International Standard 4327

INTERNATIONAL ORGANIZATION FOR STANDARDIZATION•МЕЖДУНАРОДНАЯ ОРГАНИЗАЦИЯ ПО СТАНДАРТИЗАЦИИ•ORGANISATION INTERNATIONALE DE NORMALISATION

Non-ionic surface active agents — Polyalkoxylated derivatives — Determination of hydroxyl value — Phthalic anhydride method

Agents de surface non ioniques — Dérivés polyoxyalkylénés — Détermination de l'indice d'hydroxyle — Méthode à l'anhydride phtalique

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FOREWORD

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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.

International Standard ISO 4327 was developed by Technical Committee ISO/TC 91, *Surface active agents*, and was circulated to the member bodies in June 1976.

It has been approved by the member bodies of the following countries :

Australia	Ireland	Romania
Austria	Japan	South Africa, Rep. of
Belgium	Korea, Rep. of	Switzerland
Brazil	Mexico	Turkey
France	Netherlands	United Kingdom
Germany, F.R.	New Zealand	
India	Poland	

The member bodies of the following countries expressed disapproval of the document on technical grounds :

Chile
Spain

Printed in Switzerland

Non-ionic surface active agents — Polyalkoxylated derivatives — Determination of hydroxyl value — Phthalic anhydride method

0 INTRODUCTION

The classical method for the determination of the hydroxyl value described in this International Standard requires, because of the toxic effects of pyridine and phthalic anhydride, that all handling and the titration be conducted under a well ventilated fume hood. However, annex C provides a procedure using a special apparatus which reduces the danger due to pyridine and phthalic anhydride.

1 SCOPE

This International Standard specifies a method for the determination of the hydroxyl value of polyalkoxylated condensates by esterification of the hydroxyl groups with phthalic anhydride.

2 FIELD OF APPLICATION

This method is applicable to the determination of the hydroxyl groups of polyalkoxylated condensates of aliphatic and alicyclic compounds (in particular, of ethylene oxide, propylene oxide or mixed adducts of primary and secondary fatty alcohols, alkylphenols and fatty acids, and can be used for the determination of hydroxyl values from 10 to 1 000.

However, certain substances present in these materials may react with the phthalic anhydride or with the standard volumetric sodium hydroxide solution used and consequently falsify the results.

The possible interferences are detailed below :

— Primary and secondary amines and amides, tertiary alcohols, thiols and epoxides undergo side reactions which affect the accuracy of the method.

— Long-chain fatty acids and esters may interfere by forming anhydrides which are more stable than phthalic anhydride and are not completely decomposed at the end of the method.

— Other free acids interfere by reacting with the standard volumetric sodium hydroxide solution; bases, including some tertiary amines, interfere by reacting with the phthalic acid produced. In these cases a correction may be made for the acidity or alkalinity (see ISO 4314).

Although epoxides interfere, the method may still be used if the epoxides can be eliminated, without altering the hydroxyl value, by cold vacuum distillation.

The presence of water in the sample is revealed by reaction with the phthalic anhydride, but the method may nevertheless be used without risk if the precautions described in the procedure are followed.

3 REFERENCES

ISO 607, *Surface active agents and detergents — Methods of sample division.*[1)]

ISO 1392, *Determination of crystallizing point — General method.*

ISO 2211, *Liquid chemical products — Measurement of colour in Hazen units (platinum-cobalt scale).*

ISO 4314, *Surface active agents — Determination of free alkalinity or free acidity — Titrimetric method.*

ISO 4317, *Surface active agents — Determination of water content — Karl Fischer method.*

4 DEFINITION

hydroxyl value $I(OH)$: The number of milligrams of potassium hydroxide needed to neutralize the acidity which appears during the esterification, by phthalic anhydride, of the hydroxyl groups in 1 g of the material, or the number of milligrams of potassium hydroxide corresponding to the hydroxyl groups in 1 g of the material.

NOTE — The number of moles of potassium hydroxide corresponding to the hydroxyl value is equal to the number of hydroxyl groups present in 1 kg of the material.

1) In preparation. (Revision of ISO/R 607.)

5 PRINCIPLE

Esterification of the hydroxyl groups by phthalic anhydride in pyridine solution.

Hydrolysis of the excess of phthalic anhydride with water contained in the sodium hydroxide solution used for the neutralization.

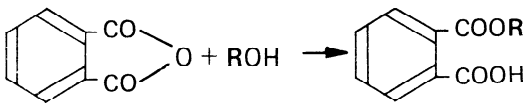
Neutralization of the acidity which appears during the esterification, and of the phthalic acid formed during the hydrolysis, by sodium hydroxide solution in the presence of phenolphthalein as indicator.

Calculation of the hydroxyl value from the difference between the volumes of sodium hydroxide solution used for the titration of the blank and of the test solution.

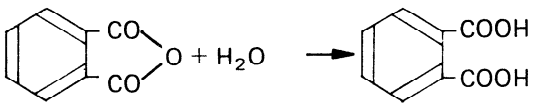
6 REACTIONS

The reactions occurring are as follows :

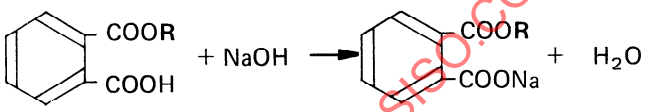
a) Esterification



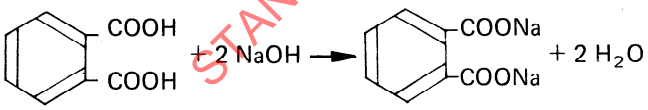
b) Hydrolysis of the excess phthalic anhydride



c) Neutralization of the acid formed during the esterification



d) Neutralization of the phthalic acid formed during hydrolysis



7 REAGENTS

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

7.1 Pyridine, if necessary distilled in the presence of 5 % of phthalic anhydride. The boiling temperature shall be between 114,5 and 115,5 °C.

7.2 Phthalic anhydride solution in pyridine (phthalation reagent).

7.2.1 *Preparation*

Place 140 ± 1 g of phthalic anhydride (melting point 131 ± 1 °C, determined by ISO 1392; and minimum purity 99,5 %, determined by the method specified in annex A) in a brown glass bottle of capacity 2 litres.

Add 1 litre of the pyridine (7.1) and shake vigorously until completely dissolved. Do not use this solution if its colour exceeds 200 Hazen units on the platinum-cobalt scale (determined by ISO 2211).

7.2.2 *Verification of reagent concentration*

Using a pipette (8.4), transfer exactly 25,0 ml of the solution (7.2) to a 250 ml conical flask.

Titrate with the standard volumetric sodium hydroxide solution (7.3) in the presence of the phenolphthalein solution (7.4).

A volume of 83 to 87 ml of the standard volumetric sodium hydroxide solution (7.3) should be required.

7.3 Sodium hydroxide, 0,5 N standard volumetric solution.

7.4 Phenolphthalein [3,3-*bis* (4-hydroxyphenyl) phthalide], 10 g/l solution in pyridine.

Dissolve 1 g of phenolphthalein in 100 ml of the pyridine (7.1).

8 APPARATUS

Ordinary laboratory apparatus and :

8.1 Burette, capacity 50 ml, complying with the requirements of class A of ISO/R 385.

8.2 Four flat-bottomed flasks, capacity 250 ml, with conical ground glass joint.

8.3 Four condensers, of effective length 400 mm, with conical ground glass joints fitting the flasks (8.2), and complying with the requirements of ISO 4799.

8.4 One-mark pipettes, capacity 25 ml, complying with the requirements of ISO 648.

9 SAMPLING

Laboratory samples of polyalkoxylated surface active agents shall be prepared and stored according to the instructions given in ISO 607.

10 PROCEDURE

All the necessary apparatus shall be absolutely clean and dry. Consequently, prepare all apparatus necessary for carrying out two simultaneous determinations on two different test portions, and two blank tests.

10.1 Test portion

It is essential that the approximate water content of the test portion be known; if necessary, determine the water content of the sample by the method specified in ISO 4317.

Weigh, to the nearest 0,001 g, into a dry and previously tared flask (8.2), a mass of the laboratory sample calculated as follows :

— For a water content lower than 1 % (*m/m*), the mass, in grams, of the test portion shall be such that :

$$m_0 = \frac{365}{I(\mathrm{OH})}$$

where $I(\mathrm{OH})$ is the estimated hydroxyl value, in milligrams of potassium hydroxide per gram.

The maximum mass of the test portion will therefore be 36,5 g as the method is restricted to a minimum hydroxyl value of 10.

— For a water content greater than 1 % (*m/m*) and up to 40 % (*m/m*), the mass, in grams, of the test portion shall be such that :

$$m_0 \geqslant \frac{31\,000}{\{100 - [H_2O]\}\, I(\mathrm{OH}) + 740\,[H_2O]}$$

and

$$m_0 \leqslant \frac{42\,000}{\{100 - [H_2O]\}\, I(\mathrm{OH}) + 1\,040\,[H_2O]}$$

where

$[H_2O]$ is the percentage, by mass, of water in the test sample;

$I(\mathrm{OH})$ is the estimated hydroxyl value, in milligrams of potassium hydroxide per gram.

The table in annex B gives the limiting values of m_0 for water contents from 1 to 40 % (*m/m*) and estimated hydroxyl values from 10 to 1 100.

WARNING – All the operations specified below shall be conducted under a well ventilated fume hood.

10.2 Determination

10.2.1 *Esterification*

Using a pipette (8.4), add 25,0 ml of the phthalation reagent (7.2) to the flask containing the test portion (10.1). Attach a condenser (8.3), previously rinsed with the pyridine (7.1), to the flask. Swirl to mix the contents. Heat the flask at gentle reflux for 1 h. Allow to cool to room temperature.

10.2.2 *Hydrolysis and titration*

Rinse the condenser with the pyridine (7.1). Remove the flask from its condenser and rinse the ground glass joints with water from a wash bottle. Place a bar magnet in the flask, place the flask on a magnetic stirrer and switch on the stirrer.

Introduce exactly 50,0 ml of the standard volumetric sodium hydroxide solution (7.3) into the flask, from the burette (8.1).

Add, by means of a 1 ml pipette, 4 or 5 drops of the phenolphthalein solution (7.4). Continue the titration with the standard volumetric sodium hydroxide solution (7.3) until the solution remains pink for 15 s.

10.3 Blank tests

Carry out two blank tests at the same time as the determination, using the same reagents, but without the test portion.

NOTE – For the results to be valid, the difference between the volume V_0 for the blank test and the volume V_1 used for each test portion should lie between 10 and 15 ml.

If this difference is greater than 15 ml, the test portion is too large, and it is necessary to recommence the test with smaller test portions [the hydroxyl value, $I(\mathrm{OH})$, will have been greater than the value estimated initially].

If the difference is less than 10 ml, the test portion is too small, and it is necessary to recommence the test with larger test portions [the hydroxyl value, $I(\mathrm{OH})$, will have been lower than estimated initially].

11 EXPRESSION OF RESULTS

11.1 Method of calculation

The hydroxyl value, $I(\mathrm{OH})$, corresponding to the test portion, is given by the formula

$$\frac{(V_0 - V_1) \times T \times 56{,}10}{m_0} - C$$

where

V_0 is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (7.3) used for the blank test;

V_1 is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (7.3) used for the determination;

T is the exact normality of the standard volumetric sodium hydroxide solution (7.3);

m_0 is the mass, in grams, of the test portion;

C is the positive acid value, or the negative alkali value, of the material (see ISO 4314); this value shall be ignored if it is 0,3 or less.

Take as the result the arithmetic mean of the duplicate determinations.

11.2 Precision

The precision of the determination is 1,5 % of the result, which should be rounded in consequence.

11.3 Reproducibility

The following information is the result of analyses carried out in 21 laboratories, in each by an analyst giving at least two results.

Sample	A	B
Mean I(OH)	51,9	172,3
Standard deviation of reproducibility, σ_R	1,15	3,80

12 TEST REPORT

The test report shall include the following particulars :

a) all information necessary for the complete identification of the sample;

b) the reference of the method used (reference to this International Standard);

c) the results and the method of expression used;

d) the test conditions;

e) any operational details not specified in this International Standard, or regarded as optional, as well as any incidents likely to have affected the results.

ANNEX A

DETERMINATION OF THE PURITY OF THE PHTHALIC ANHYDRIDE

Place 1,5 g, weighed to the nearest 0,001 g, of phthalic anhydride in a 250 ml conical flask. Add 100 ml of a 50 % (*V*/*V*) mixture of pyridine (7.1) and water, previously neutralized with a 0,1 N sodium hydroxide or hydrochloric acid solution in the presence of the phenolphthalein solution (7.4). Titrate with the standard volumetric sodium hydroxide solution (7.3) to a permanent pink colour.

The purity, expressed as a percentage by mass, is given by the formula

$$\frac{V_2 \times T \times 74 \times 100}{1\,000\, m_1}$$

where

V_2 is the volume, in millilitres, of the standard volumetric sodium hydroxide solution (7.3) used;

T is the exact normality of the standard volumetric sodium hydroxide solution (7.3);

m_1 is the mass, in grams, of the sample of phthalic anhydride;

74 is a factor representing the fact that 2 moles of sodium hydroxide are needed to neutralize the phthalic acid formed by the hydrolysis of 1 mole of phthalic anhydride (relative molecular mass = 148). (See clause 6.)

ANNEX B

MASS OF THE TEST PORTION, IN GRAMS, AS A FUNCTION OF I(OH) AND WATER CONTENT

Estimated I(OH)	Water content, % (m/m)															
	1	2	3	4	5	6	7	8	9	10	15	20	25	30	35	40
10	18 21															
20	11,5 14	10,3														
30	8,0 10,5	7,0 8,3	6,9													
40	6,6 8,4	5,7 7,0	5,1 6,0	5,25												
50	5,5 7,0	4,9 6,0	4,4 5,3	4,0 4,7	4,2											
60	4,6 6,0	4,2 5,3	3,9 4,7	3,6 4,2	3,3 3,9											
100	2,9 3,8	2,8 3,5	2,6 3,3	2,5 3,0	2,4 2,9	2,7										
200	1,5 2,0	1,5 1,9	1,4 1,9	1,4 1,9	1,4 1,7	1,3 1,7	1,6									
300	1,0 1,4	1,0 1,3	1,0 1,3	0,98 1,3	0,96 1,2	0,95 1,2	0,94 1,2	1,2								
400	0,77 1,0	0,76 1,0	0,75 1.0	0,75 0,98	0,74 0,97	0,74 0,96	0,73 0,94	0,73 0,93	0,92							
500	0,61 0,83	0,61 0,82	0,61 0,81	0,60 0,80	0,60 0,80	0,60 0,79	0,60 0,78	0,60 0,77	0,60 0,76	0,76						
600	0,51 0,69	0,51 0,69	0,51 0,68	0,51 0,68	0,51 0,68	0,51 0,67	0,51 0,67	0,51 0,66	0,50 0,66	0,50 0,65	0,63					
700	0,44 0,59	0,44 0,59	0,44 0,59	0,44 0,59	0,44 0,59	0,44 0,58	0,44 0,58	0,44 0,58	0,44 0,57	0,44 0,57	0,44 0,56	0,55				
800	0,39 0,52	0,39 0,52	0,39 0,52	0,39 0,52	0,39 0,52	0,39 0,52	0,39 0,51	0,39 0,51	0,39 0,51	0,39 0,51	0,39 0,50	0,39 0,49	0,49			
1 000	0,31 0,42	0,31 0,42	0,31 0,42	0,31 0,42	0,31 0,42	0,31 0,42	0,32 0,42	0,32 0,42	0,32 0,42	0,32 0,42	0,32 0,42	0,33 0,42	0,33 0,42	0,41	0,41	0,41
1 100	0,28 0,38	0,28 0,38	0,28 0,38	0,28 0,38	0,28 0,38	0,29 0,38	0,29 0,38	0,30 0,38	0,29 0,38	0,29 0,38	0,29 0,38	0,30 0,38	0,30 0,39	0,31 0,39	0,32 0,39	0,32 0,39

Example : For a sample with an estimated hydroxyl value of between 100 and 200, the mass of the test portion will depend on the water content as follows :

a) if the water content is 1 % (m/m), take a test portion of between 2,9 and 2,0 g;

b) if the water content is 4 % (m/m), take a test portion of between 2,5 and 1,9 g;

c) if the water content is 10 % (m/m), the table does not indicate a mass of test portion; it is necessary to eliminate part of the water, which can be left at a maximum of 5 % (m/m), and then between 2,4 and 1,7 g of the sample can be taken.

ANNEX C

SPECIAL METHOD APPLICABLE WITHOUT FUME HOOD

C.0 INTRODUCTION

This annex specifies a special apparatus and a special procedure for the determination of hydroxyl value for the case where the determination has to be carried out outside a ventilated fume hood.

C.1 APPARATUS (See figure 1)

Ordinary laboratory apparatus and :

C.1.1 Burette, capacity 50 ml, complying with the requirements of class A of ISO/R 385.

C.1.2 Flat-bottomed flasks, capacity 250 ml, with conical ground glass joint.

C.1.3 Condensers, of effective length 400 mm, with conical ground glass joints, fitting the flasks (C.1.2), and with drip collectors (see figure 2).

C.1.4 Ground glass stoppers fitting the flasks (C.1.2).

C.1.5 Ground glass stoppers fitting the flasks (C.1.2), with central holes [see figure 1 a)].

C.1.6 Ground glass stoppers fitting the flasks (C.1.2), with central holes and side-arms [see figure 1 b)].

C.1.7 Special burette, capacity 25 ml [see figure 1 c)].

C.1.8 Rinsing test tubes, capacity 200 ml [see figure 1 d)].

C.2 PROCEDURE

C.2.1 Preparation of the apparatus

All the necessary apparatus shall be absolutely clean and dry.

Rinse the condensers (C.1.3) in succession, using the rinsing test tubes (C.1.8) with about 10 ml of the pyridine (7.1), collecting the washings in the flasks (C.1.2).

After rinsing, close the tops of the condensers with one of the stoppers (C.1.4).

Fit a stopper (C.1.5) on the flask (C.1.2) reserved for the test portion and weigh to the nearest 0,001 g.

C.2.2 Test portion

Remove the stopper (C.1.5). Place the test portion (10.1) in the flask (C.1.2) reserved for this purpose. Refit the stopper (C.1.5). Reweigh the assembly to the nearest 0,001 g. Let m_0 be the mass, in grams, of the test portion.

C.2.3 Determination

C.2.3.1 *Esterification*

Introduce exactly 25,0 ml portions of the phthalation reagent (7.2) from the special burette (C.1.7) into the flask through the central hole of the stopper (C.1.5).

Fit the flask onto the lower end of the condenser, i.e. in the place of the flask which was used to collect the pyridine washings. Then close this flask, using a stopper (C.1.4) at the upper end of the condenser.

Heat the flask, fitted with its condenser, at gentle reflux for 1 h. Allow to cool to room temperature.

C.2.3.2 *Hydrolysis and titration*

Rinse the condenser with the pyridine (7.1) from the rinsing test tube (C.1.8).

Remove the flask from its condenser and rinse the ground glass joints with distilled water from a wash bottle.

Refit the flask containing the initial rinsing pyridine to the condenser and close the condenser using a solid stopper (C.1.4).

Place a bar magnet in the flask. Fit the stopper with central hole and side-arm (C.1.6) to the flask. Attach the side-arm to a vent by means of rubber tube (in order to avoid release of pyridine into the laboratory atmosphere). Place the assembly on the magnetic stirrer and switch on the stirrer.

Introduce exactly 50,0 ml of the standard volumetric sodium hydroxide solution (7.3) through the central opening of the stopper, from the burette (C.1.1).

Add, by means of a 1 ml pipette, again through the central hole in the stopper, 4 to 5 drops of the phenolphthalein solution (7.4).

Continue the titration with the standard volumetric sodium hydroxide solution (7.3) until the solution remains pink for 15 s.

Record the volume of the standard volumetric sodium hydroxide solution (7.3) used for the titration of the test solution.

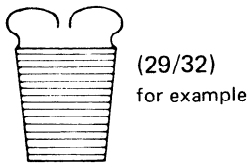
Carry out two simultaneous determinations on two different test portions.

C.2.4 Blank tests

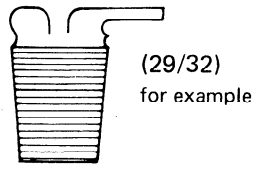
See 10.3.

C.3 EXPRESSION OF RESULTS

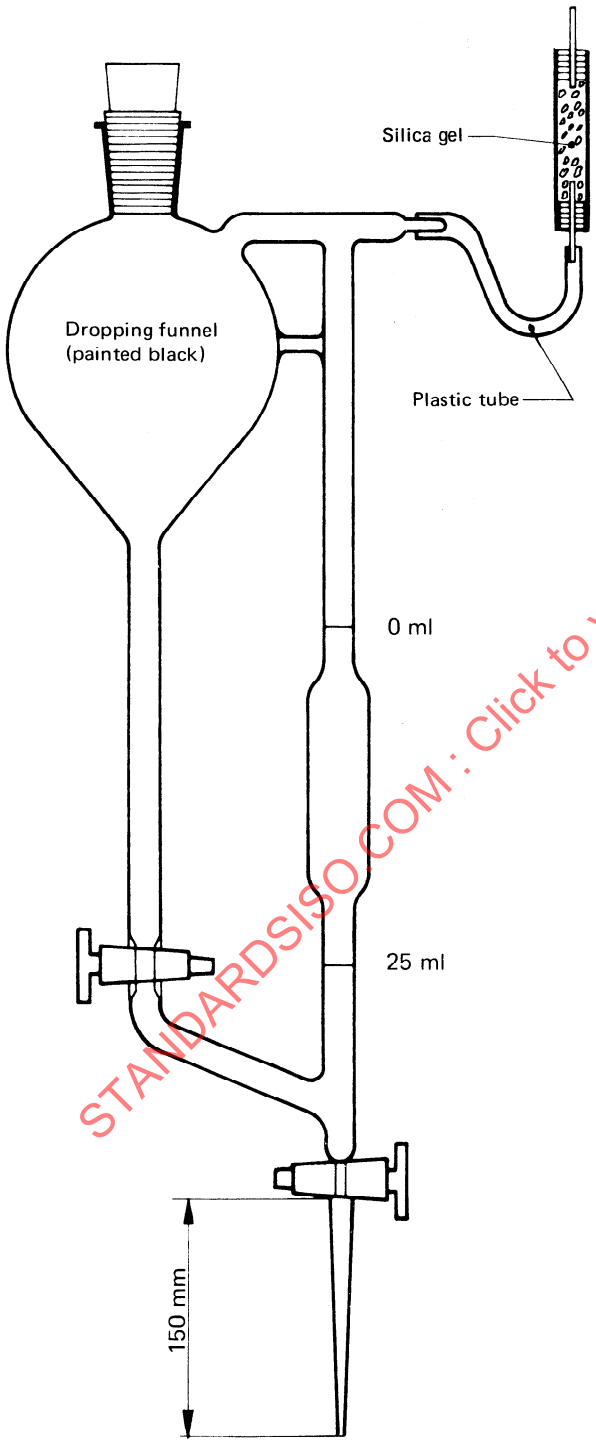
See clause 11.



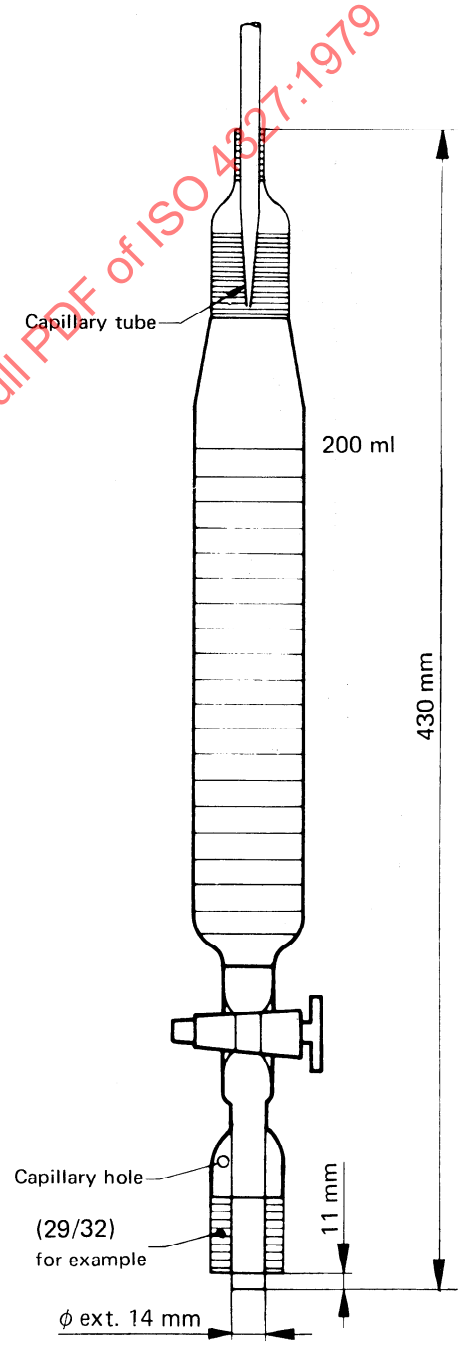
a) **Ground glass stopper (C.1.5)**



b) **Ground glass stopper (C.1.6)**



c) **Special burette (C.1.7)**



d) **Rinsing test tube (C.1.8)**

FIGURE 1 – **Apparatus**

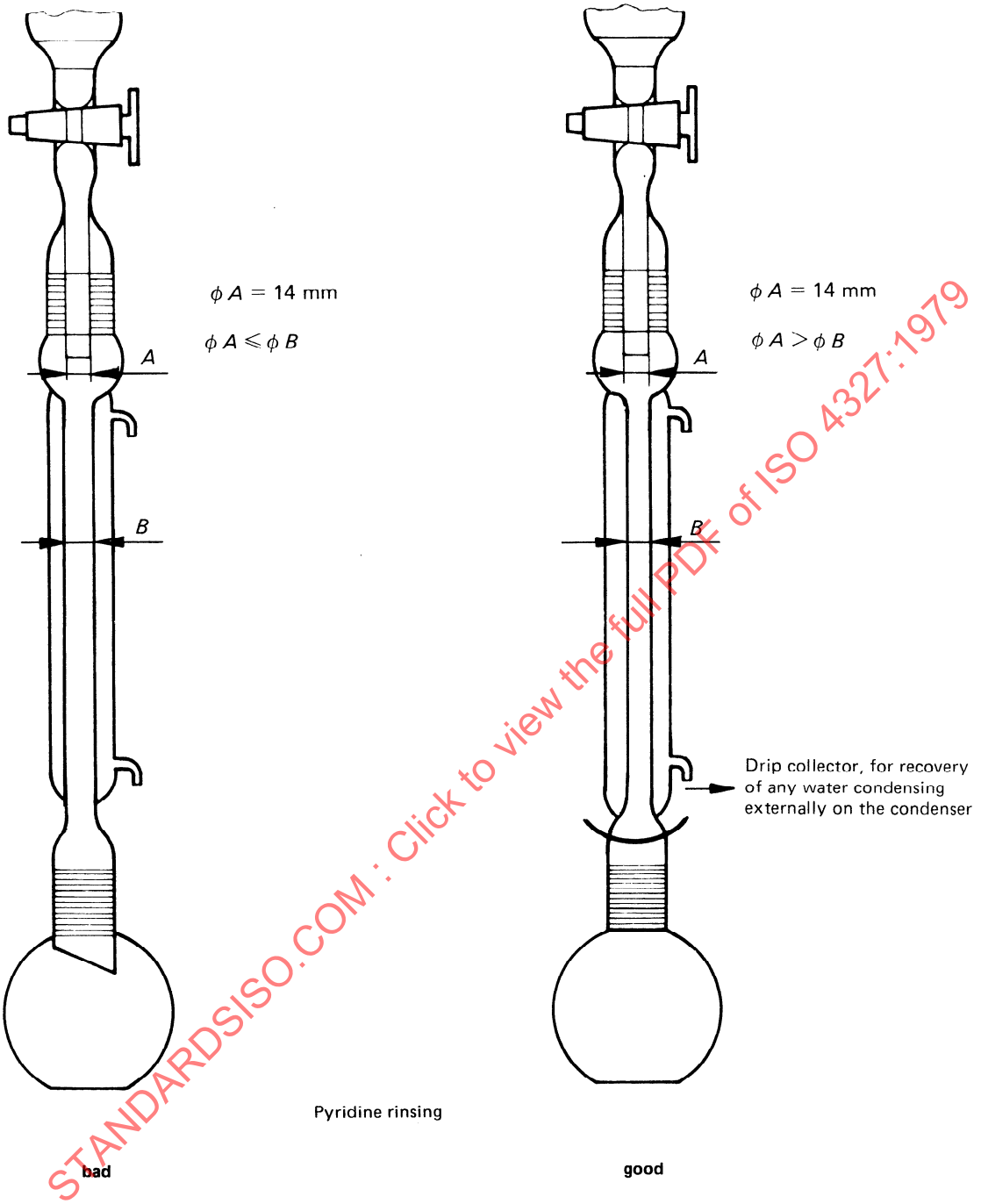


FIGURE 2 — **Examples of condensers (C.1.3)**

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