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

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

ISO 2977:1989

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Reference number
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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 approval before their acceptance as International Standards by the ISO Council. They are approved in accordance with ISO procedures requiring at least 75 % approval by the member bodies voting.

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

This second edition cancels and replaces the first edition (ISO 2977 : 1974), which has been revised to include two additional methods suitable for the determination of the aniline point of samples which may vaporize appreciably at this temperature.

Users should note that all International Standards undergo revision from time to time and that any reference made herein to any other International Standard implies its latest edition, unless otherwise stated.

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International Organization for Standardization
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Petroleum products and hydrocarbon solvents — Determination of aniline point and mixed aniline point

WARNING — Aniline should not be pipetted directly by mouth because of its extreme toxicity. Aniline is also toxic by absorption through the skin, even in very small quantities, and should be handled with great caution.

1 Scope and field of application

1.1 This International Standard specifies the test procedures for determining the aniline point of petroleum products and hydrocarbon solvents.

1.2 It also provides a procedure for determining the mixed aniline point of petroleum products and hydrocarbon solvents having aniline points below the temperature at which aniline will crystallize from the aniline-sample mixture.

1.3 Method 1 is suitable for transparent samples with an initial boiling point above room 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, is suitable for samples too dark for testing by method 1.

Methods 3 and 4 are for samples that may vaporize appreciably at the aniline point. Method 4 is particularly suitable where only small quantities of sample are available.

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

1.4 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 and paraffins the highest values.

Cycloparaffins and olefins exhibit values that lie between those for paraffins and aromatics.

In a homologous series, the aniline points increase with increasing molecular weight.

Although it occasionally is used in combination with other physical properties in correlative methods for hydrocarbon analysis, the aniline point is most often used to provide an estimate of the aromatic hydrocarbon content of mixtures.

2 References

ISO 2049, *Petroleum products — Determination of colour.*

ISO 3838, *Crude petroleum and liquid or solid petroleum products — Determination of density or relative density — Capillary-stoppered pyknometer and graduated bicapillary pyknometer methods.*

ISO 5163, *Motor and aviation-type fuels — Determination of knock characteristics — Motor method.*

ISO 5661, *Petroleum products — Hydrocarbon liquids — Determination of refractive index.*

ASTM D 41015, *Standard test method for freezing points of high-purity hydrocarbons.*

3 Definitions

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

5.1 Aniline

Dry aniline of analytical reagent quality over potassium hydroxide pellets, decant and distill fresh on the day of use, discarding the first and last 10 %. Aniline thus prepared shall give an aniline point of $69,3 \pm 0,2$ °C as determined from the average of two independent tests having a difference of not more than 0,1 °C when tested with heptane in accordance with 8.1.

As an alternative to distilling the aniline on the day of use, the aniline may be distilled as described above and the distillate collected 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 must be taken to avoid contamination by atmospheric moisture (see note to 6.2). Experience shows that, under these conditions, the aniline should remain unchanged for at least six months.

NOTE — For routine purposes, the distillation process is not mandatory provided the aniline meets the requirements of the test with heptane.

The aniline point of aniline and heptane determined with automatic apparatus shall be $69,3 \pm 0,2$ °C when corrected using the formula given in E.2.1.

5.2 Calcium sulfate, anhydrous, or sodium sulfate, anhydrous.

5.3 Heptane, conforming to the following requirements as determined by the specified or equivalent methods.

Motor octane number (ISO 5163)	$0,0 \pm 0,2$
Density at 20 °C (ISO 3838)	$0,683\ 80 \pm 0,000\ 15$ g/ml
Refractive index n_D^{20} (ISO 5661)	$1,387\ 70 \pm 0,000\ 15$
Freezing point (ANSI/ASTM D 1015) ¹⁾	-90,710 °C min.
Distillation temperature ²⁾ : 50 % recovered (at 101,3 kPa)	$98,427 \pm 0,025$ °C
differential, 80 % recovered minus 20 % recovered	0,020 °C max.

1) 1984 edition.

2) For equipment and method used, see *Journal of Research*, U.S. National Bureau of Standards, Volume 44, No. 3, 1950, pp. 309 and 310 (RP 2079).

6 Apparatus

6.1 For details of the aniline point apparatus required for each method see:

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 — Alternative apparatus may be used, such as the U-tube method for dark oils, provided it has been shown to give results of the same precision and accuracy as those described in the annexes.

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 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. For example, the aniline point of the heptane reagent as measured with dry aniline is increased, from that specified, by approximately 0,5 °C if the aniline reagent contains 0,1 % of 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 Aniline point thermometers, partial immersion type, having ranges of -38 to +42 °C, 25 to 105 °C and 90 to 170 °C, and conforming to the specifications in the table.

6.4 Pipettes, with capacities of $10 \pm 0,04$ ml and $5 \pm 0,02$ ml (see note). Provide a rubber suction bulb for use with the pipettes when measuring out aniline.

NOTE — The 10 ml and 5 ml one-mark pipettes specified in ISO 648, Class B, and ISO 648, Class A, respectively, are suitable.

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, to guard against eye splashes.

6.7 Plastic gloves, impervious to aniline.

7 Preparation of the test sample

Dry the sample by shaking vigorously for 3 to 5 min with about 10 % (V/V) of a suitable drying agent such as anhydrous calcium sulfate or anhydrous sodium sulfate. Reduce the

viscosity of viscous samples by warming to a temperature below that which would cause the loss of light ends or the dehydration of the drying agent.

Remove any suspended drying agent by centrifugation or filtration. Heat samples containing separated wax until they are homogenous and keep heated during filtration or centrifugation to ensure no separation of wax. When suspended water is visibly present and when the sample material is known to dissolve less than 0,03 % (m/m) of water, centrifuging for the removal of suspended water is an acceptable procedure.

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 colour, as determined in accordance with 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. It is suitable for 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 colour, as determined by ISO 2049, having initial boiling points sufficiently low to give incorrect aniline point readings by method 1; for example, aviation gasoline.

— Method 4: described in detail in annex D, is applicable to the same type of sample as method 3. It is particularly useful when only limited quantities of sample are available.

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

8.2 Procedure for 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 (see warning), 5 ml of the sample and 5 ml of heptane into a clean, dry apparatus. Determine the aniline point of the mixture by method 1 or 2 as described in annex A or B.

9 Expression of results

9.1 Recording of results

9.1.1 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 observations, corrected for thermometer calibration errors, to the nearest 0,05 °C, as the aniline point.

9.1.2 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.

Table — Thermometer specifications

Range	−38 to +42 °C	25 to 105 °C	90 to 170 °C
Immersion	50 mm	50 mm	50 mm
Graduation at each	0,2 °C	0,2 °C	0,2 °C
Longer lines at each	1 °C	1 °C	1 °C
Figured at each	2 °C	2 °C	2 °C
Scale error, not to exceed	0,2 °C	0,2 °C	0,2 °C
Expansion chamber permitting heating to	100 °C	150 °C	220 °C
Overall length	420 ± 5 mm	420 ± 5 mm	420 ± 5 mm
Stem diameter	6 to 7 mm	6 to 7 mm	6 to 7 mm
Bulb length	10 to 20 mm	10 to 20 mm	10 to 20 mm
Bulb diameter	5 to 6 mm	5 to 6 mm	5 to 6 mm
Distance from bottom of bulb to line at	−35 °C: 112 to 124 mm	25 °C: 106 to 120 mm	90 °C: 101 to 115 mm
Distance from bottom of bulb to line at	40 °C: 352 to 377 mm	105 °C: 358 to 379 mm	170 °C: 358 to 384 mm
Distance from bottom of bulb to top of contraction chamber	—	—	35 mm max.

9.2 Precision¹⁾

The precision (i.e. repeatability and reproducibility) of the method, as obtained by statistical examination of interlaboratory test results, is as follows:

9.2.1 Repeatability

The difference between successive test results obtained by the same operator with the same apparatus under constant operating conditions and on identical test material will, in the long run, in the normal and correct operation of the test method, exceed the values shown below only in one case in 20.

	Repeatability
Aniline point of:	
— clear light-coloured samples	0,16 °C
— moderately dark to very dark samples	0,3 °C ²⁾
Mixed aniline point of:	
— clear light-coloured samples	0,16 °C ²⁾
— moderately dark to very dark samples	0,3 °C ²⁾

9.2.2 Reproducibility

The difference between two single and independent results obtained by different operators working in different labora-

tories on identical test material will in the long run, in the normal and correct operation of the test method, exceed the values shown below only in one case in 20.

	Reproducibility
Aniline point of:	
— clear light-coloured samples	0,7 °C
— moderately dark to very dark samples	1,0 °C ²⁾
Mixed aniline point of:	
— clear light-coloured samples	0,7 °C
— moderately dark to very dark samples	1,0 °C

10 Test report

The test report shall contain at least the following information:

- a) the type and identification of the product tested;
- b) a reference to this International Standard;
- c) the result of the test (see 9.1);
- d) any deviation, by agreement or otherwise, from the procedure specified;
- e) the date of the test.

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1) The precision of the method for the determination of the aniline point of moderately dark to very dark samples and the precision of the method for the determination of the mixed aniline point were not determined from recent co-operative tests. Co-operative tests are being carried out. It is believed that the results of these tests will contribute towards obtaining reliable values.

2) Not determined from recent co-operative tests.

Annex A

(This annex forms an integral part of the Standard.)

Method 1

A.1 Apparatus

The apparatus shown in figure 1 shall be used, consisting of the following:

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 to 42 mm in diameter and 175 mm in length, made of heat-resistant glass.

A.1.3 Stirrer, manually operated, of soft iron wire approximately 2 mm in diameter, having a concentric ring of diameter approximately 19 mm at the bottom (see figure 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. Any suitable mechanical device for operating the stirrer as specified is an approved alternative to manual operation.

jacketed test tube fitted with 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 at room temperature. Centre the thermometer in the test tube so that the immersion mark is at the liquid level, making sure that the mercury bulb does not touch the side of the tube. Centre the test tube in the jacket tube.

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 approximately 1 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 to 1 °C/min. Continue cooling to a temperature of 1 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). This temperature, and not the temperature of the separation of small amounts of material, is the minimum equilibrium solution temperature.

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

A.2 Procedure

A.2.1 Clean and dry the apparatus. Pipette 10 ml of aniline (see warning) and 10 ml of the dried sample into the air-

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

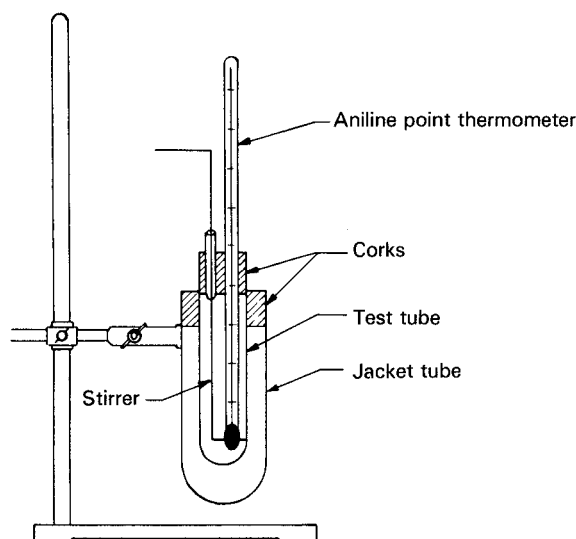


Figure 1 – Aniline point apparatus

Annex B

(This annex forms an integral part of the Standard.)

Method 2

B.1 Apparatus

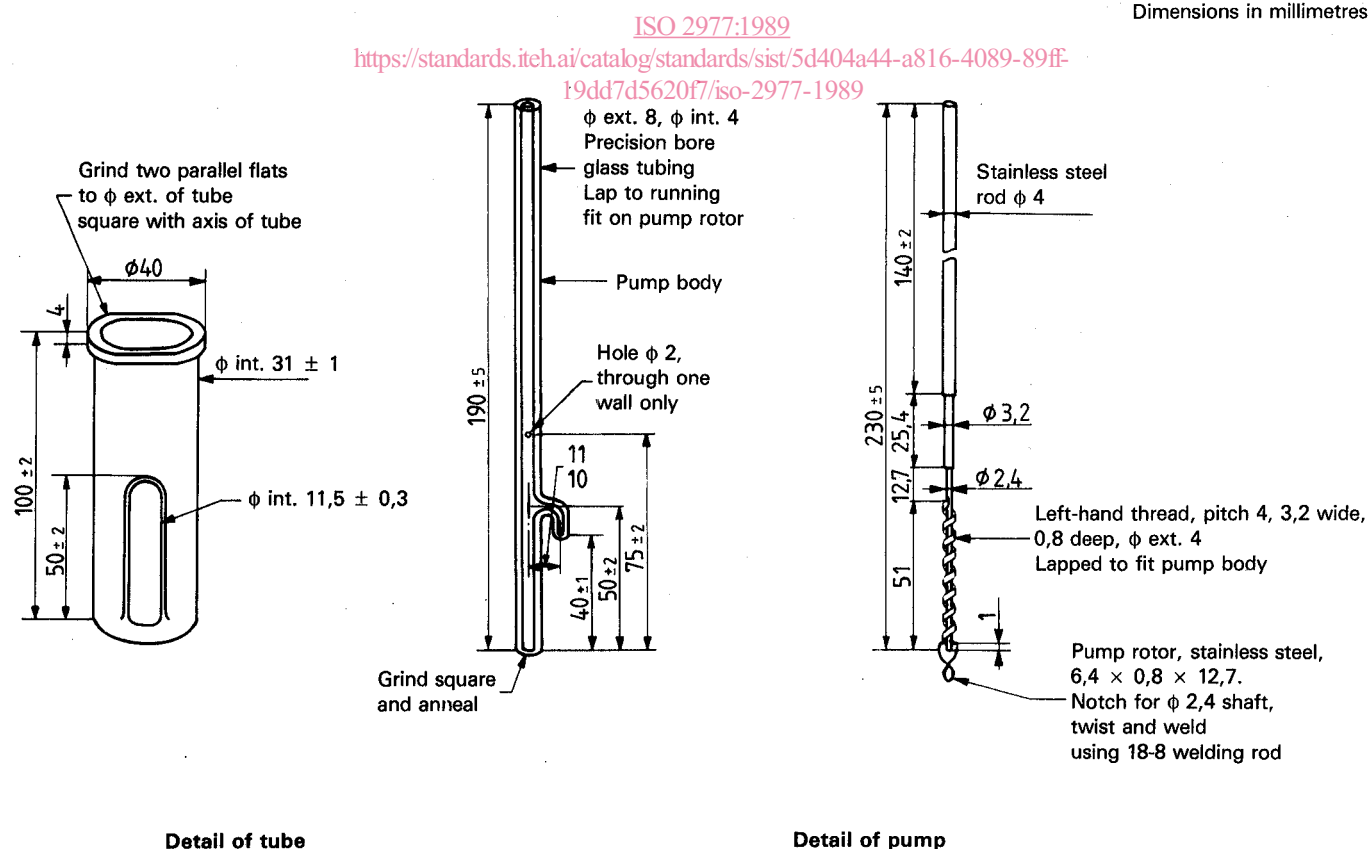
Thin-film apparatus, made of heat-resistant glass and stainless steel, conforming to the dimensions given in figure 2. A suggested assembly is shown in figure 3.

B.2 Procedure

B.2.1 Clean and dry the apparatus. Pipette 10 ml of aniline (see warning) and 10 ml of the dried sample into the tube fitted with stirrer and thermometer. If the material is too viscous for pipetting, weigh, to the nearest 0,01 g, a quantity of sample corresponding to 10 ml at room temperature. Place the thermometer in the tube so that the contraction chamber is below the liquid level, making sure that the mercury bulb does not touch the side of the tube.

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 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). 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 to 1,0 °C/min and note the appearance of the film and light filament. Record as the aniline point the temperature, to the nearest 0,1 °C, at which a second phase appears, as evidenced

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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.

At temperatures above the aniline point, the edge of the light 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 — For those making the test for the first time, the following procedure may be helpful. Make preliminary operational adjustments

and tests, using a colourless sample-aniline mixture and observing the changes taking place in the body of the liquid and film. Make 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, make 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.

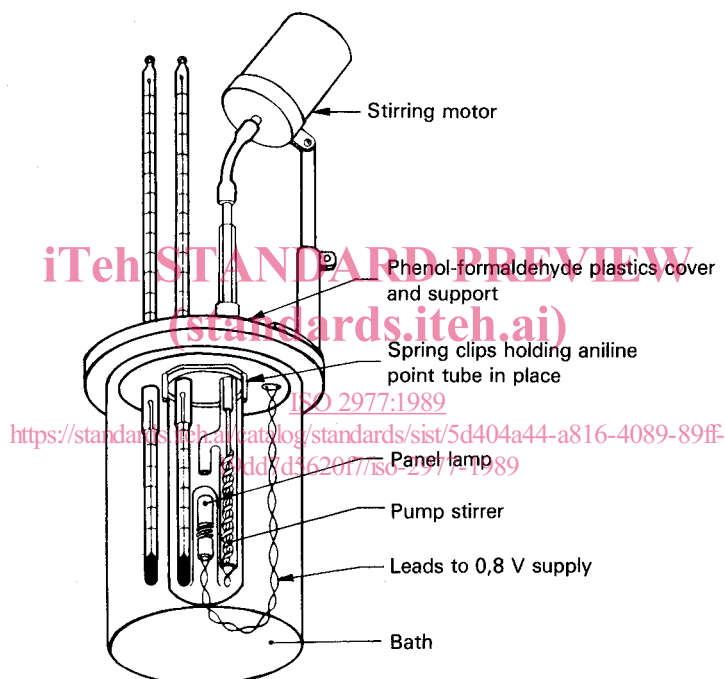


Figure 3 — Assembly of thin-film apparatus