sample table is used as a support for the temperature-controlled measurement vessel holding the liquid to be tested. Together with the force measuring system, it is mounted on a stand.

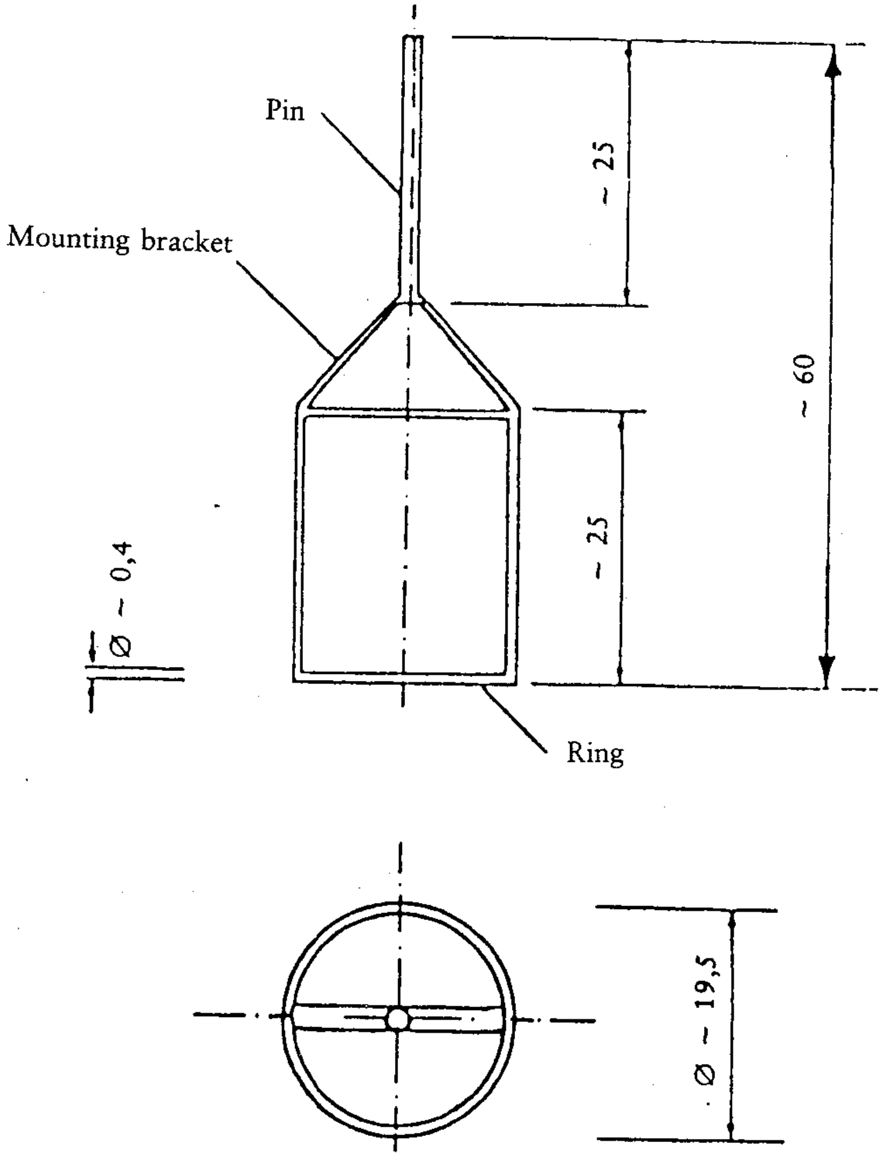
1.6.4.1.2. Force measuring system

The force measuring system (see figure) is located above the sample table. The error of the force measurement shall not exceed ± 10^{-6} N, corresponding to an error limit of ± 0,1 mg in a mass measurement. In most cases, the measuring scale of commercially available tensiometers is calibrated in mN/m so that the surface tension can be read directly in mN /m with an accuracy of 0,1 mN/m.

1.6.4.1.3. Measuring body (ring)

The ring is usually made of a platinum-iridium wire of about 0,4 mm thickness and a mean circumference of 60 mm. The wire ring is suspended horizontally from a metal pin and a wire mounting bracket to establish the connection to the force measuring system (see figure).

Figure
Measuring body
(All dimensions expressed in millimetres)



1.6.4.1.4. Measurement vessel

The measurement vessel holding the test solution to be measured shall be a temperature-controlled glass vessel. It shall be designed so that during the measurement the temperature of the test solution liquid and the gas phase above its surface remains constant and that the sample cannot evaporate. Cylindrical glass vessels having an inside diameter of not less than 45 mm are acceptable.

1.6.4.2. Preparation of the apparatus

1.6.4.2.1. Cleaning

Glass vessels shall be cleaned carefully. If necessary they shall be washed with hot chromo-sulphuric acid and subsequently with syrupy phosphoric acid (83 to 98% by weight of H_3PO_4), thoroughly rinsed in tap water and finally washed with double-distilled water until a neutral reaction is obtained and subsequently dried or rinsed with part of the sample liquid to be measured.

The ring shall first be rinsed thoroughly in water to remove any substances which are soluble in water, briefly immersed in chromo-sulphuric acid, washed in double-distilled water until a neutral reaction is obtained and finally heated briefly above a methanol flame.

Note:

Contamination by substances which are not dissolved or destroyed by chromo-sulphuric acid or phosphoric acid, such as silicones, shall be removed by means of a suitable organic solvent.

1.6.4.2.2. Calibration of the apparatus

The validation of the apparatus consists of verifying the zero point and adjusting it so that the indication of the instrument allows reliable determination in mN/m.

Mounting:

The apparatus shall be levelled, for instance by means of a spirit level on the tensiometer base, by adjusting the levelling screws in the base.

Zero point adjustment:

After mounting the ring on the apparatus and prior to immersion in the liquid, the tensiometer indication shall be adjusted to zero and the ring checked for parallelism to the liquid surface. For this purpose, the liquid surface can be used as a mirror.

Calibrations:

The actual test calibration can be accomplished by means of either of two procedures:

(a) Using a mass: procedure using riders of known mass between 0,1 and 1,0 g placed on the ring. The calibration factor, Φ_a by which all the instrument readings must be multiplied, shall be determined according to equation (1).

$$\Phi_a = \frac{\sigma_r}{\sigma_a}$$

where:

$$\sigma_r = \frac{mg}{2b}(\mathrm{mN/m})$$

m = mass of the rider (g)

g = gravity acceleration (981 cm s^{-2} at sea level)

b = mean circumference of the ring (cm)

σ_a = reading of the tensiometer after placing the rider on the ring (mN/m).

(b) Using water: procedure using pure water whose surface tension at, for instance, 23 °C is equal to 72,3 mN/m. This procedure is accomplished faster than the weight calibration but there is always the danger that the surface tension of the water is falsified by traces of contamination by surfactants.

The calibration factor, Φ_b by which all the instrument readings shall be multiplied, shall be determined in accordance with the equation (2):

$$\Phi_b = \frac{\sigma_o}{\sigma_g}$$

where:

σ_o = value cited in the literature for the surface tension of water (mN/m)

σ_g = measured value of the surface tension of the water (mN/m)

both at the same temperature.

1.6.4.3. Preparation of samples

Aqueous solutions shall be prepared of the substances to be tested, using the required concentrations in water, and shall not contain any non-dissolved substances.

The solution must be maintained at a constant temperature (± 0,5 °C). Since the surface tension of a solution in the measurement vessel alters over a period of time, several measurements shall be made at various times and a curve plotted showing surface tension as a function of time. When no further change occurs, a state of equilibrium has been reached.

Dust and gaseous contamination by other substances interfere with the measurement. The work shall therefore be carried out under a protective cover.

1.6.5. Test conditions

The measurement shall be made at approximately 20 °C and shall be controlled to within ± 0,5 °C.

1.6.6. Performance of test

The solutions to be measured shall be transferred to the carefully cleaned measurement vessel, taking care to avoid foaming, and subsequently the measurement vessel shall be placed onto the table of the test apparatus. The table-top with measurement vessel shall be raised until the ring is immersed below the surface of the solution to be measured. Subsequently, the table-top shall be lowered gradually and evenly (at a rate of approximately 0,5 cm/min) to detach the ring from the surface until the maximum force has been reached. The liquid layer attached to the ring must not separate from the ring. After completing the measurements, the ring shall be immersed below the surface again and the measurements repeated until a constant surface tension value is reached. The time from transferring the solution to the measurement vessel shall be recorded for each determination. Readings shall be taken at the maximum force required to detach the ring from the liquid surface.

2. DATA

In order to calculate the surface tension, the value read in mN/m on the apparatus shall be first multiplied by the calibration factor Φ_a or Φ_b (depending on the calibration procedure used). This will yield a value which applies only approximately and therefore requires correction.

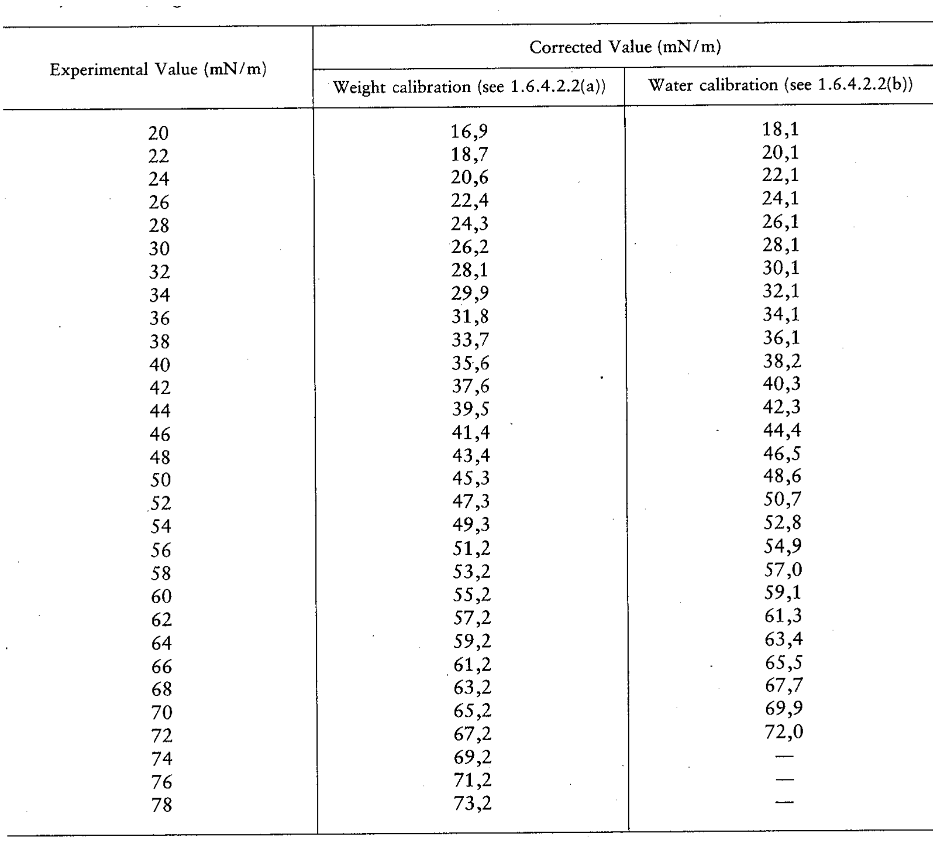
Harkins and Jordan (4) have empirically determined correction factors for surface-tension values measured by the ring method which are dependent on ring dimensions, the density of the liquid and its surface tension.

Since it is laborious to determine the correction factor for each individual measurement from the Harkins and Jordan tables, in order to calculate the surface tension for aqueous solutions the simplified procedure of reading the corrected surface-tension values directly from the table may be used. (Interpolation shall be used for readings ranging between the tabular values.)

TABLE: CORRECTION OF THE MEASURED SURFACE TENSION

Only for aqueous solutions, $\rho \cong 1$ g/cm3

R	= 9,55 mm (average ring radius)
r	= 0,185 mm (ring wire radius)



Experimental Value (mN/m)	Corrected Value (mN/m)	
	Weight calibration (see 1.6.4.2.2(a))	Water calibration (see 1.6.4.2.2(b))
20	16,9	18,1
22	18,7	20,1
24	20,6	22,1
26	22,4	24,1
28	24,3	26,1
30	26,2	28,1
32	28,1	30,1
34	29,9	32,1
36	31,8	34,1
38	33,7	36,1
40	35,6	38,2
42	37,6	40,3
44	39,5	42,3
46	41,4	44,4
48	43,4	46,5
50	45,3	48,6
52	47,3	50,7
54	49,3	52,8
56	51,2	54,9
58	53,2	57,0
60	55,2	59,1
62	57,2	61,3
64	59,2	63,4
66	61,2	65,5
68	63,2	67,7
70	65,2	69,9
72	67,2	72,0
74	69,2	—
76	71,2	—
78	73,2	—

This table has been compiled on the basis of the Harkins-Jordan correction. It is similar to that in the DIN Standard (DIN 53914) for water and aqueous solutions (density ρ = 1 g/cm^3) and is for a commercially available ring having the dimensions R = 9,55 mm (mean ring radius) and r = 0,185 mm (ring wire radius). The table provides corrected values for surface-tension measurements taken after calibration with weights or calibration with water.

Alternatively, without the preceding calibration, the surface tension call be calculated according to the following formula:

$$\sigma = \frac{\mathrm{fxF}}{4\pi \mathrm{R}}$$

where:

F = the force measured on the dynamometer at the breakpoint of the film

R = the radius of the ring

f = the correction factor (1)

3. REPORTING

3.1. TEST REPORT

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

- method used,
- type of water or solution used,
- precise specification of the substance (identity and impurities),
- measurement results: surface tension (reading) stating both the individual readings and their arithmetic mean as well as the corrected mean (taking into consideration the equipment factor and the correction table),
- concentration of the solution,
- test temperature,
- age of solution used; in particular the time between preparation and measurement of the solution,
- description of time dependence of surface tension after transferring the solution to the measurement vessel,
- 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.

3.2. INTERPRETATION OF RESULTS

Considering that distilled water has a surface tension of 72,75 mN/m at 20 °C, substances showing a surface tension lower than 60 mN/m under the conditions of this method should be regarded as being surface-active materials.

4. REFERENCES

(1) OECD, Paris, 1981, Test Guideline 115, Decision of the Council C(81) 30 final.

(2) R. Weissberger ed.: Technique of Organic Chemistry, Physical Methods of Organic Chemistry, 3rd ed., Interscience Publ., New York, 1959, Vol. I, Part I, Chapter XIV

(3) Pure Appl. Chem., 1976, vol. 48,511.

(4) Harkins, W.D., Jordan, H.F., J. Amer. Chem. Soc., 1930, vol. 52, 1751.

A.6 WATER SOLUBILITY

1. METHOD

The methods described are based on the OECD Test Guideline (1).

1.1 INTRODUCTION

It is useful to have preliminary information on the structural formula, the vapour pressure, the dissociation constant and the hydrolysis (as a function of pH) of the substance to perform this test.

No single method is available to cover the whole range of solubilities in water.

The two test methods described below cover the whole range of solubilities but are not applicable to volatile substances:

-one which applies to essentially pure substances with low solubilities, ($< 10^{-2}$ grams per litre), and which are stable in water, referred to as the 'column elution method',

-the other which applies to essentially pure substances with higher solubilities ($> 10^{-2}$ grams per litre), and which are stable in water, referred to as the 'flask method'.

The water solubility of the test substance can be considerably affected by the presence of impurities.

1.2. DEFINITION AND UNITS

The solubility in water of a substance is specified by the saturation mass concentration of the substance in water at a given temperature. The solubility in water is specified in units of mass per volume of solution. The SI unit is kg/m^3 (grams per litre may also be used).

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.

1.4. PRINCIPLE OF THE TEST METHOD

The approximate amount of the sample and the time necessary to achieve the saturation mass concentration should be determined in a simple preliminary test.

1.4.1. Column elution method

This method is based on the elution of a test substance with water from a micro-column which is charged with an inert support material, such as glass beads or sand, coated with an excess of test substance. The water solubility is determined when the mass concentration of the eluate is constant. This is shown by a concentration plateau as a function of time.

1.4.2. Flask method

In this method, the substance (solids must be pulverized) is dissolved in water at a temperature somewhat above the test temperature. When saturation is achieved the mixture is cooled and kept at the test temperature, stirring as long as necessary to reach equilibrium. Alternatively, the measurement can be performed directly at the test temperature, if it is assured by appropriate sampling that the saturation equilibrium is reached. Subsequently, the mass concentration of the substance in the aqueous solution, which must not contain any undissolved particles, is determined by a suitable analytical method.

1.5. QUALITY CRITERIA

1.5.1. Repeatability

For the column elution method, < 30 % may be obtainable; for the flask method, < 15 % should be observed.

1.5.2. Sensitivity

This depends upon the method of analysis, but mass concentration determinations down to 10^{-6} grams per litre can be determined.

1.6. DESCRIPTION OF THE METHOD

1.6.1. Test conditions

The test is preferably run at 20 ± 0,5 °C. If a temperature dependence is suspected in the solubility (> 3 % per °C), two other temperatures at least 10 °C above and below the initially chosen temperature should also be used. In this case, the temperature control should be ± 0,1 °C. The chosen temperature should be kept constant in all relevant parts of the equipment.

1.6.2. Preliminary test

To approximately 0,1 g of the sample (solid substances must be pulverized) in a glass-stoppered 10 ml graduated cylinder, increasing volumes of distilled water at room temperature are added according to the steps shown in the table below:

0,1 g soluble in 'x' ml of water	0,1	0,5	1	2	10	100	>100
Approximative solubility (grams per litre)	>1000	1000 to 200	200 to 1000	100 to 50	50 to 10	10 to 1	<1

After each addition of the indicated amount of water, the mixture is shaken vigorously for 10 minutes and is visually checked for any undissolved parts of the sample. If, after addition of 10 ml of water, the sample or parts of it remain undissolved, the experiment has to be repeated in a 100 ml measuring cylinder with larger volumes of water. At lower solubilities the time required to dissolve a substance can be considerably longer (at least 24 h should be allowed). The approximate solubility is given in the table under that volume of added water in which complete dissolution of the sample occurs. If the substance is still apparently insoluble, more than 24 h should be allowed (96 h maximum), or further dilution should be undertaken to ascertain whether the column elution or flask solubility method should be used.

1.6.3. Column elution method

1.6.3.1. Support material, solvent and eluent

The support material for the column elution method should be inert. Possible materials which can be employed are glass beads and sand. A suitable volatile solvent of analytical reagent quality should be used to apply the test substance to the support material. Water which has been double distilled in glass or quartz apparatus should be employed as the eluent.

Note:

Water directly from an organic ion exchanger must not be used.

1.6.3.2. Loading of the support

Approximately 600 mg of support material is weighed and transferred to a 50 ml round-bottom flask.

A suitable, weighed amount of test substance is dissolved in the chosen solvent. An appropriate amount of this solution is added to the support material. The solvent must be completely evaporated, e.g. in a rotary evaporator; otherwise water saturation of the support is not achieved due to partition effects on the surface of the support material.

The loading of support material may cause problems (erroneous results) if the test substance is deposited as an oil or a different crystal phase. The problem should be examined experimentally and the details reported.

The loaded support material is allowed to soak for about two hours in approximately 5 ml of water, and then the suspension is added to the microcolumn. Alternatively, dry loaded support material may be poured into the microcolumn, which has been filled with water, and then equilibrated for approximately two hours.

Test procedure:

The elution of the substance from the support material can be carried out in one of two different ways:

- recirculating pump (see figure 1),
- levelling vessel (see figure 4).

1.6.3.3. Column elution method with recirculating pump

Apparatus

A schematic arrangement of a typical system is presented in figure 1. A suitable microcolumn is shown in figure 2, although any size is acceptable, provided it meets the criteria for reproducibility and sensitivity .The column should provide for a headspace of at least five bed volumes of water and be able to hold a minimum of five samples. Alternatively, the size can be reduced if make-up solvent is employed to replace the initial five bed volumes removed with impurities.

The column should be connected to a recirculating pump capable of controlling flows of approximately 25 ml/h. The pump is connected with polytetrafluoroethylene (P .T .F.E.) and/ or glass connections. The column and pump, when assembled, should have provision for sampling the effluent and equilibrating the headspace at atmospheric pressure. The column material is supported with a small (5 mm) plug of glass wool, which also serves to filter out particles. The recirculating pump can be, for example, a peristaltic pump or a membrane pump (care must be taken that no contamination and/or absorption occurs with the tube material).

Measurement procedure

The flow through the column is started. It is recommended that a flow rate of approximately 25 ml/hr be used (this corresponds to 10 bed volumes/hr for the column described). The first five bed volumes (minimum) are discarded to remove water-soluble impurities. Following this, the recirculating pump is allowed to run until equilibration is established, as defined by five successive samples whose concentrations do not differ by more than ± 30 % in a random fashion. These samples should be separated from each other by time intervals corresponding to the passage of at least 10 bed volumes of the eluent.

1.6.3.4. Column elution method with levelling vessel

Apparatus (see figures 4 and 3)

Levelling vessel: The connection to the levelling vessel is made by using a ground glass joint which is connected by PTFE tubing. It is recommended that a flow rate of approximately 25 ml/hr be used. Successive eluate fractions should be collected and analyzed by the chosen method.

Measurement procedure

Those fractions from the middle eluate range where the concentrations are constant (± 30 %) in at least five consecutive fractions are used to determine the solubility in water .

In both cases (using a recirculating pump or a levelling vessel), a second run is to be performed at half the flow rate of the first. If the results of the two runs are in agreement, the test is satisfactory; if there is a higher apparent solubility with the lower flow rate, then the halving of the flow rate must continue until two successive runs give the same solubility.

In both cases (using a recirculating pump or a levelling vessel) the fractions should be checked for the presence of colloidal matter by examination for the Tyndall effect (light scattering). Presence of such particles invalidates the results, and the test should be repeated with improvements in the filtering action of the column.

The pH of each sample should be recorded. A second run should be performed at the same temperature.

1.6.4. Flask method

1.6.4.1. Apparatus

For the flask method the following material is needed:

- normal laboratory glassware and instrumentation,
- a device suitable for the agitation of solutions under controlled constant temperatures,
- a centrifuge (preferably thermostated), if required with emulsions, and
- equipment for analytical determination.

1.6.4.2. Measurement procedure

The quantity of material necessary to saturate the desired volume of water is estimated from the preliminary test. The volume of water required will depend on the analytical method and the solubility range. About five times the quantity of material determined above is weighed into each of three glass vessels fitted with glass stoppers (e.g. centrifuge tubes, flasks). The chosen volume of water is added to each vessel, and the vessels are tightly stoppered. The closed vessels are then agitated at 30 °C. (A shaking or stirring device capable of operating at constant temperature should be used, e.g. magnetic stirring in a thermostatically controlled water bath). After one day, one of the vessels is removed and re-equilibrated for 24 hours at the test temperature with occasional shaking. The contents of the vessel are then centrifuged at the test temperature, and the concentration of test substance in the clear aqueous phase is determined by a suitable analytical method. The other two flasks are treated similarly after initial equilibration at 30 °C for two and three days, respectively. If the concentration results from at least the last two vessels agree with the required reproducibility , the test is satisfactory. The whole test should be repeated, using longer equilibration times, if the results from vessels 1, 2 and 3 show a tendency to increasing values.

The measurement procedure can also be performed without preincubation at 30 °C. In order to estimate the rate of establishment of the saturation equilibrium, samples are taken until the stirring time no longer influences the concentration of the test solution.

The pH of each sample should be recorded.

1.6.5. Analysis

A substance-specific analytical method is preferred for these determinations, since small amounts of soluble impurities can cause large errors in the measured solubility. Examples of such methods are: gas or liquid chromatography, titration methods, photometric methods, voltammetric methods.

2. DATA

2.1. COLUMN ELUTION METHOD

The mean value from at least five consecutive samples taken from the saturation plateau should be calculated for each run, as should the standard deviation. The results should be given in units of mass per volume of solution.

The means calculated on two tests using different flows are compared and should have a repeatability of less than 30 %.

2.2. FLASK METHOD

The individual results should be given for each of the three flasks and those results deemed to be constant (repeatability of less than 15 %) should be averaged and given in units of mass per volume of solution. This may require the reconversion of mass units to volume units, using the density when the solubility is very high (> 100 grams per litre).

3. REPORTING

3.1. COLUMN ELUTION METHOD

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

- the results of the preliminary test,
- precise specification of the substance (identity and impurities),
- the individual concentrations, flow rates and pH of each sample,
- the means and standard deviations from at least five samples from the saturation plateau of each run,
- the average of the two successive, acceptable runs,
- the temperature of the water during the saturation process,
- the method of analysis employed,
- the nature of the support material employed,
- loading of support material,
- solvent used,
- evidence of any chemical instability of the substance during the test and the method used,
- all information relevant for the interpretation of the results, especially with regard to impurities and physical state of the substance.

3.2. FLASK METHOD

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

- the results of the preliminary test,
- precise specification of rhe substance (identity and impurities),
- the individual analytical determinations and the average where more than one value was determined for
- each flask,
- the pH of each sample,
- the average of the value for the different flasks which were in agreement,
- the test temperature,
- the analytical method employed,
- evidence of any chemical instability of the substance during the test and the method used,
- all information relevant for the interpretation of the results, especially with regard to impurities and physical state of the substance.

4. REFERENCES

(1) OECD, Paris, 1981, Test Guideline 105, Decision of the Council C(81) 30 final.

(2) NF T 20-045 (AFNOR) (Sept. 85). Chemical products for industrial use - Determination of water solubility of solids and liquids with low solubility -Column elution method

(3) NF T 20-046 (AFNOR) (Sept. 85). Chemical products for industrial use - Determination of water solubility of solids and liquids with high solubility -Flask method

APPENDIX

Figure 1
Column elution method with recirculating pump

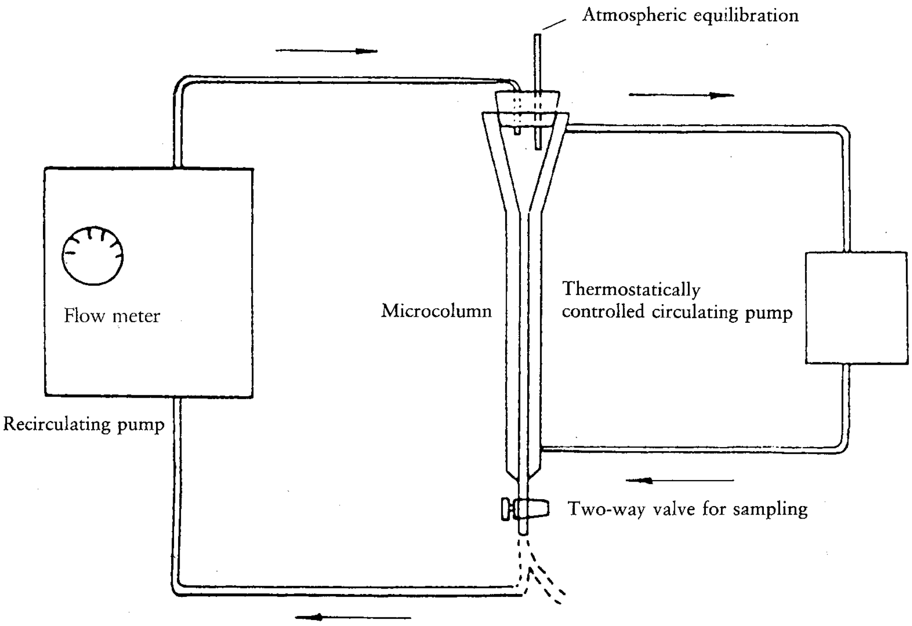

Atmospheric equilibration
Flow meter
Microcolumn
Thermostatically controlled circulating pump
Recirculating pump
Two-way valve for sampling

Figure 2

A typical microcolumn
(All dimensions in millimetres)

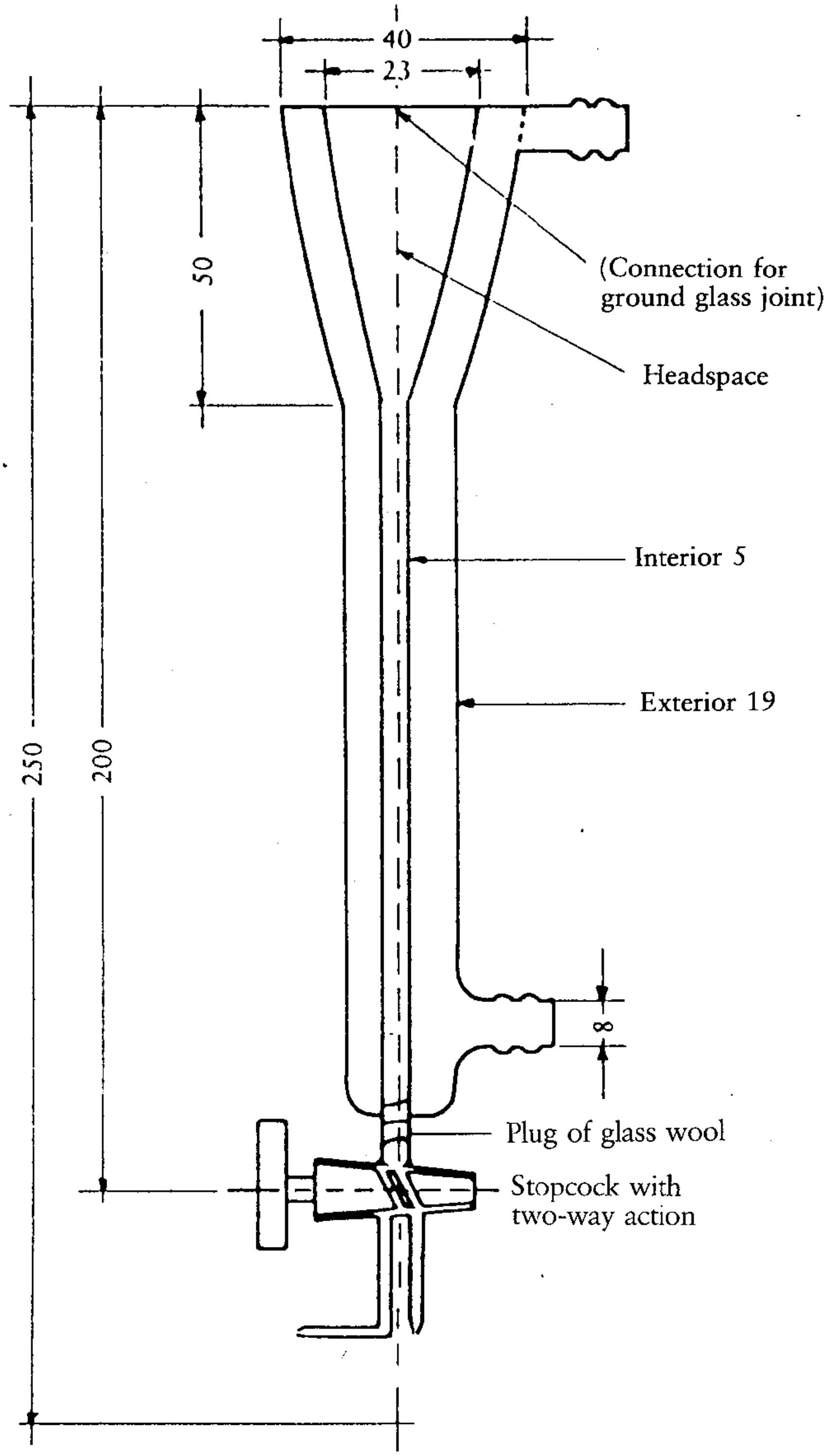


Figure 3

A typical microcolumn
(All dimensions in millimetres)

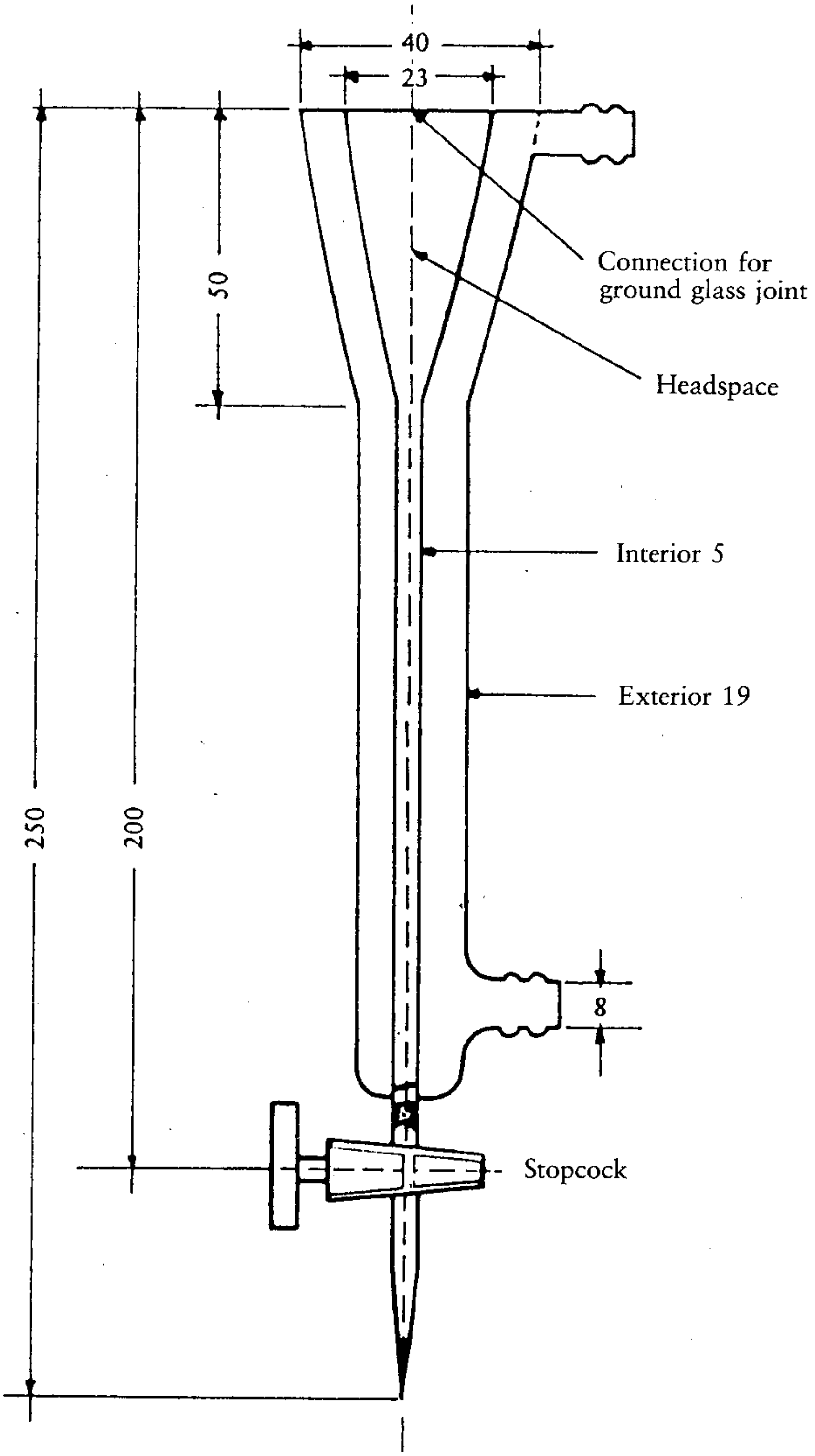
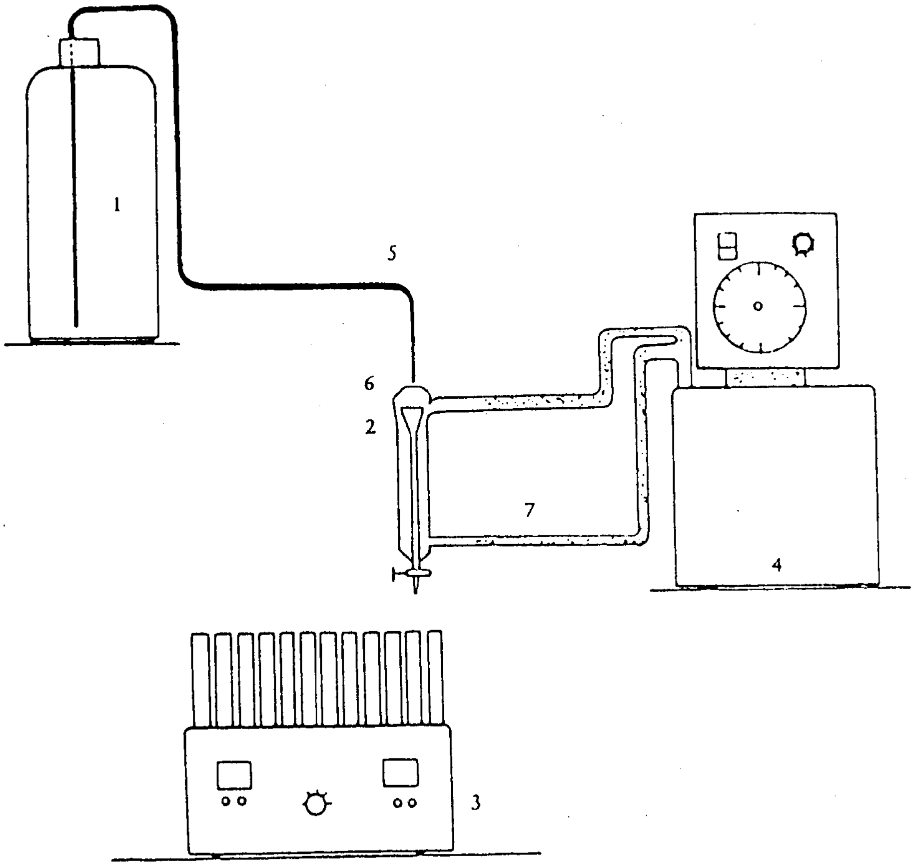


Figure 4

Column elution method with levelling vessel



1 = Levelling vessel (e.g. 2,5 litre flask)
2 = Column (see figure 3)
3 = Fraction collector
4 = Thermostat
5 = Teflon tubing
6 = Ground glass joint
7 = Water line (between thermostat and column, inner diameter: approximately 8 mm)

A.8 PARTITION COEFFICIENT

1. METHOD

The 'shake flask' method described is based on the OECD Test Guideline (1).

1.1. INTRODUCTION

It is useful to have preliminary information on structural formula, dissociation constant, water solubility, hydrolysis, n-octanol solubility and surface tension of the substance to perform this test.

Measurements should be made on ionizable substances only in their non-ionized form (free acid or free base) produced by the use of an appropriate buffer with a pH of at least one pH unit below (free acid) or above (free base) the pK.

This test method includes two separate procedures: the shake flask method and high performance liquid chromatography (HPLC). The former is applicable when the log P_{ow} value (see below for definitions) falls within the range -2 to 4 and the latter within the range 0 to 6. Before carrying out either of the experimental procedures a preliminary estimate of the partition coefficient should first be obtained.

The shake-flask method applies only to essentially pure substances soluble in water and n-octanol. It is not applicable to surface active materials (for which a calculated value or an estimate based on the individual n-octanol and water solubilities should be provided).

The HPLC method is not applicable to strong acids and bases, metal complexes, surface-active materials or substances which react with the eluent. For these materials, a calculated value or an estimate based on individual n-octanol and water solubilities should be provided.

The HPLC method is less sensitive to the presence of impurities in the test compound than is the shake-flask method. Nevertheless, in some cases impurities can make the interpretation of the results difficult because peak assignment becomes uncertain. For mixtures which give an unresolved band, upper and lower limits of log P should be stated.

1.2. DEFINITION AND UNITS

The partition coefficient (P) is defined as the ratio of the equilibrium concentrations (c_i) of a dissolved substance in a two-phase system consisting of two largely immiscible solvents. In the case n-octanol and water:

$$P_{ow} = \frac{c_{n-octanol}}{c_{water}}$$

The partition coefficient (P) therefore is the quotient of two concentrations and is usually given in the form of its logarithm to base 10 (log P).

1.3. REFERENCE SUBSTANCES

Shake-flask method

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.

HPLC method

In order to correlate the measured HPLC data of a compound with its P value, a calibration graph of log P vs. chromatographic data using at least 6 reference points has to be established. It is for the user to select the appropriate reference substances. Whenever possible, at least one reference compound should have a P_{ow} above that of the test substance, and another a P_{ow} below that of the test substance. For log P values less than 4, the calibration can be based on data obtained by the shake-flask method. For log P values greater than 4, the calibration can be based on validated literature values if these are in agreement with calculated values. For better accuracy, it is preferable to choose reference compounds which are structurally related to the test substance.

Extensive lists of values of log P_{ow} for many groups of chemicals are available (2)(3). If data on the partition coefficients of structurally related compounds are not available, then a more general calibration, established with other reference compounds, may be used.

A list of recommended reference substances and their P_{ow} values is given in Appendix 2.

1.4. PRINCIPLE OF THE METHOD

1.4.1. Shake-flask method

In order to determine a partition coefficient, equilibrium between all interacting components of the system must be achieved, and the concentrations of the substances dissolved in the two phases must be determined. A study of the literature on this subject indicates that several different techniques can be used to solve this problem, i.e. the thorough mixing of the two phases followed by their separation in order to determine the equilibrium concentration for the substance being examined.

1.4.2. HPLC method

HPLC is performed on analytical columns packed with a commercially available solid phase containing long hydrocarbon chains (e.g. C_8, C_{18}) chemically bound onto silica. Chemicals injected onto such a column move along it at different rates because of the different degrees of partitioning between the mobile phase and the hydrocarbon stationary phase. Mixtures of chemicals are eluted in order of their hydrophobicity , with water-soluble chemicals eluted first and oil-soluble chemicals last, in proportion to their hydrocarbon-water partition coefficient. This enables the relationship between the retention time on such a (reverse phase) column and the n-octanol/water partition coefficient to be established. The partition coefficient is deduced from the *capacity factor* k, given by the expression:

$$k = \frac{t_r - t_o}{t_o}$$

in which, t_r = retention time of the test substance, and t_o = average time a solvent molecule needs to pass through the column (dead-time).

Quantitative analytical methods are not required and only the determination of elution times is necessary.

1.5. QUALITY CRITERIA

1.5.1. Repeatability

Shake-flask method

In order to assure the accuracy of the partition coefficient, duplicate determinations are to be made under three different test conditions, whereby the quantity of substance specified as well as the ratio of the solvent volumes may be varied. The determined values of the partition coefficient expressed as their common logarithms should fall within a range of ± 0,3 log units.

HPLC method

In order to increase the confidence in the measurement, duplicate determinations must be made. The values of log P derived from individual measurements should fall within a range of ± 0,1 log units.

1.5.2. Sensitivity

Shake-flask method

The measuring range of the method is determined by the limit of detection of the analytical procedure. This should permit the assessment of values of log P_{ow} in the range of -2 to 4 (occasionally when conditions apply, this range may be extended to log P_{ow} up to 5) when the concentration of the solute in either phase is not more than 0,01 mol per litre.

HPLC method

The HPLC method enables partition coefficients to be estimated in the log P_{ow} range 0 to 6.

Normally, the partition coefficient of a compound can be estimated to within ± l log unit of the shake-flask value. Typical correlations can be found in the literature (4)(5)(6)(7)(8). Higher accuracy can usually be achieved when correlation plots are based on structurally-related reference compounds (9).

1.5.3. Specificity

Shake-flask method

The Nernst Partition Law applies only at constant temperature, pressure and pH for dilute solutions. It strictly applies to a pure substance dispersed between two pure solvents. If several different solutes occur in one or both phases at the same time, this may affect the results.

Dissociation or association of the dissolved molecules result in deviations from the Nernst Partition Law. Such deviations are indicated by the fact that the partition coefficient becomes dependent upon the concentration of the solution.

Because of the multiple equilibria involved, this test method should not be applied to ionizable compounds without applying a correction. The use of buffer solutions in place of water should be considered for such compounds; the pH of the buffer should be at least 1 pH unit from the pKa of the substance and bearing in mind the relevance of this pH for the environment.

1.6. DESCRIPTION OF THE METHOD

1.6.1. Preliminary estimate of the partition coefficient

The partition coefficient is estimated preferably by using a calculation method (see Appendix 1), or where appropriate, from the ratio of the solubilities of the test substance ill the pure solvents (10).

1.6.2. Shake-flask method

1.6.2.1. Preparation

n-Octanol: The determination of the partition coefficient should be carried out with high purity analytical grade reagent.

Water: water distilled or double distilled in glass or quartz apparatus should be employed. For ionizable compounds, buffer solutions in place of water should be used if justified.

Note:

Water taken directly from an ion exchanger should not be used.

1.6.2.1.1. Pre-saturation of the solvents

Before a partition coefficient is determined, the phases of the solvent system are mutually saturated by shaking at the temperature of the experiment. To do this, it is practical to shake two large stock bottles of high purity analytical grade n-octanol or water each with a sufficient quantity of the other solvent for 24 hours on a mechanical shaker and then to let them stand long enough to allow the phases to separate and to achieve a saturation state.

1.6.2.1.2. Preparation for the test

The entire volume of the two-phase system should nearly fill the test vessel. This will help prevent loss of material due to volatilization. The volume ratio and quantities of substance to be used are fixed by the following:

- the preliminary assessment of the partition coefficient (see above),
- the minimum quantity of test substance required for the analytical procedure, and
- the limitation of a maximum concentration in either phase of 0,01 mol per litre.

Three tests are carried out. In the first, the calculated volume ratio of n-octanol to water is used; in the second, this ratio is divided by two; and in the third, this ratio is multiplied by two (e.g. 1:1, 1:2,2:1).

1.6.2.1.3. Test substance

A stock solution is prepared in n-octanol pre-saturated with water. The concentration of this stock solution should be precisely determined before it is employed in the determination of the partition coefficient. This solution should be stored under conditions which ensure its stability.

1.6.2.2. Test conditions

The test temperature should be kept constant (± 1 °C) and lie in the range of 20 to 25 °C.

1.6.2.3. Measurement procedure

1.6.2.3.1. Establishment of the partition equilibrium

Duplicate test vessels containing the required, accurately measured amounts of the two solvents together with the necessary quantity of the stock solution should be prepared for each of the test conditions.

The n-octanol phases should be measured by volume. The test vessels should either be placed in a suitable shaker or shaken by hand. When using a centrifuge tube, a recommended method is to rotate the tube quickly through 180° about its transverse axis so that any trapped air rises through the two phases. Experience has shown that 50 such rotations are usually sufficient for the establishment of the partition equilibrium. To be certain, 100 rotations in five minutes are recommended.

1.6.2.3.2. Phase separation

When necessary, in order to separate the phases, centrifugation of the mixture should be carried out. This should be done in a laboratory centrifuge maintained at room temperature, or, if a non-temperature controlled centrifuge is used, the centrifuge tubes should be kept for equilibration at the test temperature for at least one hour before analysis.

1.6.2.4. Analysis

For the determination of the partition coefficient, it is necessary to determine the concentrations of the test substance in both phases. This may be done by taking an aliquot of each of the two phases from each tube for each test condition and analyzing them by the chosen procedure. The total quantity of substance present in both phases should be calculated and compared with the quantity of the substance originally introduced.

The aqueous phase should be sampled by a procedure that minimizes the risk of including traces of n-octanol: a glass syringe with a removable needle can be used to sample the water phase. The syringe should initially be partially filled with air. Air should be gently expelled while inserting the needle through the n-octanol layer. An adequate volume of aqueous phase is withdrawn into the syringe. The syringe is quickly removed from the solution and the needle detached. The contents of the syringe may then be used as the aqueous sample. The concentration in the two separated phases should preferably be determined by a substance-specific method. Examples of analytical methods which may be appropriate are:

- photometric methods,
- gas chromatography,

– high-performance liquid chromatography.

1.6.3. HPLC method

1.6.3.1. Preparation

Apparatus

A liquid chromatograph, fitted with a pulse-free pump and a suitable detection device, is required. The use of an injection valve with injection loops is recommended. The presence of polar groups in the stationary phase may seriously impair the performance of the HPLC column. Therefore, stationary phases should have the minimal percentage of polar groups (11). Commercial microparticulate reverse-phase packings or ready-packed columns can be used. A guard column may be positioned between the injection system and the analytical column.

Mobile phase

HPLC grade methanol and HPLC grade water are used to prepare the eluting solvent, which is degassed before use. Isocratic elution should be employed. Methanol/water ratios with a minimum water content of 25% should be used. Typically a 3:1 (v/v) methanol-water mixture is satisfactory for eluting compounds of log P 6 within an hour, at a flow rate of 1 ml/min. For compounds of high log P it may be necessary to shorten the elution time (and those of the reference compounds) by decreasing the polarity of the mobile phase or the column length.

Substances with very low solubility in n-octanol tend to give abnormally low log P_{ow} values with the HPLC method; the peaks of such compounds sometimes accompany the solvent front. This is probably due to the fact that the partitioning process is too slow to reach the equilibrium in the time normally taken by an HPLC separation. Decreasing the flow rate and/or lowering the methanol/water ratio may then be effective to arrive at a reliable value.

Test and reference compounds should be soluble in the mobile phase in sufficient concentrations to allow their detection. Only in exceptional cases may additives be used with the methanol-water mixture, since additives will change the properties of the column. For chromatograms with additives it is mandatory to use a separate column of the same type. If methanol-water is not appropriate, other organic solvent-water mixtures call be used, e.g. ethanol-water or acetonitrile-water .

The pH of the eluent is critical for ionizable compounds. It should be within the operating pH range of the column, which is usually between 2 and 8. Buffering is recommended. Care must be taken to avoid salt precipitation and column deterioration which occur with some organic phase/buffer mixtures. HPLC measurements with silica-based stationary phases above pH 8 are not advisable since the use of an alkaline, mobile phase may cause rapid deterioration in the performance of the column.

Solutes

The reference compounds should be the purest available. Compounds to be used for test or calibration purposes are dissolved in the mobile phase if possible.

Test conditions

The temperature during the measurements should not vary by more than ± 2 K.

1.6.3.2. Measurement

Calculation of dead time t_o

The dead time to can be determined by using either a homologous series (e.g. n-alkyl methyl ketones) or unretained organic compounds (e.g. thiourea or formamide). For calculating the dead time to by using a homologous series, a set of at least seven members of a homologous series is injected and the respective retention times are determined. The raw retention times $t_{r\,(n\,c\,+\,1)}$ are plotted as a function of $t_{r(n\,c)}$ and the intercept a and slope b of the regression equation:

$$t_{r\,(n\,c\,+\,1)} = a + b\, t_{r\,(n\,c)}$$

are determined (n_c = number of carbon atoms). The dead time to is then given by:

$$t_o = a/(l\ -b)$$

Calibration graph

The next step is to construct a correlation plot of log k values versus log p for appropriate reference compounds. In practice, a set of between 5 and 10 standard reference compounds whose log p is around the expected range are injected simultaneously and the retention times are determined, preferably on a recording integrator linked to the detection system. The corresponding logarithms of the capacity factors, log k, are calculated and plotted as a function of the log p determined by the shake-flask method. The calibration is performed at regular intervals, at least once daily, so that possible changes in column performance can be allowed for.

Determination of the capacity factor of the test substance

The test substance is injected in as small a quantity of mobile phase as possible. The retention time is determined (in duplicate), permitting the calculation of the capacity factor k. From the correlation graph of the reference compounds, the partition coefficient of the test substance can be interpolated. For very low and very high partition coefficients, extrapolation is necessary. In those cases particular care has to be taken of the confidence limits of the regression line.

2. DATA

Shake-flask method

The reliability of the determined values of P can be tested by comparison of the means of the duplicate determinations with the overall mean.

3. REPORTING

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

- precise specification of the substance (identity and impurities),

- when the methods are not applicable (e.g. surface active material), a calculated value or an estimate based on the individual n-octanol and water solubilities should be provided,

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

For shake-flask method:

- the result of the preliminary estimation, if any,

- temperature of the determination,

- data on the analytical procedures used in determining concentrations,

- time and speed of centrifugation, if used,

- the measured concentrations in both phases for each determination (this means that a total of 12 concentrations will be reported),

- the weight of the test substance, the volume of each phase employed in each test vessel and the total calculated amount of test substance present in each phase after equilibration,

- the calculated values of the partition coefficient (P) and the mean should be reported for each set of test conditions as should the mean for all determinations. If there is a suggestion of concentration dependency of the partition coefficient, this should be noted in the report,

- the standard deviation of individual P values about their mean should be reported,

- the mean P from all determinations should also be expressed as its logarithm (base 10),

- the calculated theoretical P_{ow} when this value has been determined or when the measured value is $> 10^4$,

- pH of water used and of the aqueous phase during the experiment,

- if buffers are used, justification for the use of buffers in place of water, composition, concentration and pH of the buffers, pH of the aqueous phase before and after the experiment.

For HPLC method:

- the result of the preliminary estimation, if any,

- test and reference substances, and their purity ,

- temperature range of the determinations,

- pH at which the determinations are made,

- details of the analytical and guard column, mobile phase and means of detection,

- retention data and literature log P values for reference compounds used in calibration,
- details of fitted regression line (log k versus log P),
- average retention data and interpolated log P value for the test compound,
- description of equipment and operating conditions,
- elution profiles,
- quantities of test and references substances introduced in the column,
- dead-time and how it was measured.

4. REFERENCES

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APPENDIX 1 – CALCULATION / ESTIMATION METHODS

INTRODUCTION

A general introduction to calculation methods, data and examples are provided in the Handbook of Chemical Property Estimation Methods (a).

Calculated values of P_{ow} can be used:

- for deciding which of the experimental methods is appropriate (shake-flask range: log P_{ow}: -2 to 4, HPLC range: log P_{ow}: 0 to 6),
- for selecting the appropriate test conditions (e.g. reference substances for HPLC procedures, volume ratio n-octanol/water for shake flask method),
- as a laboratory internal check on possible experimental errors,
- for providing a P_{ow}-estimate in cases where the experimental methods cannot be applied for technical reasons.

ESTIMATION METHOD

Preliminary estimate of the partition coefficient

The value of the partition coefficient can be estimated by the use of the solubilities of the test substance in the pure solvents:

For this:

$$P_{estimate} = \frac{saturation\,c_{n-octanol}}{saturation\,c_{water}}$$

CALCULATION METHODS

Principle of the Calculation Methods

All calculation methods are based on the formal fragmentation of the molecule into suitable substructures for which reliable log P_{ow}-increments are known. The log P_{ow} of the whole molecule is then calculated as the sum of its corresponding fragment values plus the sum of correction terms for intramolecular interactions.

Lists of fragment constants and correction terms ate available (b)(c)(d)(e;. Some ate regularly updated (b).

Quality Criteria

In general, the reliability of the calculation method decreases with increasing complexity of the compound under study. In the case of simple molecules with low molecular weight and one or two functional groups, a deviation of 0,1 to 0,3 log P_{ow} units between the results of the different fragmentation methods and the measured value can be expected. In the case of more complex molecules the margin of error can be greater. This will depend on the reliability and availability of fragment constants, as well as on the ability to recognize intramolecular interactions (e.g. hydrogen bonds) and the correct use of the correction terms (less of a problem with the computer software CLOGP-3) (b). In the case of ionizing compounds the correct consideration of the charge or degree of ionization is important.

Calculation Procedures

Hansch π-Method

The original hydrophobic substituent constant, π, introduced by Fujira et al. (f) is defined as:

$$\pi_X = \log P_{ow}\ (PhX) - \log P_{ow}\ (PhH)$$

where P_{ow} (PhX) is the partition coefficient of an aromatic derivative and P_{ow} (PhH) that of the parent compound

(e.g. $\pi_{Cl} = \log P_{ow}\ (C_6H_5Cl) - \log P_{ow}\ (C_6H_6) = 2,84 - 2,13 = 0,71$).

According to its definition the π-method is applicable predominantly for aromatic substitution. π-values for a large number of substituents have been tabulated (b)(c)(d). They are used for the calculation of log P_{ow} for aromatic molecules or substructures.

Rekker Method

According to Rekker (g) the log P_{ow} value is calculated as follows:

$$\log P_{ow} = \sum_i a_i f_j + \sum_j \text{(interaction terms)}$$

where f_i represents the different molecular fragment constants and a_i the frequency of their occurrence in the molecule under investigation. The correction terms can be expressed as an integral multiple of one single constant C_m (so-called 'magic constant'). The fragment constants f_i and C_m were determined from a list of 1054 experimental P_{ow} values (825 compounds) using multiple regression analysis (c)(h). The determination of the interaction terms is carried out according to set rules described in the literature (e)(h)(i).

Hansch-Leo Method

According to Hansch and Leo (c), the log P_{ow} value is calculated from:

$$\log P_{ow} = \sum_i a_i f_i + \sum_j b_j F_j$$

where f_i represents the different molecular fragment constants, F_j the correction terms and a_i, b_j the corresponding frequencies of occurrence. Derived from experimental P_{ow} values, a list of atomic and group fragmental values and a list of correction terms F_j (so-called 'factors') were determined by trial and error. The correction terms have been ordered into several different classes (a)(c). It is relatively complicated and time consuming to take into account all the rules and correction terms. Software packages have been developed (b).

Combined Method

The calculation of log P_{ow} of complex molecules can be considerably improved, if the molecule is dissected into larger substructures for which reliable log P_{ow} values are available, either from tables (b)(c) or from one's own measurements. Such fragments (e.g. heterocycles, anthraquinone, azobenzene) can then be combined with the Hansch π-values or with Rekker or Leo fragment constants.

Remarks

i) The calculation methods can only be applied to partly - or fully-ionized compounds when it is possible to take the necessary correction factors into account.

ii) If intramolecular hydrogen bonds can be assumed, the corresponding correction terms (approx. + 0,6 to + 1,0 log P_{ow} units) have to be added (a). Indications for the presence of such bonds can be obtained from stereo models or spectroscopic data of the molecule.

iii) If several tautomeric forms are possible, the most likely form should be used as the basis of the calculation.

iv) The revisions of lists of fragment constants should be followed carefully.

Report

When using calculation/estimation methods, the test report shall, if possible, include the following information:

– description of the substance (mixture, impurities, etc.),

– indication of any possible intramolecular hydrogen bonding, dissociation, charge and any other unusual effects (e.g. tautomerism),

- description of the calculation method,
- identification or supply of database,
- peculiarities in the choice of fragments,
- comprehensive documentation of the calculation.

LITERATURE

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APPENDIX 2 - RECOMMENDED REFERENCE SUBSTANCES FOR THE HLPC METHOD

Appendix 2

Recommended Reference Substances for the HPLC-Method

No.	Reference Substance	log P_{ow}	pKa
1	2-Butanone	0,3	
2	4-Acetylpyridine	0,5	
3	Aniline	0,9	
4	Acetanilide	1,0	
5	Benzylalcohol	1,1	
6	p-Methoxyphenol	1,3	pKa = 10,26
7	Phenoxy acetic acid	1,4	pKa = 3,12
8	Phenol	1,5	pKa = 9,92
9	2,4-Dinitrophenol	1,5	pKa = 3,96
10	Benzonitrile	1,6	
11	Phenylacetonitrile	1,6	
12	4-Methylbenzyl alcohol	1,6	
13	Acetophenone	1,7	
14	2-Nitrophenol	1,8	pKa = 7,17
15	3-Nitrobenzoic acid	1,8	pKa = 3,47
16	4-Chloraniline	1,8	pKa = 4,15
17	Nitrobenzene	1,9	
18	Cinnamic alcohol	1,9	
19	Benzoic acid	1,9	pKa = 4,19
20	p-Cresol	1,9	pKa = 10,17
21	Cinnamic acid	2,1	pKa = 3,89 cis 4,44 trans
22	Anisole	2,1	
23	Methylbenzoate	2,1	
24	Benzene	2,1	
25	3-Methylbenzoic acid	2,4	pKa = 4,27
26	4-Chlorophenol	2,4	pKa = 9,1
27	Trichloroethylene	2,4	
28	Atrazine	2,6	
29	Ethylbenzoate	2,6	
30	2,6-Dichlorobenzonitrile	2,6	
31	3-Chlorobenzoic acid	2,7	pKa = 3,82
32	Toluene	2,7	
33	1-Naphthol	2,7	pKa = 9,34
34	2,3-Dichloroaniline	2,8	
35	Chlorobenzene	2,8	
36	Allyl-phenylether	2,9	
37	Bromobenzene	3,0	
38	Ethylbenzene	3,2	
39	Benzophenone	3,2	
40	4-Phenylphenol	3,2	pKa = 9,54
41	Thymol	3,3	
42	1,4-Dichlorobenzene	3,4	
43	Diphenylamine	3,4	pKa = 0,79
44	Naphthalene	3,6	
45	Phenylbenzoate	3,6	
46	Isopropylbenzene	3,7	
47	2,4,6-Trichlorophenol	3,7	pKa = 6
48	Biphenyl	4,0	
49	Benzylbenzoate	4,0	
50	2,4-Dinitro-6 sec. butylphenol	4,1	
51	1,2,4-Trichlorobenzene	4,2	
52	Dodecanoic acid	4,2	
53	Diphenylether	4,2	
54	n-Butylbenzene	4,5	
55	Phenanthrene	4,5	
56	Fluoranthene	4,7	
57	Dibenzyl	4,8	
58	2,6-Diphenylpyridine	4,9	
59	Triphenylamine	5,7	
60	DDT	6,2	
		Other reference substances of low log P_{ow}	
1	Nicotinic acid	-0,07	

A.9 FLASH-POINT

1. METHOD

1.1. INTRODUCTION

It is useful to have preliminary information on the flammability of the substance before performing this test. The test procedure is applicable to liquid substances whose vapours can be ignited by ignition sources. The test methods listed in this text are only reliable for flash-point ranges which are specified in the individual methods.

The possibility of chemical reactions between the substance and the sample holder should be considered when selecting the method to be used.

1.2. DEFINITIONS AND UNITS

The flash-point is the lowest temperature, corrected to a pressure of 101,325 kPa, at which a liquid evolves vapours, under the conditions defined in the test method, in such an amount that a flammable vapour / air mixture is produced in the test vessel.

Units: °C

$t = T - 273{,}15$

(t in °C and T in 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.

1.4. PRINCIPLE OF THE METHOD

The substance is placed in a test vessel and heated or cooled to the test temperature according to the procedure described in the individual test method. Ignition trials are carried out in order to ascertain whether or not the sample flashed at the test temperature.

1.5. QUALITY CRITERIA

1.5.1. Repeatability

The repeatability varies according to flash-point range and the test method used; maximum 2 °C.

1.5.2. Sensitivity

The sensitivity depends on the test method used.

1.5.3. Specificity

The specificity of some test methods is limited to certain flash-point ranges and subject to substance-related data (e.g. high viscosity).

1.6. DESCRIPTION OF THE METHOD

1.6.1. Preparations

A sample of the test substance is placed in a test apparatus according to 1.6.3.1 and/or 1.6.3.2.

For safety, it is recommended that a method utilizing a small sample size, circa 2 cm^3, be used for energetic or toxic substances.

1.6.2. Test conditions

The apparatus should, as far as is consistent with safety , be placed in a draught-free position.

1.6.3. Performance of the test

1.6.3.1. Equilibrium method

See ISO 1516, ISO 3680, ISO 1523, ISO 3679.

1.6.3.2. Non-equilibrium method

Abel apparatus:

See BS 2000 part 170, NF M07-011, NF T66-009.

Abel-Pensky apparatus:

See EN 57, DIN 51755 part 1 (for temperatures from 5 to 65 °C), DIN 51755 part 2 (for temperatures below 5 °C), NF M07-036.

Tag apparatus:

See ASTM D 56.

Pensky-Martens apparatus:

See ISO 2719, EN 11, DIN 51758, ASTM D 93, BS 2000-34, NF M07-019.

Remarks:

When the flash-point, determined by a non-equilibrium method in 1.6.3.2., is found to be 0 ± 2 °C, 21 ± 2 °C or 55 ± 2 °C, it should be confirmed by an equilibrium method using the same apparatus.

Only the methods which can give the temperature of the flash-point may be used for a notification.

To determine the flash-point of viscous liquids (paints, gums and similar) containing solvents, only apparatus and test methods suitable for determining the flash-point of viscous liquids may be used.

See ISO 3679, ISO 3680, ISO 1523, DIN 53213 part 1.

2. DATA

3. REPORTING

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

-the precise specification of the substance (identification and impurities),

-the method used should be stated as well as any possible deviations,

-the results and any additional remarks relevant for the interpretation of results.

4. REFERENCES

None.

A.10 FLAMMABILITY (SOLIDS)

1. METHOD

1.1. INTRODUCTION

It is useful to have preliminary information on potentially explosive properties of the substance before performing this test.

This test should only be applied to powdery, granular or paste-like substances.

In order not to include all substances which can be ignited but only those which burn rapidly or those whose burning behaviour is in any way especially dangerous, only substances whose burning velocity exceeds a certain limiting value are considered to be highly flammable.

It can be especially dangerous if incandescence propagates through a metal powder because of the difficulties in extinguishing a fire. Metal powders should be considered highly flammable if they support spread of incandescence throughout the mass within a specified time.

1.2. DEFINITION AND UNITS

Burning time expressed in seconds.

1.3. REFERENCE SUBSTANCES

Not specified.

1.4. PRINCIPLE OF THE METHOD

The substance is formed into an unbroken strip or powder train about 250 mm long and a preliminary screening test performed to determine if, on ignition by a gas flame, propagation by burning with flame or smouldering occurs. If propagation over 200 mm of the train occurs within a specified time then a full test programme to determine the burning rate is carried out.

1.5. QUALITY CRITERIA

Not stated.

1.6. DESCRIPTION OF METHOD

1.6.1. Preliminary screening test

The substance is formed into an unbroken strip or powder train about 250 mm long by 20 mm wide by 10 mm high on a non-combustible, non-porous and low heat-conducting base plate.

A hot flame from a gas burner (minimum diameter 5 mm) is applied to one end of the powder train until the powder ignites or for a maximum of 2 minutes (5 minutes for powders of metals or metal-alloys). It should be noted whether combustion propagates along 200 mm of the train within the 4 minutes test period (or 40 minutes for metal powders). If the substance does not ignite and propagate combustion either by burning with flame or smouldering along 200 mm of the powder train within the 4 minutes (or 40 minutes) test period, then the substance should not be considered as highly flammable and no further testing is required. If the substance propagates burning of a 200 mm length of the powder train in less than 4 minutes, or less than 40 minutes for metal powders, the procedure described below (point 1.6.2. and following) should be carried out.

1.6.2. Burning rate test

1.6.2.1. Preparation

Powdery or granular substances are loosely filled into a mould 250 mm long with a triangular cross-section of inner height 10 mm and width 20 mm. On both sides of the mould in a longitudinal direction two metal plates are mounted as lateral limitations which project 2 mm beyond the upper edge of the triangular cross section (figure). The mould is then dropped three times from a height of 2 cm onto a solid surface. If necessary the mould is then filled up again. The lateral limitations are then removed and the excess substance scraped off. A non-combustible, non-porous and low heat-conducting base plate is placed on top of the mould, the apparatus inverted and the mould removed.

Paste-like substances are spread on a non-combustible, non-porous and low heat-conducting base plate in the form of a rope 250 mm in length with a cross section of about 1 cm^2.

1.6.2.2. Test conditions

In the case a moisture-sensitive substance, the test should be carried out as quickly as possible after its removal from the container.

1.6.2.3. Performance of the test

Arrange the pile across the draught in a fume cupboard.

The air-speed should be sufficient to prevent fumes escaping into the laboratory and should not be varied during the test. A draught screen should be erected around the apparatus.

A hot flame from a gas burner (minimum diameter of 5 mm) is used to ignite the pile at one end. When the pile has burned a distance of 80 mm, the rate of burning over the next 100 mm is measured. The test is performed six times, using a clean cool plate each time, unless a positive result is observed earlier.

2. DATA

The burning time from the preliminary screening test (1.6.1.) and the shortest burning time in up to six tests (1.6.2.3.) are relevant for evaluation.

3. REPORTING

3.1. TEST REPORT

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

- the precise specification of the substance (identification and impurities),
- a description of the substance to be tested, its physical state including moisture content,
- results from the preliminary screening test and from the burning rate test if performed,
- all additional remarks relevant to the interpretation of results.

3.2. INTERPRETATION OF THE RESULT

Powdery, granular or paste-like substances are to be considered as highly flammable when the time of burning in any tests carried out according to the test procedure described in 1.6.2 is less than 45 seconds. Powders of metals or metal-alloys are considered to be highly flammable when they can be ignited and the flame or the zone of reaction spreads over the whole sample in 10 minutes or less.

4. REFERENCES

NF T 20-042 (SEPT 85). Chemical products for industrial use. Determination of the flammability of solids.

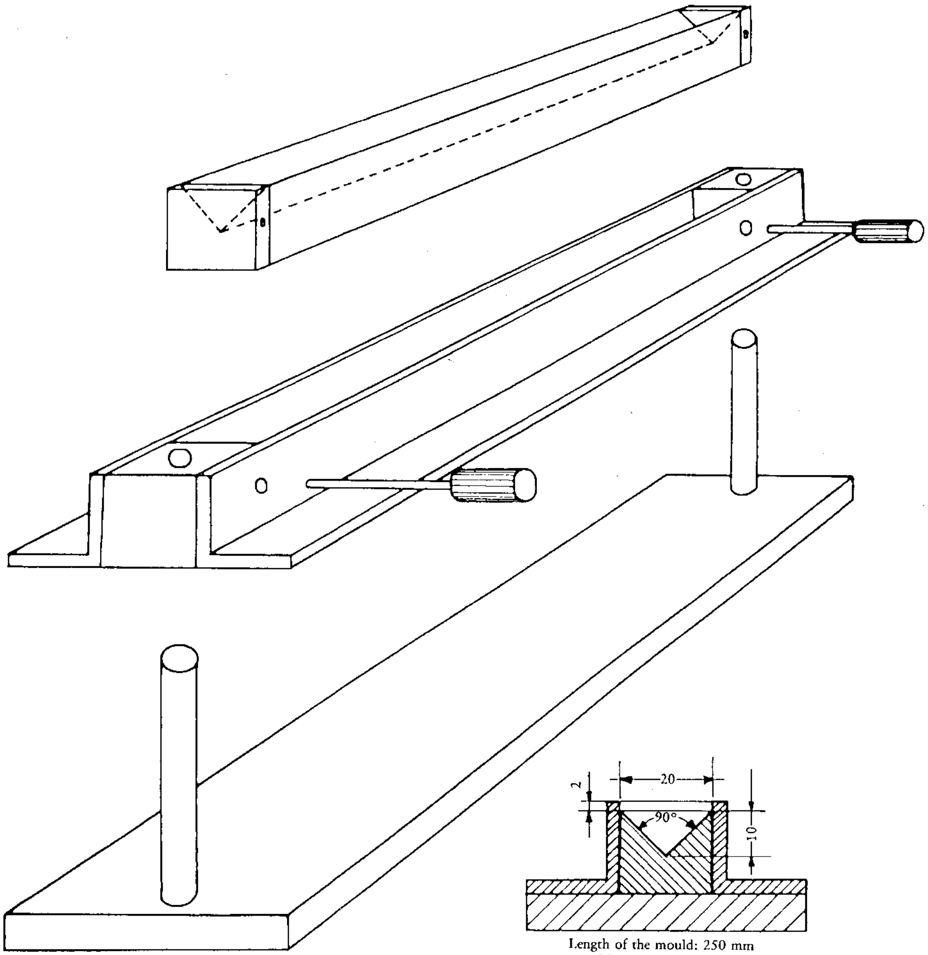
APPENDIX

Appendix

Figure

Mould and accessories for the preparation of the pile

(All dimensions in millimetres)



Length of the mould: 250 mm
Material: aluminium

A.11 FLAMMABILITY (GASES)

1. METHOD

1.1. INTRODUCTION

This method allows a determination of whether gases mixed with air at room temperature (circa 20 °C) and atmospheric pressure are flammable and, if so, over what range of concentrations. Mixtures of increasing concentrations of the test gas with air are exposed to an electrical spark and it is observed whether ignition occurs.

1.2. DEFINITION AND UNITS

The range of flammability is the range of concentration between the lower and the upper explosion limits. The lower and the upper explosion limits are those limits of concentration of the flammable gas in admixture with air at which propagation of a flame does not occur.

1.3. REFERENCE SUBSTANCES

Not specified.

1.4. PRINCIPLE OF THE METHOD

The concentration of gas in air is increased step by step and the mixture is exposed at each stage to an electrical spark.

1.5. QUALITY CRITERIA

Not stated.

1.6. DESCRIPTION OF THE METHOD

1.6.1. Apparatus

The test vessel is an upright glass cylinder having a minimum inner diameter of 50 mm and a minimum height of 300 mm. The ignition electrodes are separated by a distance of 3 to 5 mm and are placed 60 mm above the bottom of the cylinder. The cylinder is fitted with a pressure-release opening. The apparatus has to be shielded to restrict any explosion damage.

A standing induction spark of 0,5 sec. duration, which is generated from a high voltage transformer with an output voltage of 10 to 15 kV (maximum of power input 300 W), is used as the ignition source. An example of a suitable apparatus is described in reference (2).

1.6.2. Test conditions

The test must be performed at room temperature (circa 20 °C).

1.6.3. Performance of the test

Using proportioning pumps, a known concentration of gas in air is introduced into the glass cylinder. A spark is passed through the mixture and it is observed whether or not a flame detaches itself from the ignition source and propagates independently. The gas concentration is varied in steps of 1 % vol. until ignition occurs as described above.

If the chemical structure of the gas indicates that it would be non-flammable and the composition of the stoichiometric mixture with air can be calculated, then only mixtures in the range from 10 % less than the stoichiometric composition to 10% greater than this composition need be tested in 1 % steps.

2. DATA

The occurrence of flame propagation is the only relevant information data for the determination of this property.

3. REPORTING

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

- the precise specification of the substance (identification and impurities),
- a description, with dimensions, of the apparatus used
- the temperature at which the test was performed,
- the tested concentrations and the results obtained,
- the result of the test: non-flammable gas or highly flammable gas,
- if it is concluded that the gas is non-flammable then the concentration range over which it was tested in 1 % steps should be stated,
- all information and remarks relevant to the interpretation of results have to be reported.

4. REFERENCES

(1) F T 20-041 (SEPT 85). Chemical products for industrial use. Determination of the flammability of gases.

(2) W.Berthold, D.Conrad, T.Grewer, H.Grosse- einer Standard-Apparatur zur Messung von Explosionsgrenzen'. Chem.-Ing.- Tech. 1984, vo156, 2, 126-127.Wortmann, T.Redeker und H.Schacke. 'Entwicklung

A.12 FLAMMABILITY (CONTACT WITH WATER)

1. METHOD

1.1. INTRODUCTION

This test method can be used to determine whether the reaction of a substance with water or damp air leads to the development of dangerous amounts of gas or gases which may be highly flammable.

The test method can be applied to both solid and liquid substances. This method is not applicable to substances which spontaneously ignite when in contact with air.

1.2. DEFINITIONS AND UNITS

Highly flammable: substances which, in contact with water or damp air, evolve highly flammable gases in dangerous quantities at a minimum rate of 1 litre/kg pet hour.

1.3. PRINCIPLE OF THE METHOD

The substance is tested according to the step by step sequence described below; if ignition occurs at any step, no further testing is necessary. If it is known that the substance does not react violently with water then proceed to step 4 (1.3.4).

1.3.1. Step 1

The test substance is placed in a trough containing distilled water at 20 °C and it is noted whether or not the evolved gas ignites.

1.3.2. Step 2

The test substance is placed on a filter paper floating on the surface of a dish containing distilled water at 20 °C and it is noted whether or not the evolved gas ignites. The filter paper is merely to keep the substance in one place to increase the chances of ignition.

1.3.3. Step 3

The test substance is made into a pile approximately 2 cm high and 3 cm diameter. A few drops of water are added to the pile and it is noted whether or not the evolved gas ignites.

1.3.4. Step 4

The test substance is mixed with distilled water at 20 °C and the rate of evolution of gas is measured over a period of seven hours, at one-hour intervals. If the rate of evolution is erratic, or is increasing, after seven hours, the measuring time should be extended to a maximum time of five days. The test may be stopped if the rate at any time exceeds 1 litre/kg per hour.

1.4. REFERENCE SUBSTANCES

Not specified.

1.5. QUALITY CR1TERIA

Not stated.

1.6. DESCRIPTION OF METHODS

1.6.1. Step 1

1.6.1.1. Test conditions

The test is performed at room temperature (circa 20 ◦C).

1.6.1.2. Performance of the test

A small quantity (approximately 2 mm diameter) of the test substance should be placed in a trough containing distilled water. A note should be made of whether (i) any gas is evolved and (ii) if ignition of the gas occurs. If ignition of the gas occurs then no further testing of the substance is needed because the substance is regarded as hazardous.

1.6.2. Step 2

1.6.2.1. Apparatus

A filter-paper is floated flat on the surface of distilled water in any suitable vessel, e.g. a 100 mm diameter evaporating dish.

1.6.2.2. Test conditions

The test is performed at room temperature (circa 20 °C).

1.6.2.3. Performance of the test

A small quantity of the test substance (approximately 2 mm diameter) is placed onto the centre of the filter-paper. A note should be made of whether (i) any gas is evolved and (ii) if ignition of the gas occurs. If ignition of the gas occurs then no further testing of the substance is needed because the substance is regarded as hazardous.

1.6.3. Step 3

1.6.3.1. Test conditions

The test is performed at room temperature (circa 20 °C).

1.6.3.2. Performance of the test

The test substance is made into a pile approximately 2 cm high and 3 cm diameter with an indentation in the top. A few drops of water are added to the hollow and a note is made of whether (i) any gas is evolved and (ii) if ignition of the gas occurs. If ignition of the gas occurs then no further testing of the substance is needed because the substance is regarded as hazardous.

1.6.4. Step 4

1.6.4.1. Apparatus

The apparatus is set up as shown in the figure.

1.6.4.2. Test conditions

Inspect the container of the test substance for any powder < 500 μm (particle size). If the powder constitutes more than 1 % w/w of the total, or if the sample is friable, then the whole of the substance should be ground to a powder before testing to allow for a reduction in particle size during storage and handling; otherwise the substance is to be tested as received. The test should be performed at room temperature (circa 20 °C) and atmospheric pressure.

1.6.4.3. Performance of the test

10 to 20 ml of water are put into the dropping funnel of the apparatus and 10 g of substance are put in the conical flask. The volume of gas evolved can be measured by any suitable means. The tap of the dropping funnel is opened to let the water into the conical flask and a stop watch is started. The gas evolution is measured each hour during a seven hour period. If, during this period, the gas evolution is erratic, or if, at the end of this period, the rate of gas evolution is increasing, then measurements should be continued for up to five days. If, at any time of measurement, the rate of gas evolution exceeds 1 litre/kg per hour, the test can be discontinued. This test should be performed in triplicate.

If the chemical identity of the gas is unknown, the gas should be analyzed. When the gas contains highly flammable components and it is unknown whether the whole mixture is highly flammable, a mixture of the same composition has to be prepared and tested according to the method A.11.

2. DATA

The substance is considered hazardous if:

- spontaneous ignition takes place in any step of the test procedure,

or

- there is evolution of flammable gas at a rate greater than 1 litre/kg of the substance per hour.

3. REPORTING

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

- the precise specification of the substance (identification and impurities),
- details of any initial preparation of the test substance,
- the results of the tests (steps 1,2,3 and 4),
- the chemical identity of gas evolved,
- the rate of evolution of gas if step 4 (1.6.4) is performed,
- any additional remarks relevant to the interpretation of the results.

4. REFERENCES

(1) Recommendations on the transport of dangerous goods, test and criteria, 1990, United Nations, New York.

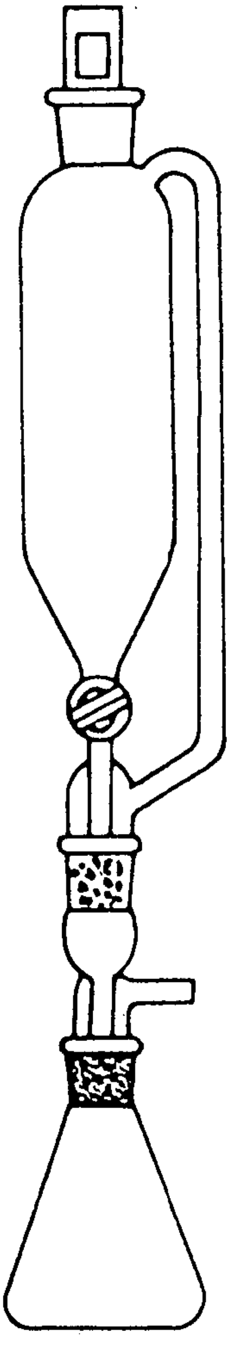
(2) NF T 20-040 (SEPT 85). Chemical products for industrial use. Determination of the flammability of gases formed by the hydrolysis of solid and liquid products.

APPENDIX

Appendix

Figure

Apparatus



A.13 PYROPHORIC PROPERTIES OF SOLIDS AND LIQUIDS

1. METHOD

1.1. INTRODUCTION

The test procedure is applicable to solid or liquid substances, which, in small amounts, will ignite spontaneously a short time after coming into contact with air at room temperature (circa 20 °C).

Substances which need to be exposed to air for hours or days at room temperature or at elevated temperatures before ignition occurs are not covered by this test method.

1.2 DEFINITIONS AND UNITS

Substances are considered to have pyrophoric properties if they ignite or cause charring under the conditions described in 1.6.

The auto-flammability of liquids may also need to be tested using method A.15 Auto-ignition temperature (liquids and gases).

1.3. REFERENCE SUBSTANCES

Not specified.

1.4. PRINCIPLE OF THE METHOD

The substance, whether solid or liquid, is added to an inert carrier and brought into contact with air at ambient temperature for a period of five minutes. If liquid substances do not ignite then they are absorbed onto filter paper and exposed to air at ambient temperature (circa 20 °C) for five minutes. If a solid or liquid ignites, or a liquid ignites or chars a filter paper, then the substance is considered to be pyrophoric.

1.5. QUALITY CRITERIA

Repeatability: because of the importance in relation to safety, a single positive result is sufficient for the substance to be considered pyrophoric.

1.6. DESCRIPTION OF THE TEST METHOD

1.6.1. Apparatus

A porcelain cup of circa 10 cm diameter is filled with diatomaceous earth to a height of about 5 mm at room temperature (circa 20 °C).

Note:

Diatomaceous earth or any other comparable inert substance which is generally obtainable shall be taken as representative of soil onto which the test substance might be spilt in the event of an accident. Dry filter paper is required for testing liquids which do not ignite on contact with air when in contact with an inert carrier.

1.6.2. Performance of the Test

a) Powdery Solids

1 to 2 cm^3 of the substance to be tested is poured from circa 1 m height onto a non-combustible surface and it is observed whether the substance ignites during dropping or within five minutes of settling.

The test is performed six times unless ignition occurs.

b) Liquids

Circa 5 cm^3 of the liquid to be tested is poured into the prepared porcelain cup and it is observed whether the substance ignites within five minutes.

If no ignition occurs in the six tests, perform the following tests:

A 0,5 ml test sample is delivered from a syringe to an indented filter paper and it is observed whether ignition or charring of the filter paper occurs within five minutes of the liquid being added. The test is performed three times unless ignition or charring occurs.

2. DATA

2.1. TREATMENT OF RESULTS

Testing can be discontinued as soon as a positive result occurs in any of the tests.

2.2. EVALUATION

If the substance ignites within five minutes when added to an inert carrier and exposed to air, or a liquid substance chars or ignites a filter paper within five minutes when added and exposed to air, it is considered to be pyrophoric.

3. REPORTING

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

- the precise specification of the substance (identification and impurities),
- the results of the tests,
- any additional remark relevant to the interpretation of the results.

4. REFERENCES

(1) NF T 20-039 (SEPT 85). Chemical products for industrial use. Determination of the spontaneous flammability of solids and liquids.

(2) Recommendations on the Transport of Dangerous Goods, Test and criteria, 1990, United Nations, New York.

A.14 EXPLOSIVE PROPERTIES

1. METHOD

1.1. INTRODUCTION

The method provides a scheme of testing to determine whether a solid or a pasty substance presents a danger of explosion when submitted to the effect of a flame (thermal sensitivity), or to shock or friction (sensitivity to mechanical stimuli), and whether a liquid substance presents a danger of explosion when submitted to the effect of a flame or shock.

The method comprises three parts:

(a) test of thermal sensitivity (1);

(b) a test of mechanical sensitivity with respect to shock (1);

(c) a test of mechanical sensitivity with respect to friction (1).

The method yields data to assess the likelihood of initiating an explosion by means of certain common stimuli. The method is not intended to ascertain whether a substance is capable of exploding under any conditions.

The method is appropriate for determining whether a substance will present a danger of explosion (thermal and mechanical sensitivity) under the particular conditions specified in the directive. It is based on a number of types of apparatus which are widely used internationally (1) and which usually give meaningful results. It is recognised that the method is not definitive. Alternative apparatus to that specified may be used provided that it is internationally recognised and the results can be adequately correlated with those from the specified apparatus.

The tests need not be performed when available thermodynamic information (e.g. heat of formation, heat of decomposition) and/ or absence of certain reactive groups (2) in the structural formula establishes beyond reasonable doubt that the substance is incapable of rapid decomposition with evolution of gases or release of heat (i.e. the material does not present any risk of explosion). A test of mechanical sensitivity with respect to friction is not required for liquids.

1.2. DEFINITIONS AND UNITS

Explosive:

Substances which may explode under the effect of flame or which are sensitive to shock or friction in the specified apparatus (or are more mechanically sensitive than 1,3-dinitrobenzene in alternative apparatus).

1.3. REFERENCE SUBSTANCES

1,3-dinitrobenzene, technical crystalline product sieved to pass 0,5 mm, for the friction and shock methods.

Perhydro-l,3,5-trinitro-l,3,5-triazine (RDX, hexogen, cyclonite -CAS 121-82-4), recrystallised from aqueous cyclohexanone, wet-sieved through a 250 μm and retained on a 150 μm sieve and dried at 103 ± 2 °C (for 4 hours) for the second series of friction and shock tests.

1.4. PRINCIPLE OF THE METHOD

Preliminary tests are necessary to establish safe conditions for the performance of the three tests of sensitivity.

1.4.1. Safety-in-handling tests (3)

For safety reasons, before performing the main tests, very small samples (circa 10 mg) of the substance are subjected to heating without confinement in a gas flame, to shock in any convenient form of apparatus and to friction by the use of a mallet against an anvil or any form of friction machine. The objective is to ascertain if the substance is so sensitive and explosive that the prescribed sensitivity tests, particularly that of thermal sensitivity , should be performed with special precautions so as to avoid injury to the operator.

1.4.2. Thermal sensitivity

The method involves heating the substance in a steel tube, closed by orifice plates with differing diameters of hole, to determine whether the substance is liable to explode under conditions of intense heat and defined confinement.

1.4.3. Mechanical sensitivity (shock)

The method involves subjecting the substance to the shock from a specified mass dropped from a specified height.

1.4.4. Mechanical sensitivity (friction)

The method involves subjecting solid or pasty substances to friction between standard surfaces under specified conditions of load and relative motion.

1.5. QUALITY CRITERIA

Not stated.

1.6. DESCRIPTION OF METHOD

1.6.1. Thermal sensitivity (effect of a flame)

1.6.1.1. Apparatus

The apparatus consists of a non-reusable steel tube with its re-usable closing device (figure 1), installed in a heating and protective device. Each tube is deep-drawn from sheet steel (see Appendix) and has an internal diameter of 24 mm, a length of 75 mm and wall thickness of 0,5 mm. The tubes are flanged at the open end to enable them to be closed by the orifice plate assembly. This consists of a pressure-resistant orifice plate, with a central hole, secured firmly to a tube using a two-part screw joint (nut and threaded collar). The nut and threaded collar are made from chromium-manganese steel (see Appendix) which is spark-free up to 800 °C. The orifice plates are 6 mm thick, made from heat-resistant steel (see Appendix), and are available with a range of diameters of opening.

1.6.1.2. Test conditions

Normally the substance is tested as received although in certain cases, e.g. if pressed, cast or otherwise condensed, it may be necessary to test the substance after crushing. For solids, the mass of material to be used in each test is determined using a two-stage dry run procedure. A tared tube is filled with 9 cm^3 of substance and the substance tamped with 80 N force applied to the total cross-section of the tube. For reasons of safety or in cases where the physical form of the sample can be changed by compression other filling procedures may be used; e.g. if the substance is very friction sensitive then tamping is not appropriate. If the material is compressible then more is added and tamped until the tube is filled to 55 mm from the top. The total mass used to fill the tube to the 55 mm level is determined and two further increments, each tamped with 80 N force, are added. Material is then either added with tamping, or taken out, as required, to leave the tube filled to a level 15 mm from the top. A second dry run is performed, starting with a tamped quantity of a third of the total mass found in the first dry run. Two more of these increments are added with 80 N tamping and the level of the substance in the tube adjusted to 15 mm from the top by addition or subtraction of material as required. The amount of solid determined in the second dry run is used for each trial; filling being performed in three equal amounts, each compressed to 9 cm^3 by whatever force is necessary. (This may be facilitated by the use of spacing rings).

Liquids and gels are loaded into the tube to a height of 60 mm taking particular care with gels to prevent the formation of voids. The threaded collar is slipped onto the tube from below, the appropriate orifice plate is inserted and the nut tightened after applying some molybdenum disulphide based lubricant. It is essential to check that none of the substance is trapped between the flange and the plate, or in the threads.

Heating is provided by propane taken from an industrial cylinder, fitted with a pressure regulator (60 to 70 mbar), through a meter and evenly distributed (as indicated by visual observation of the flames from the burners) by a manifold to four burners. The burners are located around the test chamber as shown in figure 1. The four burners have a combined consumption of about 3.2 litres of propane per minute. Alternative fuel gases and burners may be used but the heating rate must be as specified in figure 3. For all apparatus, the heating rate must be checked periodically using tubes filled with dibutyl phthalate as indicated in figure 3.

1.6.1.3. Performance of the tests

Each test is performed until either the tube is fragmented or the tube has been heated for five minutes. A test resulting in the fragmentation of the tube into three or more pieces, which in some cases may be connected to each other by narrow strips of metal as illustrated in figure 2, is evaluated as giving an explosion. A test resulting in fewer fragments or no fragmentation is regarded as not giving an explosion.

A series of three tests with a 6,0 mm diameter orifice plate is first performed and, if no explosions are obtained, a second series of three tests is performed with a 2,0 mm diameter orifice plate. If an explosion occurs during either test series then no further tests are required.

1.6.1.4. Evaluation

The test result is considered positive if an explosion occurs in either of the above series of tests.

1.6.2. Mechanical sensitivity (shock)

1.6.2.1. Apparatus (figure 4)

The essential parts of a typical fall hammer apparatus are a cast steel block with base, anvil, column, guides, drop weights, release device and a sample holder. The steel anvil 100 mm (diameter) x 70 mm (height) is screwed to the top of a steel block 230 mm (length) x 250 mm (width) x 200 mm (height) with a cast base 450 mm (length) x 450 mm (width) x 60 mm (height). A column, made from seamless drawn steel tube, is secured in a holder screwed on to the back of the steel block. Four screws anchor the apparatus to a solid concrete block 60 x 60 x 60 cm such that the guide rails are absolutely vertical and the drop weight falls freely. 5 and 10 kg weights, made from solid steel, are available for use. The striking head of each weight is of hardened steel, HRC 60 to 63, and has a minimum diameter of 25 mm.

The sample under test is enclosed in a shock device consisting of two coaxial solid steel cylinders, one above the other, in a hollow cylindrical steel guide ring. The solid steel cylinders should be of 10 (-0,003, -0,005) mm diameter and 10 mm height and have polished surfaces, rounded edges (radius of curvature 0,5 mm) and a hardness of HRC 58 to 65. The hollow cylinder must have an external diameter of 16 mm, a polished bore of 10 (+ 0,005, + 0,010) mm and a height of 13 mm. The shock device is assembled on an intermediate anvil (26 mm diameter and 26 mm height) made of steel and centred by a ring with perforations to allow escape of fumes.

1.6.2.2. Test conditions

The sample volume should be 40 mm^3, or a volume to suit any alternative apparatus. Solid substances should be tested in the dry state and prepared as follows:

(a) powdered substances are sieved (sieve size 0,5 mm); all that has passed through the sieve is used for testing;

(b) pressed, cast or otherwise condensed substances are broken into small pieces and sieved; the sieve fraction from 0,5 to 1 mm diameter is used for testing and should be representative of the original substance.

Substances normally supplied as pastes should be tested in the dry state where possible or, in any case, following removal of the maximum possible amount of diluent. Liquid substances are tested with a 1 mm gap between the upper and lower steel cylinders.

1.6.2.3. Performance of the tests

A series of six tests are performed dropping the 10 kg mass from 0,40 m (40 J). If an explosion is obtained during the six tests at 40 J, a further series of 6 tests, dropping a 5 kg mass from 0,15 m (7,5 J), must be performed. In other apparatus, the sample is compared with the chosen reference substance using an established procedure (e.g. up-and-down technique etc.).

1.6.2.4. Evaluation

The test result is considered positive if an explosion (bursting into flame and/ or a report is equivalent to explosion) occurs at least once in any of the tests with the specified shock apparatus or the sample is more sensitive than 1,3-dinitrobenzene or RDX in an alternative shock test.

1.6.3. Mechanical sensitivity (friction)

1.6.3.1. Apparatus (figure 5)

The friction apparatus consists of a cast steel base plate on which is mounted the friction device. This consists of a fixed porcelain peg and moving porcelain plate. The porcelain plate is held in a carriage which runs in two guides. The carriage is connected to an electric motor via a connecting rod, an eccentric cam and suitable gearing such that the porcelain plate is moved, once only, back and forth beneath the porcelain peg for a distance of 10 mm. The porcelain peg may be loaded with, for example, 120 or 360 newtons.

The flat porcelain plates are made from white technical porcelain (roughness 9 to 32 μm) and have the dimensions 25 mm (length) x 25 mm (width) x 5 mm (height). The cylindrical porcelain peg is also made of white technical porcelain and is 15 mm long, has a diameter of 10 mm and roughened spherical end surfaces with a radius of curvature of 10 mm.

1.6.3.2. Test conditions

The sample volume should be 10 mm^3 or a volume to suit any alternative apparatus.

Solid substances are tested in the dry state and prepared as follows:

(a) powdered substances are sieved (sieve size 0,5 mm); all that has passed through the sieve is used for testing;

(b) pressed, cast or otherwise condensed substances are broken into small pieces and sieved; the sieve fraction < 0,5 mm diameter is used for testing.

Substances normally supplied as pastes should be tested in the dry state where possible. If the substance cannot be prepared in the dry state, the paste (following removal of the maximum possible amount of diluent) is tested as a 0,5 mm thick, 2 mm wide, 10 mm long film, prepared with a former.

1.6.3.3. Performance of the tests

The porcelain peg is brought onto the sample under test and the load applied. When carrying out the test, the sponge marks of the porcelain plate must lie transversely to the direction of the movement. Care must be taken that the peg rests on the sample, that sufficient test material lies under the peg and also that the plate moves correctly under the peg. For pasty substances, a 0,5 mm thick gauge with a 2 x 10 mm slot is used to apply the substance to the plate. The porcelain plate has to move 10 mm forwards and backwards under the porcelain peg in a time of 0,44 seconds. Each part of the surface of the plate and peg must only be used once; the two ends of each peg will serve for two trials and the two surfaces of a plate will each serve for three trials.

A series of six tests are performed with a 360 N loading. If a positive event is obtained during these six tests, a further series of six tests must be performed with a 120 N loading. In other apparatus, the sample is compared with the chosen reference substance using an established procedure (e.g. up-and-down technique, etc.).

1.6.3.4. Evaluation

The test result is considered positive if an explosion (crepitation and/or a report or bursting into flame are equivalent to explosion) occurs at least once in any of the tests with the specified friction apparatus or satisfies the equivalent criteria in an alternative friction test.

2. DATA

In principle, a substance is considered to present a danger of explosion in the sense of the directive if a positive result is obtained in the thermal, shock or friction sensitivity test.

3. REPORTING

3.1. TEST REPORT

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

- identity, composition, purity, moisture content etc. of the substance tested,
- the physical form of the sample and whether or not it has been crushed, broken and/or sieved,

- observations during the thermal sensitivity tests (e.g. sample mass, number of fragments etc.),
- observations during the mechanical sensitivity tests (e.g. formation of considerable amounts of smoke or complete decomposition without a report, flames, sparks, report, crepitation etc.),
- results of each type of test,
- if alternative apparatus has been used, scientific justification as well as evidence of correlation between results obtained with specified apparatus and those obtained with equivalent apparatus must be given,
- any useful comments such as reference to tests with similar products which might be relevant to a proper interpretation of the results,
- all additional remarks relevant for the interpretation of the results.

3.2. INTERPRETATION AND EVALUATION OF RESULTS

The test report should mention any results which are considered false, anomalous or unrepresentative. If any of the results should be discounted, an explanation and the results of any alternative or supplementary testing should be given. Unless an anomalous result can be explained, it must be accepted at face value and used to classify the substance accordingly.

4. REFERENCES

(1) Recommendations on the Transport of Dangerous Goods: Tests and criteria, 1990, United Nations, New York.

(2) Bretherick, L., Handbook of Reactive Chemical Hazards, 4th edition, Butterworths, London, ISBN 0-750-60103-5, 1990.

(3) Koenen, H., Ide, K.H. and Swart, K.H., Explosivstoffe, 1961, vol.3, 6-13 and 30-42.

(4) NF T 20-038 (Sept. 85). Chemical products for industrial use -Determination of explosion risk.

APPENDIX - EXAMPLE OF MATERIAL SPECIFICATION FOR THERMAL SENSITIVITY TEST (SEE DIN 1623)

(1) Tube: Material specification No 1.0336.505 g

(2) Orifice plate: Material specification No 1.4873

(3) Threaded collar and nut: Material specification No 1.3817

Figure 1

Thermal sensitivity test apparatus (all dimensions in millimetres)

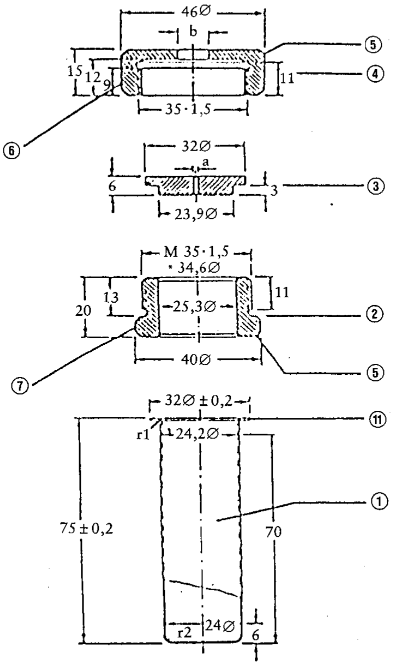


Fig. 1a Steel tube and accessories

(1) tube
(1a) outer flange
(2) threaded collar; low-friction thread
(3) orifice plate a = 2,0 or 6,0 mm diameter
(4) nut b = 10 mm diameter
(5) chamfered surface
(6) 2 flat for spanner size 41

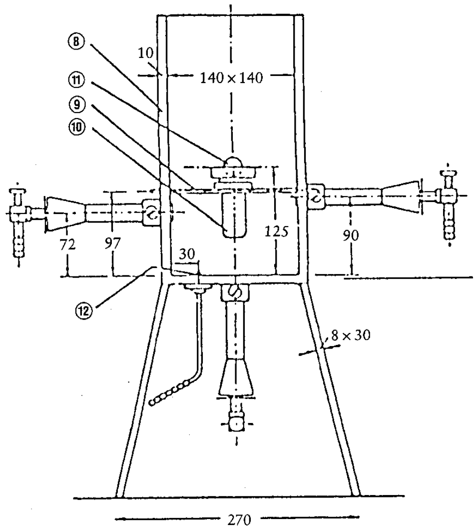
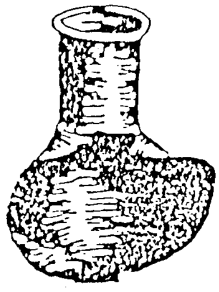


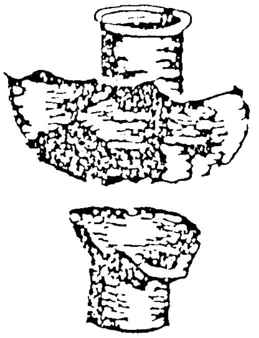
Fig. 1b Heating and protective device

(7) 2 flat for spanner size 36
(8) splinter-proof box
(9) 2 supporting rods for tube
(10) assembled tube
(11) position for rear burner; the other burners are visible
(12) pilot jet

Figure 2
Thermal sensitivity test (example of fragmentation)

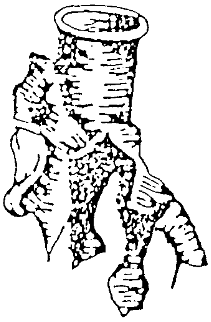


No explosion

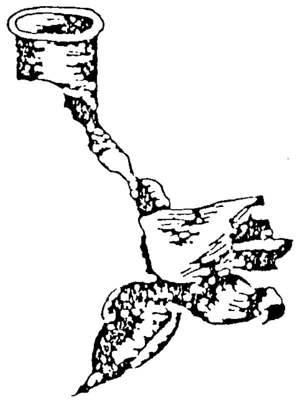


No explosion

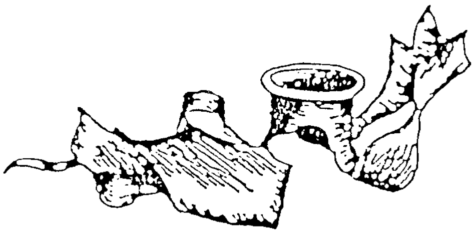
Explosion



Explosion



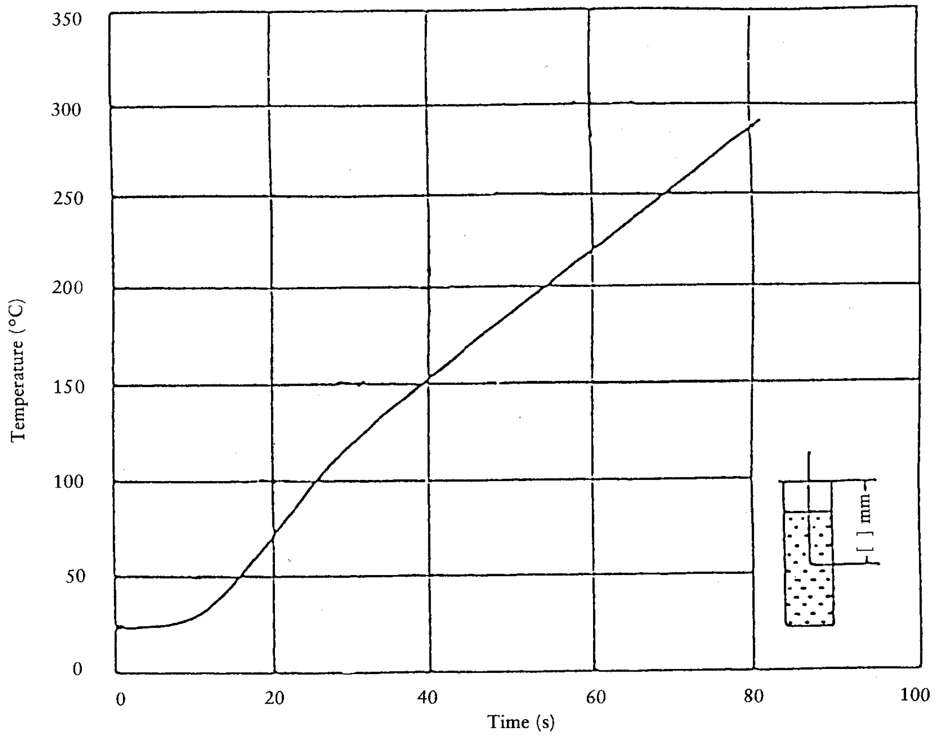
Explosion



Explosion

Figure 3

Heating rate calibration for thermal sensitivity test



Temperature/time curve obtained on heating dibutyl phtalate (27 cm^3) in a closed (1,5 mm orifice plate) tube using a propane flow rate of 3,2 litre/minute. The temperature is measured with a 1mm diameter stainless steel sheathed chromel/alumel thermocouple, placed centrally 43 mm below the rim of the tube. The heating rate between 135 °C and 285 °C should be between 185 and 215 K/minute.

Figure 4

Shock test apparatus

(all dimensions in millimetres)

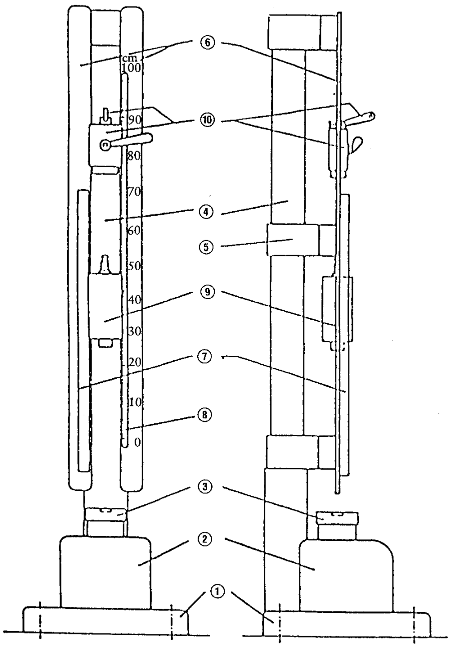


Fig. 4a Fall-hammer, front and side, general view

(1) base, 450 x 450 x 60
(2) steel block, 230 x 250 x 200
(3) anvil, 100 diameter x 70
(4) colum
(5) median cross-member
(6) 2 guides
(7) toothed rack

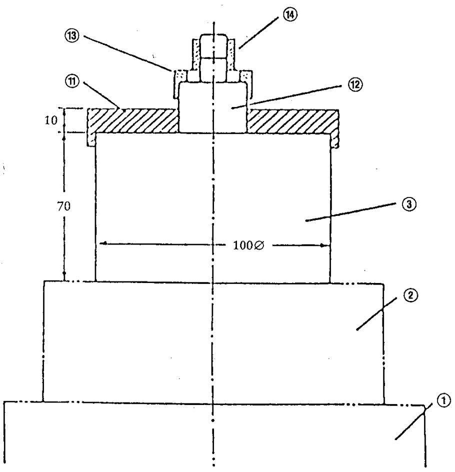


Fig. 4b Fall-hammer, lower part

(8) graduated scale
(9) fall-hammer(drop mass)
(10) holding and releasing device
(11) locating plate
(12) intermediate anvil (interchangeable), 26 diameter x 26
(13) locating ring with orifices
(14) impact device

Figure 4

Continued

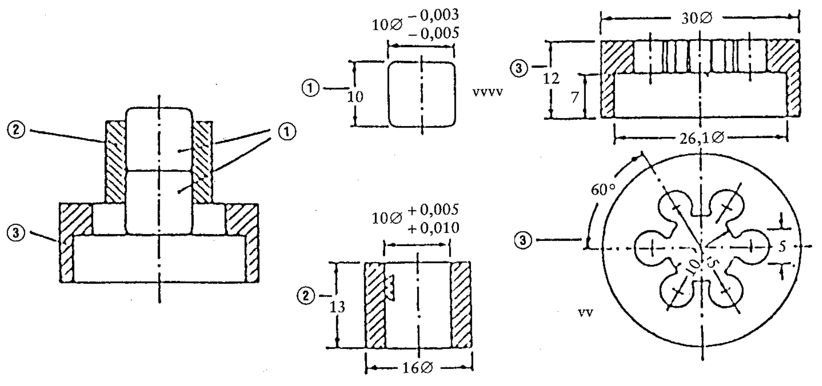
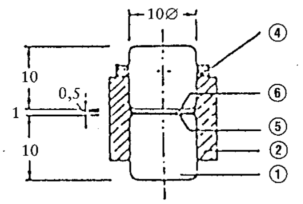


Fig. 4c Shock device for substances in powdered or paste-like form

(1) steel cylinders
(2) guide ring for steel cylinders
(3) locating ring with orifices
  (a) vertical section
  (b) plan
(4) rubber ring
(5) liquid substance (40 mm^3)
(6) space free from liquid

Fig. 4d Shock device for liquid substances



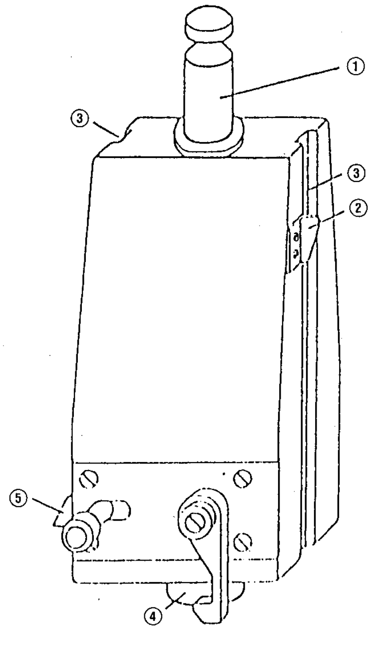


Fig. 4e Hammer (drop mass of 5 kg)

(1) suspension spigot
(2) height marker
(3) positioning groove
(4) cylindrical striking head
(5) rebound catch

Figure 5

Friction sensitivity apparatus

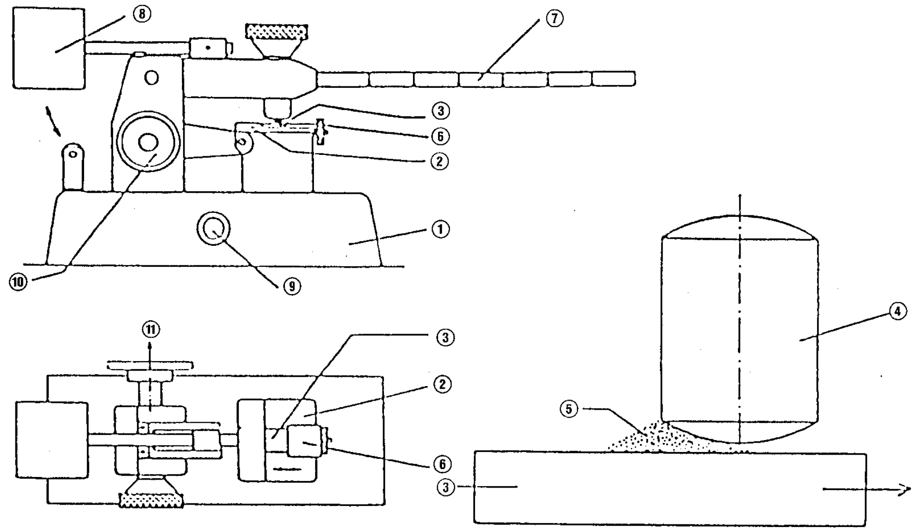


Fig. 5a Friction apparatus; elevation and plan view

(1) steel base
(2) movable carriage
(3) porcelain plate, 25 x 25 x 5 mm,
hel on carriage
(4) fixed porcelain peg, 10 diameter x 15 mm
(5) sample under test, approximately 10 mm^3

Fig. 5b Starting position of peg on sample

(6) peg-holder
(7) loading arm
(8) counterweight
(9) switch
(10) wheel for setting carriage at starting position
(11) direction to electric drive motor

A.15 AUTO-IGNITION TEMPERATURE (LIQUIDS AND GASES)

1. METHOD

1.1. INTRODUCTION

Explosive substances and substances which ignite spontaneously in contact with air at ambient temperature should not be submitted to this test. The test procedure is applicable to gases, liquids and vapours which, in the presence of air, can be ignited by a hot surface.

The auto-ignition temperature can be considerably reduced by the presence of catalytic impurities, by the surface material or by a higher volume of the test vessel.

1.2. DEFINITIONS AND UNITS

The degree of auto-ignitability is expressed in terms of the auto-ignition temperature. The auto-ignition temperature is the lowest temperature at which the test substance will ignite when mixed with air under the conditions defined in the test method.

1.3. REFERENCE SUBSTANCES

Reference substances are cited in the standards (see 1.6.3). They should primarily serve to check the performance of the method from time to time and to allow comparison with results from other methods.

1.4. PRINCIPLE OF THE METHOD

The method determines the minimum temperature of the inner surface of an enclosure that will result in ignition of a gas, vapour or liquid injected into the enclosure.

1.5. QUALITY CRITERIA

The repeatability varies according to the range of auto-ignition temperatures and the test method used.

The sensitivity and specificity depend on the test method used.

1.6. DESCRIPTION OF THE METHOD

1.6.1. Apparatus

The apparatus is described in the method referred to in 1.6.3.

1.6.2. Test conditions

A sample of the test substance is tested according to the method referred to in 1.6.3.

1.6.3. Performance of the test

See IEC 79-4, DIN 51794, ASTM-E 659-78, BS 4056, NF T 20-037.

2. DATA

Record the test-temperature, atmospheric pressure, quantity of sample used and time-lag until ignition occurs.

3. REPORTING

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

- the precise specification of the substance (identification and impurities),
- the quantity of sample used, atmospheric pressure,
- the apparatus used,
- the results of measurements (test temperatures, results concerning ignition, corresponding time-lags),
- all additional remarks relevant to the interpretation of results.

4. REFERENCES

None.

A.16 RELATIVE SELF-IGNITION TEMPERATURE FOR SOLIDS

1. METHOD

1.1 INTRODUCTION

Explosive substances and substances which ignite spontaneously in contact with air at ambient temperature should not be submitted to this test.

The purpose of this test is to provide preliminary information on the auto-flammability of solid substances at elevated temperatures.

If the heat developed either by a reaction of the substance with oxygen or by exothermic decomposition is not lost rapidly enough to the surroundings, self-heating leading to self-ignition occurs. Self-ignition therefore occurs when the rate of heat-production exceeds the rate of heat loss.

The test procedure is useful as a preliminary screening test for solid substances. In view of the complex nature of the ignition and combustion of solids, the self-ignition temperature determined according to this test method should be used for comparison purposes only.

1.2. DEFINITIONS AND UNITS

The self-ignition temperature as obtained by this method is the minimum ambient temperature expressed in °C at which a certain volume of a substance will ignite under defined conditions.

1.3. REFERENCE SUBSTANCE

None.

1.4. PRINCIPLE OF THE METHOD

A certain volume of the substance under test is placed in an oven at room temperature; the temperature/time curve relating to conditions in the centre of the sample is recorded while the temperature of the oven is increased to 400 °C, or to the melting point if lower, at a rate of 0,5 °C/min. For the purpose of this test, the temperature of the oven at which the sample temperature reaches 400 °C by self-heating is called the self-ignition temperature.

1.5. QUALITY CRITERIA

None.

1.6. DESCRIPTION OF THE METHOD

1.6.1. Apparatus

1.6.1.1. Oven

A temperature-programmed laboratory oven (volume about 2 litres) fitted with natural air circulation and explosion relief. In order to avoid a potential explosion risk, any decomposition gases must not be allowed to come into contact with the electric heating elements.

1.6.1.2. Wire mesh cube

A piece of stainless steel wire mesh with 0,045 mm openings should be cut according to the pattern in figure 1. The mesh should be folded and secured with wire into an open-topped cube.

1.6.1.3. Thermocouples

Suitable thermocouples.

1.6.1.4. Recorder

Any two-channel recorder calibrated from 0 to 600 °C or corresponding voltage.

1.6.2. Test conditions

Substances are tested as received.

1.6.3. Performance of the test

The cube is filled with the substance to be tested and is tapped gently, adding more of the substance until the cube is completely full. The cube is then suspended in the centre of the oven at room temperature. One thermocouple is placed at the centre of the cube and the other between the cube and the oven wall to record the oven temperature.

The temperatures of the oven and sample are continuously recorded while the temperature of the oven is increased to 400 °C, or to the melting point if lower, at a rate of 0,5 °C/min.

When the substance ignites the sample thermocouple will show a very sharp temperature rise above the oven temperature.

2. DATA

The temperature of the oven at which the sample temperature reaches 400 °C by self-heating is relevant for evaluation (see figure 2).

3. REPORTING

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

- a description of the substance to be tested,

- the results of measurement including the temperature/time curve,
- all additional remarks relevant for the interpretation of the results.

4. REFERENCES

NF T 20-036 (September 85). Chemical products for industrial use. Determination of the relative temperature of the spontaneous flammability of solids.

Figure 1

Pattern of 20 mm test cube

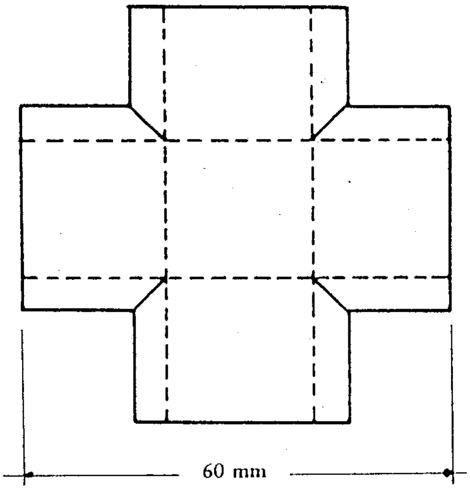
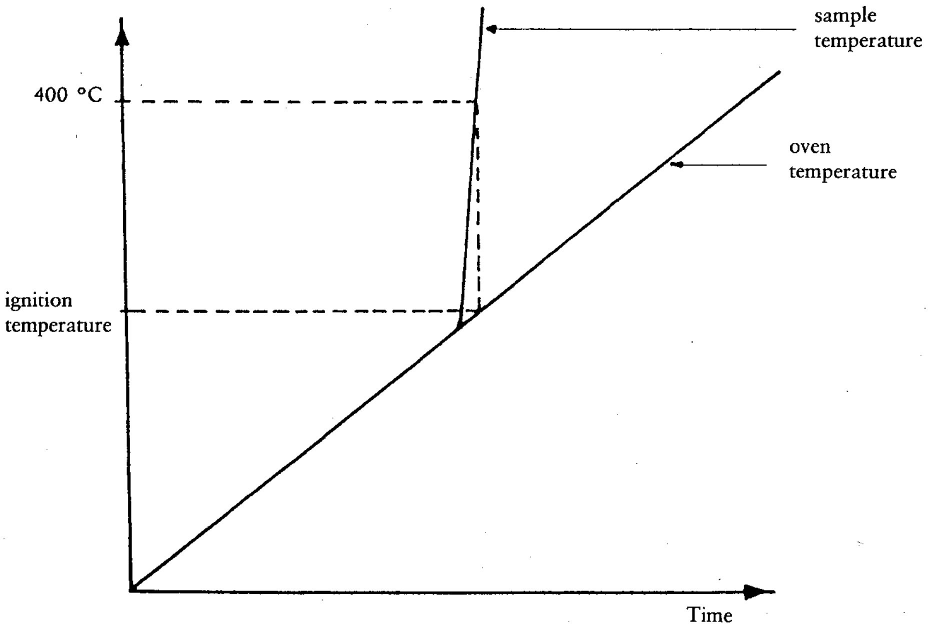


Figure 2

Typical temperature/time curve



A.17 OXIDIZING PROPERTIES (SOLIDS)

1. METHOD

1.1. INTRODUCTION

It is useful to have preliminary information on any potentially explosive properties of the substance before performing this test.

This test is not applicable to liquids, gases, explosive or highly flammable substances, or organic peroxides.

This test need not be performed when examination of the structural formula establishes beyond reasonable doubt that the substance is incapable of reacting exothermically with a combustible material.

In order to ascertain if the test should be performed with special precautions, a preliminary test should be performed.

1.2. DEFINITION AND UNITS

Burning time: reaction time, in seconds, taken for the reaction zone to travel along a pile, following the procedure described in 1.6.

Burning rate: expressed in millimetres per second.

Maximum burning rate: the highest value of the burning rates obtained with mixtures containing 10 to 90 % by weight of oxidizer.

1.3. REFERENCE SUBSTANCE

Barium nitrate (analytical grade) is used as reference substance for the test and the preliminary test.

The reference mixture is that mixture of barium nitrate with powdered cellulose, prepared according to 1.6, which has the maximum burning rate (usually a mixture with 60% barium nitrate by weight).

1.4. PRINCIPLE OF THE METHOD

A preliminary test is carried out in the interests of safety. No further testing is required when the preliminary test clearly indicates that the test substance has oxidizing properties. When this is not the case, the substance should then be subject to the full test.

In the full test, the substance to be tested and a defined combustible substance will be mixed in various ratios. Each mixture is then formed into a pile and the pile is ignited at one end.

The maximum burning rate determined is compared with the maximum burning rate of the reference mixture.

1.5. QUALITY CRITERIA

If required, any method of grinding and mixing is valid provided that the difference in the maximum rate of burning in the six separate tests differs from the arithmetic mean value by no more than 10 %.

1.6. DESCRIPTION OF THE METHOD

1.6.1. Preparation

1.6.1.1. Test substance

Reduce the test sample to a particle size < 0,125 mm using the following procedure: sieve the test substance, grind the remaining fraction, repeat the procedure until the whole test portion has passed the sieve.

Any grinding and sieving method satisfying the quality criteria may be used.

Before preparing the mixture the substance is dried at 105 °C, until constant weight is obtained. If the decomposition temperature of the substance to be tested is below 105 °C, the substance has to be dried at a suitable lower temperature.

1.6.1.2. Combustible substance

Powdered cellulose is used as a combustible substance. The cellulose should be a type used for thin-layer chromatography or column chromatography. A type with fibre-lengths of more than 85% between 0,020 and 0,075 mm has proved to be suitable. The cellulose powder is passed through a sieve with a mesh-size of 0,125 mm. The same batch of cellulose is to be used throughout the test.

Before preparing the mixture, the powdered cellulose is dried at 105 °C until constant weight is obtained.

If wood-meal is used in the preliminary test, then prepare a soft-wood wood-meal by collecting the portion which passes through a sieve mesh of 1,6 mm, mix thoroughly, then dry at 105 °C for four hours in a layer not more than 25 mm thick. Cool and store in an air-tight container filled as full as practicable until required, preferably within 24 hours of drying.

1.6.1.3. Ignition source

A hot flame from a gas burner (minimum diameter 5 mm) should be used as the ignition source. If another ignition source is used (e.g. when testing in an inert atmosphere), the description and the justification should be reported.

1.6.2. Performance of the test

Note:

Mixtures of oxidizers with cellulose or wood-meal must be treated as potentially explosive and handled with due care.

1.6.2.1. Preliminary test

The dried substance is thoroughly mixed with the dried cellulose or wood-meal in the proportions 2 of test substance to 1 of cellulose or wood-meal by weight and the mixture is formed into a small cone-shaped pile of dimensions 3,5 cm (diameter of base) x 2,5 cm (height) by filling, without tamping, a cone-shaped former (e.g. a laboratory glass funnel with the stem plugged).

The pile is placed on a cool, non-combustible, non-porous and low heat-conducting base plate. The test should be carried out in a fume cupboard as in 1.6.2.2.

The ignition source is put in contact with the cone. The vigour and duration of the resultant reaction are observed and recorded.

The substance is to be considered as oxidizing if the reaction is vigorous.

In any case where the result is open to doubt, it is then necessary to complete the full train test described below.

1.6.2.2. Train test

Prepare oxidizer cellulose-mixtures containing 10 to 90 % weight of oxidizer in 10 % increments. For borderline cases, intermediate oxidizer cellulose mixtures should be used to obtain the maximum burning rate more precisely.

The pile is formed by means of a mould. The mould is made of metal, has a length of 250 mm and a triangular cross-section with an inner height of 10 mm and an inner width of 20 mm. On both sides of the mould, in the longitudinal direction, two metal plates are mounted as lateral limitations which project 2 mm beyond the upper edge of the triangular cross-section (figure). This arrangement is loosely filled with a slight excess of mixture. After dropping the mould once from a height of 2 cm onto a solid surface, the remaining excess substance is scraped off with an obliquely positioned sheet. The lateral limitations are removed and the remaining powder is smoothed, using a roller. A non-combustible, non-porous and low heat-conducting base plate is then placed on the top of the mould, the apparatus inverted and the mould removed.

Arrange the pile across the draught in a fume cupboard.

The air-speed should be sufficient to prevent fumes escaping into the laboratory and should not be varied during the test. A draught screen should be erected around the apparatus.

Due to hygroscopicity of cellulose and of some substances to be tested, the test should be carried out as quickly as possible.

Ignite one end of the pile by touching with the flame.

Measure the time of reaction over a distance of 200 mm after the reaction zone has propagated an initial distance of 30 mm.

The test is performed with the reference substance and at least once with each one of the range of mixtures of the test substance with cellulose.

If the maximum burning rate is found to be significantly greater than that from the reference mixture, the test can be stopped; otherwise the test should be repeated five times for each of the three mixtures giving the fastest burning rate.

If the result is suspected of being a false positive, then the test should be repeated using an inert substance with a similar particle size, such as kieselguhr, in place of cellulose. Alternatively, the test substance cellulose mixture, having the fastest burning rate, should be retested in an inert atmosphere (< 2 % v/v oxygen content).

2. DATA

For safety reasons the maximum burning rate - not the mean value - shall be considered to be the characteristic oxidizing property of the substance under test.

The highest value of burning rate within a run of six tests of a given mixture is relevant for evaluation.

Plot a graph of the highest value of burning rate for each mixture versus the oxidizer concentration. From the graph take the maximum burning rate.

The six measured values of burning rate within a run obtained from the mixture with the maximum burning rate must not differ from the arithmetic mean value by more than 10 %; otherwise the methods of grinding and mixing must be improved.

Compare the maximum burning rate obtained with the maximum burning rate of the reference mixture (see 1.3).

If tests are conducted in an inert atmosphere, the maximum reaction rate is compared with that from the reference mixture in an inert atmosphere.

3. REPORT

3.1. TEST REPORT

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

- the identity, composition, purity, moisture content etc. of the substance tested;
- any treatment of the test sample (e.g. grinding, drying);
- the ignition source used in the tests;
- the results of measurements;

- the mode of reaction (e.g. flash burning at the surface, burning through the whole mass, any information concerning the combustion products, ...);
- all additional remarks relevant for the interpretation of results, including a description of the vigour (flaming, sparking, fuming, slow smouldering, etc.) and approximate duration produced in the preliminary safety / screening test for both test and reference substance;
- the results from tests with an inert substance, if any;
- the results from tests in an inert atmosphere, if any.

3.2. INTERPRETATION OF THE RESULT

A substance is to be considered as an oxidizing substance when:

(a) in the preliminary test, there is a vigorous reaction;

(b) in the full test, the maximum burning rate of the mixtures tested is higher than or equal to the maximum burning rate of the reference mixture of cellulose and barium nitrate.

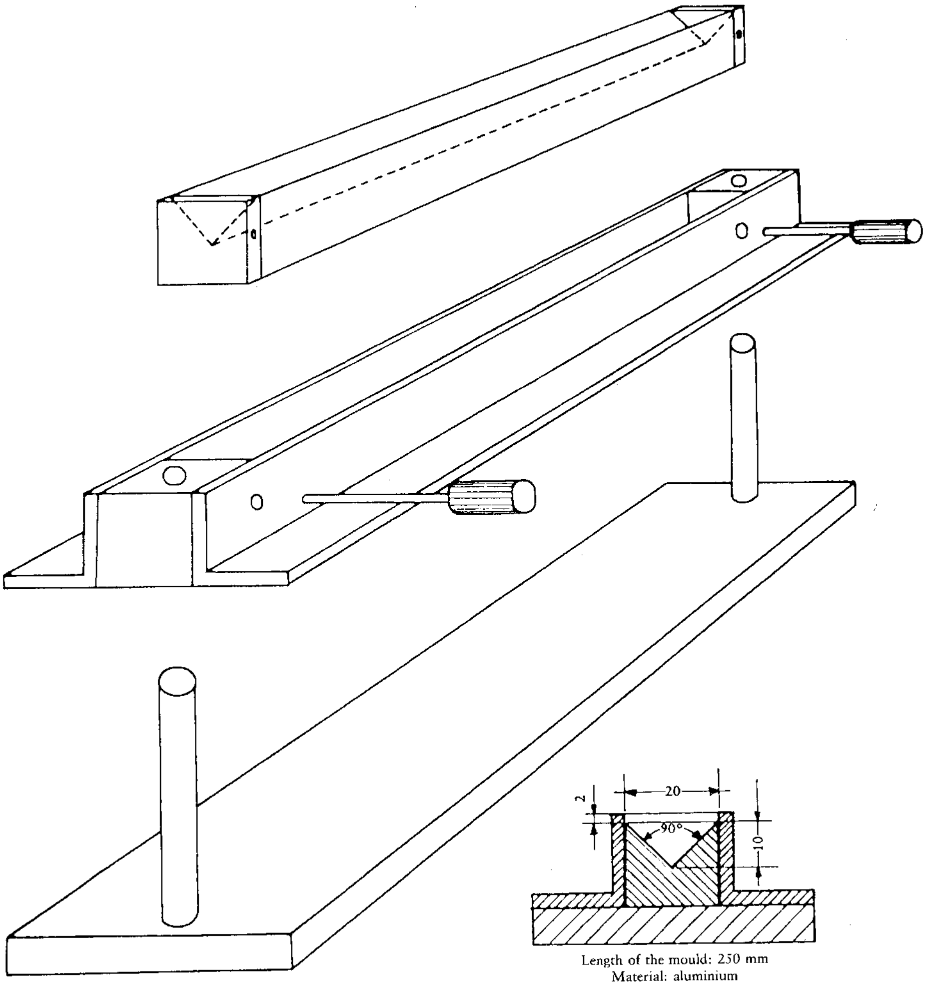
In order to avoid a false positive, the results obtained when testing the substance mixed with an inert material and/ or when testing under an inert atmosphere should also be considered when interpreting the results.

4. REFERENCES

NF T 20-035 (SEPT 85). Chemical products for industrial use. Determination of the oxidizing properties of solids.

APPENDIX

Figure
Mould and accessories for the preparations of the pile
(All dimensions in millimetres)



Length of the mould: 250 mm
Material: aluminium

A.18. NUMBER - AVERAGE MOLECULAR WEIGHT AND MOLECULAR WEIGHT DISTRIBUTION OF POLYMERS

1. METHOD

This Gel Permeation Chromatographic method is a replicate of the OECD TG 118 (1996). The fundamental principles and further technical information are given in reference (1).

1.1 INTRODUCTION

Since the properties of polymers are so varied, it is impossible to describe one single method setting out precisely the conditions for separation and evaluation which cover all eventualities and specificities occurring in the separation of polymers. In particular complex polymer systems are often not amenable to gel permeation chromatography (GPC). When GPC is not practicable, the molecular weight may be determined by means of other methods (see Annex). In such cases, full details and justification should be given for the method used.

The method described is based on DIN Standard 55672 (1). Detailed information about how to carry out the experiments and how to evaluate the data can be found in this DIN Standard. In case modifications of the experimental conditions are necessary, these changes must be justified. Other standards may be used, if fully referenced. The method described uses polystyrene samples of known polydispersity for calibration and it may have to be modified to be suitable for certain polymers, e.g. water soluble and long-chain branched polymers.

1.2. DEFINITIONS AND UNITS

The number-average molecular weight M_n and the weight average molecular weight M_w are determined using the following equations:

$$M_n = \frac{\sum_{i=1}^{n} H_i}{\sum_{i=1}^{n} H_i / M_i} \qquad M_w = \frac{\sum_{i=1}^{n} H_i x M_i}{\sum_{i=1}^{n} H_i}$$

where,

H_i is the level of the detector signal from the baseline for the retention volume V_i,

M_i is the molecular weight of the polymer fraction at the retention volume V_i, and

n is the number of data points.

The breadth of the molecular weight distribution, which is a measure of the dispersity of the system, is given by the ratio M_w/M_n.

1.3. REFERENCE SUBSTANCES

Since GPC is a relative method, calibration must be undertaken. Narrowly distributed, linearly constructed polystyrene standards with known average molecular weights M_n and M_w and a known molecular weight distribution are normally used for this. The calibration curve can only be used in the determination of the molecular weight of the unknown sample if the conditions for the separation of the sample and the standards have been selected in an identical manner.

A determined relationship between the molecular weight and elution volume is only valid under the specific conditions of the particular experiment. The conditions include, above all, the temperature, the solvent (or solvent mixture), the chromatography conditions and the separation column or system of columns.

The molecular weights of the sample determined in this way are relative values and are described as 'polystyrene equivalent molecular weights'. This means that dependent on the structural and chemical differences between the sample and the standards, the molecular weights can deviate from the absolute values to a greater or a lesser degree. If other standards are used, e.g. polyethylene glycol, polyethylene oxide, polymethyl methacrylate, polyacrylic acid, the reason should be stated.

1.4. PRINCIPLE OF THE TEST METHOD

Both the molecular weight distribution of the sample and the average molecular weights (M_n, M_w) can be determined using GPC. GPC is a special type of liquid chromatography in which the sample is separated according to the hydrodynamic volumes of the individual constituents (2).

Separation is effected as the sample passes through a column which is filled with a porous material, typically an organic gel. Small molecules can penetrate the pores whereas large molecules are excluded. The path of the large molecules is thereby shorter and these are eluted first. The medium-sized molecules penetrate some of the pores and are eluted later. The smallest molecules, with a mean hydrodynamic radius smaller than the pores of the gel, can penetrate all of the pores. These are eluted last.

In an ideal situation, the separation is governed entirely by the size of the molecular species, but in practice it is difficult to avoid at least some absorption effects interfering. Uneven column packing and dead volumes can worsen the situation (2).

Detection is effected by e.g. refractive index or UV-absorption and yields a simple distribution curve. However, to attribute actual molecular weight values to the curve, it is necessary to calibrate the column by passing down polymers of known molecular weight and, ideally, of broadly similar structure e.g. various polystyrene standards. Typically a Gaussian curve results, sometimes distorted by a small tail to the low molecular weight side, the vertical axis indicating the quantity, by weight, of the various molecular weight species eluted, and the horizontal axis the log molecular weight.

1.5. QUALITY CRITERIA

The repeatability (Relative Standard Deviation : RSD) of the elution volume should be better than 0.3 %. The required repeatability of the analysis has to be ensured by correction via an internal standard if a chromatogram is evaluated time-dependently and does not correspond to the above mentioned criterion (1). The polydispersities are dependent on the molecular weights of the standards. In the case of polystyrene standards typical values are:

$M_p < 2000$	$M_w/M_n < 1.20$
$2000 \leq M_p \leq 10^6$	$M_w/M_n < 1.05$
$M_p > 10^6$	$M_w/M_n < 1.20$

(M_p is the molecular weight of the standard at the peak maximum)

1.6. DESCRIPTION OF THE TEST METHOD

1.6.1. Preparation of the standard polystyrene solutions

The polystyrene standards are dissolved by careful mixing in the chosen eluent. The recommendations of the manufacturer must be taken into account in the preparation of the solutions.

The concentrations of the standards chosen are dependent on various factors, e.g. injection volume, viscosity of the solution and sensitivity of the analytical detector. The maximum injection volume must be adapted to the length of the column, in order to avoid overloading. Typical injection volumes for analytical separations using GPC with a column of 30 cm x 7.8 mm are normally between 40 and 100 µl. Higher volumes are possible, but they should not exceed 250 µl. The optimal ratio between the injection volume and the concentration must be determined prior to the actual calibration of the column.

1.6.2. Preparation of the sample solution

In principle, the same requirements apply to the preparation of the sample solutions. The sample is dissolved in a suitable solvent, e.g. tetrahydrofuran (THF), by shaking carefully. Under no circumstances should it be dissolved using an ultrasonic bath. When necessary, the sample solution is purified via a membrane filter with a pore size of between 0.2 and 2 µm.

The presence of undissolved particles must be recorded in the final report as these may be due to high molecular weight species. An appropriate method should be used to determine the percentage by weight of the undissolved particles. The solutions should be used within 24 hours.

1.6.3. Apparatus

- solvent reservoir
- degasser (where appropriate)
- pump
- pulse dampener (where appropriate)
- injection system
- chromatography columns

- detector
- flowmeter (where appropriate)
- data recorder-processor
- waste vessel

It must be ensured that the GPC system is inert with regard to the utilised solvents (e.g. by the use of steel capillaries for THF solvent).

1.6.4. Injection and solvent delivery system

A defined volume of the sample solution is loaded onto the column either using an auto-sampler or manually in a sharply defined zone. Withdrawing or depressing the plunger of the syringe too quickly, if done manually, can cause changes in the observed molecular weight distribution. The solvent-delivery system should, as far as possible, be pulsation-free ideally incorporating a pulse dampener. The flow rate is of the order of 1 ml/min.

1.6.5. Column

Depending on the sample, the polymer is characterised using either a simple column or several columns connected in sequence. A number of porous column materials with defined properties (e.g. pore size, exclusion limits) are commercially available. Selection of the separation gel or the length of the column is dependent on both the properties of the sample (hydrodynamic volumes, molecular weight distribution) and the specific conditions for separation such as solvent, temperature and flow rate (1)(2)(3).

1.6.6. Theoretical plates

The column or the combination of columns used for separation must be characterised by the number of theoretical plates. This involves, in the case of THF as elution solvent, loading a solution of ethyl benzene or other suitable non-polar solute onto a column of known length. The number of theoretical plates is given by the following equation:

$$N = 5.54\left(\frac{V_e}{W_{1/2}}\right)^2 \quad \text{or} \quad N = 16\left(\frac{V_e}{W}\right)^2$$

where,

N = the number of theoretical plates

V_e = the elution volume at the peak maximum

W = the baseline peak width

$W_{1/2}$ = the peak width at half height

1.6.7. Separation efficiency

In addition to the number of theoretical plates, which is a quantity determining the bandwidth, a part is also played by the separation efficiency, this being determined by the steepness of the calibration curve. The separation efficiency of a column is obtained from the following relationship:

$$\frac{V_{e,Mx} - V_{e,(10Mx)}}{\textit{cross sectional area of the column}} \geq 6.0 \left[\frac{cm^3}{cm^2}\right]$$

where,

$V_{e,Mx}$ = the elution volume for polystyrene with the molecular weight M_x

$V_{e,(10.Mx)}$ = the elution volume for polystyrene with a ten times greater molecular weight

The resolution of the system is commonly defined as follows:

$$R_{1,2} = 2x \frac{V_{e1} - V_{e2}}{W_1 + W_2} x \frac{1}{\log_{10}(M_2 / M_1)}$$

where,

V_{e1}, V_{e2} = the elution volumes of the two polystyrene standards at the peak maximum

W_1, W_2 = the peak widths at the base-line

M_1, M_2 = the molecular weights at the peak maximum (should differ by a factor of 10).

The R-value for the column system should be greater than 1.7 (4).

1.6.8. Solvents

All solvents must be of high purity (for THF purity of 99.5 % is used). The solvent reservoir (if necessary in an inert gas atmosphere) must be sufficiently large for the calibration of the column and several sample analyses. The solvent must be degassed before it is transported to the column via the pump.

1.6.9. Temperature control

The temperature of the critical internal components (injection loop, columns, detector and tubing) should be constant and consistent with the choice of solvent.

1.6.10. Detector

The purpose of the detector is to record quantitatively the concentration of sample eluted from the column. In order to avoid unnecessary broadening of peaks the cuvette volume of the detector cell must be kept as small as possible. It should not be larger than 10 µl except for light scattering and viscosity detectors. Differential refractometry is usually used for detection. However, if required by the specific properties of the sample or the elution solvent, other types of detectors can be used, e.g. UV/VIS, IR, viscosity detectors, etc.

2. DATA AND REPORTING

2.1. DATA

The DIN Standard (1) should be referred to for the detailed evaluation criteria as well as for the requirements relating to the collecting and processing of data.

For each sample, two independent experiments must be carried out. They have to be analysed individually.

M_n, M_w, M_w/M_n and M_p must be provided for every measurement. It is necessary to indicate explicitly that the measured values are relative values equivalent to the molecular weights of the standard used.

After determination of the retention volumes or the retention times (possibly corrected using an internal standard), log M_p values (M_p being the peak maxima of the calibration standard) are plotted against one of those quantities. At least two calibration points are necessary per molecular weight decade, and at least five measurement points are required for the total curve, which should cover the estimated molecular weight of the sample. The low molecular weight end-point of the calibration curve is defined by n-hexyl benzene or another suitable non-polar solute. The number average and the weight-average molecular weights are generally determined by means of electronic data processing, based on the formulas of section 1.2. In case manual digitisation is used, ASTM D 3536-91 can be consulted (3).

The distribution curve must be provided in the form of a table or as figure (differential frequency or sum percentages against log M). In the graphic representation, one molecular weight decade should be normally about 4 cm in width and the peak maximum should be about 8 cm in height. In the case of integral distribution curves the difference in the ordinate between 0 and 100 % should be about 10 cm.

2.2. TEST REPORT

The test report must include the following information:

2.2.1. Test substance:

- available information about test substance (identity, additives, impurities);
- description of the treatment of the sample, observations, problems.

2.2.2. Instrumentation:

- reservoir of eluent, inert gas, degassing of the eluent, composition of the eluent, impurities;
- pump, pulse dampener, injection system;
- separation columns (manufacturer, all information about the characteristics of the columns, such as pore size, kind of separation material etc., number, length and order of the columns used);
- number of the theoretical plates of the column (or combination), separation efficiency (resolution of thesystem);
- information on symmetry of the peaks;
- column temperature, kind of temperature control;
- detector (measurement principle, type, cuvette volume);
- flowmeter if used (manufacturer, measurement principle);
- system to record and process data (hardware and software).

2.2.3. Calibration of the system:

- detailed description of the method used to construct the calibration curve;
- information about quality criteria for this method (e.g. correlation coefficient, error sum of squares, etc.);
- information about all extrapolations, assumptions and approximations made during the experimental procedure and the evaluation and processing of data;
- all measurements used for constructing the calibration curve have to be documented in a table which includes the following information for each calibration point:
- name of the sample
- manufacturer of the sample
- characteristic values of the standards M_p, M_n, M_w, M_w/M_n, as provided by the manufacturer or derived by subsequent measurements, together with details about the method of determination
- injection volume and injection concentration
- M_p value used for calibration

- elution volume or corrected retention time measured at the peak maxima
- M_p calculated at the peak maximum
- percentage error of the calculated M_p and the calibration value.

2.2.4. Evaluation:

- evaluation on a time basis: methods used to ensure the required reproducibility (method of correction, internal standard etc.);
- information about whether the evaluation was effected on the basis of the elution volume or the retention time;
- information about the limits of the evaluation if a peak is not completely analysed;
- description of smoothing methods, if used;
- preparation and pre-treatment procedures of the sample;
- the presence of undissolved particles, if any;
- injection volume (µl) and injection concentration (mg/ml);
- observations indicating effects which lead to deviations from the ideal GPC profile;
- detailed description of all modifications in the testing procedures;
- details of the error ranges;
- any other information and observations relevant for the interpretation of the results.

3. REFERENCES

(1) DIN 55672 (1995) Gelpermeationschromatographie (GPC) mit Tetrahydrofuran (THF) als Elutionsmittel, Teil 1.

(2) Yau, W.W., Kirkland, J.J., and Bly, D.D. eds, (1979). Modern Size Exclusion Liquid Chromatography, J. Wiley and Sons.

(3) ASTM D 3536-91, (1991). Standard Test Method for Molecular Weight Averages and Molecular Weight Distribution by Liquid Exclusion Chromatography (Gel Permeation Chromatography-GPC). American Society for Testing and Materials, Philadelphia, Pennsylvania.

(4) ASTM D 5296-92, (1992). Standard Test Method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by High Performance Size-Exclusion Chromatography. American Society for Testing and Materials, Philadelphia, Pennsylvania.

APPENDIX - EXAMPLES OF OTHER METHODS FOR DETERMINATION OF NUMBER AVERAGE MOLECULAR WEIGHT (MN) FOR POLYMERS

Gel permeation chromatography (GPC) is the preferred method for determination of M_n, especially when a set of standards are available, whose structure are comparable with the polymer structure. However, where there are practical difficulties in using GPC or there is already an expectation that the substance will fail a regulatory M_n criterion (and which needs confirming), alternative methods are available, such as:

1. Use of Colligative Properties

1.1 Ebullioscopy / Cryoscopy

involves measurement of boiling point elevation (ebullioscopy) or freezing point depression (cryoscopy) of a solvent, when the polymer is added. The method relies on the fact that the effect of the dissolved polymer on the boiling/freezing point of the liquid is dependent on the molecular weight of the polymer (1) (2).

Applicability, $M_n < 20,000$.

1.2 Lowering of Vapour Pressure

involves the measurement of the vapour pressure of a chosen reference liquid before and after the addition of known quantities of polymer (1) (2).

Applicability, $M_n < 20,000$ (theoretically; in practice however of limited value).

1.3 Membrane Osmometry

relies on the principle of osmosis, i.e. the natural tendency of solvent molecules to pass through a semi-permeable membrane from a dilute to a concentrated solution to achieve equilibrium. In the test, the dilute solution is at zero concentration, whereas the concentrated solution contains the polymer. The effect of drawing solvent through the membrane causes a pressure differential that is dependent on the concentration and the molecular weight of the polymer (1) (3) (4).

Applicability, M_n between 20,000 - 200,000.

1.4 Vapour Phase Osmometry

involves comparison of the rate of evaporation of a pure solvent aerosol to at least three aerosols containing the polymer at different concentrations (1) (5) (6).

Applicability, $M_n < 20,000$.

2. End-Group Analysis

To use this method, knowledge of both the overall structure of the polymer and the nature of the chain terminating end groups is needed (which must be distinguishable from the main skeleton by e.g. NMR or titration/derivatisation). The determination of the molecular concentration of the end groups present on the polymer can lead to a value for the molecular weight (7) (8) (9).

Applicability, M_n up to 50,000 (with decreasing reliability).

3. References

(1) Billmeyer, F.W. Jr., (1984). Textbook of Polymer Science, 3rd Edn., John Wiley, New York.

(2) Glover, C.A., (1975). Absolute Colligative Property Methods. Chapter 4. In: Polymer Molecular Weights, Part I P.E. Slade, Jr. ed., Marcel Dekker, New York.

(3) ASTM D 3750-79, (1979). Standard Practice for Determination of Number-Average Molecular Weight of Polymers by Membrane Osmometry. American Society for Testing and Materials, Philadelphia, Pennsylvania.

(4) Coll, H. (1989). membrane Osmometry. In: Determination of Molecular Weight, A.R. Cooper ed., J. Wiley and Sons, pp. 25-52.

(5) ASTM 3592-77, (1977). Standard Recommended Practice for Determination of Molecular Weight by Vapour Pressure, American Society for Testing and Materials, Philadelphia, Pennsylvania.

(6) Morris, C.E.M., (1989). Vapour Pressure osmometry. In: Determinationn of Molecular Weight, A.R. Cooper ed., John Wiley and Sons.

(7) Schröder, E., Müller, G., and Arndt, K-F., (1989). Polymer Characterisation, Carl Hanser Verlag, Munich.

(8) Garmon, R.G., (1975). End-Group Determinations, Chapter 3 In: Polymer Molecular Weights, Part I, P.E. Slade, Jr. ed. Marcel Dekker, New York.

(9) Amiya, S., et al. (1990). Pure and Applied Chemistry, 62, 2139-2146.

A.19. LOW MOLECULAR WEIGHT CONTENT OF POLYMERS

1. METHOD

This Gel Permeation Chromatographic method is a replicate of the OECD TG 119 (1996). The fundamental principles and further technical information are given in the references.

1.1. INTRODUCTION

Since the properties of polymers are so varied, it is impossible to describe one single method setting out precisely the conditions for separation and evaluation which cover all eventualities and specificities occurring in the separation of polymers. In particular complex polymer systems are often not amenable to gel permeation chromatography (GPC). When GPC is not practicable, the molecular weight may be determined by means of other methods (see Annex). In such cases, full details and justification should be given for the method used.

The method described is based on DIN Standard 55672 (1). Detailed information about how to carry out the experiments and how to evaluate the data can be found in this DIN Standard. In case modifications of the experimental conditions are necessary, these changes must be justified. Other standards may be used, if fully referenced. The method described uses polystyrene samples of known polydispersity for calibration and it may have to be modified to be suitable for certain polymers, e.g. water soluble and long-chain branched polymers.

1.2. DEFINITIONS AND UNITS

Low molecular weight is arbitrarily defined as a molecular weight below 1000 dalton.

The number-average molecular weight M_n and the weight average molecular weight M_w are determined using the following equations:

$$M_n = \frac{\sum_{i=1}^{n} H_i}{\sum_{i=1}^{n} H_i / M_i} \quad M_w = \frac{\sum_{i=1}^{n} H_i x M_i}{\sum_{i=1}^{n} H_i}$$

where,

H_I = the level of the detector signal from the baseline for the retention volume V_i,

M_i = the molecular weight of the polymer fraction at the retention volume V_i, and n is the number of data points

The breadth of the molecular weight distribution, which is a measure of the dispersity of the system, is given by the ratio M_w/M_n.

1.3. REFERENCE SUBSTANCES

Since GPC is a relative method, calibration must be undertaken. Narrowly distributed, linearly constructed polystyrene standards with known average molecular weights M_n and M_w and a known molecular weight distribution are normally used for this. The calibration curve can only be used in the determination of the molecular weight of the unknown sample if the conditions for the separation of the sample and the standards have been selected in an identical manner.

A determined relationship between the molecular weight and elution volume is only valid under the specific conditions of the particular experiment. The conditions include, above all, the temperature, the solvent (or solvent mixture), the chromatography conditions and the separation column or system of columns.

The molecular weights of the sample determined in this way are relative values and are described as ‘polystyrene equivalent molecular weights’. This means that dependent on the structural and chemical differences between the sample and the standards, the molecular weights can deviate from the absolute values to a greater or a lesser degree. If other standards are used, e.g. polyethylene glycol, polyethylene oxide, polymethyl methacrylate, polyacrylic acid, the reason should be stated.

1.4. PRINCIPLE OF THE TEST METHOD

Both the molecular weight distribution of the sample and the average molecular weights (M_n, M_w) can be determined using GPC. GPC is a special type of liquid chromatography in which the sample is separated according to the hydrodynamic volumes of the individual constituents (2).

Separation is effected as the sample passes through a column which is filled with a porous material, typically an organic gel. Small molecules can penetrate the pores whereas large molecules are excluded. The path of the large molecules is thereby shorter and these are eluted first. The medium-sized molecules penetrate some of the pores and are eluted later. The smallest molecules, with a mean hydrodynamic radius smaller than the pores of the gel, can penetrate all of the pores. These are eluted last.

In an ideal situation, the separation is governed entirely by the size of the molecular species, but in practice it is difficult to avoid at least some absorption effects interfering. Uneven column packing and dead volumes can worsen the situation (2).

Detection is effected by e.g. refractive index or UV-absorption and yields a simple distribution curve. However, to attribute actual molecular weight values to the curve, it is necessary to calibrate the column by passing down polymers of known molecular weight and, ideally, of broadly similar structure e.g. various polystyrene standards. Typically a Gaussian curve results, sometimes distorted by a small tail to the low molecular weight side, the vertical axis indicating the quantity, by weight, of the various molecular weight species eluted, and the horizontal axis the log molecular weight.

The low molecular weight content is derived from this curve. The calculation can only be accurate if the low molecular weight species respond equivalently on a per mass basis to the polymer as a whole.

1.5. QUALITY CRITERIA

The repeatability (Relative Standard Deviation : RSD) of the elution volume should be better than 0.3 %. The required repeatability of the analysis has to be ensured by correction via an internal standard if a chromatogram is evaluated time-dependently and does not correspond to the above mentioned criterion (1). The polydispersities are dependent on the molecular weights of the standards. In the case of polystyrene standards typical values are:

$M_p < 2000$	$M_w/M_n < 1.20$
$2000 \leq M_p \leq 10^6$	$M_w/M_n < 1.05$
$M_p > 10^6$	$M_w/M_n < 1.20$

(M_p is the molecular weight of the standard at the peak maximum)

1.6. DESCRIPTION OF THE TEST METHOD

1.6.1. Preparation of the standard polystyrene solutions

The polystyrene standards are dissolved by careful mixing in the chosen eluent. The recommendations of the manufacturer must be taken into account in the preparation of the solutions.

The concentrations of the standards chosen are dependent on various factors e.g. injection volume, viscosity of the solution and sensitivity of the analytical detector. The maximum injection volume must be adapted to the length of the column, in order to avoid overloading.

Typical injection volumes for analytical separations using GPC with a column of 30 cm x 7.8 mm are normally between 40 and 100 µl. Higher volumes are possible, but they should not exceed 250 µl. The optimal ratio between the injection volume and the concentration must be determined prior to the actual calibration of the column.

1.6.2. Preparation of the sample solution

In principle, the same requirements apply to the preparation of the sample solutions. The sample is dissolved in a suitable solvent, e.g. tetrahydrofuran (THF), by shaking carefully. Under no circumstances should it be dissolved using an ultrasonic bath. When necessary, the sample solution is purified via a membrane filter with a pore size of between 0.2 and 2 µm.

The presence of undissolved particles must be recorded in the final report as these may be due to high molecular weight species. An appropriate method should be used to determine the percentage by weight of the undissolved particles. The solutions should be used within 24 hours.

1.6.3. Correction for content of impurities and additives

Correction of the content of species of $M < 1000$ for the contribution from non-polymer specific components present (e.g. impurities and/or additives) is usually necessary, unless the measured content is already < 1 %. This is achieved by direct analysis of the polymer solution or the GPC eluate.

In cases where the eluate, after passage through the column, is too dilute for a further analysis it must be concentrated. It may be necessary to evaporate the eluate to dryness and dissolve it again. Concentration of the eluate must be effected under conditions which ensure that no changes occur in the eluate. The treatment of the eluate after the GPC step is dependent on the analytical method used for the quantitative determination.

1.6.4. Apparatus

GPC apparatus comprises the following components:

- solvent reservoir
- degasser (where appropriate)
- pump
- pulse dampener (where appropriate)
- injection system
- chromatography columns
- detector
- flowmeter (where appropriate)
- data recorder-processor
- waste vessel

It must be ensured that the GPC system is inert with regard to the utilised solvents (e.g. by the use of steel capillaries for THF solvent).

1.6.5. Injection and solvent delivery system

A defined volume of the sample solution is loaded onto the column either using an auto-sampler or manually in a sharply defined zone. Withdrawing or depressing the plunger of the syringe too quickly, if done manually, can cause changes in the observed molecular weight distribution. The solvent-delivery system should, as far as possible, be pulsation-free ideally incorporating a pulse dampener. The flow rate is of the order of 1 ml/min.

1.6.6. Column

Depending on the sample, the polymer is characterised using either a simple column or several columns connected in sequence. A number of porous column materials with defined properties (e.g. pore size, exclusion limits) are commercially available. Selection of the separation gel or the length of the column is dependent on both the properties of the sample (hydrodynamic volumes, molecular weight distribution) and the specific conditions for separation such as solvent, temperature and flow rate (1) (2) (3).

1.6.7. Theoretical plates

The column or the combination of columns used for separation must be characterised by the number of theoretical plates. This involves, in the case of THF as elution solvent, loading a solution of ethyl benzene or other suitable non-polar solute onto a column of known length. The number of theoretical plates is given by the following equation:

$$N = 5.54\left(\frac{V_e}{W_{1/2}}\right)^2 \quad \textbf{or} \quad N = 16\left(\frac{V_e}{W}\right)^2$$

where,

N = the number of theoretical plates

V_e = the elution volume at the peak maximum

W = the baseline peak width

$W_{1/2}$ = the peak width at half height

1.6.8. Separation efficiency

In addition to the number of theoretical plates, which is a quantity determining the bandwidth, a part is also played by the separation efficiency, this being determined by the steepness of the calibration curve. The separation efficiency of a column is obtained from the following relationship:

$$\frac{V_{e,Mx} - V_{e,(10Mx)}}{\text{cross ional of the lumn}} \geq 6.0 \left[\frac{cm^3}{cm^2}\right]$$

where,

$V_{e,Mx}$ = the elution volume for polystyrene with the molecular weight M_x

$V_{e,(10.Mx)}$ = the elution volume for polystyrene with a ten times greater molecular weight

The resolution of the system is commonly defined as follows:

$$R_{1,2} = 2x\frac{V_{e1} - V_{e2}}{W_1 + W_2} x \frac{1}{\log_{10}(M_2/M_1)}$$

where,

V_{e1}, V_{e2} = the elution volumes of the two polystyrene standards at the peak maximum

W_1, W_2 = the peak widths at the base-line

M_1, M_2 = the molecular weights at the peak maximum (should differ by a factor of 10).

The R-value for the column system should be greater than 1.7 (4).

1.6.9. Solvents

All solvents must be of high purity (for THF purity of 99.5 % is used). The solvent reservoir (if necessary in an inert gas atmosphere) must be sufficiently large for the calibration of the column and several sample analyses. The solvent must be degassed before it is transported to the column via the pump.

1.6.10. Temperature control

The temperature of the critical internal components (injection loop, columns, detector and tubing) should be constant and consistent with the choice of solvent.

1.6.11. Detector

The purpose of the detector is to record quantitatively the concentration of sample eluted from the column. In order to avoid unnecessary broadening of peaks the cuvette volume of the detector cell must be kept as small as possible. It should not be larger than 10 µl except for light scattering and viscosity detectors. Differential refractometry is usually used for detection. However, if required by the specific properties of the sample or the elution solvent, other types of detectors can be used, e.g. UV/VIS, IR, viscosity detectors, etc.

2. DATA AND REPORTING

2.1. DATA

The DIN Standard (1) should be referred to for the detailed evaluation criteria as well as for the requirements relating to the collecting and processing of data.

For each sample, two independent experiments must be carried out. They have to be analysed individually. In all cases it is essential to determine also data from blanks, treated under the same conditions as the sample.

It is necessary to indicate explicitly that the measured values are relative values equivalent to the molecular weights of the standard used.

After determination of the retention volumes or the retention times (possibly corrected using an internal standard), log M_p values (M_p being the peak maxima of the calibration standard) are plotted against one of those quantities. At least two calibration points are necessary per molecular weight decade, and at least five measurement points are required for the total curve, which should cover the estimated molecular weight of the sample. The low molecular weight end-point of the calibration curve is defined by n-hexyl benzene or another suitable non-polar solute. The portion of the curve corresponding to molecular weights below 1000 is determined and corrected as necessary for impurities and additives. The elution curves are generally evaluated by means of electronic data processing. In case manual digitisation is used, ASTM D 3536-91 can be consulted (3).

If any insoluble polymer is retained on the column, its molecular weight is likely to be higher than that of the soluble fraction, and if not considered would result in an overestimation of the low molecular weight content. Guidance for correcting the low molecular weight content for insoluble polymer is provided in the Annex.

The distribution curve must be provided in the form of a table or as figure (differential frequency or sum percentages against log M). In the graphic representation, one molecular weight decade should be normally about 4 cm in width and the peak maximum should be about 8 cm in height. In the case of integral distribution curves the difference in the ordinate between 0 and 100 % should be about 10 cm.

2.2. TEST REPORT

The test report must include the following information:

2.2.1. Test substance:

- available information about test substance (identity, additives, impurities);
- description of the treatment of the sample, observations, problems.

2.2.2. Instrumentation:

- reservoir of eluent, inert gas, degassing of the eluent, composition of the eluent, impurities;
- pump, pulse dampener, injection system;
- separation columns (manufacturer, all information about the characteristics of the columns, such as pore size, kind of separation material etc., number, length and order of the columns used);
- number of the theoretical plates of the column (or combination), separation efficiency (resolution of the system);
- information on symmetry of the peaks;
- column temperature, kind of temperature control;
- detector (measurement principle, type, cuvette volume);
- flowmeter if used (manufacturer, measurement principle);
- system to record and process data (hardware and software).

2.2.3. Calibration of the system:

- detailed description of the method used to construct the calibration curve;
- information about quality criteria for this method (e.g. correlation coefficient, error sum of squares, etc.);
- information about all extrapolations, assumptions and approximations made during the experimental procedure and the evaluation and processing of data;
- all measurements used for constructing the calibration curve have to be documented in a table which includes the following information for each calibration point:

- name of the sample
- manufacturer of the sample
- characteristic values of the standards M_p, M_n, M_w, M_w/M_n, as provided by the manufacturer or derived by subsequent measurements, together with details about the method of determination
- injection volume and injection concentration
- M_p value used for calibration
- elution volume or corrected retention time measured at the peak maxima
- M_p calculated at the peak maximum
- percentage error of the calculated M_p and the calibration value.

2.2.4. Information on the low molecular weight polymer content:

- description of the methods used in the analysis and the way in which the experiments were conducted;
- information about the percentage of the low molecular weight species content (w/w) related to the total sample;
- information about impurities, additives and other non-polymer species in percentage by weight related to the total sample;

2.2.5. Evaluation:

- evaluation on a time basis: all methods to ensure the required reproducibility (method of correction, internal standard etc.);
- information about whether the evaluation was effected on the basis of the elution volume or the retention time;
- information about the limits of the evaluation if a peak is not completely analysed;
- description of smoothing methods, if used;
- preparation and pre-treatment procedures of the sample;
- the presence of undissolved particles, if any;
- injection volume (µl) and injection concentration (mg/ml);
- observations indicating effects which lead to deviations from the ideal GPC profile;
- detailed description of all modifications in the testing procedures;
- details of the error ranges;
- any other information and observations relevant for the interpretation of the results.

3. REFERENCES

(1) DIN 55672 (1995) Gelpermeationschromatographie (GPC) mit Tetrahydrofuran (THF) als Elutionsmittel, Teil 1.

(2) Yau, W.W., Kirkland, J.J., and Bly, D.D. eds. (1979). Modern Size Exclusion Liquid Chromatography, J. Wiley and Sons.

(3) ASTM D 3536-91, (1991). Standard Test method for Molecular Weight Averages and Molecular Weight Distribution by Liquid Exclusion Chromatography (Gel Permeation Chromatography-GPC). American Society for Testing and Materials, Philadelphia, Pennsylvania.

(4) ASTM D 5296-92, (1992). Standard Test method for Molecular Weight Averages and Molecular Weight Distribution of Polystyrene by High Performance Size-Exclusion Chromatography. American Society for Testing and Materials, Philadelphia, Pennsylvania.

APPENDIX - GUIDANCE FOR CORRECTING LOW MOLECULAR CONTENT FOR THE PRESENCE OF INSOLUBLE POLYMER

When insoluble polymer is present in a sample, it results in mass loss during the GPC analysis. The insoluble polymer is irreversibly retained on the column or sample filter while the soluble portion of the sample passes through the column. In the case where the refractive index increment (dn/dc) of the polymer can be estimated or measured, one can estimate the sample mass lost on the column. In that case, one makes a correction using an external calibration with standard materials of known concentration and dn/dc to calibrate the response of the refractometer. In the example hereafter a poly(methyl methacrylate) (pMMA) standard is used.

In the external calibration for analysis of acrylic polymers, a pMMA standard of known concentration in tetrahydrofuran, is analysed by GPC and the resulting data are used to find the refractometer constant according to the equation:

$$\mathbf{K = R / (C \times V \times dn/dc)}$$

where :

K = the refractometer constant (in microvolt·second/ml),

R = the response of the pMMA standard (in microvolt·second),

C = the concentration of the pMMA standard (in mg/ml),

V = the injection volume (in ml) and

dn/dc = the refractive index increment for pMMA in tetrahydrofuran (in ml/mg).

The following data are typical for a pMMA standard:

R = 2937891

C = 1.07 mg/ml

V = 0.1 ml

dn/dc = 9×10^{-5} ml/mg

The resulting K value, 3.05×10^{11} is then used to calculate the theoretical detector response if 100 % of the polymer injected had eluted through the detector.

A.20. SOLUTION / EXTRACTION BEHAVIOUR OF POLYMERS IN WATER

1. METHOD

The method described is a replicate of the revised version of OECD TG 120 (1997). Further technical information is given in reference (1).

1.1. INTRODUCTION

For certain polymers, such as emulsion polymers, initial preparatory work may be necessary before the method set out hereafter can be used. The method is not applicable to liquid polymers and to polymers that react with water under the test conditions.

When the method is not practical or not possible, the solution/extraction behaviour may be investigated by means of other methods. In such cases, full details and justification should be given for the method used.

1.2. REFERENCE SUBSTANCES

None.

1.3. PRINCIPLE OF THE TEST METHOD

The solution/extraction behaviour of polymers in an aqueous medium is determined using the flask method (see A.6 Water Solubility, Flask method) with the modifications described below.

1.4. QUALITY CRITERIA

None.

1.5. DESCRIPTION OF THE TEST METHOD

1.5.1. Equipment

The following equipment is required for the method:

- crushing device, e.g. grinder for the production of particles of known size
- apparatus for shaking with possibility of temperature control
- membrane filter system
- appropriate analytical equipment
- standardised sieves

1.5.2. Sample Preparation

A representative sample has first to be reduced to a particle size between 0.125 and 0.25 mm using appropriate sieves. Cooling may be required for the stability of the sample or for the grinding process. Materials of a rubbery nature can be crushed at liquid nitrogen temperature (1).

If the required particle size fraction is not attainable, action should be taken to reduce the particle size as much as possible, and the result reported. In the report, it is necessary to indicate the way in which the crushed sample was stored prior to the test

1.5.3. Procedure

Three samples of 10 g of the test substance are weighed into each of three vessels fitted with glass stoppers and 1000 ml of water is added to each vessel. If handling an amount of 10 g polymer proves impracticable, the next highest amount which can be handled should be used and the volume of water adjusted accordingly.

The vessels are tightly stoppered and then agitated at 20 °C. A shaking or stirring device capable of operating at constant temperature should be used. After a period of 24 hours, the content of each vessel is centrifuged or filtered and the concentration of polymer in the clear aqueous phase is determined by a suitable analytical method. If suitable analytical methods for the aqueous phase are not available, the total solubility/extractivity can be estimated from the dry weight of the filter residue or centrifuged precipitate.

It is usually necessary to differentiate quantitatively between the impurities and additives on the one hand and the low molecular weight species on the other hand. In the case of gravimetric determination, it is also important to perform a blank run using no test substance in order to account for residues arising from the experimental procedure.

The solution/extraction behaviour of polymers in water at 37 °C at pH 2 and pH 9 may be determined in the same way as described for the conduct of the experiment at 20 °C. The pH values can be achieved by the addition of either suitable buffers or appropriate acids or bases such as hydrochloric acid, acetic acid, analytical grade sodium or potassium hydroxide or NH_3.

Depending on the method of analysis used, one or two tests should be performed. When sufficiently specific methods are available for direct analysis of the aqueous phase for the polymer component, one test as described above should suffice. However, when such methods are not available and determination of the solution/extraction behaviour of the polymer is limited to indirect analysis by determining only the total organic carbon content (TOC) of the aqueous extract, an additional test should be conducted. This additional test should also be done in triplicate, using ten times smaller polymer samples and the same amounts of water as those used in the first test.

1.5.4. Analysis

1.5.4.1. Test conducted with one sample size

Methods may be available for direct analysis of polymer components in the aqueous phase. Alternatively, indirect analysis of dissolved/extracted polymer components, by determining the total content of soluble parts and correcting for non polymer-specific components, could also be considered.

Analysis of the aqueous phase for the total polymeric species is possible:

either by a sufficiently sensitive method e.g.

- TOC using persulphate or dichromate digestion to yield CO_2 followed by estimation by IR or chemical analysis;
- Atomic Absorption Spectrometry (AAS) or its Inductively Coupled Plasma (ICP) emission equivalent for silicon or metal containing polymers;
- UV absorption or spectrofluorimetry for aryl polymers;
- LC-MS for low molecular weight samples;

or by vacuum evaporation to dryness of the aqueous extract and spectroscopic (IR, UV, etc.) or AAS/ICP analysis of the residue.

If analysis of the aqueous phase as such is not practicable, the aqueous extract should be extracted with a water-immiscible organic solvent e.g. a chlorinated hydrocarbon. The solvent is then evaporated and the residue analysed as above for the notified polymer content. Any components in this residue which are identified as being impurities or additives are to be subtracted for the purpose of determining the degree of solution/extraction of the polymer itself.

When relatively large quantities of such materials are present, it may be necessary to subject the residue to e.g. HPLC or GC analysis to differentiate the impurities from the monomer and monomer-derived species present so that the true content of the latter can be determined.

In some cases, simple evaporation of the organic solvent to dryness and weighing the dry residue may be sufficient.

1.5.4.2. Test conducted with two different sample sizes

All aqueous extracts are analysed for TOC.

A gravimetric determination is performed on the undissolved/not extracted part of the sample. If, after centrifugation or filtering of the content of each vessel, polymer residues remain attached to the wall of the vessel, the vessel should be rinsed with the filtrate until the vessel is cleared from all visible residues. Following which, the filtrate is again centrifuged or filtered. The residues remaining on the filter or in the centrifuge tube are dried at 40 ^{0}C under vacuum and weighed. Drying is continued until a constant weight is reached.

2. DATA

2.1. TEST CONDUCTED WITH ONE SAMPLE SIZE

The individual results for each of the three flasks and the average values should be given and expressed in units of mass per volume of the solution (typically mg/l) or mass per mass of polymer sample (typically mg/g). Additionally, the weight loss of the sample (calculated as the weight of the solute divided by the weight of the initial sample) should also be given. The relative standard deviations (RSD) should be calculated. Individual figures should be given for the total substance (polymer+essential additives etc.) and for the polymer only (i.e. after subtracting the contribution from such additives).

2.2. TEST CONDUCTED WITH TWO DIFFERENT SAMPLE SIZES

The individual TOC values of the aqueous extracts of the two triplicate experiments and the average value for each experiment should be given expressed as units of mass per volume of solution (typically mgC/l), as well as in units of mass per weight of the initial sample (typically mgC/g).

If there is no difference between the results at the high and the low sample/water ratios, this may indicate that all extractable components were indeed extracted. In such a case, direct analysis would normally not be necessary.

The individual weights of the residues should be given and expressed in percentage of the initial weights of the samples. Averages should be calculated per experiment. The differences between 100 and the percentages found represent the percentages of soluble and extractable material in the original sample.

3. REPORTING

3.1. TEST REPORT

The test report must include the following information:

3.1.1. Test substance:

- available information about test substance (identity, additives, impurities, content of low molecular weight species).

3.1.2. Experimental conditions:

- description of the procedures used and experimental conditions;
- description of the analytical and detection methods.

3.1.3. Results:

- results of solubility/extractivity in mg/l; individual and mean values for the extraction tests in the various solutions, broken down in polymer content and impurities, additives, etc.
- results of solubility/extractivity in mg/g of polymer
- TOC values of aqueous extracts, weight of the solute and calculated percentages, if measured
- the pH of each sample
- information about the blank values

- where necessary, references to the chemical instability of the test substance, during both the testing
- process and the analytical process
- all information which is important for the interpretation of the results.

4. REFERENCES

DIN 53733 (1976) Zerkleinerung von Kunststofferzeugnissen fur Prufzwecke.