INTERNATIONAL STANDARD

ISO 2977

Third edition
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Petroleum products and hydrocarbon solvents — Determination of aniline point and mixed aniline point

Produits pétroliers et solvants hydrocarbonés — Détermination du point d'aniline et du point d'aniline en mélange

Reference number
ISO 2977:1997(E)

Foreword

ISO (the International Organization for Standardization) is a worldwide federation of national standards bodies (ISO member bodies). The work of preparing International Standards is normally carried out through ISO technical committees. Each member body interested in a subject for which a technical committee has been established has the right to be represented on that committee. International organizations, governmental and non-governmental, in liaison with ISO, also take part in the work. ISO collaborates closely with the International Electrotechnical Commission (IEC) on all matters of electrotechnical standardization.

Draft International Standards adopted by the technical committees are circulated to the member bodies for voting. Publication as an International Standard requires approval by at least 75 % of the member bodies casting a vote.

International Standard ISO 2977 was prepared by Technical Committee ISO/TC 28, *Petroleum products and lubricants*.

This third edition cancels and replaces the second edition (ISO 2977:1989), which has been technically revised, in particular with the inclusion of annex F.

Annexes A to F form an integral part of this International Standard.

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Petroleum products and hydrocarbon solvents — Determination of aniline point and mixed aniline point

WARNING — The use of this International Standard may involve hazardous materials, operations and equipment. This International Standard does not purport to address all of the safety problems associated with its use. It is the responsibility of the user of this International Standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.

1 Scope

This International Standard specifies a method for the determination of the aniline point of petroleum products and hydrocarbon solvents, and the mixed aniline point of those products having aniline points below the temperature at which aniline will crystallize from the aniline-sample mixture.

Method 1 describes a procedure for transparent samples with an initial boiling point above ambient temperature, and for those with an aniline point below the bubble point and above the solidification point of the aniline-sample mixture.

Method 2, a thin film method, describes a procedure for samples too dark for testing by method 1.

Methods 3 and 4 are for samples that may vaporize appreciably at the aniline point.

NOTE 1 Method 4 is particularly suitable where only small quantities of sample are available.

Method 5 describes a procedure using automated or automatic apparatus suitable for the range covered by methods 1 and 2.

NOTE 2 The aniline point (or mixed aniline point) is useful as an aid in the characterization of pure hydrocarbons and in the analysis of hydrocarbon mixtures. Aromatic hydrocarbons exhibit the lowest values and paraffins the highest, with cycloparaffins and olefins exhibiting intermediate values. In a homologous series, the aniline points increase with increasing molecular mass.

NOTE 3 Although the aniline point can be used in combination with other physical properties in correlative methods for hydrocarbon analysis, the most frequent usage is to provide an estimate of the aromatic content (or "aromaticity") of hydrocarbon mixtures.

2 Normative references

The following standards contain provisions which, through reference in this text, constitute provisions of this International Standard. At the time of publication, the editions indicated were valid. All standards are subject to revision, and parties to agreements based on this International Standard are encouraged to investigate the

possibility of applying the most recent editions of the standards listed below. Members of IEC and ISO maintain registers of currently valid International Standards.

ISO 648:1977, *Laboratory glassware — One-mark pipettes.*

ISO 2049:1996, *Petroleum products — Determination of colour (ASTM scale).*

3 Definitions

For the purposes of this International Standard, the following definitions apply:

3.1 aniline point: The minimum equilibrium solution temperature, in degrees Celsius, of a mixture of equal volumes of aniline and the product under test.

3.2 mixed aniline point: The minimum equilibrium solution temperature, in degrees Celsius, of a mixture of two volumes of aniline, one volume of the product under test and one volume of heptane.

3.3 bubble point: The temperature, in degrees Celsius, noted at the moment when bubbles first appear in the body of the mixture when heated under standardized conditions.

4 Principle

Specified volumes of aniline and sample, or aniline and sample plus heptane, are placed in a tube and mixed mechanically. The mixture is heated at a controlled rate until the two phases become miscible. The mixture is then cooled at a controlled rate and the temperature at which the two phases separate is recorded as the aniline point or mixed aniline point.

5 Reagents and materials

5.1 Aniline

CAUTION — Aniline is extremely toxic, even in very small quantities, and is absorbed through the skin. Handle with great caution. Wear goggles of safety glass and gloves impervious to aniline for all operations where aniline is handled directly.

Dry analytical reagent grade aniline over potassium hydroxide pellets, decant and distil fresh on the day of use, discarding the first and last 10 % (*V*/*V*). Aniline thus prepared shall give an aniline point of 69,3 °C ± 0,2 °C as determined from the average of two independent tests having a difference of not more than 0,1 °C when tested with heptane (5.3) in accordance with the procedure described in 8.1.

As an alternative to distilling the aniline on the day of use, distil the aniline as described above and collect the distillate in ampoules which are then sealed under vacuum or dry nitrogen and stored in a cool dark place for future use. In either case, rigid precautions shall be taken to avoid contamination by atmospheric moisture (see 6.2).

NOTE 4 Experience shows that, under these conditions, the aniline should remain unchanged for at least six months.

NOTE 5 For routine analysis, distillation is not mandatory provided that the aniline meets the requirements of the test with heptane.

NOTE 6 For the purposes of this International Standard, the term "% (*V*/*V*)" is used to represent the volume fraction of a material.

The aniline point of aniline and heptane determined with automated or automatic apparatus shall be 69,3 °C ± 0,2 °C when corrected using the formula given in E.4.1.

5.2 Drying agent, consisting of anhydrous calcium sulfate or sodium sulfate.

5.3 Heptane, of minimum purity 99,75 %.

6 Apparatus

6.1 Aniline point apparatus, conforming to the individual method requirements as detailed in:

— annex A for method 1;

— annex B for method 2;

— annex C for method 3;

— annex D for method 4;

— annex E for method 5.

NOTE 7 Alternative apparatus may be used, such as the U-tube method for dark oils, provided that it has been shown to give results of the same precision as given in clause 10 and accuracy as defined by the aniline point of heptane (see 5.1), as those described in annex A to annex E.

6.2 Heating and cooling bath, consisting of a suitable air bath, a bath using a non-aqueous, non-volatile transparent liquid, or an infrared lamp (250 W to 375 W), provided with means for controlled heating.

Water shall not be used as either a heating or a cooling medium, since aniline is hygroscopic and moist aniline will give erroneous test results.

NOTE 8 As an example, the aniline point of dry aniline with heptane is increased by approximately 0,5 °C if the aniline contains 0,1 % (*V*/*V*) water.

If the aniline point is below the dew point of the atmosphere, pass a slow stream of dry inert gas into the aniline point tube to blanket the aniline-sample mixture.

6.3 Thermometers, conforming to the specifications in annex F. The thermometers shall be provided with current calibration certificates, traceable to national standards, and giving corrections over the range to 0,02 °C.

6.4 Pipettes, conforming to ISO 648 Class A, and provided with indirect suction. Capacities required are 10,0 ml, 5,0 ml and 0,5 ml. The 0,5 ml pipette (method 4) shall be provided with a long fine tip.

6.5 Balance, accurate to 0,01 g, suitable for weighing the tube and the sample when the sample cannot be pipetted conveniently.

6.6 Safety goggles, manufactured using safety glass.

6.7 Safety gloves, impervious to aniline.

7 Preparation of test sample

Dry the sample by shaking vigorously for 3 min to 5 min with approximately 10 % (*V*/*V*) of the drying agent (5.2). Reduce the viscosity of viscous or waxy samples by warming to a temperature below that which would cause the loss of light ends or the dehydration of the drying agent. If suspended water is visibly present, centrifuge the sample to remove the water before carrying out the final drying with drying agent.

Remove any suspended drying agent by centrifuge or filtration. Heat samples containing separated wax until they are homogenous and keep heated during the centrifuging or filtration operations.

8 Procedure

8.1 Choice of method

Five methods, to be used as applicable, are specified as follows:

Method 1: described in detail in annex A, is applicable to clear, light-coloured samples and to samples not darker than 6,5 by ISO 2049, having initial boiling points well above the expected aniline point.

Method 2: described in detail in annex B, is applicable to light-coloured samples, to moderately dark samples, and to very dark samples.

NOTE 9 Method 2 is applicable to samples too dark to be tested by method 1.

Method 3: described in detail in annex C, is applicable to clear samples and to samples not darker than 6,5 by ISO 2049, having initial boiling points sufficiently low to give incorrect aniline point readings by method 1.

NOTE 10 An example is aviation gasoline.

Method 4: described in detail in annex D, is a small-scale method, applicable to the same type of sample as method 3, and is applied when only limited quantities of sample are available.

Method 5: is applicable when using automated or automatic apparatus in accordance with the instructions in annex E.

8.2 Mixed aniline point

This procedure is applicable to samples having aniline points below the temperature at which aniline crystallizes from the mixture. Pipette 10 ml of aniline, 5 ml of the sample and 5 ml of heptane (5.3) into a clean, dry apparatus. Determine the aniline point of the mixture by method 1 or method 2 as described in annex A or annex B.

9 Evaluation and expression of results

9.1 If the range of three successive observations of the aniline point temperature is not greater than 0,1 °C for light-coloured samples or 0,2 °C for dark samples, report the average of these temperature readings, corrected for thermometer calibration errors, to the nearest 0,05 °C, as the aniline point or mixed aniline point.

9.2 If such a range is not obtained after five observations, repeat the test using fresh quantities of aniline and sample in a clean, dry apparatus; if consecutive temperature observations show a progressive change, or if the range of observations is greater than 0,16 °C for light-coloured samples, or 0,3 °C for dark samples, report the method as being inapplicable.

10 Precision

The precision of the method, as obtained by statistical examination of inter-laboratory test results is given in 10.1 and 10.2 below. The precision values, with the exception of those for clear, light-coloured samples, were not obtained from recent co-operative tests.

10.1 Repeatability, r

The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions on identical test material would, in the normal and correct operation of the test method, exceed the values below only in one case in twenty.

Aniline point of:

— clear light-coloured samples $r = 0{,}16$ °C

— moderately dark to very dark samples $r = 0{,}3$ °C

Mixed aniline point of:

— clear light-coloured samples $r = 0{,}16$ °C

— moderately dark to very dark samples $r = 0{,}3$ °C

10.2 Reproducibility, R

The difference between two single and independent results obtained by different operators working in different laboratories on nominally identical test material would, in the normal and correct operation of the test method, exceed the values below only in one case in twenty.

Aniline point of:

— clear light-coloured samples $R = 0{,}5$ °C

— moderately dark to very dark samples $R = 1{,}0$ °C

Mixed aniline point of:

— clear light-coloured samples $R = 0{,}7$ °C

— moderately dark to very dark samples $R = 1{,}0$ °C

11 Test report

The test report shall contain at least the following information:

a) a reference to this International Standard;

b) the type and complete identification of the product tested;

c) the result of the test (see clause 9);

d) any deviation, by agreement or otherwise, from the standard procedures specified;

e) the date of the test.

Annex A
(normative)

Method 1

A.1 Apparatus

The apparatus shown in figure A.1 shall be used. It consists of:

A.1.1 Test tube, approximately 25 mm in diameter and 150 mm in length, made of heat-resistant glass.

A.1.2 Jacket, approximately 37 mm to 42 mm in diameter and 175 mm in length, made of heat-resistant glass.

A.1.3 Stirrer, manually or mechanically operated, of soft iron wire approximately 2 mm in diameter, having a concentric ring of diameter approximately 19 mm at the bottom (see figure A.1). The length of the stirrer to the right-angle bend at the top of the stem shall be approximately 200 mm. The portion at right angles to the stem shall be approximately 55 mm long. A glass sleeve approximately 65 mm in length and of 3 mm inside diameter shall be used as a guide for the stirrer.

A.2 Procedure

A.2.1 Clean and dry the apparatus. Pipette 10 ml of aniline and 10 ml of the dried sample into the air-jacketed test tube fitted with the stirrer and thermometer. If the material is too viscous for pipetting, weigh to the nearest 0,01 g, a quantity of the sample corresponding to 10 ml ± 0,02 ml at room temperature. Centre the thermometer in the test tube such that the immersion mark is at the liquid level, ensuring that the mercury bulb does not touch the side of the tube. Centre the test tube in the jacket tube.

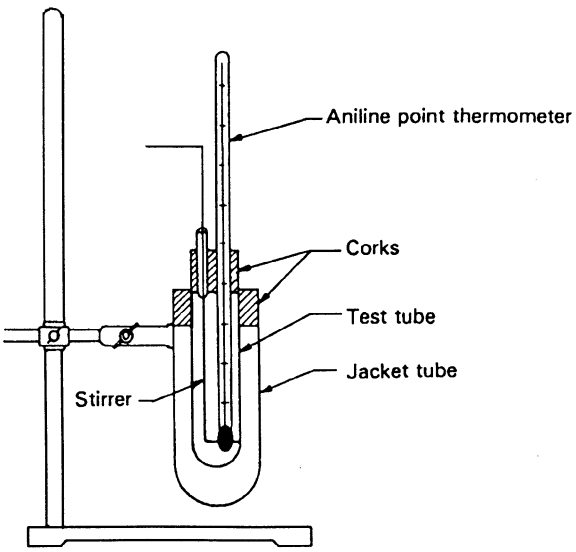

Figure A.1 — Aniline point apparatus

A.2.2 Stir the aniline-sample mixture rapidly, using a 50 mm stroke, avoiding the inclusion of air bubbles and, if necessary, heating at a rate of 1 °C/min to 3 °C/min until complete miscibility is obtained by applying heat directly to the jacket tube. If the aniline-sample mixture is completely miscible at room temperature, substitute a non-aqueous cooling bath for the heat source. Continue stirring and allow the mixture to cool slowly at a rate of 0,5 °C/min to 1 °C/min. Continue cooling to a temperature of 1 °C to 2 °C below the first appearance of turbidity and record as the aniline point the temperature, to the nearest 0,1 °C, at which the mixture suddenly becomes cloudy throughout (see note 11). This temperature, and not the temperature of the separation of small amounts of material, is the minimum equilibrium solution temperature.

NOTE 11 The true aniline point is characterized by a turbidity which increases sharply as the temperature is lowered.

A.2.3 Repeat the observation of the aniline point temperature by heating and cooling repeatedly until a report as specified in 9.1 can be made.

Annex B
(normative)

Method 2

B.1 Apparatus

B.1.1 Thin-film apparatus, made of heat-resistant glass and stainless steel, conforming to the dimensions given in figure B.1. Figure B.2 illustrates a suggested assembly.

B.2 Procedure

B.2.1 Clean and dry the apparatus. Pipette 10 ml of aniline and 10 ml of the dried sample into the tube fitted with the stirrer and thermometer. If the material is too viscous for pipetting, weigh, to the nearest 0,1 g, a quantity of the sample corresponding to 10 ml ± 0,02 ml at room temperature. Place the thermometer in the tube such that the contraction chamber is below the liquid level, ensuring that the mercury bulb does not touch the side of the tube.

Dimensions in millimetres

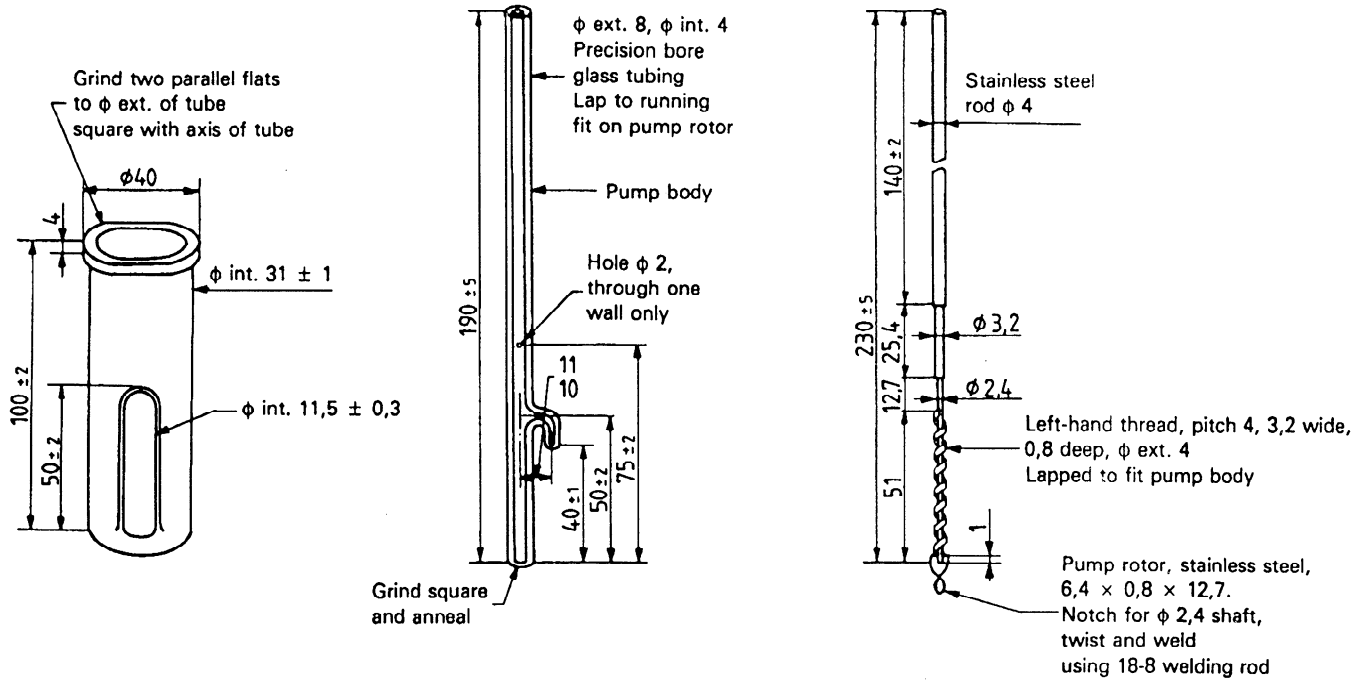

Figure B.1 — Details of aniline point thin-film apparatus

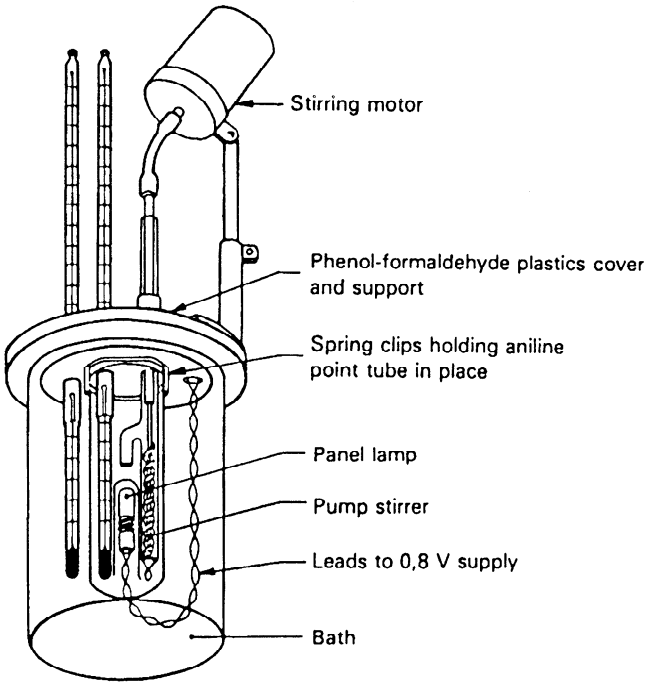

Figure B.2 — Assembly of thin-film apparatus

B.2.2 Adjust the speed of the pump to produce a continuous stream of the sample-aniline mixture in the form of a thin film flowing over the light well. With extremely dark samples, operate the pump slowly and lower it so that the delivery tube nearly touches the top of the light well, thus obtaining a film that is continuous and thin enough to permit observation of the aniline point. Adjust the voltage on the lamp until just enough light is given for the filament to be visible through the film. Raise the temperature of the mixture at a rate of 1 °C/min to 2 °C/min until the aniline point has just been passed, as denoted by definite, sudden brightening of the lamp filament and by the disappearance of the more or less opalescent condition of the film (see note 12). Discontinue heating and adjust the lamp voltage so that the filament appears clear and distinct but not uncomfortably bright to the eye. Adjust the temperature of the bath so that the sample-aniline mixture cools at a rate of 0,5 °C/min to 1,0 °C/min and note the appearance of the film and lamp filament. Record as the aniline point the temperature, to the nearest 0,1 °C, at which a second phase appears, as evidenced by the reappearance of the opalescent condition of the film (usually causing a halo to appear around the lamp filament) or by a sudden dimming of the lamp filament, or both.

NOTE 12 At temperatures above the aniline point, the edge of the lamp filament appears clear and distinct. At the aniline point temperature, a halo or haze forms around the filament, replacing the distinct lines of the filament edge with lines which appear cloudy or hazy. Further darkening of the cloud over the filament occurs at lower temperatures, but is not to be confused with the aniline point.

NOTE 13 For those users carrying out the test for the first time, the following procedure may be helpful. Make preliminary operational adjustments and tests, using a colourless aniline-sample mixture and observing the changes taking place in the body of the liquid and film. Carry out rough tests with dark oils to become familiar with the appearance of the film and light source as the mixture passes from the clear state above the aniline point to the opalescent state below. If the sample is such that there is difficulty in observing the exact point of the phase change, carry out experiments with the sample, using various intensities of light and paying particular attention to the appearance of the light in the immediate vicinity of the lamp filament.

B.2.3 Repeat the observation of the aniline point temperature by heating and cooling repeatedly until a report as specified in 9.1 can be made.