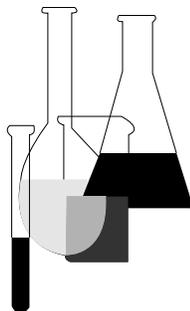




# Product Properties Test Guidelines

## OPPTS 830.7220 Boiling Point/Boiling Range



## INTRODUCTION

This guideline is one of a series of test guidelines that have been developed by the Office of Prevention, Pesticides and Toxic Substances, United States Environmental Protection Agency for use in the testing of pesticides and toxic substances, and the development of test data that must be submitted to the Agency for review under Federal regulations.

The Office of Prevention, Pesticides and Toxic Substances (OPPTS) has developed this guideline through a process of harmonization that blended the testing guidance and requirements that existed in the Office of Pollution Prevention and Toxics (OPPT) and appeared in Title 40, Chapter I, Subchapter R of the Code of Federal Regulations (CFR), the Office of Pesticide Programs (OPP) which appeared in publications of the National Technical Information Service (NTIS) and the guidelines published by the Organization for Economic Cooperation and Development (OECD).

The purpose of harmonizing these guidelines into a single set of OPPTS guidelines is to minimize variations among the testing procedures that must be performed to meet the data requirements of the U. S. Environmental Protection Agency under the Toxic Substances Control Act (15 U.S.C. 2601) and the Federal Insecticide, Fungicide and Rodenticide Act (7 U.S.C. 136, *et seq.*).

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## **OPPTS 830.7220 Boiling point/boiling range.**

(a) **Scope**—(1) **Applicability.** This guideline is intended to meet testing requirements of both the Federal Insecticide, Fungicide, and Rodenticide Act (FIFRA) (7 U.S.C. 136, *et seq.*) and the Toxic Substances Control Act (TSCA) (15 U.S.C. 2601).

(2) **Background.** The source materials used in developing this harmonized OPPTS test guideline are the OPPT guideline under 40 CFR 796.1220 Boiling Point/Boiling Range, OPP guideline 63–6 Boiling Point (Pesticide Assessment Guidelines, Subdivision D: Product Chemistry, EPA Report 540/9–82–018, October 1982) and OECD guideline 103 Boiling Point/Boiling Range.

(b) **Introduction.** (1) Five methods used to determine the boiling point are described in this guideline: The ebulliometric method is based on the ASTM D 1120–72; the distillation method is based on the standards ISO R 918 and the draft ISO DIS 4626, BS 4359/68, BS 4591/71, DIN 53171; the Siwoloboff method is based on JIS K 0064–1966; the photocell detection method is based on the manufacturer’s manual under paragraph (e)(4) of this guideline; the Dynamic Method was tested in the OECD Laboratory Intercomparison Testing Programme, part I, 1979, for vapor pressure determination.

(2) **Qualifying statement.** The methods and devices described in this test guideline can be applied to liquids, provided that these do not undergo chemical reaction at temperatures below the boiling point (e.g., autoxidation, rearrangement, degradation, etc.).

(c) **Method.** (1) Application and limits of test. The boiling point of a substance is an environmentally relevant physical chemical property because it is important for identification purposes and is one factor influencing the states in which the substance will exist in the environment.

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

(3) The dynamic method has the advantage that it can also be applied for the determination of vapor pressure and that it is not necessary to correct the boiling temperature to the normal pressure (101.325 kPa) because the standard pressure can be adjusted during the measurement. However, this method is not at present automated. (For a detailed description, see OPPTS 830.7950 for the vapor pressure curve.

(4) Note: In the literature, different boiling points are sometimes quoted for the same substance. These differences are due to such variables as the dimension of the apparatus (for example, the fit of the thermometer), the type of the thermometer, the stem correction, the pressure correction,

and the accuracy of the pressure measurement. Therefore, the above-mentioned international and national standardized methods contain precise requirements for these specified conditions.

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

(6) Definitions and units. (i) The standard **boiling point** is described as the temperature at which the pressure of the saturated vapor of a liquid is the same as the standard pressure.

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

$$\log p = - \Delta H_v / 2.3 RT$$

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

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

(iv) Conversions:

Pressure (units kPa)	Temperature (units K)
100 kPa = 1 bar = 0.1 MPa <sup>1</sup> .....	$t = T - 273.15$
133 Pa = 1 mm Hg = 1 torr <sup>2</sup> .....	$t$ in °C, and $T$ in K

<sup>1</sup> "Bar" units are still permissible but not recommended.

<sup>2</sup> The units mm Hg and torr are no longer permissible.

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

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

where:

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

$p$  = barometer measurement in kPa

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

T = measured boiling temperature in K

T<sub>n</sub> = boiling temperature corrected to normal pressure in K

(B) The temperature-correction factors  $f_T$  and equations for their approximation are included in the international and national standards mentioned in paragraph (e)(2) of this guideline for many substances. For example, the DIN 53171 method mentions the following rough corrections for solvents included in paints under the following table 1:

**Table 1.—Temperature Correction Factors  $f_T$**

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

(C) A table of temperature-correction factors for organic solvents (see ISO/DIS 4626 is included in the following table 2:

**Table 2.—Temperature-Correction Factors for Organic Solvents (See ISO/DIS 4626)**

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

Table 2.—Temperature-Correction Factors for Organic Solvents (See ISO/DIS 4626)—Continued

Product	Thermometer °C	Boiling point °C at 101.325 kPa	Rate of change of boiling point with pressure	
			K' °C/0.1 kPa (°C/mbar)	K °C/mmHg
Dimethyl formamide .....	102	153.0	0.033	0.044
Dipropylene glycol .....	106	232.8	0.038	0.051
Diisopropyl ether .....	39	68.3	0.031	0.041
Ethyl acetate .....	39	77.2	0.031	0.041
Ethyl alcohol .....	39	78.3	0.025	0.033
Ethyl benzene .....	41	136.2	0.037	0.049
Ethylene glycol .....	104	197.6	0.032	0.043
Ethylene glycol mono- <i>n</i> -butyl ether .....	103	171.2	0.035	0.047
Ethylene glycol monoethyl ether	102	135.1	0.033	0.044
Ethylene glycol monoethyl ether acetate .....	102	156.3	0.035	0.046
Ethylene glycol monomethyl ether .....	41	124.5	0.031	0.041
Ethylene glycol monoisopropyl ether .....	102	142.8	0.033	0.044
2-Ethyl hexanol .....	104	184.8	0.034	0.046
Ethyl isoamyl ketone .....	103	158.2	0.037	0.049
<i>n</i> -Hexyl acetate .....	103	171.6	0.038	0.050
Hexylene glycol .....	104	197.1	0.034	0.045
Isophorone .....	105	215.3	0.043	0.057
Mesityl oxide .....	41	129.8	0.035	0.047
4-Methoxy-4-methyl-2-pentanone	103	160.6	0.037	0.049
Methanol .....	39	64.6	0.025	0.033
Methyl isoamyl acetate .....	102	146.2	0.036	0.048
Methyl isoamyl ketone .....	102	144.9	0.036	0.048
Methyl isobutyl carbinol .....	41	131.8	0.031	0.041
Methyl isobutyl ketone .....	41	116.2	0.035	0.046
Monoethanol amine .....	103	170.7	0.030	0.040
Perchloroethylene .....	41	121.2	0.036	0.048
<i>n</i> -Propyl acetate .....	40	101.6	0.032	0.042
<i>iso</i> -Propyl acetate .....	40	88.5	0.031	0.041
<i>n</i> -Propyl alcohol .....	40	97.2	0.026	0.034
Isopropyl alcohol .....	40	82.3	0.025	0.033
Propylene glycol .....	104	187.6	0.032	0.043
Propylene oxide .....	38	34.3	0.027	0.036
Pyridine .....	41	115.4	0.035	0.046
Toluene .....	41	110.6	0.035	0.046
Triethylene glycol .....	107	287.6	0.038	0.050
Triethylene glycol monoethyl ether .....	106	255.4	0.038	0.051
Trichloroethylene .....	40	87.1	0.032	0.043
Vinyl acetate .....	39	72.7	0.030	0.040
White spirit .....	103	.....	0.041	0.055
Xylene (isomer mixture) .....	41	.....	0.037	0.049
<i>m</i> -Xylene .....	41	139.1	0.037	0.049
<i>o</i> -Xylene .....	41	144.4	0.037	0.050
<i>p</i> -Xylene .....	41	138.3	0.037	0.049

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

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

(i) Determination by use of the ebulliometer. See paragraphs (e)(1) and (e)(4) of this guideline. Ebulliometers were originally developed for the determination of molecular weight by boiling point elevation, but they are also suited for exact boiling point measurements. A very simple apparatus is described in ASTM D 1120–72. The liquid is heated in this apparatus under equilibrium conditions at atmospheric pressure until it boils. The determined temperature of the liquid, corrected to standard pressure, is the boiling point.

(ii) Dynamic method. See paragraph (e)(2) of this guideline. This method measures the vapor recondensation temperature by means of a thermocouple in the reflux while boiling. The pressure can be varied in this method.

(iii) Distillation method for boiling point (and boiling range). This method involves distillation of the liquid and measurement of the vapor recondensation temperature and determination of the amount of distillate.

(iv) Method according to Siwoloboff. See paragraph (e)(2) of this guideline. A sample is heated in a sample tube which is immersed in a heat-bath liquid. A fused capillary, containing an air bubble in the lower part, is dipped in the sample tube. The temperature at which a regular string of bubbles escapes from the capillary or the temperature at which the string of bubbles stops and the fluid suddenly starts rising in the capillary (Siwoloboff under paragraph (e)(2) of this guideline) is determined.

(v) Photocell detection. See paragraph (e)(3) of this guideline. Using the principle according to Siwoloboff. Measurements are automatic, the rising bubbles being detected photo-electrically.

(9) Quality criteria. The different methods for the determination of the boiling point (boiling range) are compared with regard to their use and precision and possibility to standardize/automate in the following table 3:

**Table 3.—Comparison of the Methods**

Method of measurement	Approximate accuracy	Ability to standardize	Automation
Ebulliometer .....	±1.4 K (up to 373 K) <sup>1</sup> .....	Existing standard ASTM D 1120–72 <sup>1</sup> .	Difficult as yet
Dynamic method .....	±2.5 K (above 373 K) <sup>1</sup> .....	Possible .....	Difficult
Distillation process (boiling range).	±0.5 K .....	Existing standards, e.g., ISO/R 918, DIN 53171, BS 4591/17.	Difficult as yet
According to Siwoloboff .....	±1K to ±2K .....	Possible .....	Automatic method exists (see photocell detection)
Photocell detection .....	±0.3 K (at 373 K) .....	Possible .....	Measurement process works automatically
Differential scanning calorimetry.	±0.5 K (up to 600 K) .....	Existing standard .....	Automatic method

**Table 3.—Comparison of the Methods—Continued**

Method of measurement	Approximate accuracy	Ability to standardize	Automation
Differential thermal analysis ...	±2.0 K (up to 1273 K) ±0.5 K (up to 600 K) ..... ±2.0 K (up to 1273 K)	ASTM E537-76 Existing standard ..... ASTM E537-76	exists Automatic method exists

<sup>1</sup>This accuracy is only valid for pure substances and for the simple device as, for example, described in ASTM D 1120-72; it can be improved with more sophisticated ebulliometer devices.

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

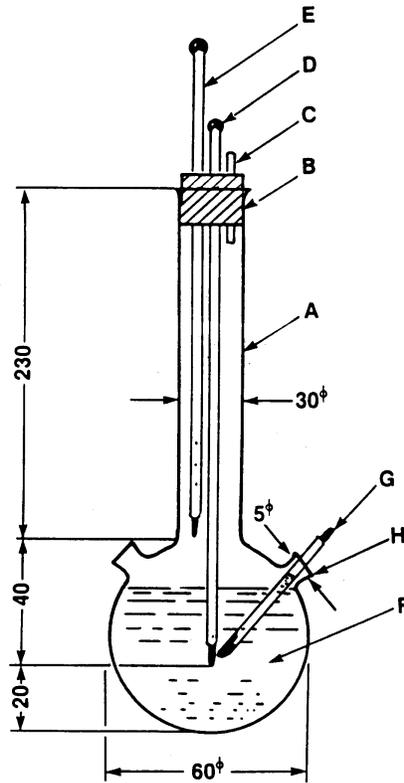
(i) Ebulliometer. See ASTM D 1120-72, Standard Test Method for Boiling Point of Engine Antifreezes, and reference under paragraph (e)(4) of this guideline.

(ii) Dynamic method. See OPPTS 830.7950 for Vapour Pressure Curve, Principle of the test methods. The boiling temperature observed with an applied pressure of 101.325 kPa is recorded.

(iii) Distillation process (boiling range). See ISO/R 918, Test Method for Distillation (Distillation Yield and Distillation Range); ISO 4626/1980, Volatile Organic Liquids—Determination of Boiling Range of Organic Solvents Used as Raw Materials; BS 4349/68, Method for Determination of Distillation of Petroleum Products; BS 4591/71, Method for the Determination of Distillation Characteristics; DIN 53171, Lösungsmittel für Anstrichstoffe, Bestimmung des Siedeverlaufes; DIN 51751, Prüfung flüssiger Mineralkohlenwasserstoffe—Bestimmung des Siedeverlaufes.

(iv) Method according to Siwoloboff. (A) The sample is heated in a melting point apparatus in a sample tube, with a diameter of approximately 5 mm in the following figure 1:

FIGURE 1—APPARATUS FOR THE DETERMINATION OF MELTING AND BOILING POINT (JISK 0064—1966), WITH SPECIFICATIONS IN MILLIMETERS

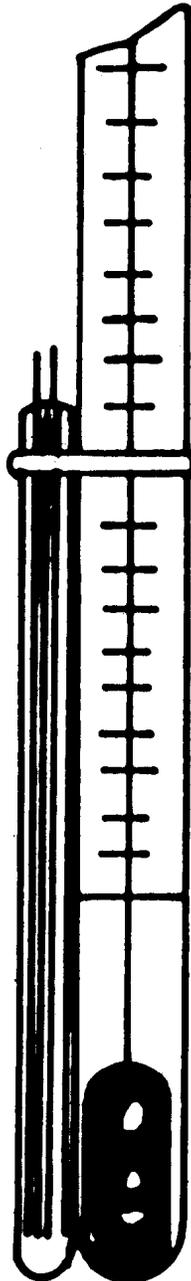


- A: MEASURING TUBE
- B: CORK STOPPER
- C: VENT
- D: THERMOMETER
- E: AUXILIARY THERMOMETER
- F: BATH LIQUID
- G: SAMPLE TUBE; MAX. 5mm OUTER DIAMETER;  
CAPILLARY TUBE, APPROX. 1mm INNER  
DIAMETER, AND APPROX. 0.2mm TO  
0.3mm WALL-THICKNESS
- H: SIDE TUBE

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

is fastened either to the thermometer with a rubber-band or is fixed with a support from the side under the following figure 2:

FIGURE 2—PRINCIPLE ACCORDING TO SIWOLOBOFF

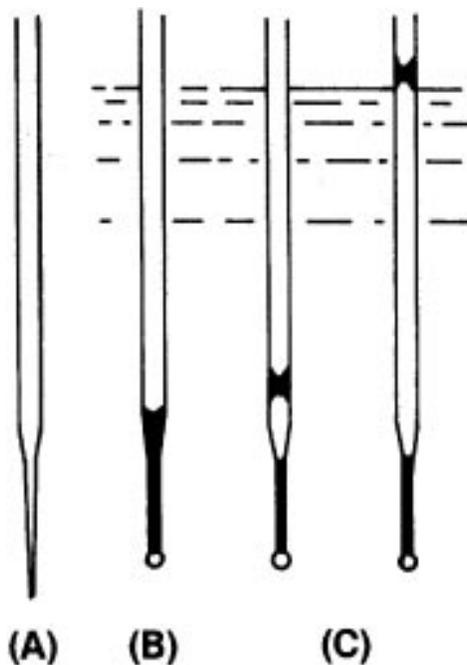


(C) The bath liquid is chosen according to boiling temperature. At temperatures of up to 573 K sulfuric acid or silicon oil can be used; if sulfuric acid is used, this liquid must be handled with extreme care. Liquid paraffin may only be used up to 473 K. The heating of the bath liquid should be adjusted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

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

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

FIGURE 3—MODIFIED PRINCIPLE



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

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

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

(vi) Differential scanning calorimetry. See ASTM E 537-76 and OECD 103. Samples of the test substance and a reference material are subjected to the same controlled temperature program. The difference in energy input necessary to maintain identical temperatures in the substance and the reference material is recorded. When the sample undergoes a transition involving a change in enthalpy (endothermic on boiling), that change is indicated by a departure from the base line of the heat flow record.

(vii) Differential thermal analysis. See ASTM E 537-76 and OECD 103. The difference in temperature between the substance and a reference material, which are both subjected to the same controlled temperature program, are recorded. When the sample undergoes a transition involving a change in enthalpy (endothermic in the case of boiling), that change is indicated by a departure from the base line of the temperature record.

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

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

(d) **Data and reporting—(1) Treatment of results.** (i) The boiling point to be determined should be a mean of at least two measurements, which are in the range of approximate accuracy indicated in table 2 under

paragraph (c)(9) of this guideline. If determinations are not reproducible, other methods should be considered (see General remarks, above).

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

(iii) The method used should be indicated, including any deviations from procedures described in this test guideline.

(2) [Reserved]

(e) **Literature references.** The following references should be consulted for additional background material on this test guideline.

(1) Kienitz, H. *Methoden der Organischen Chemie* ed. Houben-Weyl, Vol. 2, (Georg Thieme Verlag, Stuttgart, 1953, pp. 815–821.

(2) *Test Guideline 104 for Vapour Pressure Curve*, A 80/5 Umweltbundesamt, Berlin (1980).

(3) Siwoloboff, A. *Berichte-Deutsche Chemische Gesellschaft* 19: 795 (1886).

(4) Manual of Apparatus FP 5+FP 51, FP 52 and FP 53, Mettler Instrumente AG, CH–8606 Greifensee-Zürich, Switzerland.

(5) *European Pharmacopoeia*, 1:75 (1974).

(6) *Organization for Economic Cooperation and Development*, Guidelines for The Testing of Chemicals, OECD 103, Boiling Point/Boiling Range, OECD, Paris, France.

(7) ASTM Standard Method E 537-76, Standard Method for Assessing the thermal stability of Chemicals by Methods of Differential Thermal Analysis (ASTM Annual Index, latest edition).