INTERNATIONAL STANDARD ISO 3840

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Petroleum distillates — Determination of olefinic plus aromatic hydrocarbons content

Distillats du pétrole — Détermination de la teneur en hydrocarbures oléfiniques et aromatiques

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FOREWORD

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International Standard ISO 3840 was drawn up by Technical Committee ISO/TC 28, *Petroleum products*, and was circulated to the Member Bodies in August 1975.

It has been approved by the Member Bodies of the following countries :

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Petroleum distillates — Determination of olefinic plus aromatic hydrocarbons content

1 SCOPE AND FIELD OF APPLICATION

1.1 This International Standard specifies a method for the determination of the olefinic plus aromatic hydrocarbons content of gasolines, naphthas, kerosines, and other petroleum distillates which are substantially free from butanes and butenes and which have a 90 % recovery point not over 315 °C when determined in accordance with ISO 3405. The method is not directly applicable to determinations above 98,5 % (*V/V*) olefins plus aromatics if a 10 ml test portion is used, nor above 97,0 % (*V/V*) if a 5 ml test portion is used.

NOTE — *For best results, depentanized test portions should be used.*

1.2 The results obtained by the prescribed procedure represent all acid-absorbable materials in the test portion. These, besides aromatic and olefinic hydrocarbons, comprise a variable portion of compounds containing sulphur, nitrogen, oxygen or combinations thereof. Hence, in the interpretation of results, the presence or absence of appreciable proportions of non-hydrocarbon materials should be considered. In petroleum distillates, the proportion of non-hydrocarbon materials is generally low enough for the acid absorption to be taken as a measure of total olefinic plus aromatic hydrocarbons and, in the absence of olefins (bromine number less than 1), as a measure of aromatics, after an empirical correction for co-absorbed saturates has been applied. This solubility correction is subject to variation depending on the material analysed. Also, the contraction of volume may include certain minor effects such as the volume change which occurs when hydrocarbons of different types are mixed; these effects are usually considerably less than the precision of the method, and, therefore, are negligible.

2 REFERENCES

ISO 3405, *Petroleum products — Determination of distillation characteristics.*

ISO 3839, *Petroleum distillates and commercial aliphatic olefins — Determination of bromine number — Electrometric method.*[1]

3 PRINCIPLE

A measured volume of the test portion, contained in a specified flask, is shaken in a prescribed manner, at the temperature of melting ice, with a solution of phosphorus(V) oxide in concentrated sulphuric acid. After the test portion has reacted, the flask is centrifuged to separate the phases and the unreacted portion is measured.

4 REAGENTS

During the analysis, use only reagents of recognized analytical grade, and only distilled water or water of equivalent purity.

4.1 Sulphonation acid.

Prepare (CAUTION, see below) a mixture containing 70 % (*m/m*) of the sulphuric acid (H_2SO_4) (4.2) and 30 % (*m/m*) of phosphorus(V) oxide (P_2O_5). This is done conveniently as follows : add 500 g of phosphorus(V) oxide to 633 ± 5 ml of the sulphuric acid (4.2) contained in a conical flask. Stir with a glass rod or mechanical stirrer until only a small amount of residue remains, cover with a beaker while the mixture cools to room temperature, and decant into acid bottles provided with a closure which will protect the reagent from dilution with moisture from the atmosphere. Prepare the reagent as rapidly as possible to minimize absorption of moisture from the air during preparation.

CAUTION — While preparing the reagent, the operator should wear the face mask or safety goggles (5.5) and place the flask in a basin.

4.2 Sulphuric acid, 95 to 96 % (*m/m*).

5 APPARATUS

5.1 Standard and precision sulphonation flasks, of heat-resistant glass, well annealed, and meeting the requirements shown in figures 1, 2 and 3.

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[1] At present at the stage of draft.

Dimensions in millimetres

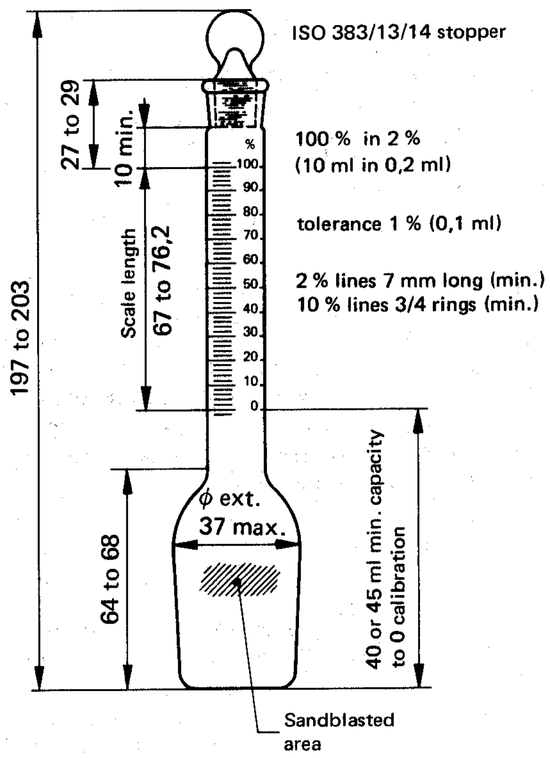

FIGURE 1 – **Standard sulphonation flask**

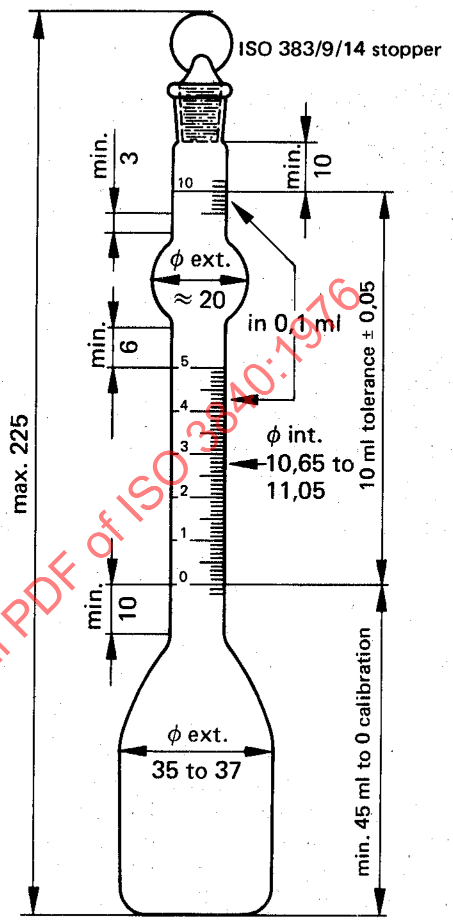

FIGURE 2 – **Precision sulphonation flask for 10 ml test portion**

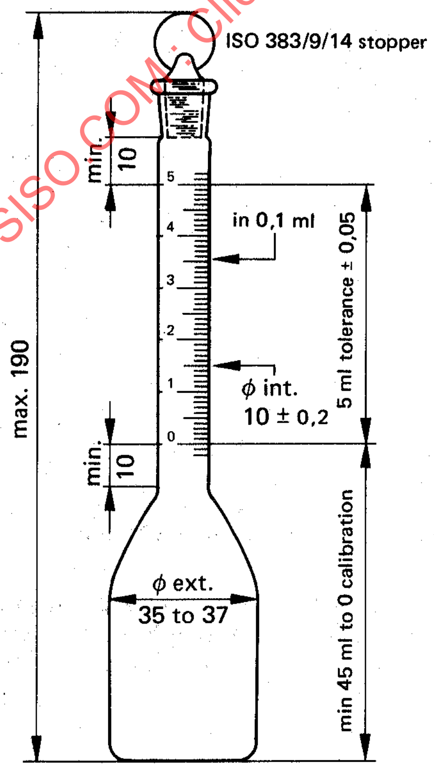

FIGURE 3 – **Precision sulphonation flask for 5 ml test portion**

5.2 Pipettes, of capacity 5 and 10 ml, calibrated to deliver respectively 5,0 ± 0,02 ml and 10,0 ± 0,04 ml of water at 20 °C.

5.3 Centrifuge, capable of whirling two or more filled sulphonation flasks (5.1) at a speed that can be controlled to give a relative centrifugal force (rcf) of between 250 and 400 *g* at the bottom of the flasks. The revolving head, trunnion rings and trunnion cups, including the cushions, shall be soundly constructed to withstand the maximum centrifugal force capable of being delivered by the power source. The trunnion cups and cushions shall firmly support the flasks, and the construction shall be such that no part of the neck of the flask touches the centrifuge head when the centrifuge is in motion. The centrifuge shall be enclosed by a metal shield or case strong enough to eliminate danger if any breakage occurs.

Calculate the speed of the rotating head, in revolutions per minute, from the formula

$$1\,336\sqrt{\frac{\mathrm{rcf}}{d}}$$

where

rcf is the relative centrifugal force;

d is the diameter of swing, in millimetres, measured between bottoms of opposite flasks when in rotating position.

5.4 Mechanical shaker and ice-water bath.

Any type of mechanical shaker may be used provided that it gives accurate results with the test mixtures (clauses 6 and 7). Shaking can also be done by hand if all precautions are observed.

Annex A gives the design and procedure for a suitable shaking machine with a stationary ice-water bath. Annex B describes a shaking machine using individual ice-water baths. Annex C gives a suitable procedure using hand shaking.

5.5 Face mask or safety goggles, for the operator.

THE USE OF THIS PROTECTIVE EQUIPMENT IS A SAFEGUARD AGAINST POTENTIAL HAZARDS IN PROCEDURES WITH MATERIALS AND EQUIPMENT DESCRIBED IN : 4.1; 6.1; 6.2 7.1; 7.2; 7.3; 7.4; 7.5; annex A, annex B; annex C.

6 DETERMINATION OF SHAKING TIME USING TEST MIXTURES

Time of shaking to the nearest minute must be established for each shaking machine according to the procedure given in clause 7. This is done by determining the minimum time necessary to achieve complete sulphonation with test mixture A, without causing over-sulphonation using test mixture B.

6.1 Test mixture A for complete sulphonation

This test mixture is a 40 ± 0,1 % (*V*/*V*) blend of benzene in isooctane. This blend is difficult to sulphonate completely. The temperature of the test mixture should not be below 0 °C. Purify the isooctane by percolating 200 ml through 50 g of activated silica gel packed tightly in a 10 mm diameter column. Prepare the mixture by placing 60 ± 0,1 ml of isooctane in a 100 ml volumetric flask and dilute to 100 ml using pure benzene. The aromatic content of this test mixture, determined by this method, should be 40 ± 1 % (*V*/*V*), and the mixture after sulphonation treatment and neutralization with a pellet of potassium hydroxide (KOH) should have a refractive index, n_D^{20}, within 0,000 2 of that of the original isooctane.

NOTE — Pipetting isooctane into the flask first and filling to the mark with benzene is specified since benzene expands on dilution with a saturated hydrocarbon. The mixture would contain too little saturated hydrocarbon if the benzene were put in the flask first. Expansion with toluene is less, so this point is not important in preparing test mixture B.

6.2 Test mixture B for over-sulphonation

This mixture is a 30 ± 0,1 % (*V*/*V*) blend of toluene in methylcyclohexane. This mixture is particularly susceptible to over-sulphonation if the temperature goes above 2 °C. Purify the methylcyclohexane by percolation through silica gel (see 6.1). Prepare this blend by placing 30 ± 0,1 ml of toluene in a 100 ml volumetric flask and dilute to 100 ml using methylcyclohexane. The aromatic content of this mixture as determined by this method should be 30 ± 1 % (*V*/*V*).

7 PROCEDURE

7.1 Introduce 25 ± 1 ml of the sulphonation acid (4.1) into either the standard or precision 10 ml sulphonation flask (5.1) (depending on the desired precision) and close the flask with the glass stopper. Place the flask in its holder in the mechanical shaker (5.4). Flasks held in a vertical position must be submerged at least to the 20 % (2 ml) mark in the ice-water bath (5.4) (0 to 2 °C). Flasks held in the oblique position, i.e. more than 10° from the vertical, must be immersed above the top graduation in an ice pack or ice water (see note). Keep the flask in the ice pack or ice water for at least 10 min before adding the test portion. CAUTION — At this point, the operator should put on the face mask or safety goggles (5.5).

Record the temperature of the test portion.

NOTE — One suitable form of ice pack for the inclined flask is shown in figure 9.

7.2 By means of a pipette (5.2), add 10 ml of the test portion at room temperature to the sulphonation acid, allowing the test portion to run slowly down the walls of the flask in order to minimize mixing with the acid (see note 1). Stopper the flask (CAUTION, see below) and secure it in place in the mechanical shaker by means of the clamp (see note 2).

CAUTION — Excessive pressure, which may develop in blends of high olefin content, can cause breakage if the stopper is fastened rigidly to the flask. Therefore, it is important that the stopper be fastened in such a way that it can move slightly and thus release the pressure. Either a sponge rubber disk placed between the stopper and the clamp, or a spring tension clamp, is satisfactory.

NOTES

1 Highly volatile test samples, which bubble in the pipette at room temperature, must be cooled in the ice-water bath and transferred to the sulphonation flask by means of a cooled pipette.

2 If a mechanical shaker is not available and the bromine number of the test sample is not over 20, as determined in accordance with ISO 3839, it is possible to obtain satisfactory results by manual shaking provided the instructions in annex C are rigidly adhered to.

7.3 Allow the flask to stand for 10 min after introduction of the test portion; then operate the mechanical shaker (see note 2 to 7.2) for 5 min at a rate such that it makes two or three cycles (a cycle consists of a forward and a return stroke) every 10 s. Then shake the flask continuously for as many minutes as were determined necessary to obtain good results with the test mixtures for each mechanical shaker (see clause 6 and note 2 to 7.2). (CAUTION, see below.) In general, 10 min shaking is adequate using the mechanical shaker described in annex A and B, or hand shaking (annex C).

CAUTION — Put on the face mask or safety goggles before proceeding with the next step in the procedure.

7.4 Vent the flask momentarily while still in the ice-water bath, then immediately remove it from the bath and centrifuge it for 3 min at a speed calculated from the formula given in 5.3 to give a relative centrifugal force (rcf) of between 250 and 400 at the bottom of the flask. Pour the sulphuric acid (4.2) down the side of the neck of the flask until the hydrocarbon layer is entirely within the graduated portion of the neck, then centrifuge for an additional 5 min.

7.5 Bring the acid-hydrocarbon mixture to a temperature within 1 °C (see note) of that at which the test portion was measured by immersing the sulphonation flask for 15 min in water maintained at the desired temperature. Wipe the outside of the flask and place it in front of a plain, non-reflective, white or light-coloured background illuminated by a diffused light. Read the scale to the nearest quarter division (that is, to the nearest 0,05 ml) on a standard flask, and to the nearest 0,2 division (that is, to the nearest 0,02 ml) on a precision flask, at the upper and lower levels on the hydrocarbon layer as represented by points A and B in figure 4. Point A denotes the nearly flat boundary between the clear hydrocarbon and the darkest part of the air-liquid interface and point B refers to the lower and more distinct interface between the clear hydrocarbon and the sulphonation acid. (In figure 4 these readings are, respectively, 9,4 and 7,15 ml.)

NOTE — A temperature change of 1 °C corresponds to a volume change of about 0,1 %.

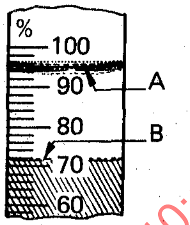

FIGURE 4 — **Illustration of method for reading volume of unreacted hydrocarbon in sulphonation flask** (see 7.5)

7.6 If the residual volume is less than 5 ml and the bromine number of the test sample is over 35 when using ISO 3839, make a second determination using only 5 ml of test sample. For such test portions, the prescribed centrifuging may not be sufficient to separate completely all unreacted hydrocarbons from the acid layer. Therefore, recentrifuge the flask after the volume reading and reread the volume. If the second volume reading differs from the first by more than 0,02 ml on the precision flask or 0,05 ml on the standard flask, repeat centrifuging and reading until two successive volume readings agree within the above limits. If, after four centrifugings, the agreement of successive readings is still outside the above limits, the applicability of the test and the results obtained are subject to doubt.

7.7 Check the shaking time necessary to give results accurate within ± 1 % on each test mixture daily until concordant results are obtained for 3 consecutive days. Then check once a week. Repeat this test sequence for each new operator, mechanical shaker, or bath of sulphonation acid.

NOTE — For good results with this method, careful control of both the conditions of shaking and the temperature of the reaction mixture is essential. Under-sulphonation can be corrected by more vigorous shaking; over-sulphonation usually results from too high a temperature. If the inclined position of the flask is used, the neck of the flask needs to be packed in ice, otherwise the sulphonation acid may become too warm by being splashed up in the neck of the flask.

8 EXPRESSION OF RESULTS

Calculate the olefinic plus aromatic hydrocarbons content (O + A), as a percentage by volume, from the formula

$$\frac{(V_1 - V_0)\,100}{V_1} - \frac{10\,C}{V_1}$$

where

V_0 is the volume, in millilitres, of the residue;

V_1 is the volume, in millilitres of the test portion;

C is the correction, in millilitres, for the solubility of the residue in the acid (see table).

TABLE – **Solubility corrections**

$(V_1 - V_0)\ 100/V_1$	C
0 to 5,0	0,7
5,1 to 20,0	0,8
20,1 to 35,0	0,9
35,1 to 45,0	1,0
45,1 to 60,0	1,1
60,1 to 70,0	1,2
70,1 to 85,0	1,3
85,1 to 100,0	1,4

9 PRECISION

The precision of the method, as obtained by statistical examination of inter-laboratory test results, is as follows :

9.1 Repeatability

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

Standard flask : 1,3 %
Precision flask : 0,6 %

9.2 Reproducibility

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

Standard flask : 2,6 %
Precision flask : 2,0 %

NOTE – When 5 ml test portions are used, the percentage differences to be expected are approximately twice as great.

10 TEST REPORT

Report the result as olefinic plus aromatic hydrocarbons content and make reference to this International Standard.

When results are obtained with both 5 and 10 ml test portions and differ from each other by not more than 1,5 %, report the values obtained with the 10 ml test portion; if the two values differ by more than 1,5 %, report the values obtained with the 5 ml test portion.

ANNEX A

SHAKING MACHINE WITH STATIONARY ICE-WATER BATH

A.1 Figure 5 shows a commercial shaking machine with a stationary ice-water bath and reciprocating flask holders designed for this method. Ice is packed in two compartments made of open-mesh screen so that the bottles can be shaken in water at a temperature between 0 and 2 °C which is free from floating ice.

A.2 The shaking apparatus, with the cover and one of the screen ice containers removed to illustrate the mounting of the flask carrier on the reciprocating part of the machine, is shown in figure 6. The carrier assembly shown holds eight flasks, supported in pairs by clamps which screw down firmly over the tops of the flasks as shown in figure 7. The clamp consists of two inverted cups, each containing a sponge rubber disk, mounted on a plate. The cups cover the stoppers and upper necks of the flasks and serve as relief valves, should excessive pressures develop in the flasks during shaking.

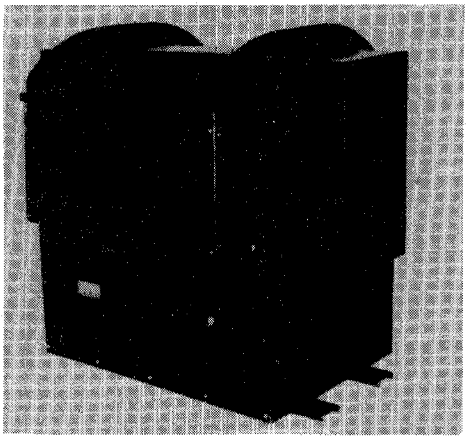

FIGURE 5 — **Shaking machine with stationary ice-water bath**

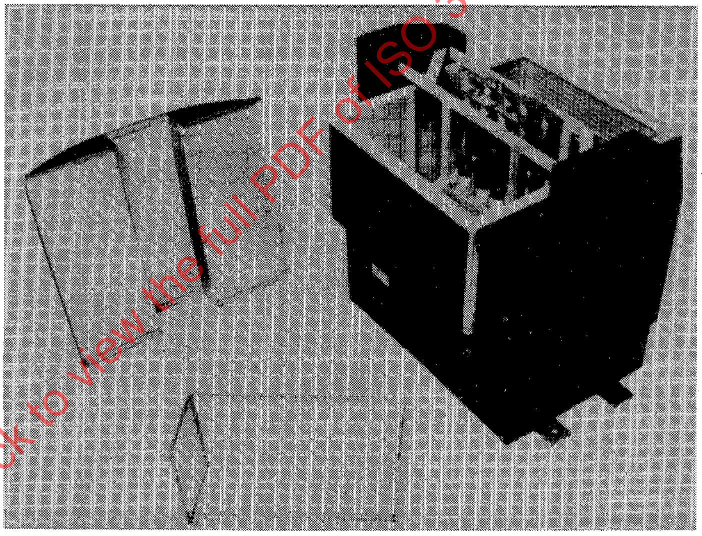

FIGURE 6 — **Shaking machine with ice-water bath removed**

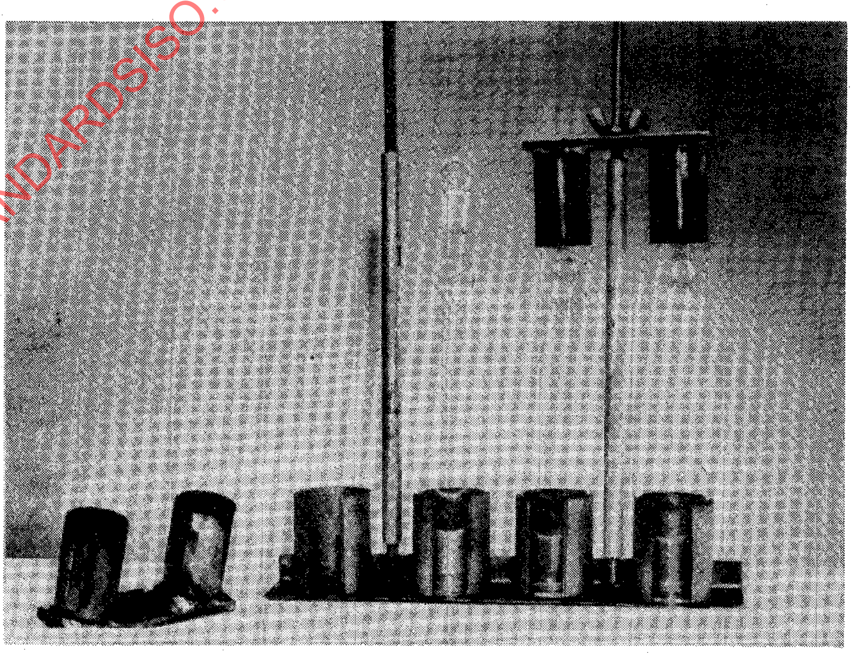

FIGURE 7 — **Sulphonation flask holder and clamp for shaking machine**

ANNEX B

SHAKING MACHINE FOR INDIVIDUAL ICE-WATER BATH

B.1 Figure 8 shows a shaking machine with a carriage fitted with a wooden block and clamp arrangement for holding four cooling jars rigidly at an angle of 45° and pointing in the direction of motion. These cooling jars provide a means for shaking sulphonation flasks which are immersed in an ice-water slurry. A suitable jar may be made by drilling a hole of appropriate size through the plastics lid of a 500 ml capacity chemical reagent jar, as shown in figure 9. The neck of the flask extends through this opening and is cushioned by a short piece of rubber tubing. The stopper of the flask is held in place by a modified Sligh oxidation flask clamp, the head of the stopper being ground, if necessary, to permit use of this clamp.

B.2 The stoppered sulphonation flask containing the acid is placed in the empty cooling jar which is then packed with finely crushed ice, keeping the flask properly centred. The jar is completely filled with water to displace all the air, and the lid screwed on the jar. After the sample is pipetted into the flask, the stopper is clamped in position. It is important that spring tension of the modified Sligh clamp (see figure 9) is adjusted so as to allow a slight movement of the stopper of the sulphonation flask under pressures that may develop when shaking highly olefinic samples. The apparatus is covered with a cloth during shaking to catch any spray released if excessive pressures develop.

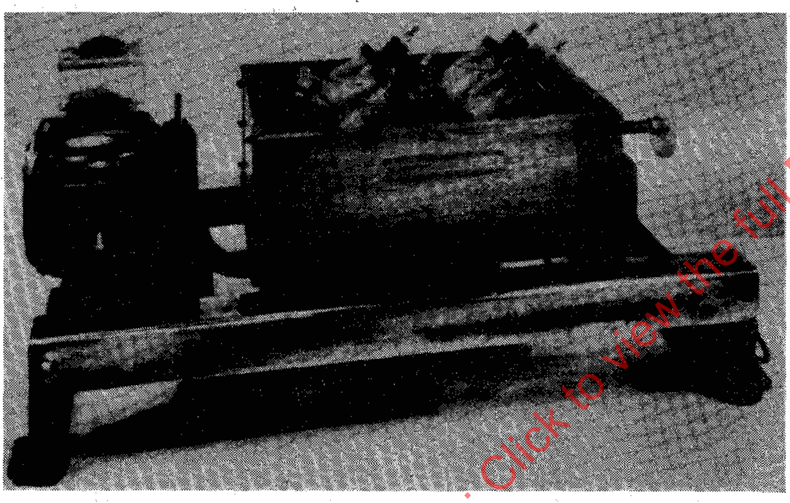

FIGURE 8 – **Arrangement for shaking individual sulphonation flasks**

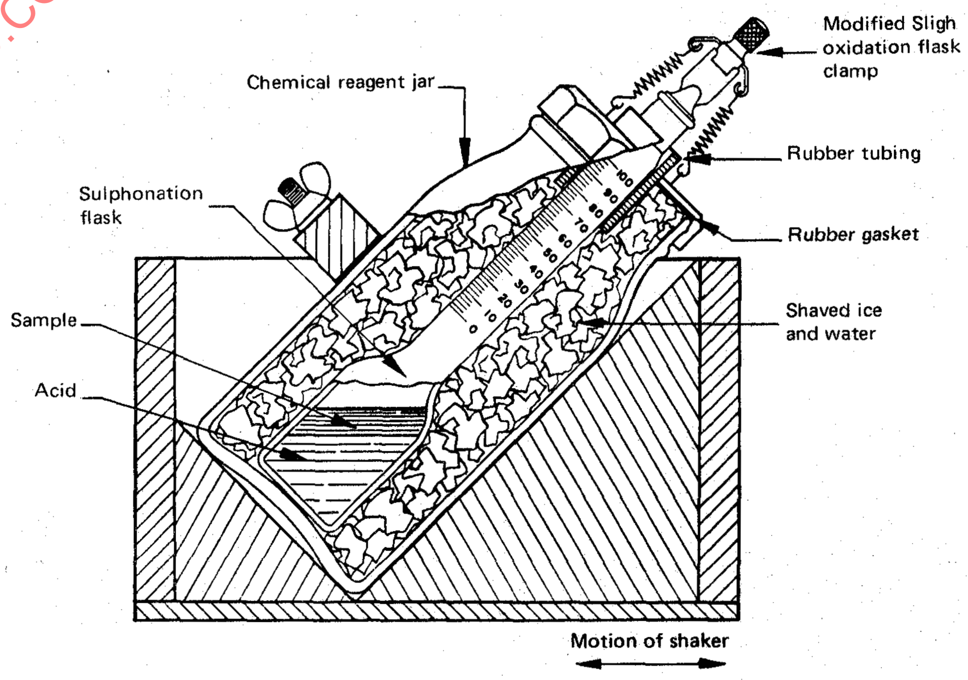

FIGURE 9 – **Ice-water bath and clamp arrangement for individual sulphonation flask**