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Nickel-based alloys — Determination of resistance to intergranular corrosion

Alliages à base de nickel — Détermination de la résistance à la corrosion intergranulaire

Reference number
ISO 9400:1990(E)

Foreword

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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 9400 was prepared by Technical Committee ISO/TC 156, *Corrosion of metals and alloys.*

Annex A of this International Standard is for information only.

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Nickel-based alloys — Determination of resistance to intergranular corrosion

Section 1: General

1.1 Scope

This International Standard specifies four methods for determination of the susceptibility of nickel-based alloys to intergranular corrosion.

These methods are for laboratory testing of susceptibility only, and a direct correlation with intergranular corrosion in actual service may not occur unless the service medium is the same as the test medium.

The methods covered are as follows:

- **Method A:** iron(III) sulfate — sulfuric acid test (section 2);
- **Method B:** copper — copper-sulfate — 16 % sulfuric acid test (section 3);
- **Method C:** hydrochloric acid test (section 4);
- **Method D:** nitric acid test (section 5);

The appropriate method for use with a given alloy, the selection of sensitizing treatment, and the acceptance criteria to be used in any evaluation have to be agreed between the buyer and seller of the alloy. As a guide, the methods specified in this International Standard should be applicable to those nickel-based alloys used for corrosion service and listed in ISO 6207[1].

1.2 Definition

For the purposes of this International Standard, the following definition applies.

nickel-based alloy: An alloy which includes nickel as the predominant element.

NOTE 1 This definition is consistent with that given in ISO 6372-1[2].

1.3 Apparatus

The recommended apparatus is shown in figure 1. The cold-finger type of condenser with standard Erlenmeyer flasks should not be used except for method D.

The following items are required.

1.3.1 Four-bulb Allihn or Soxhlet condenser with 45/50 ground glass joint.

1.3.2 Erlenmeyer flask, capacity 1 dm^3, with 45/50 ground glass joint.

NOTE 2 The use of round flasks with a heating jacket is also acceptable.

1.3.3 Glass cradle or other equivalent means of specimen support, such as glass hooks or stirrups. The cradle should have three or four holes in it, to increase circulation of the test solution around the specimen (see figure 1).

1.3.4 Boiling chips to promote uniform boiling and to prevent bumping.

For method A, these boiling chips should be made of pure alundum.

1.3.5 Silicone grease for application to the ground glass joint of the condenser and flask.

A PTFE sleeve for the joint is also acceptable.

1.3.6 Heating device such as an electrically heated hot-plate, for continuous boiling of the test solution.

1.3.7 Analytical balance capable of weighing to at least the nearest 1 mg (if mass loss is to be determined).

1.3.8 Stereoscopic microscope capable of magnification of 5× to 20×, with a good light source, for examination of the tested specimen (for method B).

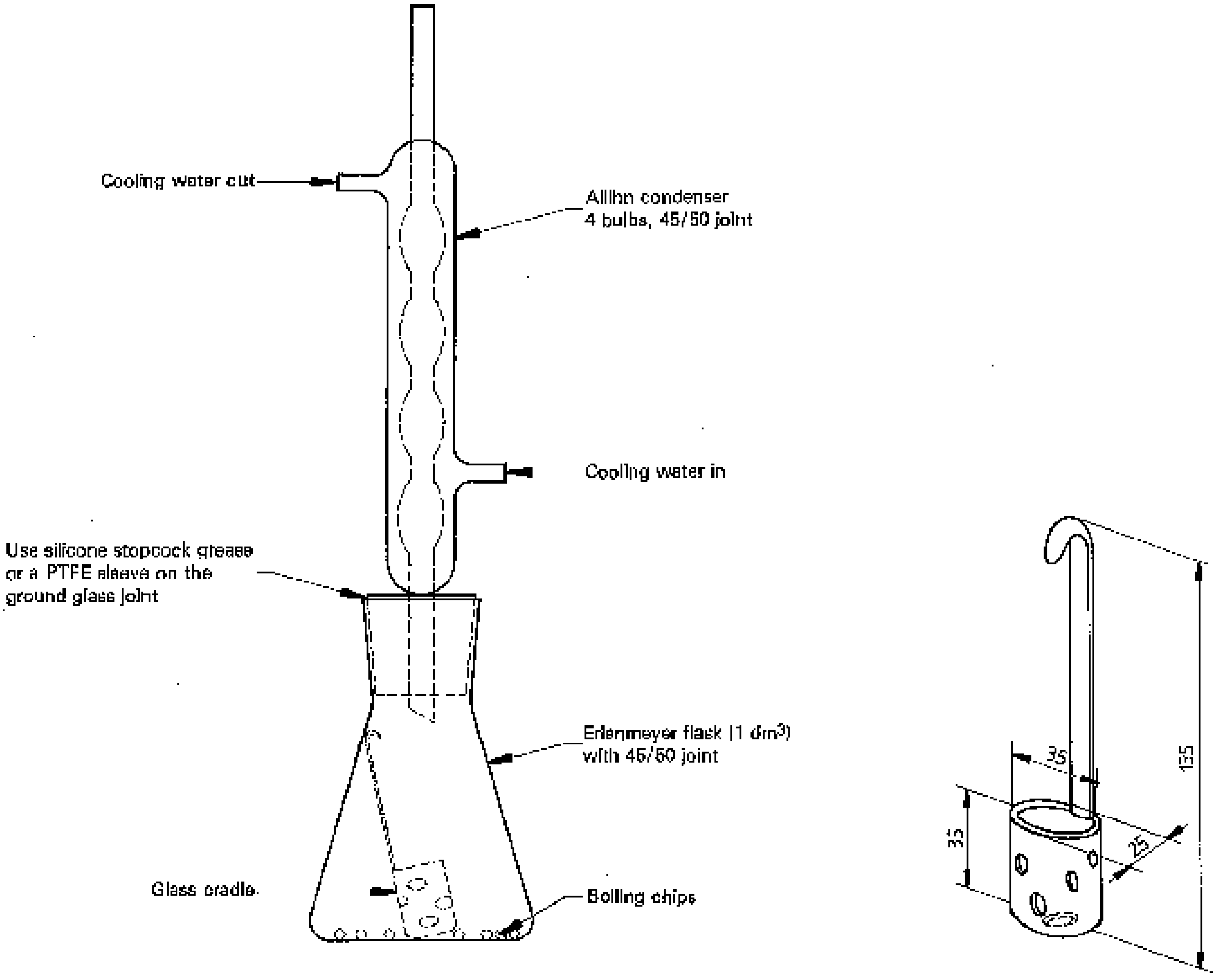
1.4 Preparation of test specimens

The following requirements for the preparation of test specimens are common to all four test methods. Additional requirements are given, where necessary, in the section describing the particular method.

A specimen having a total surface area of 20 cm² to 30 cm² is recommended. As-welded specimens should be cut so that no more than a 13 mm width of unaffected base metal is included on either side of the weld and heat-affected zone.

It is intended to test a specimen representing as nearly as possible the surface of the material used in service. Surface finishing should be performed only as required to remove foreign material and obtain a standard, uniform finish to represent the appropriate surface, while maintaining reasonable specimen size for convenience in testing. Normally, removal of more material than necessary will have little influence on the test results. However, in the special case of surface carburization (sometimes encountered, for instance, in tubing when carbonaceous lubricants are employed), it may only be possible to remove the carburized layer completely by heavy grinding or machining. Such treat-

Dimensions in millimetres



a) Assembled apparatus

b) Glass cradle

Figure 1 — Recommended apparatus

ment of non-carburized test specimens is not permissible, except in tests undertaken to demonstrate specific surface effects. When samples are cut by shearing, the deformed metal shall be removed by grinding or machining prior to testing.

Prior to testing, the test specimens shall be degreased with a chlorine-free solvent and rinsed.

1.5 Sensitization of test specimens

1.5.1 Specimens to be given a thermal treatment prior to testing shall be clean of carbonaceous material prior to the thermal treatment. Otherwise, carburization may invalidate the test results. A light surface grinding or pickling followed by washing and rinsing in a non-chlorinated solvent should provide a clean surface. It is recommended that the effect of the pickling bath on the specimen be tested prior to the environmental exposure.

1.5.2 Specimens of alloys to be given a sensitization treatment prior to testing shall be placed in a furnace at the required temperature and for the required time, and shall then be water quenched. The use of a sensitization treatment shall be agreed upon between buyer and seller.

1.5.3 Specimens of alloys that are not given a sensitization treatment shall be tested in a condition simulating end-use conditions. Specimens from material that is intended to be welded or heat treated shall be welded or heat treated in nearly the same manner as the material will experience in fabrication or service. The specific treatment shall be agreed upon between buyer and seller.

Section 2: Method A — Iron(III) sulfate — Sulfuric acid test

2.1 Scope

This section describes the procedure for conducting the boiling iron(III) sulfate — sulfuric acid test to determine the susceptibility of nickel-based alloys to intergranular attack.

2.2 Iron(III) sulfate — sulfuric acid test solution

Prepare 600 cm³ of test solution as follows.

Measure 400 cm³ of distilled water into a 500 cm³ graduated cylinder and pour into the Erlenmeyer flask (1.3.2).

Measure 236 cm³ of reagent grade 95 to 98 % (*m/m*) sulfuric acid into a 250 cm³ graduated cylinder. Add the acid slowly to the water in the Erlenmeyer flask to avoid boiling by the heat evolved. (Loss of vapour results in an increase in the acid concentration.)

Weigh 25 g of reagent grade iron(III) sulfate nonahydrate [$Fe_2(SO_4)_3 \cdot 9H_2O$, containing about 75 % $Fe_2(SO_4)_3$], and add it to the sulfuric acid solution. A trip balance may be used.

Drop several boiling chips (1.3.4) into the flask.

Lubricate the ground glass joint with silicone grease (1.3.5).

Fit the flask to the condenser (1.3.1) and circulate cooling water.

Boil the solution until all the iron(III) sulfate is dissolved.

2.3 Preparation of test specimens

See clause 1.4.

2.4 Procedure

Measure the dimensions of the specimen to the nearest 0,5 mm, including the inner dimensions of any holes, and calculate the total exposed surface area.

Degrease the specimen using a non-chlorinated solvent, dry and then weigh to the nearest 1 mg.

Place the specimen in a glass cradle (1.3.3) and immerse it in boiling test solution (clause 2.2).

Testing of a single specimen in a flask is preferred. However, several specimens may be tested simultaneously. The number is limited only by the number of glass cradles that can be fitted into the flask (usually three or four). In no case shall different alloys be tested together. Each specimen shall be in a separate cradle so that the specimens do not touch.

Mark the liquid level on the flask with a heat-resistant marker to provide a check on vapour loss. If there is an appreciable change in the level, repeat the test with fresh solution and a new specimen.

Continue immersion of the specimen for a period of 24 h or 120 h, then remove the specimen, rinse in water and acetone, and dry. For alloys containing less than 18 % chromium the exposure time is typically 24 h. For alloys containing more than 18 % chromium the exposure time is 120 h.

Weigh the specimen and subtract the mass from the original mass.

NOTES

3 No intermediate weighings are usually necessary. The tests can be run without interruption; however, if preliminary results are desired, the specimen can be removed at any time for weighing.

4 No changes in the test solution are necessary during the test period.

5 Additional iron(III) sulfate inhibitor may have to be added during the test if the corrosion rate is unusually high, as evidenced by a change in the colour of the solution. More iron(III) sulfate has to be added if the total mass loss of all specimens exceeds 2 g [during the test, iron(III) sulfate is consumed at a rate of approximately 10 g for each 1 g of dissolved metal].

6 During testing, there is some deposition of iron oxides on the upper part of the Erlenmeyer flask. This can be readily removed, after completion of the test, by boiling a 10 % (*m/m*) solution of hydrochloric acid in the flask.

2.5 Evaluation

2.5.1 The effect of the test solution on the material can be measured by determining the loss of mass of the specimen. Calculate the corrosion rate as follows:

$$\text{corrosion rate} = \frac{k \times \Delta m}{A \times t \times \rho}$$

where

k is a constant (see note 7);

t is the exposure time, in hours;

A is the exposed area, in square centimetres, of the specimen;

Δm is the mass loss, in grams;

ρ is the density, in grams per cubic centimetre, of the specimen.

NOTE 7 Using the above units for t, A, Δm and ρ, the corrosion rate can be calculated in a variety of units using the appropriate value of k:

Corrosion rate units desired	Value of k to be used
mils [milliinches] per year (mpy)	$3{,}45 \times 10^6$
inches per year (ipy)	$3{,}45 \times 10^3$
inches per month (ipm)	$2{,}85 \times 10^2$
millimetres per year (mm/y)	$8{,}76 \times 10^4$
micrometres per year (μm/y)	$8{,}76 \times 10^7$
picometres per second (pm/s)	$2{,}78 \times 10^6$

2.5.2 The presence of intergranular attack is usually determined by comparing the calculated corrosion rate to that for properly annealed material. Even in the absence of intergranular attack, the rate of general or grain-face corrosion of properly annealed material will vary from one alloy to another. The corrosion rate considered acceptable shall be determined between buyer and seller.

2.5.3 As an alternative or in addition to calculating a corrosion rate from mass loss data, metallographic examination may be used to evaluate the degree of intergranular attack. The depth of attack considered acceptable shall be determined between buyer and seller.

Section 3: Method B — Copper — Copper sulfate — 16 % sulfuric acid test

3.1 Scope

3.1.1 This section describes the procedure for conducting the copper — copper sulfate — 16 % sulfuric acid test to determine the susceptibility of certain nickel-based alloys to intergranular attack. This test detects susceptibility to intergranular attack associated with the precipitation of chromium carbides or nitrides.

3.1.2 This test may be used to evaluate the heat treatment accorded to as-received material. It may also be used to evaluate the effectiveness of stabilizing element additions (Nb, Ti, etc.) and reduction in interstitial content to aid in resistance to intergranular attack. It may be applied to all wrought products and weld metal.

3.1.3 This test does not detect susceptibility associated with chi-phase, sigma-phase, or titanium carbides or nitrides. For detecting susceptibility in environments known to cause intergranular attack due to these phases use method D.

3.2 Acidified copper sulfate test solution

Dissolve 100 g of copper(II) sulfate pentahydrate ($CuSO_4.5H_2O$) in 700 cm^3 of distilled water, add 100 cm^3 of sulfuric acid (H_2SO_4, reagent grade ρ 1,84 g/cm^3), and dilute to 1 000 cm^3 with distilled water. The solution will contain approximately 6 % (*m/m*) of anhydrous copper(II) sulfate ($CuSO_4$) and 16 % (*m/m*) of H_2SO_4.

3.3 Copper

Electrolytic grade copper shot or turnings may be used. Shot is preferred for its ease of handling before and after the test.

The copper shot or turnings may be reused if cleaned in warm water after each test.

3.4 Preparation of test specimens

See clause 1.4

Since the evaluation is done by bending, the shape of the test specimen shall be such as to allow bending to be accomplished with the original surface on the outside of the bend.

3.5 Procedure

The volume of test solution (clause 3.2) used shall be sufficient to completely immerse the specimen(s) and provide a minimum ratio of solution volume to total specimen surface area of 8 cm^3/cm^2.

As many as three specimens can be tested in the same flask, provided that all of the specimens are of the same grade and that the ratio of solution volume to total specimen surface area is maintained.

The specimen(s) shall be immersed in the test solution. A sufficient quantity of copper shot or turnings (clause 3.3) shall be used to cover all surfaces of the specimen, whether it is in a vented cradle or embedded in a layer of copper shot or turnings on the bottom of the flask. The amount of copper used, provided that an excess of metallic copper is present, is not critical.

Heat the solution to boiling and maintain boiling throughout the test period. Begin timing the test period when the solution reaches the boiling point. Mark the liquid level on the flask with a heat-resistant marker to provide a check on vapour loss. If there is an appreciable change in the level, repeat the test with fresh solution and a new specimen.

NOTE 8 Measures should be taken to minimize bumping of the solution when glass cradles are used to support specimens. A small amount of copper shot (8 to 10 pieces) on the bottom of the flask will conveniently serve this purpose.

The test shall consist of a 24 h period. However, longer periods may be employed, in which case the exposure time shall be included in the test report. Fresh test solution is not needed for test periods up to 72 h. (If any adherent copper remains on the specimen, it may be removed by a brief immersion in concentrated nitric acid at room temperature. The sample is then rinsed in water and dried.)

3.6 Evaluation

3.6.1 The specimen shall be bent through 180° over a radius equal to twice the thickness of the specimen. In no case shall the specimen be bent over a smaller radius or through a greater angle than that specified in the product specification. In cases of material having low ductility, such as severely cold-worked material, a 180° bend may prove impractical. Determine the maximum angle of bend without causing cracks in such material by bending an untested specimen of the same configuration as the specimen to be tested.

Welded samples shall be bent in such a manner that the weld and heat-affected zone are strained.

Samples machined from thick sections shall have the original surface on the outside of the bend.

3.6.2 In the case of tubes up to 40 mm in outside diameter, the specimen shall be flattened. The distance between the platens after flattening, measured under load, shall not be greater than the following value, h, in millimetres:

$$h = \frac{1{,}09D\delta}{0{,}09D + \delta}$$

where

δ is the specified wall thickness, in millimetres;

D is the outside diameter of the tube, in millimetres.

In the case of welded tube, the weld shall be at the point of maximum flattening.

3.6.3 The bent or flattened specimen shall be examined using a stereoscopic microscope (1.3.8). The appearance of fissures or cracks indicates the presence of intergranular attack. Cracking that originates at the edge of the specimen should be disregarded. The appearance of deformation without accompanying cracks or fissures should also be disregarded.

3.6.4 When an evaluation is questionable or as an alternative to 3.6.3, the presence or absence of intergranular attack shall be determined by metallographic examination of the specimen.

NOTE 9 Cracks suspected of arising through poor ductility may be investigated by bending a similar specimen which was not exposed to the boiling test solution. A visual comparison between the exposed and unexposed specimens should assist in interpretation.

Section 4: Method C — Hydrochloric acid test

4.1 Scope

This section describes the procedure for conducting the hydrochloric acid test to determine the susceptibility of certain high molybdenum nickel-based alloys to intergranular attack.

4.2 Hydrochloric acid test solution

Prepare 600 cm³ of test solution as follows.

Measure 306 cm³ of distilled water into a 500 cm³ graduated cylinder and pour into the Erlenmeyer flask (1.3.2).

Measure 300 cm³ of reagent grade 37 to 38 % (*m/m*) hydrochloric acid into a 500 cm³ graduated cylinder. Add the acid slowly to the water in the Erlenmeyer flask.

Drop several boiling chips (1.3.4) into the flask.

Lubricate the ground glass joint with silicone grease (1.3.5).

Fit the flask to the condenser (1.3.1) and circulate cooling water.

NOTE 10 For nickel-chromium-molybdenum alloys, the same test procedure can be used except that a 10 % (*m/m*) solution of hydrochloric acid should be used.

4.3 Preparation of test specimens

See clause 1.4.

4.4 Procedure

Measure the dimensions of the specimen to the nearest 0,5 mm, including the inner dimensions of any holes, and calculate the total exposed surface area.

Degrease the specimen using a non-chlorinated solvent, dry and then weigh it to the nearest 1 mg.

Place the specimen in a glass cradle (1.3.3) and immerse it in the boiling test solution (clause 4.2).

Testing of a single specimen in a flask is preferred. However, several specimens may be tested simultaneously. The number is limited only by the number of glass cradles that can be fitted into the flask (usually three or four). In no case shall different alloys be tested together. Each specimen shall be in a separate cradle so that the specimens do not touch.

Mark the liquid level on the flask with a heat-resistant marker to provide a check on vapour loss. If there is an appreciable change in the level, repeat the test with fresh solution and a new specimen.

Continue immersion of the specimen for a period of 168 h, then remove the specimen, rinse in water and then in a non-chlorinated solvent and dry.

Weigh the specimen and subtract the mass from the original mass.

NOTES

11 No intermediate weighings are usually necessary. The tests can be run without interruption; however, if preliminary results are desired, the specimen can be removed at any time for weighing.

12 No changes in the test solution are necessary during the test period.

4.5 Evaluation

Evaluate the results of the test in accordance with clause 2.5.

Section 5: Method D — Nitric acid test

5.1 Scope

This section describes the procedure for conducting the nitric acid test to determine the susceptibility of certain nickel-based alloys to intergranular attack.

5.2 Nitric acid test solution

The test solution shall be (65 ± 0,2) % (*m*/*m*) nitric acid determined by analysis. This solution may be prepared by adding distilled water to concentrated nitric acid (reagent grade HNO_3, ρ 1,42 g/cm^3) in the proportion of 108 cm^3 of distilled water per cubic decimetre of concentrated nitric acid.

The acid used shall be of analytical reagent grade, with the following maximum residual contents:

Fixed residue	50 mg/kg
Pb	5 mg/kg
Fe	2 mg/kg
Mn	negative test
As	0,05 mg/kg
Cl	1 mg/kg
SO_4	10 mg/kg
PO_4	2 mg/kg
F	1 mg/kg

Care shall be taken to prevent contamination of the test solution, especially by fluorides, either before or during the test. Experience has shown that the presence of even small amounts of hydrofluoric acid will increase the corrosion rate. It is not permissible, for example, to conduct nitric-hydrofluoric acid tests under the same hood as nitric acid tests.

5.3 Apparatus

When evaluating stainless steels using this test, a 1 dm^3 wide mouth Erlenmeyer flask with a cold-finger type of condenser (see figure 2) is commonly used. The use of this apparatus is acceptable if agreed upon between buyer and seller.

As an alternative to the apparatus specified in clause 1.3, it is permissible to use a multi-specimen testing apparatus[3] designed to permit the testing of a large number of specimens simultaneously, by providing for replacement of the acid in contact with the specimens several times per hour with redistilled acid. Because of the lesser accumulation of corrosion products in the test solution, the corrosion rates obtained with the multi-specimen testing apparatus are consistently lower than those obtained with the conventional apparatus; the differences are small on properly annealed or stabilized material, which will show low rates in both types of test, but can be very large for sensitized specimens. For research purposes or where results are to be compared directly, it is essential that the same type of apparatus be used for all tests.

5.4 Preparation of test specimens

See clause 1.4.

5.5 Procedure

Measure the dimensions of the specimen to the nearest 0,5 mm, including the inner dimensions of any holes, and calculate the total exposed surface area.

Degrease the specimen using a non-chlorinated solvent, dry and then weigh to the nearest 1 mg.

The volume of test solution (clause 5.2) used shall be sufficient to completely immerse the specimen(s) and provide a minimum ratio of solution volume to total specimen surface area of 20 cm^3/cm^2. Normally, a volume of about 600 cm^3 is used.

The best practice is to use a separate container for each specimen. For routine evaluations, it is acceptable to test as many as three specimens in the same container provided that they all are of the same grade and all show satisfactory resistance to corrosion. However, if more than one of the specimens tested in the same container fail to pass the test, it is necessary to retest all specimens in separate containers since excessive corrosion of one specimen may result in accelerated corrosion of the other specimens tested with it. Excessive corrosion may often be detected by changes in the colour of the test solution, and it may be appropriate to provide separate containers for such specimens without waiting until the end of the test period. A record should be made showing which specimens were tested together.

NOTE 13 If a multi-specimen testing apparatus (clause 5.3) is employed, a large number of specimens may be tested in the large container provided.

Place the specimens in the test solution in the container, pass cooling water through the condenser, heat the solution to boiling and maintain boiling throughout the test period.

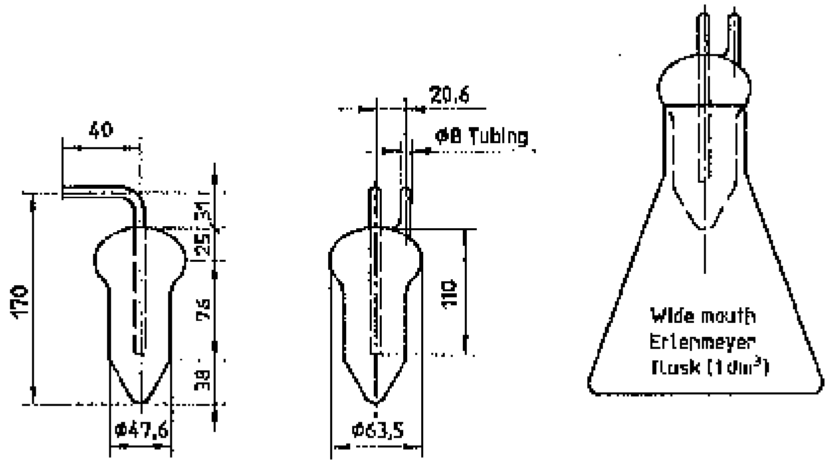
After each test period, rinse the specimens with water, scrub with a nylon or natural bristle brush under running water to remove any adhering corrosion products, rinse in acetone, dry and weigh.

To obtain the most consistent results, the test should consist of five boiling periods of 48 h each, with a fresh test solution being used in each period. By mutual agreement, a combination of one 48 h period and two 96 h periods (not necessarily in that order) instead of five 48 h periods may be acceptable for routine evaluations.

5.6 Evaluation

Evaluate the results of the test in accordance with clause 2.5.

Dimensions in millimetres



Condenser

Flask with condenser in place

NOTE - The condenser is made of Pyrex or equivalent heat-resisting glass.

Figure 2 — Alternative flask and condenser for nitric acid test

Annex A
(informative)

Bibliography

[1] ISO 6207:—[1], *Seamless nickel and nickel alloy tube.*

[2] ISO 6372-1:1989, *Nickel and nickel alloys -- Terms and definitions — Part 1: Materials.*

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[1] To be published.

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