

## OECD GUIDELINE FOR THE TESTING OF CHEMICALS

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

### Vapour Pressure

#### INTRODUCTION

1. This guideline is a revised version of the original Guideline 104 which was adopted in 1981. Two additional methods are described in this version. These are the effusion cell and the spinning rotor techniques. Moreover, an estimation method has been added in an appendix. The main change otherwise concerns the format. The revision was based on the EC method "Vapour Pressure", published in 1992 (1).

#### INITIAL CONSIDERATIONS

2. At the thermodynamic equilibrium, the vapour pressure of a pure substance is a function of temperature only. The fundamental principles are given in references 2 and 3.

3. No single measurement procedure is applicable to the entire range of pressures from less than  $10^4$  to  $10^5$  Pa. Seven methods are proposed in this guideline which can be applied in different vapour pressure ranges. The various methods are compared as to application, repeatability, reproducibility, measuring range in Table 1. Vapour pressure can also be calculated and a calculation method is set out in the appendix. For vapour pressures higher than 10 Pa, experimental determination is preferred over calculation.

#### DEFINITIONS AND UNITS

4. The vapour pressure of a substance is defined as the saturation pressure above a solid or liquid substance.

5. The SI unit of pressure which should be used is the pascal (Pa). Units which have been employed historically are given hereafter, together with their conversion factors:

$$\begin{aligned}1 \text{ Torr} &= 1 \text{ mm Hg} = 1.333 \times 10^2 \text{ Pa} \\1 \text{ atmosphere} &= 1.013 \times 10^5 \text{ Pa} \\1 \text{ bar} &= 10^5 \text{ Pa}\end{aligned}$$

The SI unit of temperature is the kelvin (K). The conversion of kelvins to degrees Celsius is according to the formula

$$T = t + 273.15$$

where

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

Table 1

Measuring method	Substances		Estimated repeatability	Estimated reproducibility	Recommended range
	solid	liquid			
Dynamic method	low melting	yes	up to 25%	up to 25%	10 <sup>3</sup> Pa to 2x10 <sup>3</sup> Pa
			1 to 5%	1 to 5 %	2x10 <sup>3</sup> Pa to 10 <sup>5</sup> Pa
Static method	yes	yes	5 to 10%	5 to 10 %	10 Pa to 10 <sup>5</sup> Pa
Isoteniscope	yes	yes	5 to 10%	5 to 10 %	10 <sup>2</sup> Pa to 10 <sup>5</sup> Pa
Effusion method vap. pres. balance	yes	yes	5 to 20 %	up to 50 %	10 <sup>-3</sup> Pa to 1 Pa
Effusion method weight loss	yes	yes	10 to 30%	--	10 <sup>-3</sup> Pa to 1 Pa
Gas saturation method	yes	yes	10 to 30%	up to 50%	10 <sup>-5</sup> Pa to 10 <sup>3</sup> Pa
Spinning rotor method	yes	yes	10 to 20 %	--	10 <sup>-4</sup> Pa to 0,5 Pa

### REFERENCE SUBSTANCES

6. Reference substances do not need to be employed. They serve primarily to check the performance of a method from time to time as well as to allow comparison between results of different methods.

### PRINCIPLE OF THE TEST

7. In general, 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 thermodynamic temperature according to the simplified Clapeyron-Clausius equation

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

where

$p$  = the vapour pressure in pascals

$\Delta H_v$  = the heat of vaporization in J mol<sup>-1</sup>

$R$  = the universal gas constant, 8.314 J mol<sup>-1</sup> K<sup>-1</sup>

$T$  = the temperature in K

### DESCRIPTION OF THE METHODS

#### Dynamic method (Cottrell's method)

##### Principle

8. The vapour pressure is determined by measuring the boiling temperature of the substance at various specified pressures between roughly 10<sup>3</sup> and 10<sup>5</sup> Pa. This method is also recommended for the determination of the boiling temperature. It is useful for that purpose up to 600 K. The boiling temperatures of liquids are approximately 0.1 °C higher at a depth of 3 to 4 cm than at the surface because of the hydrostatic pressure of the column of liquid. In Cottrell's method (4) the thermometer

is placed in the vapour above the surface of the liquid and the boiling liquid is made to pump itself continuously over the bulb of the thermometer. A thin layer of liquid which is in equilibrium with vapour at atmospheric pressure covers the bulb. The thermometer thus reads the true boiling point, without errors due to superheating or hydrostatic pressure. The pump originally employed by Cottrell is shown in figure 1. The tube A contains the boiling liquid. A platinum wire B sealed into the bottom facilitates uniform boiling. The side tube C leads to a condenser, and the sheath D prevents the cold condensate from reaching the thermometer E. When the liquid in A is boiling, bubbles and liquid trapped by the funnel are poured via the two arms of the pump F over the bulb of the thermometer.

Figure 1

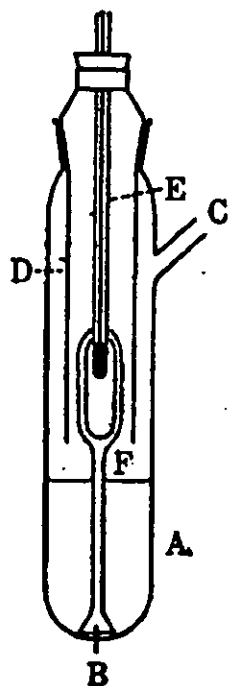
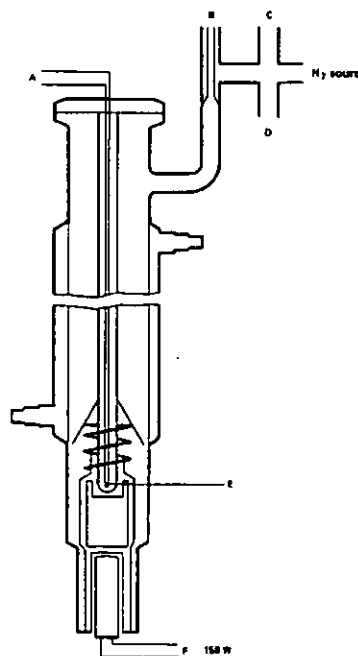


Figure 2



Cottrell pump (source: ref. 4)

- A. Thermocouple
- B. Vacuum buffer volume
- C. Pressure gauge
- D. Vacuum
- E. Measuring point
- F. Heating element circa 150 W

#### Apparatus

9. A very accurate apparatus, employing the Cottrell principle, is shown in figure 2. It consists of a tube with a boiling section in the lower part, a cooler in the middle part, and an outlet and flange in the upper part. The Cottrell pump is placed in the boiling section which is heated by means of an electrical cartridge. The temperature is measured by a jacketed thermocouple or resistance thermometer inserted through the flange at the top. The outlet is connected to the pressure regulation system. The latter consists of a vacuum pump, a buffer volume, a manostat for admitting nitrogen for pressure regulation and a manometer.

**Procedure**

10. The substance is placed in the boiling section. Problems may be encountered with non-powder solids but these can sometimes be solved by heating the cooling jacket. The apparatus is sealed at the flange and the substance degassed. Frothing substances cannot be measured using this method.
11. 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.
12. 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.
13. 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.

**Static method****Principle**

14. In the static method (5), the vapour pressure at thermodynamic equilibrium is determined at a specified temperature. This method is suitable for substances and multicomponent liquids and solids in the range from 10 to  $10^5$  Pa and, provided care is taken, also in the range 1 to 10 Pa.

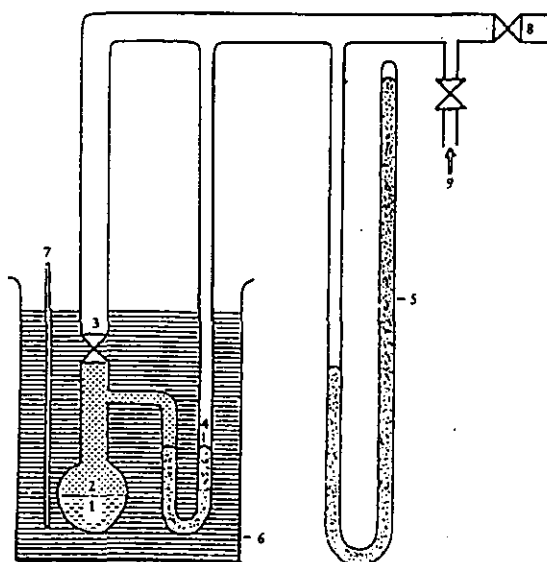
**Apparatus**

15. The equipment consists of a constant-temperature bath (precision of  $\pm 0.2$  K), a container for the sample connected to a vacuum line, a manometer and a system to regulate the pressure. The sample chamber (figure 3a) is connected to the vacuum line via a valve and a differential manometer (U-tube containing a suitable manometer fluid) which serves as zero indicator. Mercury, silicones and phthalates are suitable for use in the differential manometer, depending on the pressure range and the chemical behaviour of the test substance. The test substance must not dissolve noticeably in, or react with, the U-tube fluid. A pressure gauge can be used instead of a U-tube (figure 3b). For the manometer, mercury can be used in the range from normal pressure down to  $10^2$  Pa, while silicone fluids and phthalates are suitable for use below  $10^2$  Pa down to 10 Pa. There are other pressure gauges which can be used below  $10^2$  Pa and heatable membrane capacity manometers can even be used at below  $10^{-1}$  Pa. The temperature is measured on the outside wall of the vessel containing the sample or in the vessel itself.

**Procedure**

16. Using the apparatus as described in figure 3a, 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 and degassed at reduced temperature. In the case of a multiple-component sample, the temperature should be low enough to ensure that the composition of the material is not altered. Equilibrium can be established more quickly by stirring. The sample can be cooled with liquid nitrogen or dry ice, but care should be taken to avoid condensation of air or pump-fluid. With the valve over the sample vessel open, suction is applied for several minutes to remove the air. If necessary, the degassing operation is repeated several times.

Figure 3 a



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/nitrogen

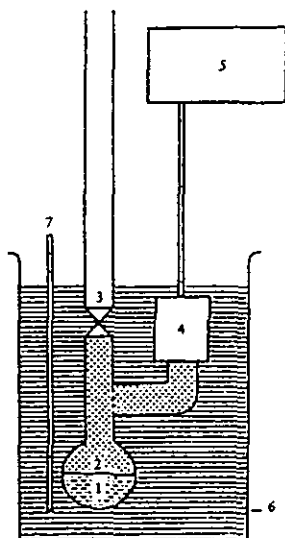
17. When the sample is heated with the valve closed, the vapour pressure increases. This alters the equilibrium of the fluid in the U-tube. To compensate for this, nitrogen or air is admitted to the apparatus until the differential pressure indicator is at zero again. The pressure required for this can be read off the manometer or an instrument of higher precision. This pressure corresponds to the vapour pressure of the substance at the temperature of the measurement. Using the apparatus described in figure 3 b, the vapour pressure is read off directly.

18. The vapour pressure is determined at suitably small temperature intervals (approximately 5 to 10 measuring points in all) up to the desired temperature maximum.

19. 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 situations:

- i) the sample still contains air (e.g. in the case of highly viscous materials) or low-boiling substances which is or are released during heating;
- ii) the substance undergoes a chemical reaction in the temperature range investigated (e.g. decomposition, polymerization).

Figure 3b



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

### Isotenoscope

#### **Principle**

20. The isotenoscope (6) is based on the principle of the static method. The method involves placing a sample in a bulb maintained at constant temperature and connected to a manometer and a vacuum pump. Impurities more volatile than the substance are removed by degassing at reduced pressure. The vapour pressure of the sample at selected temperatures is balanced by a known pressure of inert gas. The isotenoscope was developed to measure the vapour pressure of certain liquid hydrocarbons but it is appropriate for the investigation of solids as well. The method is usually not suitable for multicomponent systems. Results are subject to only slight errors for samples containing non-volatile impurities. The recommended range is  $10^2$  to  $10^5$  Pa.

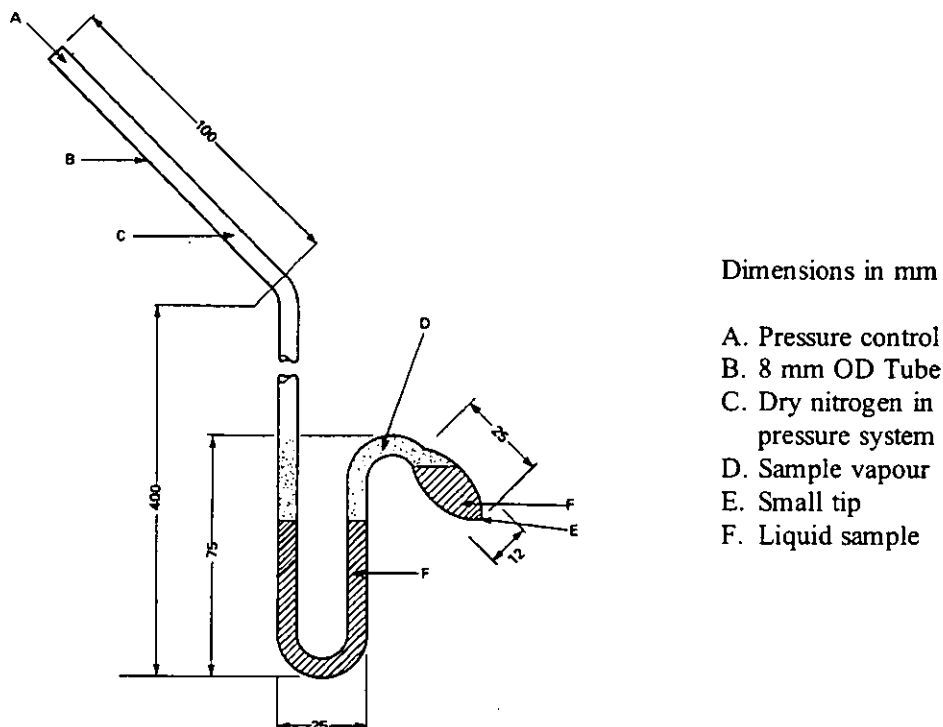
#### **Apparatus**

21. An example of a measuring device is shown in figure 4 [a complete description can be found in ASTM D 2879-86 (6)].

#### **Procedure**

22. In the case of liquids, the substance itself serves as the fluid in the differential manometer. A quantity of the liquid, sufficient to fill the bulb and the short leg of the manometer, is put in the isotenoscope. The isotenoscope 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 isotenoscope is placed in a horizontal position so that the sample spreads out into a thin layer in the sample bulb and manometer. The pressure of the system is reduced to 133 Pa and the sample gently warmed until it just boils (removal of dissolved gases). The isotenoscope is then placed so that the sample returns to the bulb and fills the short leg of the manometer. The pressure is maintained at 133 Pa. 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, creating a vapour-filled, nitrogen-free space. The isotenoscope is then placed in a constant temperature bath, and the pressure of nitrogen is adjusted until it equals that of the sample. At the equilibrium, the pressure of nitrogen equals the vapour pressure of the substance.

Figure 4



23. In the case of solids and depending on the pressure and temperature ranges, manometer liquids such as silicon fluids or phthalates are used. The degassed manometer liquid is put in a bulge provided on the long arm of the isoteniscope. Then the solid to be investigated is placed in the sample bulb and is degassed at elevated temperature. After that the isoteniscope is inclined so that the manometer liquid can flow into the U-tube.

#### **Effusion method: vapour pressure balance (7)**

##### **Principle**

24. A sample of the test substance is heated in a small furnace, placed in an evacuated bell jar. The furnace is covered by a lid which carries small holes of known diameters. The vapour of the substance, escaping through one of the holes, is directed onto a balance pan of a highly sensitive balance which is also enclosed in the evacuated bell jar. In some designs, the balance pan is surrounded by a refrigeration box, providing heat dissipation to the outside by thermal conduction, and is cooled by radiation so that the escaping vapour condenses on it. The momentum of the vapour jet acts as a force on the balance. The vapour pressure can be derived in two ways: directly from the force on the balance pan and also from the evaporation rate using the Hertz-Knudsen equation (2):

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

where

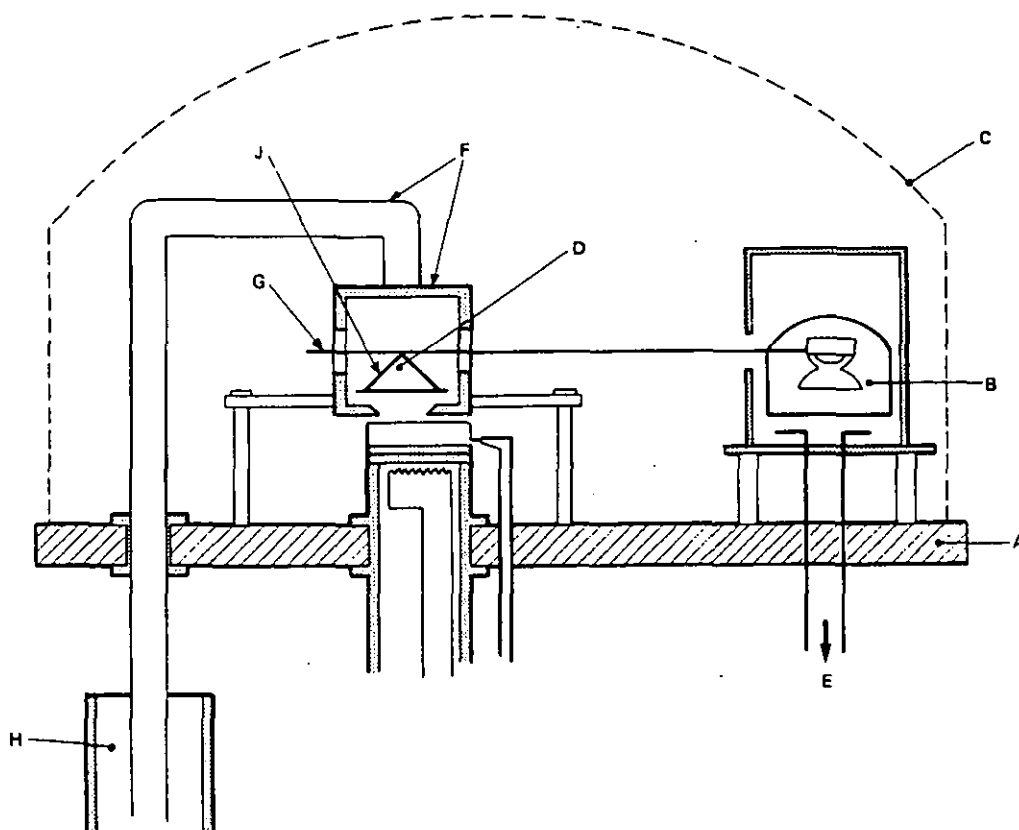
- G = evaporation rate ( $\text{kg s}^{-1} \text{m}^{-2}$ )  
 M = molar mass ( $\text{g mol}^{-1}$ )  
 T = temperature (K)  
 R = universal gas constant ( $\text{J mol}^{-1} \text{K}^{-1}$ )  
 p = vapour pressure (Pa)

The recommended range is  $10^{-3}$  to 1 Pa.

#### Apparatus

25. The general principle of the apparatus is illustrated in figure 5.

Figure 5



- |    |                         |    |                                   |
|----|-------------------------|----|-----------------------------------|
| A. | Base plate              | F. | Refrigeration box and cooling bar |
| B. | Moving coil instrument  | G. | Evaporator furnace                |
| C. | Bell jar                | H. | Dewar flask with liquid nitrogen  |
| D. | Balance with scalepan   | J. | Shield                            |
| E. | Vacuum measuring device |    |                                   |



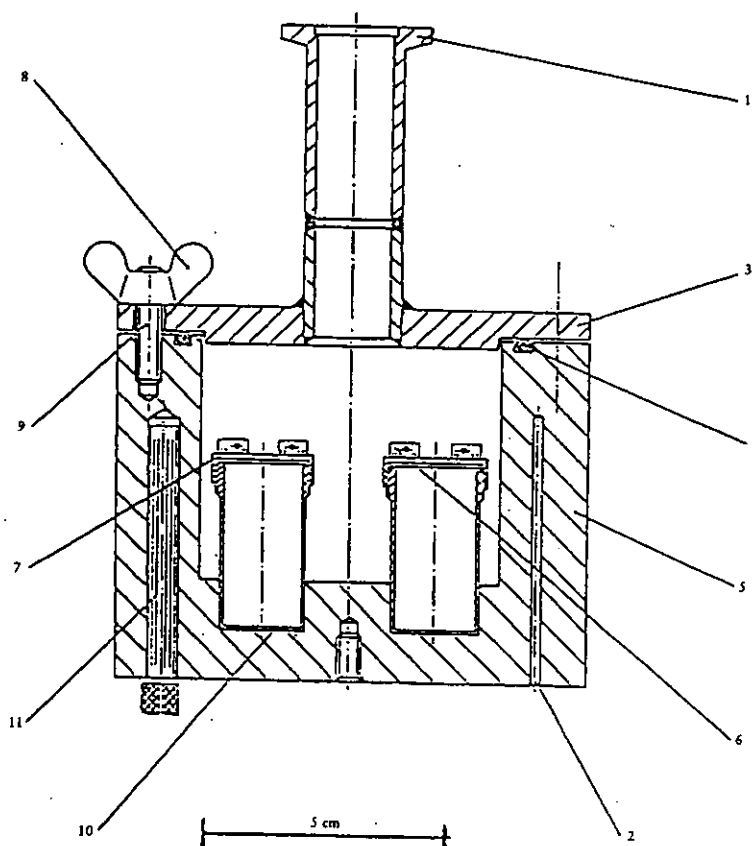
**Effusion method: loss of weight****Principle**

26. The method is based on the estimation of the mass of test substance flowing out per unit of time of a Knudsen cell (8) 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 chromatography. The vapour pressure is calculated by applying the Hertz-Knudsen relation (see paragraph 24) with correction factors that depend on parameters of the apparatus (9). The recommended range is  $10^{-3}$  to 1 Pa.

**Apparatus**

27. The general principle of the apparatus is illustrated in figure 6.

Figure 6



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

Gas saturation method (10)**Principle**

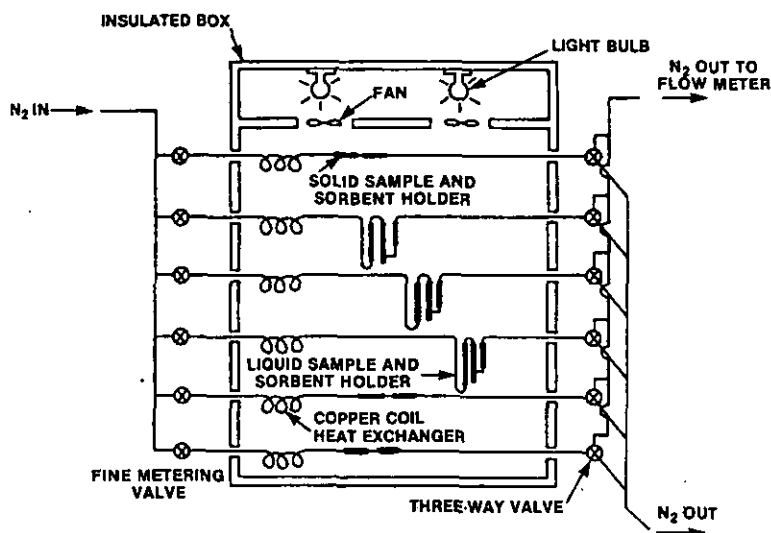
28. Inert gas is passed, at ambient temperature and at a known flow rate, through or over a sample of the test substance, slowly enough to ensure saturation. Achieving saturation in the gas phase is of critical importance. The transported substance is trapped, generally using a sorbent, and its amount is determined. As an alternative to vapour trapping and subsequent analysis, in-train analytical techniques, like gas chromatography may be used to determine quantitatively the amount of material transported. The vapour pressure is calculated on the assumption that the ideal gas law is obeyed and that the total pressure of a mixture of gases is equal to the sum of the pressures of the component gases. The partial pressure of the test substance, i.e. the vapour pressure, is calculated from the known total gas volume and the weight of the material transported.

29. The gas saturation procedure is applicable to solid or liquid chemicals. It can be used for vapour pressures down to  $10^{-5}$  Pa. The method is most reliable for vapour pressures below  $10^3$  Pa. Above  $10^3$  Pa, the vapour pressures are generally overestimated, probably due to aerosol formation. Since the vapour pressure measurements are made at ambient temperatures, the need to extrapolate data from high temperatures is not necessary and high temperature extrapolation, which can often cause serious errors, is avoided.

**Apparatus**

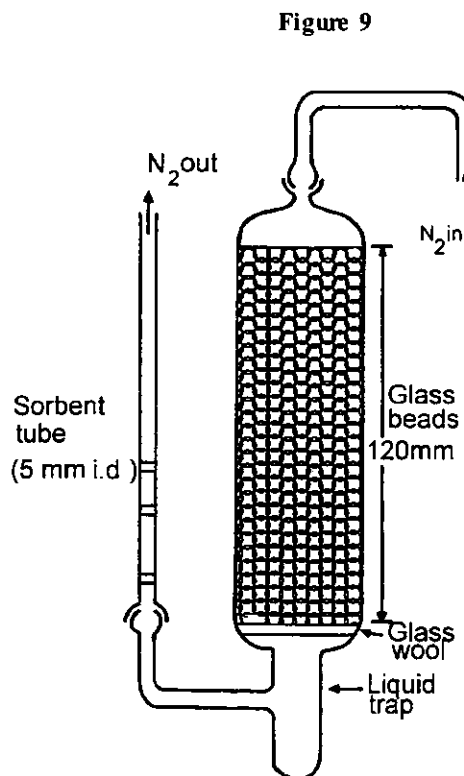
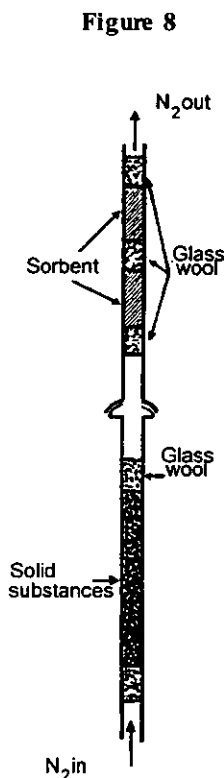
30. The procedure requires the use of a constant-temperature box. The sketch in Figure 7 shows a box containing three solid and three liquid sample holders, which allow for the triplicate analysis of either a solid or a liquid sample. The temperature is controlled to  $\pm 0.5^\circ\text{C}$  or better.

Figure 7



31. In general, nitrogen is used as an inert carrier gas but, occasionally, another gas may be required (11). The carrier gas must be dry. The gas stream is split into 6 streams, controlled by needle valves (approximately 0.79 mm orifice), and flows into the box via 3.8 mm i.d. copper tubing. After temperature equilibration, the gas flows through the sample and the sorbent trap and exits from the box.

32. Solid samples are loaded into 5 mm i.d. glass tubing between glass wool plugs (see Figure 8). Figure 9 shows a liquid sample holder and sorbent system. The most reproducible method for measuring the vapour pressure of liquids is to coat the liquid on glass beads and to pack the holder with these beads. As an alternative, the carrier gas may be made to pass a coarse frit and bubble through a column of the liquid test substance.



33. The sorbent system contains a front and a backup sorbent section. At very low vapour pressures, only small amounts are retained by the sorbent and the adsorption on the glass wool and the glass tubing between the sample and the sorbent may be a serious problem.

34. Traps cooled with solid  $CO_2$  are another efficient way for collecting the vapourized material. They do not cause any back pressure on the saturator column and it is also easy to remove quantitatively the trapped material.

#### Procedure

35. The flow rate of the effluent carrier gas is measured at room temperature. The flow rate is checked frequently during the experiment to assure that there is an accurate value for the total volume of carrier gas. Continuous monitoring with a mass flow-meter is preferred. Saturation of the gas phase may require considerable contact time and hence quite low gas flow rates (12).

36. At the end of the experiment, both the front and backup sorbent sections are analysed separately. The compound on each section is desorbed by adding a solvent. The resulting solutions are analysed quantitatively to determine the weight desorbed from each section. The choice of the analytical method (also the choice of sorbent and desorbing solvent) is dictated by the nature of the test material. The desorption efficiency is determined by injecting a known amount of sample onto

the sorbent, desorbing it and analysing the amount recovered. It is important to check the desorption efficiency at or near the concentration of the sample under the test conditions.

37. To assure that the carrier gas is saturated with the test substance, three different gas flow rates are used. If the calculated vapour pressure shows no dependence on flow rate, the gas is assumed to be saturated.

38. The vapour pressure is calculated through the equation

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

where

p = vapour pressure (Pa)

W = mass of evaporated test substance (g)

V = volume of saturated gas (m<sup>3</sup>)

R = universal gas constant 8.314 (J mol<sup>-1</sup> K<sup>-1</sup>)

T = temperature (K)

M = molar mass of test substance (g mol<sup>-1</sup>)

Measured volumes must be corrected for pressure and temperature differences between the flow meter and the saturator.

### Spinning rotor

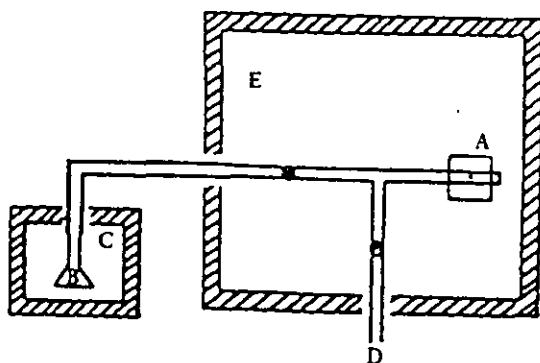
#### **Principle**

39. This method uses a spinning rotor viscosity gauge, in which the measuring element is a small steel ball which, suspended in a magnetic field, is made to spin by rotating fields (13, 14, 15). Pick-up coils allow its spinning rate to be measured. When the ball has reached a given rotational speed, usually about 400 revolutions per second, energizing is stopped and deceleration, due to gas friction, takes place. The drop of rotational speed is measured as a function of time. The vapour pressure is deduced from the pressure-dependent slow-down of the steel ball. The recommended range is 10<sup>-4</sup> to 0.5 Pa.

#### **Apparatus**

40. A schematic drawing of the experimental set-up is shown in figure 10. The measuring head is placed in a constant-temperature enclosure, regulated within 0.1°C. The sample container is placed in a separate enclosure, also regulated within 0.1°C. All other parts of the set-up are kept at a higher temperature to prevent condensation. The whole apparatus is connected to a high-vacuum system.

Figure 10



- A. Spinning rotor sensor head
- B. Sample cell
- C. Thermostat
- D. Vacuum line (turbo pump)
- E. Air thermostat

## DATA AND REPORTING

### Data

41. 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.

### Test Report

42. The test report must 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 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.

## LITERATURE

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APPENDIXESTIMATION METHODINTRODUCTION

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, e.g., less than  $10^{-3}$  Pa).

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

The vapour pressure is calculated as follows:

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

where

T = temperature of interest

$T_b$  = normal boiling point

$P_{vp}$  = vapour pressure at temperature T

$\Delta H_{vb}$  = heat of vaporization

$\Delta Z_b$  = compressibility factor (estimated at 0,97)

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

Further

$$\frac{\Delta H_{vb}}{T_b} = K_p(8.75 + R \ln T_b)$$

where

$K_p$  is an empirical factor considering the polarity of the substance. For several compound types,  $K_p$  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, the vapour pressure is calculated as follows:

$$\ln P_{vp} = \ln P_1 + \frac{\Delta H_{vl}}{\Delta Z_v RT_1} \left[ 1 - \left( 3 - 2 \frac{T_1}{T} \right) \frac{T_1}{T} - 2 m \left( 3 - 2 \frac{T_1}{T} \right)^{m-1} \ln \frac{T}{T_1} \right]$$

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

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## OECD GUIDELINE FOR THE TESTING OF CHEMICALS

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

### Water Solubility

#### INTRODUCTION

1. This guideline is a revised version of the original Guideline 105 which was adopted in 1981. There are no differences of substance between the current version and that from 1981. Mainly the format has been changed. The revision was based on the EC method "Water Solubility" (1).

#### INITIAL CONSIDERATIONS

2. The water solubility of a substance can be considerably affected by the presence of impurities. This guideline addresses the determination of the solubility in water of essentially pure substances which are stable in water and not volatile. Before determining water solubility, it is useful to have some preliminary information on the substance, like structural formula, vapour pressure, dissociation constant and hydrolysis as a function of pH.

3. Two methods, the column elution method and the flask method which cover respectively solubilities below and above  $10^{-2}$  g/l are described in this guideline. A simple preliminary test is also described. It allows to determine approximately the appropriate amount of sample to be used in the final test, as well as the time necessary to achieve saturation.

#### DEFINITIONS AND UNITS

4. The water solubility of a substance is the saturation mass concentration of the substance in water at a given temperature.

5. Water solubility is expressed in mass of solute per volume of solution. The SI unit is  $\text{kg/m}^3$  but g/l is commonly used.

#### REFERENCE SUBSTANCES

6. Reference substances do not need to be employed when investigating a substance.

#### DESCRIPTION OF THE METHODS

##### Test conditions

7. The test is preferably run at  $20 \pm 0,5$  °C. The chosen temperature should be kept constant in all relevant parts of the equipment.

**Preliminary test**

8. In a stepwise procedure, increasing volumes of water are added at room temperature to approximately 0.1 g of the sample (solid substances must be pulverized) in a 10 ml glass-stoppered measuring cylinder. After each addition of an amount of water, the mixture is shaken 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 is continued in a 100 ml measuring cylinder. The approximate solubility is given in Table 1 below under that volume of water in which complete dissolution of the sample occurs. When the solubility is low, a long time may be required to dissolve a substance and at least 24 hours should be allowed. If, after 24 hours, the substance is still not dissolved, more time (up to 96 hours) should be allowed or further dilution should be attempted to ascertain whether the column elution method or flask method should be used.

**Table 1**

ml of water for 0.1 g soluble	0.1	0.5	1	2	10	100	> 100
approximate solubility in g/l	> 1000	1000 to 200	200 to 100	100 to 50	50 to 10	10 to 1	< 1

**Column elution method****Principle**

9. 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, previously coated with an excess of the test substance (2). The water solubility is given by the mass concentration of the eluate when this has reached a plateau as a function of time.

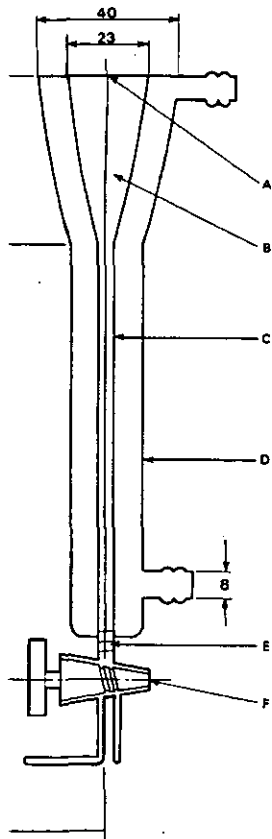
**Apparatus**

10. The apparatus consists of a microcolumn (Figure 1), maintained at constant temperature. It is connected either to a recirculating pump (Figure 2) or to a levelling vessel (Figure 3). The microcolumn contains an inert support held in place by a small plug of glasswool which also serves to filter out particles. Possible materials which can be employed for the support are glass beads, diatomaceous earth, or other inert materials.

11. The microcolumn shown in figure 1 is suitable for the set-up with recirculating pump. It has a head space providing for five bed volumes (discarded at the start of the experiment) and the volume of five samples (withdrawn for analysis during the experiment). Alternatively, the size can be reduced if water can be added to the system during the experiment to replace the initial five bed volumes removed with impurities. The column is connected with tubing made of an inert material to the recirculating pump, capable of delivering approximately 25 ml/h. The recirculating pump can be, for example, a peristaltic or membrane pump. Care must be taken that no contamination and/or adsorption occurs with the tube material.

12. A schematic arrangement using a levelling vessel is shown in figure 3. In this arrangement the microcolumn is fitted with a one way stopcock. The connection to the levelling vessel consists of a ground glass joint and tubing made of an inert material. The flow rate from the levelling vessel should be approximately 25 ml/h.

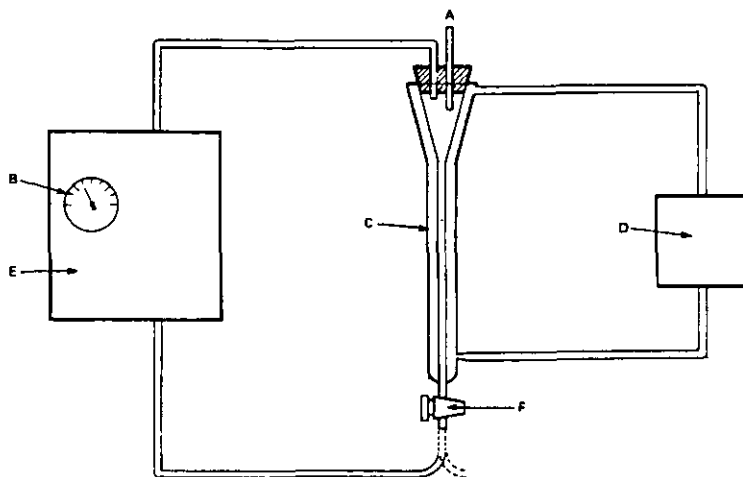
Figure 1



Dimensions in mm

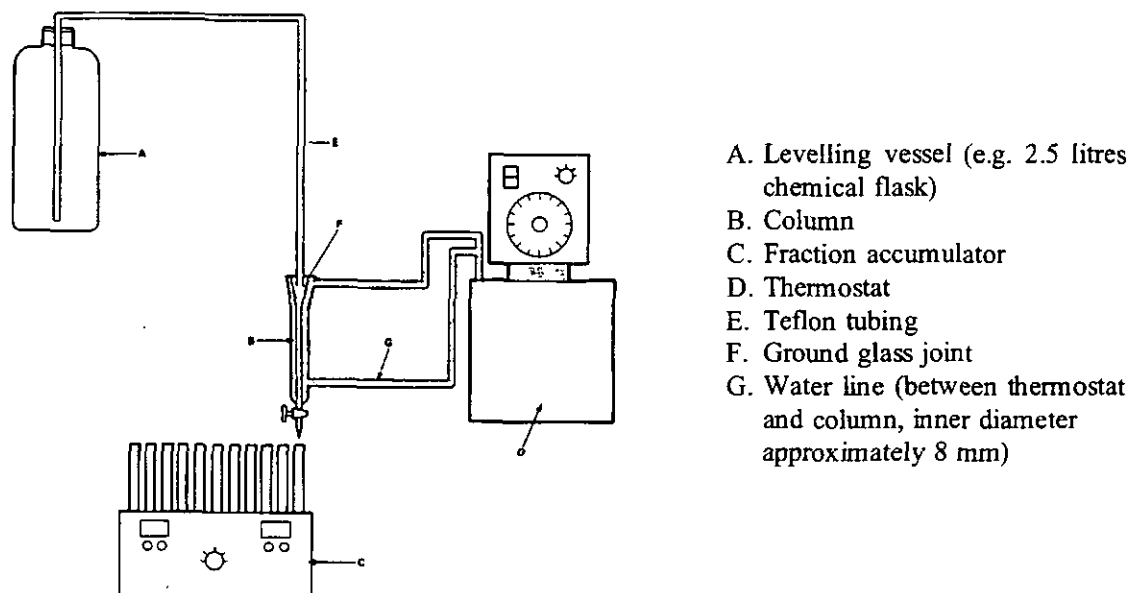
- A. Connection for ground glass joint
- B. Headspace
- C. Interior 5
- D. Exterior 19
- E. Plug of glass wool
- F. Stopcock

Figure 2



- A. Atmospheric equilibration
- B. Flowmeter
- C. Microcolumn
- D. Thermostatically controlled circulating pump
- E. Recirculating pump
- F. Two-way valve for sampling

Figure 3



#### Loading of the support

13. Approximately 600 mg of support material is transferred to a 50 ml round-bottom flask. A suitable amount of test substance is dissolved in a volatile solvent of analytical reagent quality and an appropriate amount of this solution is added to the support material. The solvent is completely evaporated, e.g. using a rotary evaporator, as otherwise water saturation of the support will not be achieved during the elution step because of partitioning on the surface. The loaded support material is soaked for two hours in approximately 5 ml of water and the suspension is poured into the microcolumn. Alternatively, dry loaded support material may be poured into the water-filled microcolumn and two hours are allowed for equilibrating.

14. The loading of the support material may cause problems, leading to erroneous results, e.g. when the test substance is deposited as an oil. These problems should be examined and the details reported.

#### Procedure using a recirculating pump

15. The flow through the column is started. It is recommended that a flow rate of approximately 25 ml/h, corresponding to 10 bed volumes per hour for the column described, be used. At least the first five bed volumes are discarded to remove water soluble impurities. Following this, the pump is allowed to run until equilibrium is established, as defined by five successive samples whose concentrations do not differ by more than  $\pm 30\%$  in a random fashion. These samples should be separated from each other by time intervals corresponding to the passage of at least ten bed volumes. Depending on the analytical method used, it may be preferable to establish a concentration/time curve to show that equilibrium is reached.

#### Procedure using a levelling vessel

16. Successive eluate fractions should be collected and analyzed by the chosen method. Fractions from the middle eluate range, where the concentrations are constant within  $\pm 30\%$  in at least five consecutive fractions, are used to determine the solubility.