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Recommendations for

Treatment of water for marine boilers

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Committees responsible for this British Standard

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Department of Industry (Laboratory of the Government Chemist)
Fabric Care Research Association
Health and Safety Executive
Institute of Energy
Institution of Chemical Engineers
Institution of Corrosion Science and Technology
Institution of Gas Engineers
Ministry of Defence
National Coal Board
Royal Society of Chemistry
Society of Laundry Engineers and Allied Trades Limited

The following bodies were also represented in the drafting of the standard, through subcommittees and panels:

Association of Shell Boilermakers
British Water and Effluent Treatment Plant Association
Department of Industry (National Physical Laboratory)
Institute of Marine Engineers
Water-tube Boilermakers' Association

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Contents

Foreword

This British Standard, having been prepared under the direction of the Environment and Pollution Standards Committee, supersedes BS 1170:1968 which is withdrawn.

The first British Standard intended as an introduction to water treatment for marine boilers was published in December 1947. Since that time marine engineers have come to realize that the water in ships, boilers has to conform to recognized standards if efficiency is to be maintained. Since the publication of BS 1170:1968, boiler pressures and steam temperatures have again been increased in the never-ending search for more economic working. These increases in pressure and temperature have demanded a purer supply of water and more sophisticated treatment. This revised edition caters for boilers operating at pressures up to 130 bar1) by adding a sixth range of pressure to the five previously dealt with. For boilers operating above 130 bar, the control of treatment and the requirements for the limits of impurities in the feed water would be even more stringent.

Other changes made for this edition include considerable expansion of the glossary of terms (Appendix A), explanation of the concepts of pH value, acidity and alkalinity (Appendix B), inclusion of a section on safe handling of chemicals (Appendix C), new ship-board methods for determination of copper, iron, silica and suspended solids (Appendix D), 16 additions to the list of reagents (Appendix E), and the inclusion of a brief outline on on-line instrumentation and automation (Appendix F).

Each of the control tests in Appendix D is preceded by a short introduction to the principles underlying the chemical reactions. No method of test for nitrate is available that can readily be carried out on board ship; to obtain an estimate of this contaminant, a sample is taken and sent ashore for analysis.

The standard should enable an engineer to control boiler water and feed water treatment under all normal working conditions. Detailed instructions for use when conditions are abnormal are beyond the scope of this standard and expert advice should be obtained from qualified advisers.

Basic methods of chemical treatment are described from which it should be possible to select a suitable treatment for most ships, bearing in mind the quality of make-up feed water, the boiler pressure and whether a deaerator is fitted or not. In all cases alkaline treatment chemicals are used, often with various oxygen scavengers. The use of neutralizing and filming amines for protection against corrosion of the steam and condensate systems, hydrazine for oxygen removal and anti-foams for preventing carry-over are included.

Summary of pages

This document comprises a front cover, an inside front cover, pages i to iv, pages 1 to 86, an inside back cover and a back cover.

This standard has been updated (see copyright date) and may have had amendments incorporated. This will be indicated in the amendment table on the inside front cover.

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1) 1 bar = 10^5 N/m^2 = 100 kPa = approximately 14 lbf/in^2.

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Section 1. General

1 Scope

This British Standard gives recommendations on the treatment of water for marine boilers with working pressures up to 130 bar. It applies to six groups of boilers, classified according to their operating pressures as follows (see also **17.1**).

Group 1. Boilers up to 17.5 bar

Group 2. Boilers from 17.5 bar to 31 bar

Group 3. Boilers from 31 bar to 42 bar

Group 4. Boilers from 42 bar to 60 bar

Group 5. Boilers from 60 bar to 80 bar

Group 6. Boilers from 80 bar to 130 bar

Section 6 of the standard gives detailed information on each of these groups. This section gives recommendations for feed water and condensate as well as for the water in the boilers.

This standard is concerned with water conditions for boilers and associated plant, but is not intended to cover all details of the maintenance of equipment.

2 References

The titles of the publications referred to are listed on the inside back cover.

3 Definitions

For the purposes of this British Standard, the following definitions apply. (See also Appendix A.)

3.1
feed water

water fed by the feed pumps to the boiler

3.2
boiler water

water circulating within the boiler containing dissolved solids from the feed water and also conditioning chemicals

3.3
make-up water

water added to replace system water losses, e.g. from blowdown

NOTE 1 This is sometimes known as extra feed or make-up feed.

NOTE 2 Suitable water quality is normally produced by evaporation, though base exchange softening or evaporation followed by demineralization may be used.

3.4
condensate

water formed by condensation of steam from the boiler

4 Control of treatment ashore and afloat

In order to secure uniformity and continuity of water treatment throughout a fleet of vessels, it is important to organize a system of supervision and control on lines similar to those suggested in this standard. It is advisable to secure the cooperation of water treatment consultants for this purpose.

It cannot be too strongly emphasized that control, including regular testing, is the keystone upon which success of treatment depends, and if a company's own chemical staff is not available, a member of the engineer superintendent's staff should be trained in water treatment.

The application and control of any chemical treatment should be in the hands of the engineer in charge of the boilers and the success of the treatment can be assured only by close cooperation between the engineers and those responsible for specifying the treatment. It is recommended that this cooperation should include the shore staff, i.e. superintendents and those responsible for maintaining the supply of materials. There is, therefore, an administrative as well as a technical effort required, the former requiring first attention. The development of a particular case may be visualized in stages somewhat as follows.

a) Contact between consultants and the engineer superintendent. Collection of information on boiler problems, e.g. on feed water, failures and matters of general interest. General discussion of methods of treatment and control.

b) Inspection of the boilers. Discussion with ships' chief engineers.

c) Formulation of chemical treatment and methods of application and control.

d) Presentation and explanation to the engineer superintendent and discussion of arrangements to put the chosen chemical treatment into effect.

e) Training of ships' staff in control tests and routine application of chemicals, and similar training of any members of shore staff who will be responsible for supervision of water treatment and maintenance of chemical supplies throughout the fleet.

f) Arrangements for regular inspection of boilers and test records by trained members of staff.

g) Regular discussion of difficulties and improvements with specialists.

These items give some idea of the steps required to institute properly controlled water treatment.

Section 2. Sources of water and limiting impurities for various groups of boilers

5 Sources of water

5.1 General. There are three main types of water used to prepare make-up feed for marine boilers: evaporated waters, fresh or shore waters, and sea and tidal waters. River waters are used to a lesser extent.

5.2 Evaporated waters. These waters are obtained by distilling either fresh water or sea water. With sea water for boilers of groups 4, 5 and 6, it is better to double-evaporate or, alternatively, after a single evaporation, to pass the water through a mixed-bed demineralizing plant. Evaporated water should not contain more than 4 mg/L of dissolved solids and usually as little as 1 mg/L. Within certain limits contamination at this level should not affect the type of treatment. The dissolved oxygen content may be as high as 3 mg/L to 4.5 mg/L but this depends on how long ago the water was evaporated and whether a large surface area has been in contact with the air.

5.3 Fresh or shore waters. Immediately it forms, rain water is probably one of the purest waters in nature, but it subsequently dissolves various gases of which oxygen, carbon dioxide and sulphur dioxide are usually the most important as far as boiler plants are concerned. The carbon dioxide and sulphur dioxide combine with the water to form carbonic and sulphurous acids. These subsequently dissolve limestone and other minerals when the water passes through and over the earth's crust. Other substances, e.g. common salt (sodium chloride), Epsom salts (magnesium sulphate) and decaying vegetable matter, also dissolve in the water which then becomes a complex solution, depending on the composition of the ground through and over which it has passed. The dissolved oxygen content is usually of the order of 9 mg/L to 10.5 mg/L.

No two waters are exactly alike and a full analysis of shore water is usually obtainable from the water authority of the port in question. Some waters may be very soft but acid in nature, e.g. moorland or peaty waters; others may be very hard and alkaline. In addition all waters contain small amounts of silica in solution and may have varying quantities of solid matter in suspension.

The dissolved salts may be divided into two classes; salts of calcium and magnesium (commonly referred to as hardness salts) and other salts. The commonest of the former are the bicarbonates, chlorides, sulphates and sometimes nitrates; these are potential scale-forming compounds. The other salts consist principally of sodium bicarbonate, sodium chloride, sodium sulphate and sodium nitrate; these do not produce scale.

Whenever possible, waters containing the lowest quantity of calcium and magnesium salts and/or corrosive compounds (e.g. chlorides) should be used in preference to others.

All fresh water is liable to contamination by sea water once on board. The composition may also be changed as a result of attempts to prevent corrosion of storage tanks, either by adding lime to the water or by the action of the water on cement or other alkaline materials that may be used to cover the walls.

5.4 Sea and tidal waters. The sea receives an enormous contribution of water from rivers and at the same time loses a large volume of water by evaporation. River waters provide a continuous supply of dissolved solids to the seas, as a result of which the dissolved solids in sea water are concentrated to about fifty times that of a poor quality fresh water. The composition of sea water varies slightly according to the locality and the dissolved solids content varies in the oceans from about 32 000 mg/L to 38 000 mg/L. In landlocked seas greater variations are found at different seasons of the year.

A typical sample of sea water contains the following salts:

		mg/L
Calcium bicarbonate	$Ca(HCO_3)_2$	180
Calcium sulphate	$CaSO_4$	1 220
Magnesium sulphate	$MgSO_4$	1 960
Magnesium chloride	$MgCl_2$	3 300
Sodium chloride	NaCl	25 620
		32 280

In estuaries the composition of the water varies according to the state of the tide and is affected to some extent by winds and rainfall. The general composition of an estuary water more closely resembles that of sea water than that of fresh river water and, for the purposes of this standard, sea and tidal waters are considered together. The dissolved oxygen content is usually of the order of 9 mg/L to 10.5 mg/L.

Estuary waters contaminated with sewage, industrial effluents, organic matter, etc. should not be used.

5.5 River waters, canals and lakes. Whilst it may not be common practice to use fresh waters from rivers, canals and lakes as make-up feed, nevertheless many merchant vessels do navigate along such waterways. On occasions it may be necessary to use this water but it should first be filtered. The dissolved solids content may vary considerably but for practical purposes the filtered water can be regarded as fresh or shore water as in **5.3**.

It is essential that excessively dirty water or water contaminated with sewage, industrial effluents, organic matter, etc. is not used.

6 Effect of boiler plant design and operating conditions on required water quality

6.1 General. The recommended water qualities given in Table 1 to Table 7 are generally applicable to boiler plant of current design. Some of the other boiler types that require special consideration are described briefly in clause **7**. The manner in which design and operating procedures can influence the necessary water conditions is described in this clause. For convenience the subject is divided into two categories, low-pressure and high-pressure boilers. The first category covers basically all boilers in groups 1 to 3; the second category covers high-pressure main propulsion boilers.

6.2 Low pressure boilers

6.2.1 *Feed system and economizer.* The rating of the evaporator, the feed pump, the deaerator (if provided) and the feed system generally should take into account the quantity of make-up feed water required to replace water lost, for example, by blowdown.

In plant where a deaerator is not employed, it is good practice, when arranging the layout of pipework at a hot well, to avoid cold water being fed to the tank in close proximity to the outlet connection. Water at ambient temperature contains approximately 10 mg/L of oxygen in solution and therefore the extra feed water should be mixed with the hot returned condensate, in a manner that minimizes re-aeration, so to produce as constant a composition as possible for the final feed water. Deaerators, where fitted, should be brought into operation as soon as possible during start-up. If a boiler is used intermittently, it is, of course, necessary to ensure that the conditioning chemicals are applied in relation to the boiler operation.

It is generally desired that the pH value of the condensate and feed water should be in the range 8.5 to 9.5 (see appropriate table). This minimizes corrosion of the pipelines and economizer (if fitted) and also corrosion that is liable to occur when the colder feed water comes in contact with boiler water with the result that corrosive gases, such as carbon dioxide and oxygen, are released.

Boiler water conditioning chemicals, i.e. phosphate and sodium hydroxide, should preferably be dosed directly to the drum or, less satisfactorily, intermittently to the feed water. To avoid precipitation in feed-lines, phosphates (other than polyphosphates) should not be dosed continuously to the feed water. The point of injection into the drum should be remote from the steam off-take, sampling and blowdown facilities. If slug injection to the feed water is employed, the injection pump should be interlocked with the feed pump so that chemicals are introduced into the feed-line only when the feed pump is running.

Distillate from the evaporator is corrosive to both iron-based and copper-based materials. It is recommended that service tanks are protected with epoxy resin or other coating.

NOTE Several procedures are available for reducing the pick-up of iron and copper from this source, but they are outside the scope of this standard.

6.2.2 *Boiler.* Flame impingement is generally unlikely to cause overheating of tubes provided there are no significant water-side deposits. If such deposits are present the metal temperature is increased, which leads to an increased deposition rate and blistering or corrosion.

Steam purity is impaired by turbulence of water and steam within the boiler shell or steam drum. In order to maintain the desired steam purity it is important that, in addition to maintaining the recommended water conditions, the operating limits of pressure and output are observed. Operation of a boiler at significantly lower pressure than the design pressure can lead to serious carry-over due to the increase in specific volume of steam. The effect of load change on steam purity depends on the sensitivity of the automatic drum water level control. A sudden increase in load tends to reduce boiler pressure, leading to the formation of additional steam bubbles, increase in water level and possible carry-over. The operation of safety valves has a similar effect.

In water-tube boilers settling of sludge occurs in the lower drum due to the low velocity. The facility for removal of this sludge by intermittent blowdown should be provided. Small boxes incorporated in furnace wall water circuits for distribution purposes are not suitable for blowing down; indeed the operation of box drains on load for this purpose may lead to severe damage by its effect on the boiler circulation. Boilers are sometimes designed so that distribution boxes are subject to direct heating, others have nozzles or restrictors in the water circuits. These types may require feed water and boiler water of better qualities than those given in Table 1 to Table 7.

6.2.3 *Superheater.* The prevention of carry-over and consequent deposition of salts in the superheater is contingent upon maintaining concentrations in the boiler water below the maximum levels given in Table 1 to Table 7.

6.2.4 *Turbine.* It is generally accepted that steam fed to a turbine should contain less than 0.02 mg/L silica and at the pressures being considered this should present no problem. A steam purity of less than 0.03 mg/L of sodium ion should be aimed at; this corresponds to approximately 0.1 mg/L of total solids.

6.3 High pressure boilers

6.3.1 *Feed system and economizer.* The rating of the evaporator, the ion exchange plant (if provided), the feed pump, the deaerator and the feed system generally should take into account the quantity of feed water required to replace water lost, for example, by blowdown. The deaerator should be brought into use as soon as possible during start-up.

It is generally desired that the pH value of the condensate/feed water should be in the range 8.5 to 9.5 (see appropriate table). This minimizes corrosion of the pipelines and boiler internal fittings.

Boiler water conditioning chemicals, i.e. phosphate and sodium hydroxide, should be dosed directly to the drum. The point of injection into the drum should be remote from the steam off-take, sampling and blowdown facilities. Feed water conditioning chemicals for pH control and oxygen scavenging should be continuously dosed to the feed-line. If the feed water is also used as attemperator spray water, then it is essential to use only volatile chemicals for conditioning the feed water.

Distillate from the evaporator is corrosive to both iron-based and copper-based materials. It is recommended that service tanks are protected with epoxy resin or other coating.

NOTE Several procedures are available for reducing the pick-up of iron and copper from this source, but they are outside the scope of this standard.

Ingress of iron and copper debris is one of the prime causes of tube failures. The problem is most critical on tankers where the occasional use of feed water pumps as cargo pumps gives rise to very high levels of debris during their start-up. Maintenance of the correct chemical conditions serves to reduce the production of this debris, but even under ideal conditions some will be formed. Being particulate in nature this lends itself to removal by filtration, and consideration should be given to installing a 5 μm cartridge-type filter in the feed-line.

6.3.2 *Boiler*. Heat transfer surfaces are more prone to corrosion/deposition the higher the heat flux density and the operating temperature and pressure. For these reasons, generally lower impurity limits are recommended for high pressure boilers and for all boilers with a heat flux density exceeding 300 kW/m^2.

Flame impingement is generally unlikely to cause overheating of tubes, provided there are no significant waterside deposits. If such deposits are present, the metal temperature is increased which leads to an increased deposition rate and blistering or corrosion.

Steam purity is impaired by turbulence of water and steam within the steam drum. In order to maintain the desired steam purity it is important that, in addition to maintaining the recommended water conditions, the operating limits of pressure and output are observed. Operation of a boiler at significantly lower pressure than the design pressure can lead to serious carry-over due to the increase in specific volume of steam. The effect of load change on steam purity depends on the sensitivity of the automatic drum water level control. A sudden increase in load tends to reduce boiler pressure leading to the formation of additional steam bubbles, increase in water level and possible carry-over. The operation of safety valves has a similar effect.

If a boiler design incorporates a lower drum, then settling of sludge occurs in this drum due to the low velocity. The facility for removal of this sludge by intermittent blowdown should be provided. Small boxes incorporated in furnace wall water circuits for distribution purposes are not suitable for blowing down; indeed the operation of box drains on load for this purpose may lead to severe damage by its effect on the boiler circulation. Boilers are sometimes designed so that distribution boxes are subject to direct heating, others have nozzles or restrictors in the water circuits. These types may require feed water and boiler water of better qualities than those given in Table 1 to Table 7.

Surface-type attemperators are particularly susceptible to corrosion where there is a build-up of deposit. It is important that the tube surfaces are kept clean by attention to the feed water quality and blowdown routine.

6.3.3 *Superheater.* The prevention of carry-over and consequent deposition of salts in the superheater is contingent upon maintaining concentrations in the boiler water below the maximum levels given in Table 1 to Table 7. It is also vital that, where control of superheat temperature is by spray attemperation, the spray water should be of suitable quality, i.e. less than 1 mg/L of total solids. If an attemperator coil is incorporated in the steam or water drum, leakage at a joint or perforation of a tube is to be avoided to prevent boiler water entering the secondary superheater.

6.3.4 *Turbine.* It is generally accepted that steam feed to turbines should contain less than 0.02 mg/L of silica. Figure 4 gives the corresponding maximum concentrations of silica in the boiler water for various operating pressures and pH values. These silica levels are readily achieved by most boilers, except during the period following commissioning or extensive repairs or when shore water with a high silica content is used as feed to the evaporator. A steam purity of less than 0.03 mg/L of sodium ion should be aimed at; this corresponds to approximately 0.1 mg/L of total solids.

7 Effect of boiler type on required water quality

7.1 General. The recommendations for feed water quality and boiler water conditions given under the various boiler groups are for boilers of traditional design. There are many boiler designs for which the water treatment requires special consideration; the list given below includes the more commonly found types together with brief notes on the important features. The list is not intended to be comprehensive and may not cover all types of boiler encountered. In other cases it is recommended to seek advice from the boiler supplier.

7.2 Water-tube boilers. The only water that is suitable for water-tube boilers is distilled water. This should be obtained from fresh or sea water as described in **5.2**. For water-tube boilers in groups 1 to 4 (see **17.1**), the distillate from the evaporator should not contain more than 4 mg/L of dissolved solids. Any source of impurity giving rise to more than 10 mg/L of dissolved solids in the feed water cannot be treated in a satisfactory manner as the constant addition of chemicals to counteract this may result in the boiler priming. A further source of impurity is dissolved oxygen, and this should not exceed the limits given in the appropriate table.

For boilers in group 5, the distillate from the evaporator should contain not more than 2 mg/L of dissolved solids. A condenser leak giving rise to not more than 5 mg/L of dissolved solids in the feed water can be treated for a limited time. The dissolved oxygen content should be kept within the limit given in Table 5.

For boilers in group 6, the distillate from the evaporator should contain not more than 2 mg/L of dissolved solids. The distillate from the evaporator should be further purified by a demineralization process to provide extra feed water with a sodium ion content of less than 0.1 mg/L. The dissolved oxygen content should be kept within the limit given in Table 7.

Two methods of treatment are recommended for group 6 boilers, i.e. the use of congruent phosphate/pH treatment (see **28.5**) and low solids non-phosphate treatment (see **28.6**).

7.3 Scotch boilers, vertical boilers and steam/steam generators. The following waters are suitable for these types of boiler:

a) evaporated water;

b) fresh water with the lowest calcium plus magnesium content available but in general not more than 300 mg/L of total hardness as calcium carbonate.

A condenser leak giving rise to about 30 mg/L of dissolved solids in the feed water can be treated for a limited time but should be repaired as soon as possible.

7.4 Scotch boilers with impure feed. As with all boilers the purer the feed the better, but it is recognized that in certain ships, e.g. trawlers, a supply of good quality water cannot be provided. Waters for which only very limited treatment can be carried out are:

a) shore water contaminated with sea water;

b) sea water.

7.5 Exhaust gas boilers. Exhaust gas boilers are designed to produce low-pressure steam utilizing the heat contained in the exhaust gases from main propulsion (or large generating set) diesel engines and gas turbines. The boilers mostly have forced circulation, but may also have natural circulation, usually in a parallel water circuit with a conventionally fired auxiliary boiler. The water-side problems of this type of boiler are more often associated with operating procedures than with design. For instance, a reduction in steam demand should be achieved by bypassing gas and not by reducing the feed flow nor by isolation of sections on the water-side. Either of these actions can result in drying out and deposition of solids within the boiler. It is good practice to continue circulating water through the boiler for a period after steam production has ceased.

7.6 Dual pressure boilers. Dual pressure boilers have, as the name suggests, two water circuits. The primary circuit produces high-pressure steam which in turn passes through a secondary steam generator producing low-pressure steam. The primary circuit is basically a closed cycle requiring only minimal make-up water to replace incidental losses.

Sodium sulphite should be used for oxygen scavenging in the primary circuit to avoid the build-up of high levels of ammonia that would occur if hydrazine were used. If feed water to the secondary circuit contains a high level of dissolved oxygen, hydrazine is recommended as the oxygen scavenger so as to avoid the high level of solids that would result from the use of sodium sulphite. In other respects the water conditions should be as given in the appropriate table.

7.7 Coil boilers. Coil boilers have a single-pass forced circulation generating section from which a mixture of steam and boiler water is delivered to a separator or accumulator vessel. In this vessel the steam is separated from the water by a mechanical separator or by flashing, and the residual boiler water is recirculated to the feed tank or to the inlet of the coil. These boilers can tolerate a poorer quality of feed water, i.e. a higher than tabulated level of dissolved solids provided that all hardness has been removed.

7.8 Reheat boilers. Boiler/turbine systems using a reheat cycle are becoming more common. The use of reheat does not affect the boiler water conditioning in any way.

7.9 Packaged boilers. The modern packaged boiler is a highly rated shell and tube boiler, the heat flux density in the fire tube often being as high or higher than in a water-tube boiler. It is therefore given a separate entry in Table 1.

Section 3. Chemical cleaning

8 General

The high rate of heat transfer in modern marine boilers makes it essential that the heating surfaces are absolutely clean when new and remain clean in service. It is strongly recommended that chemical cleaning should be carried out by a recognized chemical cleaning contractor and that the operation be efficiently supervised, with chemical testing to ensure that the main acid stage is efficient and carried out without damage to the plant and that subsequent rinsing, flushing, neutralizing and passivation are satisfactory.

It is essential that the following safety precautions are observed.

a) Some gases given off during chemical cleaning are toxic or flammable or form an explosive mixture with air. The working area should be well ventilated and all means of ignition, including smoking, should be avoided.

b) Inhibitors used to restrain the attack by acid on boiler metal may leave toxic residues. Entry to a boiler or similar confined space after the use of inhibited acid should be made with care; the space should be vented thoroughly before entry and if necessary full protective clothing should be used with a face respirator having pressurized fresh air supply.

9 Pre-commission cleaning of boilers and feed systems

Wherever possible, boilers and their associated feed systems should be chemically cleaned before they are put into service. This cleaning should preferably be carried out after preliminary trials but before final acceptance by the owners. The process is designed to remove any oil, grease and surface rust that forms during erection, mill scale remaining from manufacturing processes and siliceous material that enters the plant during erection. These deposits, if not removed chemically, can cause boiler tube failures or lead to carry-over of silica and oxide particles which may deposit on turbine blading with consequent loss in efficiency.

Separate cleaning processes should preferably be used for the feed system and for the boiler or, alternatively, they can be combined. The following is an example of a commonly used sequence.

a) *Initial degreasing*. This is often carried out by boiling an alkaline solution in the boiler and circulating an alkaline solution through the feed pipework to remove traces of oil, grease and dirt.

b) *Main ammoniated citric acid clean*. This process is carried out at the appropriate temperature to remove surface rust and traces of mill scale.

c) *Flushing*. This is carried out several times to remove traces of acid and undissolved deposits.

d) *Passivation*. This often involves ammoniated citric acid at a pH value of 8 to 9 with an added oxidizing agent being circulated through the boiler and feed system. This is often followed by boiling hydrazine solution.

e) *Inspection*. This includes manual removal of undissolved deposits and debris.

Connections are needed for installation of the temporary pipework required for circulating the cleaning solutions. Provision should be made for such connections in the early design stages so that the temporary circuits can be quickly and easily placed in position when needed, with the minimum amount of dismantling of the permanent installation. It may also be necessary to bypass any units that are not to be cleaned, and suitable connections for this purpose should be fitted. Provision should also be made for an electricity supply to circulating pumps, for an adequate water supply, for heating the solutions and for disposing of the effluents to the satisfaction of local authorities.

10 Post-commission cleaning of boilers

Even with the purest feed water, reaction of steel with water to form magnetite (a protective iron oxide, Fe_3O_4) makes chemical cleaning necessary for boilers belonging to groups 5 and 6 from time to time during service. At the present time there is no generally accepted way of accurately assessing or "measuring" the potentially harmful effect of a deposit. It has become fairly common for boilers to be chemically cleaned on a preventative maintenance basis every 2 to 5 years; the interval between cleans should depend on a review of water conditions and on an examination of the boiler. It has also become fairly common to remove a section of tube and subject it to metallurgical examination; if it is found to have a significant thickness of dense deposit, then the boiler should be chemically cleaned. Non-destructive testing for this purpose has not yet reached a state of general acceptance as to methods and interpretation, sufficient for it to be endorsed by this standard.

If copper alloys are used in the condensate/feed system, copper will undoubtedly deposit in the boiler. This may require an additional one or two stages of copper removal but otherwise the procedure is on lines similar to that indicated above.

Section 4. Objectives of water treatment

11 General

The objectives of the treatments described in this standard are as follows:

a) to overcome the effects of scale-forming salts present in the feed water;

b) to reduce or prevent corrosion of the boiler and associated equipment;

c) to maintain a high steam purity to protect turbines and prevent deposition on ancillary equipment;

d) to prevent corrosion in systems where steam is condensed and recovered for further use.

If treatment is to be effective, these objectives should be achieved simultaneously.

Before any treatment is applied, a careful study should be made of the information given in this standard on various types of water, scale formation, corrosion, steam purity and feed-line corrosion.
(See clauses **5**, **12**, **14** and **15**.)

12 Scale formation

When water containing dissolved and suspended solids is evaporated in a boiler the solids concentrate and scale/deposit formation may occur. Any such scale/deposit will impede heat transfer and may restrict water flow, causing overheating and ultimate failure. One way of controlling this concentration is to use "blowdown" (see clause **16**).

Scales are complex mixtures and a large number of substances have been identified in samples taken from boilers. Typical constituents of scales and deposits are calcium carbonate, calcium sulphate, complex silicates of magnesium, sodium, iron, calcium and aluminium, calcium and magnesium phosphates, magnesium hydroxide, and iron and copper oxides. Some scales consist of a number of layers of differing nature and composition.

Although the physical form of scales may depend on the constituents present, the conditions giving rise to scale formation are likely to be the dominant factor governing the nature of the scale formed. It is possible for the same constituent, e.g. calcium carbonate, to form both hard and soft deposits.

When scale is found in boilers, its physical characteristics should be noted before any chemical analysis is carried out. Chemical analysis may be supplemented by, for example, X-ray diffraction examination of the deposit, since the information thus obtained may be useful in deciding the type of water treatment to be applied.

Calcium bicarbonate decomposes when its solution is heated, releasing carbon dioxide and forming calcium carbonate which can precipitate and deposit on heat transfer surfaces. Solutions of calcium sulphate do not decompose on heating but may still form deposit due to saturation and precipitation at the hot surfaces where high rates of water evaporation are encountered.

The effect of adherent scales is to hinder the flow of heat from the heating surfaces. Scale build-up, acting as a thermal insulator, leads to a rise in temperature of the underlying metal which in severe cases can cause softening or rupture of the metal surface.

13 Hideout

The disappearance or reduction in the concentration of certain normally soluble salts in an operating boiler indicates that hideout is occurring. This effect has been found mainly in boilers having a high rate of heat input per unit area of heating surface. Hideout may be expected to occur when the heat transfer rate exceeds about 300 kW/m^2.

The causes of hideout are not fully understood, though several have been suggested. One possible cause is inadequate circulation due either to poor design or faulty operation, such as boiler overload resulting in steam blanketing, producing restricted circulation.

Hideout has also been attributed to boiler deposits laid down in the tubes during the life of the boiler. The deposits normally have a high iron content, are very hard, and are invariably porous. Seepage occurs through the porous medium until the true metal surface is found. The concentration of the dissolved substances in the film of boiler water adjacent to these highly rated heating surfaces increases.

The film of concentrated boiler salts thus formed is assumed to remain fairly stationary close to the metal, its high concentration of salts resulting in a high boiling point and little disturbance from bubble formation. Boiling thus takes place mainly outside the film and the consequent evaporation helps to maintain or increase the concentrated film.

Eventually, some of the least soluble materials and especially those such as trisodium phosphate for which the solubility decreases markedly with increasing temperature, are actually deposited on the metal surfaces, the "mother liquor" tending to diffuse away. This leads to the disappearance of the deposited substances, which is characteristic of hideout.

Once hideout conditions have started, even sodium hydroxide will eventually be lost from the boiler water. This is liable to result in a direct reaction of the strong caustic solution with the boiler metal to produce ferroates which, when later deposited, increase the depth of the oxide layer and cause a vicious spiral condition. There is also a risk of tube failure from hydrogen embrittlement, the hydrogen being generated as a result of the aforementioned reaction between sodium hydroxide and the metal surface.

Hideout can therefore be identified by a rapid drop in the phosphate concentration while the boilers are under full load. The phosphate reserve returns when the boiler is operating under idle conditions or very low steaming conditions.

Under low steaming conditions the concentrated film and deposited solids mix with the boiler water and the concentrations of the salts concerned return to normal.

It should be stressed that the only satisfactory method of curing hideout conditions, which can eventually lead to tube failure as a result of overheating, is to chemically clean the boilers.

14 Corrosion

Corrosion results from the interaction of a metal with its environment in which the metal is dissolved or forms an insoluble reaction product such as oxide.

Reactions in boiler plant are generally between steel and an aqueous solution resulting in pitting, general wasting, caustic gouging, hydrogen embrittlement or corrosion fatigue.

Corrosion reactions are complex but may be summarized by saying that they are directly or indirectly associated with dissolved gases, oxygen, carbon dioxide, and dissolved salts either in the bulk solution or locally concentrated at the metal/water interface.

The presence of carbon dioxide and sulphur dioxide carried over in the steam may result in an acidic condensate causing corrosion in steam recovery systems (see clause **15**).

Corrosion may proceed undetected under a layer of scale until the metal is perforated or at least so weakened that it fails to withstand the pressure of the steam in the boiler.

Corrosion fatigue occurs when the metal is subjected to repeated or fluctuating stresses while in contact with a corrosive medium.

Historically, caustic cracking was a major corrosion concern in riveted drum boilers. The use of welded stress-relieved drums has alleviated the situation, although a few instances have been reported at or near expanded tube ends and in bolts securing flanged connections exposed to concentrated boiler water salts.

Precautions to prevent corrosion in idle boilers are dealt with in section 7.

15 Steam purity and feed-line corrosion

Provided that carry-over does not occur, the main impurities in the steam are likely to be carbon dioxide, oxygen and possibly silica and ammonia. Since silica has a limited solubility in steam, it is possible that if waters of high silica content are used for producing boiler feed, troubles may be experienced due to silica deposition in the cooler portions of the steam-using equipment. The limited solubility of silica means, however, that volatilization and deposition are only likely to give rise to trouble in groups 5 and 6 boilers.

Of the gaseous impurities mentioned, dissolved oxygen produces the more intense local attack, i.e. pitting. However, when oxygen and carbon dioxide are present in solution together, the corrosion rate is greater than the sum of the corrosion rates due to each gas acting separately.

Oxygen can enter the boiler dissolved in the feed water and this should therefore be treated to eliminate oxygen (see **18.8** and **18.9**). This is achieved by a combination of physical and chemical means. Physical removal is accomplished by passing the feed through a deaerator which removes most of the oxygen, and the remainder is chemically removed by the addition of a reducing agent.

Carbon dioxide and sulphur dioxide may be generated by the breakdown of salts within the boiler and may contaminate the steam giving rise to acid condensate and feed-line corrosion.

Corrosion by acid condensate can be reduced or prevented by the use of volatile amines of either the neutralizing or filming type (see **20.7**). Overdosing of neutralizing amines should be avoided because a pH value greater than about 9.5 in the steam condensate increasingly favours attack on copper alloys by ammonia in the presence of 20×10^{-3} mg/L or more of dissolved oxygen. Overdosing with filming amines can result in the deposition of wax-like deposits.

Feed-line filtration helps to prevent any particulate matter arising from corrosion of pre-boiler equipment being carried into the boilers (see **17.6**).

16 Blowdown

Assuming a boiler produces dry pure steam, any non-gaseous impurities present in the feed are concentrated in the boiler water and either deposit in the boiler or can be removed by operation of the boiler blowdown valve. Table 1 to Table 7 indicate maximum levels of chloride, dissolved solids and silica that are not to be exceeded, otherwise steam purity may be affected or corrosion of the boiler may occur. Suitable means for blowing down are a large valve opened intermittently or a small valve and/or orifice passing blowdown continuously.

Traditionally the blowdown operation for boilers operating at lower boiler pressures was also associated with removal of "suspended solids" from a boiler. These suspended solids were precipitated hardness salts, such as calcium carbonate, magnesium hydroxide, calcium phosphate, especially if shore water was used as evaporator feed or direct feed.

These suspended solids normally settled in areas of low velocity in a boiler and particularly in the lower drum of a bi-drum or multi-drum boiler. To remove the resultant sludge, a blowdown valve at the bottom of the drum was opened wide to subject the sludge to vigorous turbulence.

The adoption in recent years of higher boiler pressures and high heat flux densities has required lower levels of chloride in boiler waters, mainly to prevent boiler corrosion. This has been accomplished primarily by increasing evaporator distillate quality and generally tightening-up specifications and operating standards concerned with the ingress of sea water to the condensate/feed water system. This has been so successfully accomplished that the need for blowdown for concentration control has been greatly reduced. Furthermore, there is no longer any question of using shore water as evaporator feed for modern high-pressure boilers, so that voluminous quantities of sludge resulting from the calcium and magnesium hardness are never encountered in this class of plant.

The result of this development has been the decreasing use of the boiler blowdown valve. This may have contributed to the tendency observed in recent years for deposits of iron oxide and copper/copper oxide to form on boiler tubes. Some of the iron oxide arises due to the slow conversion of the tube metal to iron oxide, but much of it originates from the products of corrosion of the condensate/feed system. A high proportion of these products are swept from the feed system into the boiler during load change.

Thus, notwithstanding that visual examination of boilers may indicate insignificant quantities of deposit by the standard of previous years, the blowdown facility should not be regarded as being only for the purpose of concentration control but should also be used to remove corrosion products from the boiler. Even if its operation is not required for the control of chloride, dissolved solids or silica, the valve should nonetheless be operated at least daily and, for best results, after each load change.

It is important to note that valves on some manifolds are for emptying the boiler and it is essential that they are not operated when the boiler is steaming; reference should be made to the boilermaker's operating instructions.

Section 5. Treatment of feed water

17 Design considerations

17.1 Types of boiler. Owing to the wide range of operating conditions, marine boilers are (for the purposes of this British Standard) designated as follows.

Group 1. Boilers operating at pressures up to and including 17.5 bar. These boilers generally have open feed systems and no deaerators and may be of the vertical, Scotch, packaged or water-tube types and also steam/steam generators.

Group 2. Water-tube boilers operating at pressures between 17.5 bar and 31 bar with open or closed feed systems and with or without deaerators.

Group 3. Water-tube boilers operating at pressures between 31 bar and 42 bar with closed feed systems and with or without deaerators.

Group 4. Water-tube boilers operating at pressures between 42 bar and 60 bar with closed feed systems and deaerators, and possibly including condensate filtration.

Group 5. Water-tube boilers operating at pressures between 60 bar and 80 bar with closed feed systems and deaerators, and possibly including condensate filtration.

Group 6. Water-tube boilers with integral furnaces, operating at pressures between 80 bar and 130 bar.

17.2 Choice of treatment. The principal factors that determine the choice of water treatment for marine boilers are the nature and composition of the feed water and the type of boiler. For higher-pressure water-tube boilers, the feed water should ideally contain no oxygen, carbon dioxide, oil, scale-forming constituents or suspended solids. For lower-pressure water-tube and shell-type boilers, the requirements for feed water are less exacting and depend upon heat flux density and other design factors.

17.3 Make-up water. The quantity of make-up (extra feed) water used varies considerably from ship to ship depending upon the type of installation and the service, the amount varying from about 1 % to about 5 % of the total feed water. This make-up water may consist of distilled fresh water, distilled sea water, raw fresh water or softened fresh water. In an emergency, water of poorer quality than that given in section 6 may have to be used. The use of such water should be confined to as short a time as possible, and during this period the boiler steaming rate should be reduced whilst maintaining the normal operating boiler pressure and temperature.

For boilers in groups 3, 4 and 5, make-up water of evaporated water quality is essential under normal conditions.

For boilers in group 6, it is essential to purify evaporated sea water by a demineralization process for use as make-up water.

Reserve water storage tanks should be thoroughly cleaned and treated internally as required prior to loading with fresh water. The structural and piping arrangements should be such that it is virtually impossible to contaminate the make-up water by sea water or oil. Bituminous or synthetic resin coatings are preferred for the internal treatment of water tanks. Methods such as cement washing should be avoided.

17.4 Ion exchange processes

17.4.1 *Treatment of water by ion exchange.* Ion exchange may be used in a wide variety of ways to remove part or virtually all of the dissolved mineral impurities in make-up water or feed water. A comprehensive description of the range of treatment processes that can be performed by ion exchange on land is given in BS 2486 but for ship-board treatment only two processes are normally used, namely sodium ion exchange and mixed bed demineralization.

Ion exchange materials used in these processes are usually made from synthetic resins in the form of spherical beads of about 0.5 mm in diameter. These ion exchange resins are normally used in the form of a packed bed containing many millions of ion exchange beads, retained in a pressure vessel through which the water to be treated may be passed without loss of resin.

The resin beads have a cross-linked polymer structure and during manufacture fixed active ionic groups are incorporated which render the beads hydrophilic and water permeable. The fixed active groups have associated exchangeable ions which may be either cations or anions depending on the type of fixed active group implanted into the structure, if the exchangeable ions are cations, the resin is called a cation exchange resin and if the exchangeable ions are anions, the resin is an anion exchange resin.

The exchangeable ions in the water absorbed within the resin structure can only leave the resin and pass into the water surrounding the beads if they are replaced by similarly charged ions derived from salts, acids or alkalis dissolved in the surrounding water.

As the exchange occurs with many different cations or anions in the water, it is convenient to express the concentrations of all the cations or anions in the water in a common form, namely milligrams of calcium carbonate per litre, in order to assess the total ion exchange load imposed on the resin during the water treatment cycle.

The ion exchange reactions are reversible. When most of the original ions in the resin have been replaced by other ions from solution, the resin is restored to its original form by treatment with a solution containing the original ions. This process is called "regeneration".

Various ions have different affinities for the resin. An ion of higher affinity will displace one of lower affinity. This phenomenon permits resins to be used for selective removal of certain unwanted ions from a solution containing both beneficial or acceptable ions and those that are detrimental to the operation of boiler plant.

17.4.2 *Ion exchange resin capacity.* The capacity of an exchange resin is normally given as the weight in kilograms of the ions, expressed in a common form as calcium carbonate ($CaCO_3$), capable of being removed from the water by one cubic metre of exchange resin, i.e. kg $CaCO_3/m^3$ resin.

The capacity is a variable depending, for example, on the original ionic form of the resin and the nature and concentration of the ions being exchanged from the water and also on the operating temperature. It also depends upon the type, quantity and concentration of regenerant used and is affected by the age of the resin and by fouling.

17.4.3 *Removal of calcium and magnesium hardness.* The hardness due to calcium and magnesium salts present in fresh water or shore water can be eliminated by passing the hard water through an ion exchange column charged with a strong acid cation (s.a.c.) exchange resin in the sodium ion form. The softening process is correctly known as sodium ion exchange but is frequently referred to as base exchange. The treatment and regeneration stages are as follows.

a) *Treatment stage.* When water is passed through the ion exchange bed the calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions derived from the hardness or scale-forming salts dissolved in the water are exchanged for sodium (Na^+) ions contained in the ion exchange resin. The calcium and magnesium salts originally present in the water are thereby converted into their corresponding sodium salts which are not scale-forming.

1)	$2\ Na^+R^-$	+	$CaCl_2$	→	$Ca^{2+}R^-_2$	+	$2\ NaCl$
	s.a.c. resin (sodium form)		calcium chloride		s.a.c. resin (calcium form)		sodium chloride

The sodium ion exchange process does not reduce the total concentration of salts in solution or the total alkalinity of the water. The softened water in most cases still requires treatment to adjust the pH value to a suitable level and to remove dissolved oxygen.

b) *Regeneration stage.* Regeneration of the exhausted ion exchange resin is effected by treatment of the bed with a solution of sodium chloride. This treatment displaces the Ca^{2+} and Mg^{2+} ions from the resin and converts the resin back to its original Na^+ ion form. The waste product of regeneration is a mixed solution of sodium, calcium and magnesium chloride salts which may be discharged directly into the sea. Following regeneration, it is essential to rinse the resin bed to waste with fresh water in order to remove residual regenerant within the exchange bed before the unit is returned to service.

2)	$Ca^{2+}R_2^-$	+	2NaCl	→	$2Na^+R^-$	+	$CaCl_2$
	s.a.c. resin (calcium form)		sodium chloride (regenerant)		s.a.c. resin (sodium form)		calcium chloride (waste product)

The regeneration procedure may be carried out under manual or automatic control and the treatment stage may be monitored by a simple chemical test or by an automatic hardness detector. On automatic units, the regeneration sequence may be initiated by the hardness detector or from a water meter on a throughput basis.

17.4.4 *Purification of evaporator distillate.* The distillate from evaporators frequently contains between 1 mg/L and 4 mg/L of dissolved solids and may at times be further contaminated by excess carry-over. When operating boilers in groups 4 to 6, removal of these contaminants may be required and can be achieved by polishing the distillate with a mixed bed (ion exchange) demineralizer. The treatment and regeneration stages are as follows.

a) *Treatment stage.* The mixed bed demineralizer contains both strong acid cation (s.a.c.) and strong base anion (s.b.a.) exchange resins intimately mixed. The cation resin is in the hydrogen form and releases its hydrogen (H^+) ions in exchange for the metallic calcium (Ca^{2+}), magnesium (Mg^{2+}) and sodium (Na^+) cations derived from the salts contained in the distillate. In so doing, it converts the salts in the distillate into their corresponding acids.

3)	H^+R^-	+	NaCl	→	Na^+R^-	+	HCl
	s.a.c. resin (hydrogen form)		sodium chloride		s.a.c. resin (sodium form)		hydrochloric acid

The anion resin is in the hydroxyl form and releases its hydroxyl (OH^-) ions in exchange for the chloride (Cl^-), sulphate (SO_4^{2-}), nitrate (NO_3^-) bicarbonate (HCO_3^-) and silicate (SiO_3^{2-}) anions derived from the acids produced by cation exchange. The hydrogen (H^+) ions displaced from the cation resin and the hydroxyl ions displaced from the anion resin combine to form water.

4)	R^+OH^-	+	HCl	→	R^+Cl^-	+	H_2O
	s.b.a. resin (hydroxyl form)		hydrochloric acid		s.b.a. resin (chloride form)		water

By this two-stage reaction, which occurs repeatedly through the entire depth of the mixed bed column, virtually complete removal of all dissolved solids is achieved.

b) *Regeneration stage.* For regeneration, the two resins are hydraulically separated by backwashing. The anion resin, having a lower density, rises and forms a separate layer above the cation resin. Acid is injected into the unit via a distribution system located at the interface between the two resin layers and passes down through the cation resin and then to waste. A solution of sodium hydroxide is injected into the top of the unit and passes down through the anion resin layer, being collected and removed from the unit via the mid-collector.

Regeneration of mixed bed strong acid cation (s.a.c.) exchange resin is depicted by the following equations:

5)	$2\ Na^+R^-$	+	H_2SO_4	→	$2\ H^+R^-$	+	Na_2SO_4
	s.a.c. resin (sodium form)		sulphuric acid (regenerant)		s.a.c. resin (hydrogen form)		sodium sulphate (waste product)

or

6)	Na^+R^-	+	HCl	→	H^+R^-	+	NaCl
	s.a.c. resin (sodium form)		hydrochloric acid (regenerant)		s.a.c. resin (hydrogen form)		sodium chloride (waste product)

or

7)	$2\ Na^+R^-$	+	H_2NSO_3H	→	$2\ H^+R^-$	+	Na_2NSO_3H
	s.a.c. resin (sodium form)		sulphamic acid (regenerant)		s.a.c. resin (hydrogen form)		sodium sulphamate (waste product)

Regeneration of mixed bed strong base anion (s.b.a.) exchange resin is depicted by the following equation:

8)	R^+Cl^-	+	NaOH	→	R^+OH^-	+	NaCl
	s.b.a. resin (chloride form)		sodium hydroxide (regenerant)		s.b.a. resin (hydroxyl form)		sodium chloride (waste product)

After separate regeneration of the anion and cation resins the individual beds are rinsed with distillate to remove most of the residual regenerant and waste products. The two resins are remixed with vigorous agitation of the total bed by introducing air into the bottom of the bed. The bed is finally rinsed with distillate and is then ready to be returned to service.

17.4.5 *In situ regenerated marine mixed bed units.* With in situ regenerated marine mixed bed units, where the quantity of regenerant chemical required is fairly small and regeneration is required infrequently, strong liquid chemicals may be supplied and stored on board in drums. The hazards associated with storage and handling of very strong acid and liquid caustic soda (sodium hydroxide) on board ship are obvious and therefore solid regeneration chemicals, such as sulphamic acid (H_2NSO_3H) and caustic soda, are preferred in this situation. Dissolving and/or dilution tanks provided to permit preparation of sufficient regenerant solution for each regeneration should be designed to prevent spillage or splashing due to the motion of the ship.

17.4.6 *External regeneration.* Ships travelling regularly between fixed ports of call may sometimes be equipped with non-regenerable ion exchange units. When the ship enters port the exhausted resin is removed and replaced by a fresh charge, the regeneration being done on land.

17.4.7 *Installation of mixed bed units.* Evaporator distillate is usually slightly acidic, or at the very best neutral, and therefore tends to be corrosive. The very pure water produced by mixed bed demineralization is not corrosive to mild steel even when it is saturated with dissolved oxygen, but becomes corrosive when exposed to air due to pick-up of carbon dioxide. Mild steel pipework is therefore suitable for conveying mixed bed demineralized water that has not come into contact with air. However, the distillate tank and the interconnecting pipework to the mixed bed unit should be protected against corrosion. A suitable filter may be installed to protect the ion exchange resin bed from contamination by corrosion products that may be present in the distillate from time to time.

In order to ensure that the mixed bed demineralizer produces the highest quality of treated water at all times when the boiler is operating, the demineralizer should, if possible, be installed in a position where it can continuously recirculate a small proportion of the demineralized distillate back to the distillate storage. If the mixed bed unit is operated on an on/off basis, there may be a temporary deterioration in the treated water quality when the flow is re-established after an idle period.

The mixed bed unit should be furnished with monitoring conductivity instruments to provide continuous indication of the treated water quality and with alarm contacts to signal abnormally high conductivity and the necessity for regeneration.

Regeneration waste effluent from the mixed bed unit may be highly acidic or highly alkaline. For reasons of safety, facilities may have to be provided on board for collection, mixing and neutralization of this effluent before it is discharged, particularly if regeneration is likely to be carried out when the ship is stationary in port or in an inland waterway.

17.4.8 *Condensate polishing.* For boilers in group 6 and others designed to operate with a high rate of heat flux density, continuous full-flow condensate polishing may be required. As with the distillate from the evaporators, the condensate may be polished by mixed bed (ion exchange) units and these should be preceded by filtration to protect the ion exchange resins from corrosion products that may form in the condensate system.

Under normal conditions the ionic load on the ion exchange resins of the boiler condensate polishing mixed bed unit is very low and consequently this unit may be operated at a higher flow rate than those used for the distillate. The units provide a margin of capacity to cater for any unexpected ingress of salt water. Any ammonia or volatile amine present in the condensate is removed by the cation exchange resin in the mixed bed units, unless the cation resin is converted to the ammonium form before commencement of the treatment cycle. If the cation resin is operated in the hydrogen form, the proportions of cation and anion resin used in the mixed bed condensate polisher may be selected so that there is sufficient capacity in the cation resin to handle the ammonia in addition to the neutral salts that constitute a load on both the cation and anion exchange resins.

17.5 Impurities in the feed water. Most impurities that cause scale, corrosion or overheating are carried into the boiler with the feed water. These contaminants include sea water, carbon dioxide, oxygen and oil.

Salinity due to the ingress of sea water may be caused by leaking condensers or heat exchangers, or by the priming of evaporators. Condensers and heat exchangers should be tested, for example, with a fluorescent chemical and an ultraviolet lamp, as soon as contamination is suspected (see **18.6**).

Water from evaporator plant contains solids and carbon dioxide and it is strongly recommended that the vapour lines from the evaporators should not be coupled directly to the condensers in case evaporator carry-over occurs. Regular attention should be given to the automatic control mechanism for the heating steam and water levels, whilst automatic dumping valves should be fitted in the feed water make-up system which would operate in the event of contamination.

The main causes of contamination with oxygen are open feed tanks directly coupled to the boiler feed pumps, loss of steam on the low-pressure (LP) turbine glands, or leaking LP piston rod and LP valve spindle glands. Under normal running conditions or manoeuvring, contamination with oxygen may also be caused by reduction of the condensate temperature below the saturation temperature of the steam in the condenser.

To overcome these difficulties glandless types of extractor and feed pumps should be fitted in conjunction with an enclosed feed system. All the feed water should be fully deaerated prior to being pumped into the boilers and automatic gland steam pressure regulators should be fitted in lieu of hand control. Chemical treatment should be used for the removal of the last traces of oxygen and neutralization of carbon dixoide.

Oil contamination is prevalent with reciprocating engines and should be controlled using the minimum of oil recommended by the engine builders and by changing the filters in the low-pressure and high-pressure sections of the feed system at short, regular intervals.

17.6 Condensate filtration. The infrequent or intermittent use of steam-operated equipment on board ship frequently produces condensate that is heavily contaminated with corrosion products from steam and condensate lines associated with this equipment.

Heavily contaminated condensate should ideally be discharged to waste as the corrosion products, which are mainly iron and copper oxides, should be prevented from entering the boiler. In many cases, however, dumping of contaminated condensate is not practicable due to scarcity of make-up water and other considerations, and protection of the boiler can only be effectively achieved by full-flow condensate filtration.

The filters used are normally of the cellulose fibre porous cartridge type. The filter unit should contain a sufficient number of cartridges or elements to provide the required filtration area to handle the required flow. For 5 µm particle retention, the filtration area is normally calculated on the basis of about 45 tonnes of water per hour per square metre of filtration surface area.

As the cartridges are not regenerable they should be replaced with new cartridges when they are exhausted. The solids retention capacity depends on the nature of the suspended solids and the construction of the cartridges, which determines whether filtration is purely on the surface or in-depth. With surface filtration exhaustion is usually indicated by an increase in hydraulic head loss (manufacturer's stated value) whereas with in-depth filtration breakthrough of solids may occur without appreciable increase in head loss. In the latter case filtrate quality should be tested at intervals to determine whether replacement is required; alternatively, the cartridges may be replaced after a fixed quantity of water has been passed.

In many cases the replacement of cartridges can be carried out speedily but, to ensure continuous filtration capability, it may be necessary to use both duty and stand-by filters.

17.7 Instrumentation (see also Appendix F). Where appropriate, use should be made of instrumentation to simplify chemical testing or to give a better degree of control than can be obtained with intermittent chemical tests. Indicating or recording instruments are preferably installed while the ship is being fitted out, but portable instruments are available that may be fitted at any time. In a low-pressure system the reserves of treatment chemicals are usually sufficient to buffer it against the effects of inadvertent admission of harmful impurities. Daily analysis of the boiler water may then be adequate and fully instrumented and automated chemical treatment may not be justified.

However, as boiler operating pressures and heat flux densities increase, it becomes necessary to decrease the chemical reserves in order to avoid damage caused by local concentration of the treatment chemicals, e.g. caustic gouging attack. Feed water quality and boiler water conditions become more important and deviations from the recommended chemical limits need to be corrected promptly. On-line instrumentation and automation of the chemical treatment merit careful consideration for highly rated, high-pressure boiler installations. For boilers in groups 3 to 6, there should be continuous monitoring of dissolved oxygen in the feed water. If the feed water is treated with hydrazine or a neutralizing amine, the pH value of the feed water should also be monitored. Either recording or indicating instruments may be used for these tests.

If continuous monitoring is considered unnecessary, portable meters should be provided for dissolved oxygen (groups 2 to 6), for electrical conductivity (all groups) and for pH value (where the chemical treatment renders it of interest). If continuous monitoring is provided, portable meters may be used for checking purposes and also for testing at other points. Evaporators should be provided with an electrical conductivity meter on the distillate line.

For group 6 boilers, a pNa^+ (sodium ion) monitor should be used to monitor continuously the levels of sodium ion in the feed water and condensate. For boiler waters, a portable dissolved solids (electrical conductivity) meter is recommended for boilers in all groups as the best means of rapidly checking dissolved solids content; for boilers in groups 5 and 6, a dissolved solids (electrical conductivity) recording or indicating meter is recommended in addition. Other instruments for specific constituents, e.g. to determine and record phosphate values (and also pH values where congruent phosphate/pH treatment is used), may be justified for highly rated marine boiler installations.

The accuracy and reliability of on-line instrumentation are influenced by its environment, so it is advisable to install all the equipment in an enclosed, air-conditioned space. Such centralization simplifies the sampling requirements and makes it easier to carry out routine calibration, maintenance and repair.

All instruments that operate continuously can be fitted with an alarm (a bell or a flashing light) or can be arranged to shut down an item of plant, such as a sea water evaporator, if the maximum permitted level of the impurity being measured is exceeded.

With continuously recording or indicating electrical conductivity meters for feed water, a sample of the feed water just prior to the boiler feed pump should be passed through a hydrogen ion exchange column to remove dissolved gases, such as ammonia and neutralizing amines. This is particularly important if the feed water is being treated with hydrazine or a neutralizing amine. On-line conductivity meters at other points in the feed system are used to locate the source of contamination. With all instruments the instructions of the manufacturer about the sampling and other requirements of the instruments should be strictly followed. For instruments provided with electrodes, the manufacturer's recommendations for the care and maintenance of the electrodes should be followed.

18 Factors under the control of the engineer

18.1 The control of impurities in make-up water and feed water. For the satisfactory operation and maintenance of boilers, it is essential that the impurities in boiler feed water are kept to a minimum. Chemical means are available for controlling the effects of contamination but the main emphasis should be on the limitation of the ingress of impurities by the correct operation and maintenance of engine-room equipment.

18.2 Make-up water. It is of utmost importance that all water used for filling boilers and for make-up water is clean. Feed water tanks filled with sea or river water at any time for ballast purposes should be thoroughly washed out before replenishing with fresh water. Filling feed water tanks with sea or river waters should be avoided if possible. The make-up water taken from tanks is seldom as pure as the condensate to which it is added, so it is important to reduce to a minimum the losses that the make-up water is required to replace.

18.3 Impurities in feed water. The feed water that enters the boiler is the source of most of the impurities in the boiler water which give rise to scale formation or to corrosion. It is essential that any contamination of the feed water is traced to its source and stopped. The main contaminants in feed water result from the following causes:

a) priming of evaporators and boilers, leakage of condensers and heat exchangers, and ingress of sea water into feed water tanks;

b) oxygen dissolved in make-up water and from air leakage into condensers and other systems below atmospheric pressure;

c) carbon dioxide dissolved in make-up water, and from air leakage into condensers and decomposition of carbonates and bicarbonates in the boiler;

d) oil from the lubrication of engines or fuel oil from faulty heating coils;

e) scale-forming constituents arising from sea water contamination or from the use of unsoftened shore water as make-up water;

f) iron and copper oxides in condensate from deck steam lines and cargo heating coils;

g) impurities arising from the faulty operation of regenerable demineralization plant.

18.4 Evaporators. The salinity of the output from the evaporator should be monitored to ensure that distillate of an adequate quality is maintained. If the distillate is to be used as make-up water for water-tube boilers, the output should be monitored continuously by means of a suitable conductivity meter.

To maintain the quality of the distillate in submerged-coil type evaporators, priming or carry-over of water from the evaporator should be avoided. Adequate quality of the distillate may be achieved by the following.

a) Maintaining the water in the evaporator at the correct concentration and avoiding unsteady conditions in any part of the evaporator system. If exhaust steam is used, additional attention is required as unsteady evaporating conditions may result.

b) Ensuring that the designed output of the evaporator is not exceeded.

c) Maintaining the correct water level in the shell of submerged-coil type evaporators.

d) Keeping the heat exchanger tube expansions tight.

e) Ensuring that the baffles fitted in the shell of submerged-coil type evaporators are correctly assembled and free to operate, i.e. that drainage is correct.

NOTE Chemical treatment of the sea water fed to evaporators to minimize scale formation and carry-over is usual but is outside the scope of this standard.

18.5 Oil contamination. Although slight oil contamination can be treated chemically, all possible steps should be taken to prevent any traces of oil entering the feed system.

18.6 Condenser operation. For vessels not fitted with full feed flow deaerators, the condenser serves as the sole means of effecting mechanical deaeration of the feed water. The condenser should be operated with as high a condensate temperature as possible, consistent with the required vacuum, to minimize the extent to which the gases present dissolve in the condensate. The vacuum system should be maintained free from air leaks at all times.

The conductivity of the condensate should be checked frequently when steaming to ensure that cooling water leaks have not developed; it is recommended that a suitable conductivity meter should be fitted for this purpose. If hydrazine or a neutralizing amine is used for feed water treatment, the condensate sample should first be passed through a hydrogen ion exchange column in order to remove the ammonia (or amine) present before measuring the conductivity. It should be noted that some condensers may show traces of ammonia (or amine) in the residual condensate when standing idle. Time should therefore be allowed for the steam flow into the condenser to displace any such residual condensate from the hot well before any test result is taken as an indication that the condenser is leaking.

For detection of leakage of condensers or other heat exchangers, the following method has proved to be effective, being particularly useful for the location of small leaks otherwise difficult to trace. When the plant is shut down and the tubes and water boxes are emptied, the steam space in the condenser is filled with water up to the exhaust flange, a small amount of the sodium salt of fluorescein being added to the water during the process to give a concentration of 50 mg/L. After the fluorescein-treated water has been in the condenser for a few minutes, the tube plate and tubes are illuminated by ultraviolet light and any small leaks are immediately revealed by a bright green fluorescence. The fluorescein should be flushed out of the system after testing.

18.7 Gaseous impurities in condensate and feed systems. The steam condensate may be corrosive due to the solution of certain gaseous impurities originally present in the steam. These gaseous impurities include the following:

a) oxygen dissolved and entrained in feed water;

b) carbon dioxide dissolved in feed water and also formed by decomposition of carbonates added to the boiler water;

c) ammonia present in the condensate of all boilers using hydrazine as an oxygen scavenger owing to the thermal decomposition of hydrazine in the boiler water;

NOTE Traces of ammonia may be present in all feed waters.

d) sulphur dioxide from the decomposition of sodium sulphite.

Uncontrolled ingress of these impurities into the condensate and feed systems leads to rapid corrosion of these systems and also of the boiler. The effect of any corrosion taking place, apart from any wastage of equipment, is to transfer a proportion of the corrosion products (mainly iron and copper oxides) into the boiler where they may in turn be deposited on the steam-generating surfaces.

The degree of corrosion, due mainly to the presence of oxygen, is dependent on the alkalinity. Severe corrosion takes place if carbon dioxide or sulphur dioxide is dissolved in sufficient quantity to render the condensate acidic.

Corrosion of the feed and condensate system may be minimized by:

a) removing as much gaseous impurity from the feed water as possible by physical means;

b) chemical dosing of the feed water to maintain a slight alkalinity (pH value not less than 8.5) to neutralize any acidity present and to remove any remaining dissolved oxygen.

18.8 Mechanical removal of oxygen. Every effort should be made to remove, by efficient mechanical deaeration, as much of the dissolved oxygen as possible from the feed water before it enters the feed pump. Supplementary chemical treatment should normally only be used to remove the last traces of oxygen. The dissolved oxygen content of the feed water is critical in boilers with working pressures above 17.5 bar and particularly for high-pressure water-tube boilers. In lower-pressure boilers, particularly Scotch marine boilers, conditions are not so critical.

When feed systems open to the atmosphere are used, a large amount of air will be dissolved in the feed water.

The amount of oxygen may be minimized by attending to all possible sources of air leaks on the vacuum side, by avoiding splash of water in hot wells, drain and filter tanks, by closing snifting cocks on feed pumps, and by maintaining the optimum operating conditions in the condenser.

18.9 Chemical treatment of feed water

NOTE Attention is drawn to any regulations governing the use of volatile treatment chemicals in relation to the end use of steam.

The mechanical removal of gaseous impurities from condensate may be supplemented by the use of a suitable chemical treatment that will remove or neutralize the remaining impurities.

Chemicals that may be added to the feed water to minimize corrosion include the following.

a) *Hydrazine*. Hydrazine may be added to remove the residual oxygen. The hydrazine is continuously dosed into the feed water in order to maintain a suitable reserve (see **20.4**) in the boiler water. The residual hydrazine decomposes in the boiler to yield ammonia in the steam which raises the pH of the condensate. The quantity of hydrazine used should be sufficient to raise the pH value of the condensate, as measured by a continuously recording pH meter at the extraction pump outlet (before the addition point of hydrazine), to the figure indicated in the appropriate table.

CAUTION. Hydrazine is toxic, and suitable precautions for its handling should be observed. Its use is usually prohibited where the steam may come into contact with food or beverages.

b) *Neutralizing amines* (e.g. cyclohexylamine or morpholine). The action of these amines is similar to that of ammonia. They are volatile in steam and neutralize the acidity of the condensate. They should be injected periodically into the feed system in order to maintain the pH value of the condensate within the range 9.0 to 9.5 as measured by a continuously recording pH meter.

c) *Filming amines* (normally octadecylamine). These amines are wax-like solids and protect the system by forming a barrier between the metal and the water. The amine is added continuously as a dispersion in water in order to maintain a suitable reserve in the condensate. It may be injected into the steam lines or into the feed system at a point where the feed water temperature is above 80 °C.

Filming amines should under no circumstances be applied to water that is to be treated by ion exchange processes as the amines would permanently foul the resins.

Section 6. Treatment of water in the boiler

19 General

The criterion of correct treatment is the internal condition of the boiler. Since the boiler can be inspected only at infrequent intervals, its condition is assessed by carrying out regular control tests on the boiler water. In the light of the test results, appropriate remedial action should be taken through the addition of chemicals, repeated as necessary until the test results are again satisfactory.

Details of suitable treatment for various types of boilers are dealt with separately under each group of boilers.

20 Chemicals

CAUTION. All chemicals can be harmful if mishandled and suppliers' recommendations for safe handling should be carefully followed (see also Appendix C).

20.1 Sodium phosphate for precipitation of hardness salts. The important types of phosphate for this purpose are:

*di*sodium phosphate
*tri*sodium phosphate
glassy sodium phosphate

The principal conditions required for scale prevention are the maintenance in the boiler water of a reserve of *tri*sodium phosphate and of a small but definite alkalinity. In the boiler, under correct alkaline conditions, *di*sodium phosphate and glassy sodium phosphate are converted to *tri*sodium phosphate, and any excess of *tri*sodium phosphate is stable even at high boiler pressures and temperatures. *Tri*sodium phosphate precipitates from solution all the calcium in the boiler water in the form of basic calcium phosphate. Magnesium salts, even in the presence of phosphate, are usually precipitated as hydroxide (sometimes associated with silica) in the form of a sludge. The choice of a particular phosphate is governed by the alkalinity requirement of the feed water. Under comparable conditions, the alkalinity produced in the boiler by the phosphate increases in the order: glassy sodium phosphate, *di*sodium phosphate, *tri*sodium phosphate. With shore waters of high bicarbonate content as make-up water, *tri*sodium phosphate often gives an excessive alkalinity and therefore glassy sodium phosphate is more suitable.

20.2 Sodium hydroxide or sodium carbonate for providing alkalinity. It is often necessary to supplement the alkalinity produced even when the highly alkaline *tri*sodium phosphate is used. For this purpose sodium hydroxide (caustic soda) or sodium carbonate (soda ash) may be used. Under the action of temperature and pressure in the boiler, sodium carbonate is partly converted to sodium hydroxide which reacts with the magnesium hardness salts to form insoluble magnesium hydroxide and the corresponding sodium salts. Sodium carbonate is not normally used for the precipitation of calcium in the treatment of water in marine boilers.

For boilers in groups 3 to 6, it is preferable to use sodium hydroxide in place of sodium carbonate since decomposition of sodium carbonate would release carbon dioxide.

For boilers in group 1, it is preferable to use sodium carbonate in place of sodium hydroxide to provide alkalinity because of ease of handling. For such boilers, a carbonate/organic polymer treatment should be used in place of the more usual alkali/phosphate treatment.

For boilers in group 2, sodium hydroxide and sodium carbonate are equally suitable.

20.3 Polyelectrolytes, tannins and other chemicals for physical conditioning of precipitates (sludge conditioning). Any precipitate produced should not be allowed to adhere to the heat-transfer surfaces. To prevent this possibility many treatments include polyelectrolytes, tannins and various other chemicals that physically affect the finely divided particles and form a non-adherent sludge rather than scale. The amounts of these ingredients required are dependent on the conditions to be met and can only be prescribed when these conditions are known.

The problem of excess sludge in group 1 boilers can be overcome by using an alkali/organic polymer treatment. By avoiding the use of phosphate, cleaner boilers result since the organic polymer prevents the formation of scale, adherent deposits and sticky sludges. The elimination of phosphate sludge accumulation enables salt water contamination to be tolerated to a greater extent.

20.4 Sodium sulphite (preferably catalyzed) or hydrazine for removal of traces of oxygen. The dissolved oxygen content of the feed water is critical in the case of boilers with working pressures above 17.5 bar, and particularly so for highly rated water-tube boilers.

In certain types of low-pressure boilers, particularly with the more highly rated boilers, removal of dissolved oxygen is also necessary and this is generally carried out by chemical means alone.

For boilers in groups 1 and 2, sodium sulphite (preferably catalyzed) is used to remove residual oxygen. A reserve of 50 mg/L to 100 mg/L of sodium sulphite (as Na_2SO_3) should be maintained in the boiler water.

For group 2 boilers, the oxygen content of the feed water should not exceed 0.06 mg/L (0.04 mL/L) and efforts should be made to reduce it to below 0.03 mg/L (0.02 mL/L) especially for highly rated water-tube boilers.

For group 3 boilers, sodium sulphite or hydrazine is used to remove residual oxygen. A reserve of 20 mg/L to 50 mg/L of sodium sulphite (as Na_2SO_3) or 0.1 mg/L to 1.0 mg/L of hydrazine should be maintained in the boiler water. In boilers working at these pressures, the oxygen content of the feed water should not exceed 0.03 mg/L (0.02 mL/L).

For boilers in groups 4, 5 and 6, only hydrazine should be added to remove oxygen from the feed water. A reserve of 0.1 mg/L to 1.0 mg/L of hydrazine should be maintained in the boiler water or, if the reserve in group 6 boilers is too small to measure, the dosage of hydrazine applied continuously should be at least twice the stoichiometric requirement of the dissolved oxygen in the feed water following physical deaeration.

20.5 Chemicals for the prevention of caustic cracking

NOTE The comments and recommendations given in this subclause are the best that can be made in the light of present knowledge on a subject still under investigation. Chemicals other than those given have been suggested for the same purpose, e.g. tannins and sodium silicate.

The prevention of scale and corrosion is to a great extent dependent upon maintaining the correct kind and amount of alkalinity in the boiler water. However, the presence of caustic soda in the boiler can lead to the development of caustic cracking (intercrystalline cracking) of the boiler metal in places where an excessive concentration of sodium hydroxide occurs in contact with heavily stressed metal, e.g. within riveted overlapped seams, especially where there is a slight leakage to atmosphere.

For boilers in groups 1 and 2, the use of sodium sulphate and sodium nitrate is recommended to prevent the development of cracks (for details see Table 1 and Table 2). For boilers in groups 3, 4 and 5, persistent leakage may cause caustic cracking, and appropriate remedial action should be taken if leakage is detected. For boilers in group 6, if the feed water quality is suitable and adequate control testing facilities are available, two alternative procedures are recommended: congruent phosphate/pH treatment (see **28.5**) and low solids non-phosphate treatment (see **28.6**).

No water treatment can prevent the extension of any existing intercrystalline cracks. Any boiler with a history of persistent leakage or seepage at rivet heads or seams should therefore be examined by a responsible person with a wide experience of this class of trouble.

20.6 Antifoams for minimizing foaming. Foaming may be minimized by the application of small doses of antifoams that destroy and suppress the layers of foam on the boiler water which lead to carry-over. The use of antifoam, however, will probably not be effective if the boiler operation is faulty or if the carry-over is caused by purely mechanical factors.

Antifoams may be applied separately or as a constituent of chemical mixtures. They are complex organic compounds of high relative molecular mass and should be used according to the instructions provided by the suppliers.

20.7 Filming amines or neutralizing amines for prevention of corrosion in steam and condensate systems. Steam and condensate lines are subject to corrosion caused by oxygen, carbon dioxide or sulphur dioxide in the steam (see clause **15** and **18.7**). Such corrosion may be prevented by treatment to remove the last traces of oxygen (see **20.4**) supplemented by the use of either filming or neutralizing amines.

Filming amines may be added to boilers in groups 1 and 2 with open feed systems. Neutralizing amines (such as cyclohexylamine and morpholine) are used in boilers where the amount of make-up feed water is small and where either a deaerator is fitted or a closed feed system is in use.

The recommendations of the suppliers of both filming and neutralizing amines regarding dosage and points of application should be followed.

20.8 Chemical mixture. If a feed water has a constant composition, it may be convenient to use a phosphate, alkali and sludge conditioner ready mixed in constant proportions (see **C.11**). Such prepared mixtures allow the three constituent chemicals to be added simultaneously.

For group 1 boilers using alkali/organic polymer treatment, irrespective of whether the feed water is of constant or variable composition, it is more convenient to apply separate formulations of alkali with antifoam and of polymer with antifoam to allow for the variable alkali requirements.

21 Limits of treatment

If gross contamination occurs, either as a result of serious leakage or of unavoidable use of sea water feed, the addition of chemicals to the full extent required by the impurities would produce an excessive quantity of sludge that could lead to tube and furnace failures. Further, the amount of soluble salts left in the water would increase to such a high figure that there would be a serious risk of foaming and carry-over.

The addition of chemicals is therefore not appropriate to all feed water conditions and should be stopped if the contamination becomes excessive. The causes of such contamination should be rectified before further treatment is undertaken.

22 Sampling arrangements and equipment

For efficient sampling, the provision of a cooling coil and sampler valve panel with labelled valves is recommended (see Figure 1).

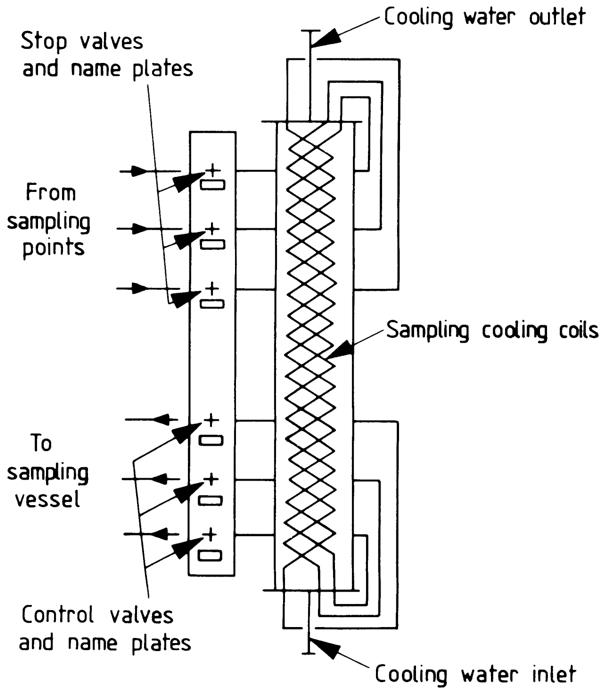

Figure 1 — Sample cooling coil for multiple sampling points

If oxygen and hydrazine tests are being carried out, the cooling coil should be made of stainless steel. The rate of flow (about 300 mL/min) should be adjusted by a control valve at the cooling coil outlet pipe.

Water-tube boilermakers provide shut-off valves at selected sampling points, which are piped individually to the stop valve on the sampler panel.

For feed water and distillate, sampling points with shut-off valves are recommended for the extraction pump outlet, the feed pump discharge line and the deaerator outlet. These points should be piped to stop valves on the sampler panel. If a deionization plant is installed, the maker's instructions for sampling should be followed. The instructions for pH meters, conductivity meters and pNa^+ (sodium ion) monitors should be carefully followed when selecting sampling points for these instruments.

To provide a sample at ambient temperature, cooling is required. Fresh or evaporated chilled water is recommended for cooling purposes, and is a necessity where stainless steel cooling coils are fitted.

Before taking the test sample, the water from the coil and pipework should be run to waste for a time sufficient to flush out the sampling lines, and then the collecting vessel should be rinsed three times with the water to be tested. Samples should not be taken within 2 h of chemical dosage. However, they should be tested as soon as possible after collection.

The special sampling procedures for individual tests should be carefully followed, and it is recommended that tests be carried out and the results recorded at the frequency given in the table applicable to the boiler pressure.

Smaller boilers in group 1 may have a sampling cock without a cooling coil for sampling. In such circumstances the sample becomes more concentrated than the water in the boiler due to the loss of flash steam when the sample is taken.

23 Group 1 boilers

23.1 Operating pressure. Group 1 boilers operate at pressures up to and including 17.5 bar.

23.2 Types of boiler. The following types of boiler are found in group 1:

Scotch boilers
vertical boilers

packaged boilers
water-tube boilers (low pressure)
steam/steam generators.

These boilers generally have open feed systems and no deaerators.

23.3 Make-up water. The make-up water used is usually fresh water, or occasionally distilled sea water or distillate water from an evaporator. Some tugs, colliers and trawlers occasionally use raw sea water in emergency as make-up (see **23.5.1**) whereas some small older steam vessels use raw sea water as make-up.

23.4 Treatment chemicals. The principal chemicals used are as follows:

a) sodium phosphate to prevent scale;

b) sodium carbonate or sodium hydroxide to give a suitable alkalinity in the boiler water and to assist in minimizing corrosion;

c) polyelectrolytes, sodium aluminate, starch and tannins to condition the sludge;

d) sodium sulphite (preferably catalysed) to remove the last traces of oxygen;

e) sodium sulphate or sodium nitrate to minimize the risk of caustic cracking in riveted boilers;

f) antifoams to minimize carry-over due to formation of a foam layer;

g) filming amines to protect against corrosion of feed and condensate systems when necessary.

23.5 Treatment

23.5.1 *Initial treatment*. Whenever a boiler is filled, suitable quantities of the appropriate chemicals should be added.

In the absence of any special instructions the appropriate chemicals may be applied in the form of a mixture similar to that described in **C.11**; 0.5 kg of this mixture should be added for every 1 000 kg of water used to fill the boiler.

If sodium sulphate or sodium nitrate is used, it should be put into the boiler as part of the initial treatment and replaced when the boiler has been blown down, or emptied and refilled. On each occasion, either 0.75 kg of anhydrous sodium sulphate or 1.5 kg of the crystalline salt or 0.2 kg of sodium nitrate should be used per 1 000 kg of water put into the boiler.

If a boiler has unavoidably to be filled with hard or moderately hard fresh water and the advice of a water treatment specialist is not available, twice the stated amounts of chemicals should be used. Any discrepancy between the resulting boiled water characteristics (measured after the boiler has steamed for at least 2 h) and those given should be corrected during the subsequent period of steaming.

23.5.2 *Subsequent treatment during steaming*. During steaming the chemicals should be added to the boiler water as described in **23.5.3**, if required, following the routine control tests and in the amounts indicated by the results of these tests. The usual control tests and the frequency of making them are stated in Table 1, together with the recommended characteristics to be maintained in a correctly treated boiler water. Other values may at times be recommended by water treatment advisers to meet special conditions.

23.5.3 *Methods of applying chemicals*. The various chemicals in the amounts required following each series of daily or weekly control tests should be dissolved in water of evaporated quality, using hot water at about 65 °C for chemicals that are difficult to dissolve. The water should be contained in a steel or plastics tank of suitable capacity and the whole of the solution should be added as a "slug". To make the solution use about 4.5 L of water for each 500 g of chemical, adding the latter slowly to the water (not vice versa) with constant stirring until solution is complete. See Appendix C for precautions to be taken in handling chemicals.

When the boiler is open it may be filled by pouring the solution through a manhole, but when the boiler is closed the solution should be conveyed through a special feed-line; suitable alternative arrangements for this are shown in Figure 2. Whichever of these arrangements is employed, the chemical solution should be followed by condensate to make sure that the interior of the dosing equipment is left in a clean condition. This prevents any chemical crystallizing and possibly blocking the pipe during the periods between applications of the chemicals.

If the aforementioned method cannot be conveniently employed, the solutions may be passed through the auxiliary feed-line, the point of application being as close as possible to the inlet side of the auxiliary feed pump. If this alternative method is used, care should be taken to pass feed water or preferably condensate through the auxiliary pump and feed-line immediately after the chemicals, and to continue this washing process for at least 15 min.

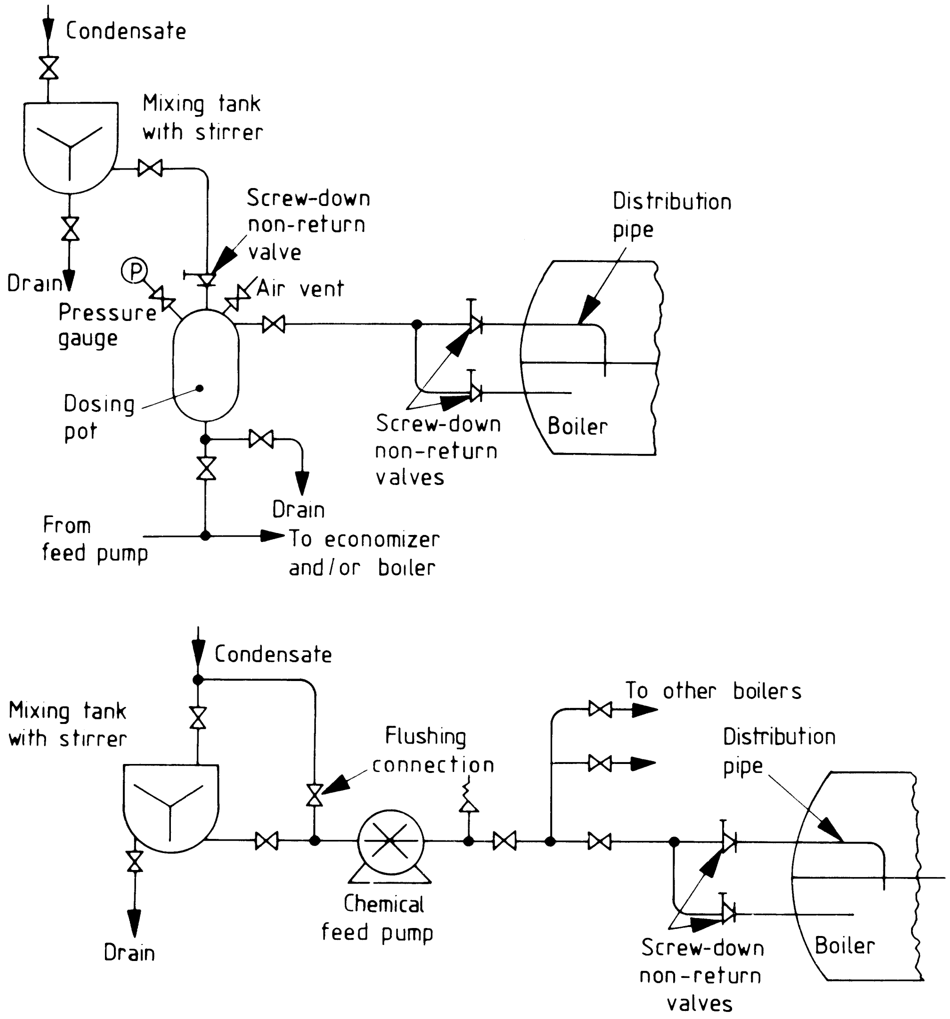

Figure 2 — Alternative methods of adding chemicals

23.5.4 *Sampling and control tests.* Samples should be taken from each boiler every day and tested within 30 min. If tests cannot be carried out within this time, samples should be stored in completely filled and sealed bottles until required. Details of control tests are given in Appendix D. If sodium sulphite is in use, the sulphite test (see **D.17**) should be carried out as soon as possible and not more than 10 min after taking the sample.

NOTE For sampling arrangements and equipment, see clause **22**.

23.5.5 *Adjustment of chemical treatment*

23.5.5.1 *Chemical mixture.* If the chemicals are used in the form of a mixture (see **20.8**), and the control tests on the boiler water show an alkalinity to phenolphthalein below the lower limit recommended in Table 1, then an appropriate amount of chemical mixture should be added in accordance with the manufacturer's instructions.

If the alkalinity to phenolphthalein is above the upper limit, treatment with chemical mixture should be suspended until the excess is consumed. If the boiler water hardness cannot be reduced below the value given in Table 1 without making the alkalinity to phenolphthalein too high, supplementary additions of sodium phosphate and sludge conditioning agent should be made.

23.5.5.2 *Separate chemicals.* If separate chemicals are used, the amounts of each should be varied individually as follows.

a) *Sodium phosphate.* If the phosphate test (see **D.14**) shows less than 30 mg/L of sodium phosphate as PO_4, the next addition should be increased by adding the appropriate amount of one of the following (in g per 1 000 kg of water in the boiler) for every 10 mg/L that the phosphate content of the boiler water is below 50 mg/L (i.e. the mean of the range given in Table 1):

	g per 1 000 kg
anhydrous *di*sodium phosphate	15
crystalline *di*sodium phosphate dodecahydrate	38
crystalline *di*sodium phosphate dihydrate	19
anhydrous *tri*sodium phosphate	17
crystalline *tri*sodium phosphate	40
glassy sodium phosphate	11

If the phosphate test shows more than 70 mg/L of phosphate as PO_4, no further phosphate should be added.

b) *Sodium carbonate or sodium hydroxide.* If the alkalinity to phenolphthalein in the boiler water is less than the lower limit recommended in Table 1, 60 g of sodium carbonate or 40 g of sodium hydroxide per 1 000 kg of water in the boiler should be added for every 50 mg/L of alkalinity deficiency.

NOTE These quantities are slightly in excess of the theoretically required amounts.

c) *Sludge conditioning agent.* This should be used in suitable quantities if and as recommended by the water treatment advisers.

d) *Antifoams.* These should be used in suitable quantities if and as recommended by the water treament advisers.

e) *Sodium sulphite.* If this chemical is used, the excess in the boiler water should be maintained within the recommended limits (see Table 1). If the excess is below 50 mg/L as Na_2SO_3, 20 g of crystalline or 10 g of anhydrous sodium sulphite per 1 000 kg of water in the boiler should be added for each 10 mg/L of sulphite deficiency below 75 mg/L.

23.5.5.3 *Alkali/organic polymer treatment.* If an alkali/organic polymer treatment is used, the amounts of each chemical should be varied individually as follows.

a) *Sodium carbonate or sodium hydroxide.* If the alkalinity to phenolphthalein in the boiler water is less than the lower limit recommended in Table 1, 60 g of sodium carbonate or 40 g of sodium hydroxide per 1 000 kg of water in the boiler should be added for every 50 mg/L of alkalinity deficiency.

NOTE These quantities are slightly in excess of the theoretically required amounts.

Organic polymer. The additions of polymer should be made daily. The daily requirements of polymer are calculated from the following

Daily evaporation of boilers	**Amount of polymer to be added daily (20 % polymer solutions in water)**
50 t per day	750 mL
100 t per day	1 500 mL
150 t per day	2 250 mL

As most of the polyacrylate polymer solutions used in this form of treatment can vary in strength from 10 % to 40 %, it is necessary to use the appropriate factor when calculating the daily requirements of polymer.

The amount of daily additions of polymer are not critical to within narrow limits and can be based on the average daily evaporation over several weeks.

23.5.6 *Protection of steam and condensate systems.* Normally, protection of steam and condensate systems of group 1 boilers are not required but if corrosion is a serious problem, recourse may be made to the use of a filming amine. If used, this is normally applied to the boiler feed tanks continuously but downstream of any filters and is controlled to maintain a reserve of amine in the condensate.

24 Group 2 boilers

24.1 Operating pressure. Group 2 boilers operate in the pressure range 17.5 bar up to and including 31 bar.

24.2 Type of boiler. A group 2 boiler is of the water-tube type with an open or closed feed system and which may or may not have a deaerator.

24.3 Make-up water. The make-up water is usually evaporated sea water or fresh water. Base-exchanged softened fresh water is also used occasionally and, rarely, raw fresh water.

Table 1 — Boiler water, feed water and condensate characteristics for group 1 boilers (up to 17.5 bar)

a) Boiler water

Type of boiler	Frequency of test								
	Daily	Weekly	Daily	Daily	Daily	Daily	Weekly		Daily where separate chemicals are used
	Alkalinity to phenolphthalein	Caustic alkalinity	Chlorides (max.)	Conductivity at 25 °C (max.)	EDTA hardness (max.)	Sulphite excess	Sodium level to deter caustic cracking		Phosphate reserve
							Sulphate	Nitrate	
	mg/L as $CaCO_3$	mg/L as $CaCO_3$	mg/L as NaCl	µS/cm[a]	mg/L as $CaCO_3$	mg/L as Na_2SO_3	mg/L as Na_2SO_4	mg/L as $NaNO_3$	mg/L as PO_4
Scotch	300 to 700	150 to 500	3 000	10 000	5	50 to 100	At least 2.0 times the caustic alkalinity expressed as $CaCO_3$	At least 50 % the caustic alkalinity expressed as $CaCO_3$	30 to 70
Vertical	300 to 500	150 to 400	1 200	4 500	5	50 to 100			
Steam/steam generators	150 to 300	75 to 250	350	3 000	5	50 to 100			
Water-tube	150 to 300	75 to 200	350	2 250	5	50 to 100			
Packaged boiler	150 to 300	75 to 250	350	3 000	5	50 to 100			

b) Feed water and condensate; daily tests

Test sample	Chloride (max.)
	mg/L as NaCl
Feed water	10
Condensate	10

NOTE 1 For simplicity in calculation of reagent strengths, alkalinity and hardness are expressed in terms of mg/L as $CaCO_3$.

NOTE 2 To convert from sodium chloride in mg/L as NaCl to mg/L in terms of $CaCO_3$ multiply by 0.85 and to convert to mg/L as Cl multiply by 0.61.

NOTE 3 If a filming amine is used for the treatment of condensate systems, a reserve of 1 mg/L as amine should be maintained in the condensate from the condensers.

[a] Microsiemens per centimetre.

24.4 Treatment chemicals. The principal chemicals used are as follows:

a) sodium phosphates to prevent scale;

b) sodium carbonate or sodium hydroxide to give a suitable alkalinity in the boiler water and to assist in minimizing corrosion;

c) polyelectrolytes, sodium aluminate, starch and tannins to condition the sludge;

d) sodium sulphite (preferably catalysed) to remove the last traces of oxygen;

e) sodium sulphate or sodium nitrate to minimize the risk of caustic cracking in riveted boilers;

f) antifoams to minimize carry-over due to formation of a foam layer;

g) neutralizing amines, e.g. cyclohexylamine or morpholine, or filming amines, e.g. octadecylamine, to protect against corrosion of feed and condensate systems.

24.5 Treatment

24.5.1 *Initial treatment.* Whenever a boiler is filled, suitable quantities of the appropriate chemicals should be added.

In the absence of any special instructions the appropriate chemicals may be applied in the form of a mixture similar to that described in **C.11**; 0.5 kg of this mixture should be added for every 1 000 kg of water used to fill the boiler.

If sodium sulphate or sodium nitrate is used, it should be put into the boiler as part of the initial treatment and replaced when the boiler has been blown down, or emptied and refilled. On each occasion, 0.75 kg of anhydrous sodium sulphate or 1.5 kg of the crystalline salt or 0.2 kg of sodium nitrate should be used per 1 000 kg of water put into the boiler.

If unavoidably a boiler has to be filled with hard or moderately hard fresh water and the advice of a water treatment specialist is not available, twice the stated amounts of chemicals should be used. Any discrepancy between the resulting boiler water characteristics (measured after the boiler has steamed for at least 2 h) and those specified should be corrected during the subsequent period of steaming.

24.5.2 *Subsequent treatment during steaming.* During steaming the chemicals should be added to the boiler water as described in **24.5.3**, if required, following the routine control tests and in the amounts indicated by the results of these tests. The usual control tests and the frequency of making them are stated in Table 2, together with the recommended characteristics to be maintained in a correctly treated boiler water. Other values may at times be recommended by water treatment advisers to meet special conditions.

24.5.3 *Methods of applying chemicals.* The various chemicals in the amounts required following each series of daily or weekly control tests should be dissolved in water of evaporated quality, using hot water at about 65 °C for chemicals that are difficult to dissolve. The water should be contained in a steel or plastics tank of suitable capacity and the whole of the solution should be added as a “slug”. To make the solution use about 4.5 L of water for each 500 g of chemical, adding the latter slowly to the water (not vice versa) with constant stirring until solution is complete. See Appendix C for precautions to be taken in handling chemicals.

When the boiler is open it may be filled by pouring the solution through a manhole, but when the boiler is closed the solution should be conveyed through a special feed-line; suitable alternative arrangements for this are shown in Figure 2. Whichever of these arrangements is employed, the chemical solution should be followed by condensate to make sure that the interior of the dosing equipment is left in a clean condition. This prevents any chemical crystallizing and possibly blocking the pipe during the periods between applications of the chemicals.

If the aforementioned method cannot be conveniently employed, the solutions may be passed through the auxiliary feed-line, the point of application being as close as possible to the inlet side of the auxiliary feed pump. If this alternative method is used, care should be taken to pass feed water or preferably condensate through the auxiliary pump and feed-line immediately after the chemicals, and to continue this washing process for at least 15 min.

24.5.4 *Sampling and control tests.* Samples should be taken from each boiler every day and tested within 30 min of being taken. If tests cannot be carried out within this time, samples should be stored in completely filled and sealed bottles until required. Details of control tests are given in Appendix D. If sodium sulphite is in use, the sulphite test (see **D.17**) should be carried out as soon as possible and not more than 10 min after taking the sample.

NOTE For sampling arrangements and equipment, see clause **22**.

24.5.5 ***Adjustment of chemical treatment***

24.5.5.1 *Chemical mixture*. If the chemicals are used in the form of a mixture (see **20.8**), and the control tests on the boiler water show an alkalinity to phenolphthalein below the lower limit recommended in Table 2, then an appropriate amount of chemical mixture should be added in accordance with the manufacturer's instructions.

If the alkalinity to phenolphthalein is above the upper limit, treatment with chemical mixture should be suspended until the excess is consumed. If the boiler water hardness cannot be reduced below the upper limit without making the alkalinity to phenolphthalein too high, supplementary additions of sodium phosphate and sludge conditioning agent should be made.

24.5.5.2 *Separate chemicals.* If separate chemicals are used, the amounts of each should be varied individually as follows.

a) *Sodium phosphate.* If the phosphate test (see **D.14**) shows less than 30 mg/L of sodium phosphate as PO_4, the next addition should be increased by adding the appropriate amount of one of the following (in g per 1 000 kg of water in the boiler) for every 10 mg/L that the phosphate content of the boiler water is below 50 mg/L:

	g per 1 000 kg
anhydrous *di*sodium phosphate	15
crystalline *di*sodium phosphate dodecahydrate	38
crystalline *di*sodium phosphate dihydrate	19
anhydrous *tri*sodium phosphate	17
crystalline *tri*sodium phosphate	40
glassy sodium phosphate	11

b) *Sodium carbonate or sodium hydroxide.* If the alkalinity to phenolphthalein in the boiler water is less than the lower limit recommended in Table 2, 60 g of sodium carbonate or 40 g of sodium hydroxide per 1 000 kg of water in the boiler should be added for every 50 mg/L of alkalinity deficiency.

NOTE These quantities are slightly in excess of the theoretically required amounts.

Table 2 — Boiler water, feed water and condensate characteristics for group 2 boilers (17.5 bar to 31 bar)

a) Boiler water

Type of boiler	Frequency of test								
	Daily	**Weekly**	**Daily**	**Daily**	**Daily**	**Daily**	**Weekly (riveted boilers only)**		**Daily**
	Alkalinity to phenolphthalein	**Caustic alkalinity**	**Chlorides (max.)**	**Conductivity at 25 °C (max.)**	**EDTA hardness (max.)**	**Sulphite excess**	**Sodium level to deter caustic cracking**		**Phosphate reserve**
							Sulphate	**Nitrate**	
	mg/L as $CaCO_3$	mg/L as $CaCO_3$	mg/L as NaCl	µS/cm[a]	mg/L as $CaCO_3$	mg/L as Na_2SO_3	mg/L as Na_2SO_4	mg/L as $NaNO_3$	mg/L as PO_4
Water-tube	150 to 300	100 to 250	150	1 500	5	50 to 100	At least 2.0 times the caustic alkalinity expressed as $CaCO_3$	At least 40 % the caustic alkalinity expressed as $CaCO_3$	30 to 70

b) Feed water and condensate; daily tests

Test sample	**Chloride (max.)**	**pH** (when a neutralizing amine is used)	**Dissolved oxygen (max.)**	
	mg/L as NaCl		mg/L	
Feed water	5	—	0.06 (0.04 mL/L)	
Condensate	5	8.5 to 9.5	—	

NOTE 1 For simplicity in calculation of reagent strengths, alkalinity and hardness are expressed in terms of mg/L as $CaCO_3$.

NOTE 2 To convert from chloride in mg/L as NaCl to mg/L in terms of $CaCO_3$ multiply by 0.85 and to convert to mg/L as Cl multiply by 0.61.

NOTE 3 If a filming amine is used for the treatment of condensate systems, a reserve of 1 mg/L as amine should be maintained in the condensate from the condensers.

[a] Microsiemens per centimetre.

c) *Sludge conditioning agent.* This should be used in suitable quantities if and as recommended by the water treatment advisers.

d) *Antifoams.* These should be used in suitable quantities if and as recommended by the water treatment advisers.

e) *Sodium sulphite.* If this chemical is used, the excess in the boiler water should be maintained within the recommended limits. If the excess is below 50 mg/L as Na_2SO_3 (see Table 2) 20 g of crystalline or 10 g of anhydrous sodium sulphite per 1 000 kg of water in the boiler should be added for each 10 mg/L of sulphite deficiency below 75 mg/L.

24.5.6 *Protection of steam and condensate systems.*

NOTE Attention is drawn to any regulations governing the use of volatile treatment chemicals in relation to the end use of the steam.

If corrosion in steam and condensate systems is a serious problem, neutralizing or filming amines can be used as follows to counteract such attack.

a) *Neutralizing amines.* Neutralizing amines may be continuously or intermittently added as a solution to the feed system at any suitable point before the main boiler feed pump. Control of the treatment should be excercised by maintaining the pH value of the condensate continuously within the range 8.5 to 9.5 as determined by a continuously recording pH meter. Only cold feed water should be used for dilution.

b) *Filming amines.* Filming amines should be added continuously using a suitable metering pump and injecting preferably into the steam main. If this method of addition is not practicable, the amine should be added to the feed water system downstream of any filter at a point where the temperature of the feed water exceeds 80 °C.

25 Group 3 boilers

25.1 Operating pressure. Group 3 boilers operate in the pressure range 31 bar up to and including 42 bar.

25.2 Type of boiler. A group 3 boiler is of the water-tube type with a closed feed system and which may or may not have a deaerator.

25.3 Make-up water. The make-up water used is evaporated water.

25.4 Treatment chemicals. The principal chemicals used are as follows:

a) sodium phosphates to prevent scale;

b) sodium carbonate or sodium hydroxide to give a suitable alkalinity in the boiler water and to assist in minimizing corrosion;

c) polyelectrolytes, starch and tannins to condition the sludge;

d) sodium sulphite (preferably catalysed) or hydrazine (preferred) to remove the last traces of oxygen;

e) antifoams to minimize carry-over due to formation of a foam layer;

f) neutralizing amines, e.g. cyclohexylamine and morpholine, or filming amines, e.g. octadecylamine to protect against corrosion of feed and condensate systems.

25.5 Treatment

25.5.1 *Initial treatment.* Whenever a boiler is filled, suitable quantities of the appropriate chemicals should be added.

In the absence of any special instructions the appropriate chemicals may be applied in the form of a mixture similar to that described in **C.11**; 0.5 kg of this mixture should be added for every 1 000 kg of water used to fill the boiler.

25.5.2 *Subsequent treatment during steaming.* During steaming the chemicals should be added to the boiler water as described in **25.5.3**, if required, following the routine control tests and in the amounts indicated by the results of these tests. The usual control tests and the frequency of making them are stated in Table 3, together with the recommended characteristics to be maintained in a correctly treated boiler water. Other values may at times be recommended by water treatment advisers to meet special conditions.

25.5.3 *Methods of applying chemicals.* The various chemicals in the amounts required following each series of daily control tests should be dissolved in water of evaporated quality, using hot water at about 65 °C for chemicals that are difficult to dissolve. The water should be contained in a steel or plastic tank of suitable capacity, and the whole of the solution should be added as a "slug". To make the solution use about 4.5 L of water for each 500 g of chemical, adding the latter slowly to the water (not vice versa) with constant stirring until solution is complete. See Appendix C for procedures to be taken in handling of chemicals.

When the boiler is open it may be filled by pouring the solution through a manhole, but when the boiler is closed the solution should be conveyed through a special feed-line; suitable alternative arrangements for this are shown in Figure 2. Whichever of these arrangements is employed, the chemical solution should be followed by condensate to make sure that the interior of the dosing equipment is left in a clean condition. This prevents any chemical crystallizing and possibly blocking the pipe during the periods between applications of the chemicals.

If the aforementioned method cannot be conveniently employed, the solutions may be passed through the auxiliary feed-line, the point of application being as close as possible to the inlet side of the auxiliary feed pump. If this alternative method is used, care should be taken to pass feed water or preferably condensate through the auxiliary pump and feed-line immediately after the chemicals, and to continue this washing process for at least 15 min.

25.5.4 *Sampling and control tests.* Samples should be taken from each boiler every day and tested within 30 min of being taken. If tests cannot be carried out within this time, samples should be stored in completely filled and sealed bottles until required. Details of control tests are given in Appendix D. If sodium sulphite or hydrazine is in use, the relevant test (see **D.11** and **D.17**) should be carried out as soon as possible and not more than 10 min after taking the sample.

NOTE For sampling arrangements and equipment, see clause **22**.

25.5.5 *Adjustment of chemical treatment*

25.5.5.1 *Chemical mixture.* If the chemicals are used in the form of a mixture (see **20.8**), and the control tests on the boiler water show an alkalinity to phenolphthalein below the lower limit recommended in Table 3, then an appropriate amount of chemical mixture should be added in accordance with the manufacturer's instructions.

If the alkalinity to phenolphthalein is above the upper limit, treatment with chemical mixture should be suspended until the excess is consumed. If the boiler water hardness cannot be reduced below the upper limit without making the alkalinity to phenolphthalein too high, supplementary additions of sodium phosphate and sludge conditioning agent should be made.

25.5.5.2 *Separate chemicals.* If separate chemicals are used, the amounts of each should be varied individually as follows.

a) *Sodium phosphate.* If the phosphate test (see **D.14**) shows less than 30 mg/L of sodium phosphate as PO_4, the next addition should be increased by adding the appropriate amount of one of the following (in g per 1 000 kg of water in the boiler) for every 10 mg/L that the phosphate content of the boiler water is below 40 mg/L:

	g per 1 000 kg
anhydrous *di*sodium phosphate	15
crystalline *di*sodium phosphate dodecahydrate	38
crystalline *di*sodium phosphate dihydrate	19
anhydrous *tri*sodium phosphate	17
crystalline *tri*sodium phosphate	40
glassy sodium phosphate	11

b) *Sodium carbonate or sodium hydroxide.* If the alkalinity to phenolphthalein in the boiler water is less than the lower limit recommended in Table 2, 60 g of sodium carbonate or 40 g of sodium hydroxide per 1 000 kg of water in the boiler should be added for every 50 mg/L of alkalinity deficiency.

NOTE These quantities are slightly in excess of the theoretically required amount.

c) *Sludge conditioning agent.* This should be used in suitable quantities if and as recommended by the water treatment advisers.

d) *Antifoams*. These should be used in suitable quantities if and as recommended by the water treatment advisers.

e) *Sodium sulphite*. If this chemical is used, the excess in the boiler water should be maintained within the recommended limits. If the excess is below 20 mg/L as Na_2SO_3 (see Table 3), 20 g of crystalline or 10 g of anhydrous sodium sulphite per 1 000 kg of water in the boiler should be added for each 10 mg/L of sulphite deficiency below 35 mg/L.

f) *Hydrazine*. If hydrazine is used to remove the last traces of oxygen, it should be added continuously, by means of a suitable metering pump, to the feed system immediately after the deaerator (if fitted) or immediately after the extraction pump if no deaerator is installed. Only cold feed water should be used for dilution.

The amount used should be sufficient to remove all oxygen in the feed water and to maintain a reserve in the boiler water of 0.1 mg/L to 1.0 mg/L as determined by the test described in **D.11**. Subject to this requirement, the quantity of hydrazine used should be sufficient to raise the pH value of the condensate, as measured by a continuously recording pH meter at the extraction pump outlet (before the addition point of hydrazine), to between 8.5 and 9.0 (between 9.0 and 9.5 if neutralizing amine treatment is also in effect).

CAUTION. Hydrazine is toxic and suitable precautions for its handling should be observed (see **C.4**).

25.5.6 *Protection of steam and condensate systems.*

NOTE Attention is drawn to any regulations governing the use of volatile treatment chemicals in relation to the end use of the steam.

If corrosion in steam and condensate systems is a serious problem, neutralizing or filming amines can be used as follows to counteract such attack.

a) *Neutralizing amines*. Neutralizing amines may be continuously or intermittently added as a solution to the feed system at any suitable point before the main boiler feed pump. Control of the treatment should be exercised by maintaining the pH value of the condensate continuously within the range 9.0 to 9.5 as determined by a continuously recording pH meter. Only cold feed water should be used for dilution.

b) *Filming amines*. Filming amines should be added continuously using a suitable metering pump and injecting preferably into the steam main. If this method of injection is not practicable, the amine should be added to the feed water system downstream of any filter at a point where the temperature of the feed water exceeds 80 °C.

26 Group 4 boilers

26.1 Operating pressure. Group 4 boilers operate in the pressure range 42 bar up to and including 60 bar.

26.2 Type of boiler. A group 4 boiler is of the water-tube type with a closed feed system and a deaerator and may include condensate filtration.

26.3 Make-up water. The make-up water used is evaporated water.

26.4 Treatment chemicals. The principal chemicals used are as follows:

a) sodium phosphates to prevent scale;

b) sodium carbonate or sodium hydroxide to give a suitable alkalinity in the boiler water and to assist in minimizing corrosion;

c) polyelectrolytes, starch and tannins to condition the sludge;

d) hydrazine to remove the last traces of oxygen;

e) antifoams to minimize carry-over due to formation of a foam layer;

f) neutralizing amines, e.g. cyclohexylamine and morpholine, or filming amines, e.g. octadecylamine to protect against corrosion of feed and condensate systems.

26.5 Treatment

26.5.1 *Initial treatment.* Whenever a boiler is filled, suitable quantities of the appropriate chemicals should be added.

In the absence of any special instructions the appropriate chemicals may be applied in the form of a mixture similar to that given in **C.11**; 0.5 kg of this mixture should be added for every 1 000 kg of water used to fill the boiler.

Table 3 — Boiler water, feed water and condensate characteristics for group 3 boilers (31 bar to 42 bar)

a) Boiler water

Type of boiler	Frequency of test							
	Daily	Daily	Daily	Daily	Daily	Daily		Daily
	Alkalinity to phenolphthalein	Caustic alkalinity	Chlorides (max.)	Conductivity at 25 °C (max.)	EDTA hardness (max.)	Sulphite excess or	Hydrazine reserve	Phosphate reserve
	mg/L as $CaCO_3$	mg/L as $CaCO_3$	mg/L as NaCl	µS/cm[a]	mg/L as $CaCO_3$	mg/L as Na_2SO_3	mg/L as N_2H_4	mg/L as PO_4
Water-tube, all welded construction	100 to 150	50 to 100	100	750	1.0	20 to 50	0.1 to 1.0	30 to 50

b) Feed water and condensate

Frequency of test	Daily or continuously using an oxygen meter	Continuously using a pH meter	Daily
Test sample	Dissolved oxygen after deaeration (max.)	pH value	Chloride (max.)
			mg/L as NaCl
Feed water	0.03 mg/L (0.02 mL/L)	—	1.0
Condensate	—	Using hydrazine 8.5 to 9.0 Using neutralizing amine 9.0 to 9.5 Using both 9.0 to 9.5	1.0

NOTE 1 For simplicity in calculation of reagent strengths, alkalinity and hardness are expressed in terms of mg/L as $CaCO_3$.

NOTE 2 To convert from chloride in mg/L as NaCl to mg/L in terms of $CaCO_3$ multiply by 0.85 and to convert to mg/L as Cl multiply by 0.61.

NOTE 3 If a filming amine is used for the treatment of condensate systems, a reserve of 1 mg/L as amine should be maintained in the condensate from the condenser.

[a] Microsiemens per centimetre.

26.5.2 *Subsequent treatment during steaming.* During steaming the chemicals should be added to the boiler water as described in **26.5.3**, if required, following the routine control tests and in the amounts indicated by the results of these tests. The usual control tests and the frequency of making them are stated in Table 4, together with the recommended characteristics to be maintained in a correctly treated boiler water. Other values may at times be recommended by water treatment advisers to meet special conditions.

26.5.3 *Methods of applying chemicals.* The various chemicals in the amounts required following each series of daily or weekly control tests should be dissolved in water of evaporated quality, using hot water at about 65 °C for chemicals that are difficult to dissolve. The water should be contained in a steel or plastics tank of suitable capacity, and the whole of the solution should be added as a "slug". To make the solution use about 4.5 L of water for each 500 g of chemical, adding the latter slowly to the water (not vice versa) with constant stirring until the solution is complete. See Appendix C for precautions to be taken in handling chemicals.

When the boiler is open it may be filled by pouring the solution through a manhole, but when the boiler is closed the solution should be conveyed through a special feed-line; suitable alternative arrangements for this are shown in Figure 2. Whichever of these arrangements is employed, the chemical solution should be followed by condensate to make sure that the interior of the dosing equipment is left in a clean condition. This prevents any chemical crystallizing and possibly blocking the pipe during the periods between applications of the chemicals.

If the aforementioned method cannot be conveniently employed, the solutions may be passed through the auxiliary feed-line, the point of application being as close as possible to the inlet side of the auxiliary feed pump. If this alternative method is used, care should be taken to pass feed water or preferably condensate through the auxiliary pump and feed-line immediately after the chemicals, and to continue this washing process for at least 15 min.

26.5.4 *Sampling and control tests.* Samples should be taken from each boiler every day and tested within 30 min of being taken. If tests cannot be carried out within this time, samples should be stored in completely filled and sealed bottles until required. Details of control tests are given in Appendix D. If hydrazine is in use, the relevant test (see **D.11**) should be carried out as soon as possible and not more than 10 min after taking the sample.

NOTE For sampling arrangements and equipment, see clause **22**.

26.5.5 *Adjustment of chemical treatment*

26.5.5.1 *Chemical mixture.* If the chemicals are used in the form of a mixture (see **20.8**), and the control tests on the boiler water show an alkalinity to phenolphthalein below the lower limit recommended in Table 4, then an appropriate amount of chemical mixture should be added in accordance with the manufacturer's instructions.

If the alkalinity to phenolphthalein is above the upper limit, treatment with chemical mixture should be entirely suspended until the excess is consumed. If the boiler water hardness cannot be reduced below the upper limit without making the alkalinity to phenolphthalein too high, supplementary additions of sodium phosphate and sludge conditioning agent should be made.

26.5.5.2 *Separate chemicals.* If separate chemicals are used, the amounts of each should be varied individually as follows.

a) *Sodium phosphate.* If the phosphate test (see **D.14**) shows less than 30 mg/L of sodium phosphate as PO_4, the next addition should be increased by adding the appropriate amount of one of the following (in g per 1 000 kg of water in the boiler) for every 10 mg/L that the phosphate content of the boiler water is below 40 mg/L:

	g per 1 000 kg
anhydrous *di*sodium phosphate	15
crystalline *di*sodium phosphate dodecahydrate	38
crystalline *di*sodium phosphate dihydrate	19
anhydrous *tri*sodium phosphate	17
crystalline *tri*sodium phosphate	40
glassy sodium phosphate	11

b) *Sodium carbonate or sodium hydroxide.* If the alkalinity to phenolphthalein in the boiler water is less than the lower limit recommended in Table 4, 60 g of sodium carbonate or 40 g of sodium hydroxide per 1 000 kg of water in the boiler should be added for every 50 mg/L of alkalinity deficiency.

NOTE These quantities are slightly in excess of the theoretically required amount.

c) *Sludge conditioning agent.* This should be used in suitable quantities if and as recommended by the water treatment advisers.

d) *Antifoams.* These should be used in suitable quantities if and as recommended by the water treatment advisers.

e) *Hydrazine.* If hydrazine is used to remove the last traces of oxygen, it should be added continuously, by means of a suitable metering pump, to the feed system immediately after the deaerator. Only cold feed water should be used for dilution.

Table 4 — Boiler water, feed water and condensate characteristics for group 4 boilers (42 bar to 60 bar)

a) Boiler water

Type of boiler	Frequency of test						
	Daily	Daily	Daily	Daily	Daily	Daily	Daily
	Alkalinity to phenolphthalein	Caustic alkalinity	Chlorides (max.)	Conductivity at 25 °C (max.)	EDTA hardness (max.)	Hydrazine reserve	Phosphate reserve
	mg/L as $CaCO_3$	mg/L as $CaCO_3$	mg/L as NaCl	µS/cm[a]	mg/L as $CaCO_3$	mg/L as N_2H_4	mg/L as PO_4
Water-tube, all welded construction	50 to 100	40 to 60	50	600	1.0	0.1 to 1.0	30 to 50

b) Feed water and condensate

Test sample	Frequency of test					
	Daily or continuously using an oxygen meter	Continuously using a pH meter	Daily	Daily	Weekly (laboratory check every 3 months to 6 months)	
	Dissolved oxygen after deaeration (max.)	pH value	EDTA hardness (max.)	Chlorides (max.)	Copper (max.)	Iron (max.)
			mg/L as $CaCO_3$	mg/L as NaCl	mg/L as Cu	mg/L as Fe
Feed water	0.015 mg/L (0.01 mL/L)	—	1.0	1.0	0.01	0.01
Condensate	—	Using hydrazine 8.5 to 9.0 Using neutralizing amine 9.0 to 9.5 Using both 9.0 to 9.5	1.0	1.0	—	—

NOTE 1 For simplicity in calculation of reagent strengths, alkalinity and hardness are expressed in terms of mg/L as $CaCO_3$.

NOTE 2 To convert from chloride in mg/L as NaCl to mg/L in terms of $CaCO_3$ multiply by 0.85 and to mg/L as Cl multiply by 0.61.

NOTE 3 If a filming amine is used for the treatment of condensate systems, a reserve of 1 mg/L as amine should be maintained in the condensate from the condenser.

NOTE 4 Figures quoted for copper and iron concentrations represent average steady load values (see **17.6**).

[a] Microsiemens per centimetre.

The amount used should be sufficient to remove all oxygen in the feed water and to maintain a reserve in the boiler water of 0.1 mg/L to 1.0 mg/L as determined by the test described in **D.11**. Subject to this requirement, the quantity of hydrazine used should be sufficient to raise the pH value of the condensate, as measured by a continuously recording pH meter at the extraction pump outlet (before the addition point of hydrazine), to between 8.5 and 9.0 (between 9.0 and 9.5 if neutralizing amine treatment is also in effect).

CAUTION. Hydrazine is toxic and suitable precautions for its handling should be observed (see **C.4**).

26.5.6 *Protection of steam and condensate systems.*

NOTE Attention is drawn to any regulations governing the use of volatile treatment chemicals in relation to the end use of the steam.

If corrosion in steam and condensate systems is a serious problem, neutralizing or filming amines can be used as follows to counteract such attack.

a) *Neutralizing amines.* Neutralizing amines may be continuously or intermittently added as a solution to the feed system at any suitable point before the main boiler feed pump. Control of the treatment should be exercised by maintaining the pH value of the condensate continuously within the range 9.0 to 9.5 as determined by a continuously recording pH meter. Only cold feed water should be used for dilution.

b) *Filming amines.* Filming amines, if used, should be added continuously using a suitable metering pump and injecting preferably into the steam main. If this method of injection is not practicable, the amine should be added to the feed water system downstream of any filter at a point where the temperature of the feed water exceeds 80 °C.

27 Group 5 boilers

27.1 Operating pressure. Group 5 boilers operate in the pressure range 60 bar up to and including 80 bar.

27.2 Type of boiler. A group 5 boiler is of the water-tube type with a closed feed system and a deaerator and may include condensate filtration.

27.3 Make-up water. The make-up water used is evaporated water, preferably purified further by a demineralization process.

27.4 Treatment chemicals. The principal chemicals used are as follows:

a) sodium phosphates to prevent scale;

b) sodium hydroxide to give a suitable alkalinity in the boiler water and to assist in minimizing corrosion;

c) polyelectrolytes, starch and tannins to condition the sludge;

d) hydrazine to remove the last traces of oxygen;

e) antifoams to minimize carry-over due to formation of a foam layer;

f) neutralizing amines, e.g. cyclohexylamine and morpholine to protect against corrosion of feed and condensate systems.

27.5 Treatment

27.5.1 *Initial treatment.* Whenever a boiler is filled, suitable quantities of the appropriate chemicals should be added.

In the absence of any special instructions the appropriate chemicals may be applied in the form of a mixture similar to that described in **C.11**; 0.5 kg of this mixture should be added for every 1 000 kg of water used to fill the boiler.

27.5.2 *Subsequent treatment during steaming.* During steaming the chemicals should be added to the boiler water as described in **27.5.3**, if required, following the routine control tests and in the amounts indicated by the results of these tests. The usual control tests and the frequency of making them are stated in Table 5, together with the recommended characteristics to be maintained in a correctly treated boiler water. Other values may at times be recommended by water treatment advisers to meet special conditions.

NOTE If there is difficulty in maintaining the phosphate level in highly rated group 5 boilers, and there is no obvious reason for this difficulty, the condition known as hideout (see clause **13**) may be occurring. If this condition is suspected, it is essential to consult the water treatment advisers.

It should be noted, however, that any substantial deviation from the limits stated in Table 5 is a clear indication of condenser leakage or other defect requiring remedial action other than the addition of chemicals. In such circumstances, the frequency of testing should be at least every 12 h rather than daily, in order to check that the faulty condition has been remedied as soon as possible.

27.5.3 *Methods of applying chemicals.* The various chemicals in the amounts required following each series of daily or weekly control tests should be dissolved in water of evaporated quality, using hot water at about 65 °C for chemicals that are difficult to dissolve. The water should be contained in a steel or plastics tank of suitable capacity, and the whole of the solution should be added as a “slug”. To make the solution use about 4.5 L of water for each 500 g of chemical, adding the latter slowly to the water (not vice versa) with constant stirring until solution is complete. See Appendix C for precautions to be taken in handling chemicals.

When the boiler is open it may be filled by pouring the solution through a manhole, but when the boiler is closed the solution should be conveyed through a special feed-line; suitable alternative arrangements for this are shown in Figure 2. Whichever of these arrangements is employed, the chemical solution should be followed by condensate to make sure that the interior of the dosing equipment is left in a clean condition. This prevents any chemical crystallizing and possibly blocking the pipe during the periods between applications of the chemicals.

If the method described above cannot be conveniently employed, the solutions may be passed through the auxiliary feed-line, the point of application being as close as possible to the inlet side of the auxiliary feed pump. If this method is used, care should be taken to pass feed water or preferably condensate through the auxiliary pump and feed-line immediately after the chemicals, and to continue this washing process for at least 15 min.

27.5.4 *Sampling and control tests.* Samples should be taken from each boiler every day and tested within 30 min. If tests cannot be carried out within this time, samples should be stored in completely filled and sealed bottles until required. Details of control tests are given in Appendix D. If hydrazine is in use, the relevant test (see **D.11**) should be carried out as soon as possible and not more than 10 min after taking the sample.

NOTE For sampling arrangements and equipment, see clause **22**.

Table 5 — Boiler water, feed water and condensate characteristics for group 5 boilers (60 bar to 80 bar)

a) Boiler water

Type of boiler	Frequency of test							
	Daily	Daily	Daily	Daily or continuously using a meter		Daily	Daily	Weekly (laboratory check every 3 months to 6 months)
	Alkalinity to phenolphthalein	Caustic alkalinity	Chlorides (max.)	Conductivity at 25 °C (max.)	EDTA hardness (max.)	Hydrazine reserve	Phosphate reserve	Silica (max.)
	mg/L as $CaCO_3$	mg/L as $CaCO_3$	mg/L as NaCl	µS/cm[a]	mg/L as $CaCO_3$	mg/L as N_2H_4	mg/L as PO_4	mg/L as SiO_2
Water-tube	50 to 80	40 to 60	30	450	1.0	0.1 to 1.0	20 to 30	3

b) Feed water and condensate

Test sample	Frequency of test					
	Daily or continuously using an oxygen meter	Continuously using a pH meter	Daily	Daily	Weekly (laboratory check every 3 to 6 months)	
	Dissolved oxygen after deaeration (max.)	pH value	EDTA hardness (max.)	Chlorides (max.)	Copper (max.)	Iron (max.)
			mg/L as $CaCO_3$	mg/L as NaCl	mg/L as Cu	mg/L as Fe
Feed water	0.01 mg/L (0.007 mL/L)	—	1.0	1.0	0.005	0.01
Condensate	—	Using hydrazine 8.5 to 9.0 Using neutralizing amine 9.0 to 9.5 Using both 9.0 to 9.5	1.0	1.0	—	—

NOTE 1 For simplicity in calculation of reagent strengths, alkalinity and hardness are expressed as mg/L in terms of $CaCO_3$.

NOTE 2 To convert from chloride in mg/L as NaCl to mg/L as $CaCO_3$ multiply by 0.85 and to mg/L as Cl multiply by 0.61.

NOTE 3 Figures quoted for copper and iron concentrations represent average steady load values (see **17.6**).

[a] Microsiemens per centimetre.

27.5.5 ***Adjustment of chemical treatment***

27.5.5.1 *Chemical mixture.* If the chemicals are used in the form of a mixture (see **20.8**), and the control tests on the boiler water show an alkalinity to phenolphthalein below the lower limit recommended in Table 5, then an appropriate amount of chemical mixture should be added in accordance with the manufacturer's instructions.

If the alkalinity to phenolphthalein is above the upper limit, treatment with chemical mixture should be entirely suspended until the excess is consumed. If the boiler water hardness cannot be reduced below the upper limit without making the alkalinity to phenolphthalein too high, supplementary additions of sodium phosphate and sludge conditioning agent should be made.

27.5.5.2 *Separate chemicals.* If separate chemicals are used, the amounts of each should be varied individually as follows.

a) *Sodium phosphate.* If the phosphate test (see **D.14**) shows less than 20 mg/L of sodium phosphate as PO_4, the next addition should be increased by adding the appropriate amount of one of the following (in g per 1 000 kg of water in the boiler) for every 10 mg/L that the phosphate content of the boiler water is below 25 mg/L:

	g per 1 000 kg
anhydrous *di*sodium phosphate	15
crystalline *di*sodium phosphate dodecahydrate	38
crystalline *di*sodium phosphate dihydrate	19
anhydrous *tri*sodium phosphate	17
crystalline *tri*sodium phosphate	40
glassy sodium phosphate	11

b) *Sodium hydroxide.* If the alkalinity to phenolphthalein in the boiler water is less than the lower limit recommended in Table 5, 8.4 g of sodium hydroxide per 1 000 kg of water in the boiler should be added for every 10 mg/L of alkalinity deficiency.

c) *Sludge conditioning agent.* This should be used in suitable quantities if and as recommended by the water treatment advisers.

d) *Antifoams.* These should be used in suitable quantities if and as recommended by the water treatment advisers.

e) *Hydrazine.* If hydrazine is used to remove the last traces of oxygen, it should be added continuously, by means of a suitable metering pump, to the feed system immediately after the deaerator. Only cold feed water should be used for dilution.

The amount used should be sufficient to remove all oxygen in the feed water and to maintain a reserve in the boiler water of 0.1 mg/L to 1.0 mg/L as determined by the test described in **D.11**. Subject to this requirement the quantity of hydrazine used should be sufficient to raise the pH value of the condensate, as measured by a continuously recording pH meter at the extraction pump outlet (before the addition point of hydrazine), to between 8.5 and 9.0 (or between 9.0 and 9.5 if neutralizing amine treatment is also in effect).

CAUTION. Hydrazine is toxic and suitable precautions for its handling should be observed (see **C.4**).

27.5.6 *Protection of steam and condensate systems.*

NOTE Attention is drawn to any regulations governing the use of volatile treatment chemicals in relation to the end use of the steam.

If corrosion in steam and condensate systems is a serious problem, neutralizing amines can be used to counteract such attack.

Neutralizing amines may be continuously or intermittently added as a solution to the feed system at any suitable point before the main boiler feed pump. Control of the treatment should be exercised by maintaining the pH value of the condensate continuously within the range 9.0 to 9.5 as determined by a continuously recording pH meter. Only cold feed water should be used for dilution.

28 Group 6 boilers

28.1 Operating pressure. Group 6 boilers operate in the pressure range 80 bar up to and including 130 bar.

28.2 Type of boiler. A group 6 boiler is of the water-tube integral furnace type and of current design and rating.

28.3 Make-up feed water. The make-up feed water used is evaporated sea water purified further by a demineralization process.

28.4 Treatment chemicals. The principal chemicals used are as follows:

a) sodium phosphates to prevent scale and for congruent control;

b) sodium hydroxide to give a suitable boiler water pH value;

c) hydrazine to remove the last traces of oxygen;

d) neutralizing amines, e.g. cyclohexylamine or morpholine, to protect against corrosion of feed and condensate systems.

For prevention of caustic cracking, two alternative treatments are available as described in **28.5** and **28.6**.

28.5 Treatment using congruent phosphate/pH treatment

28.5.1 *Introduction.* In high-pressure highly rated marine boilers, hydroxyl ions derived from an excess of sodium hydroxide can, because of localized concentration effects, lead to dissolution of iron as sodium ferroate, which is soluble and hence non-protective. Although hydrogen is liberated, tube failures usually result from wastage of the metal, rather than from hydrogen embrittlement.

It has been shown that the crystals formed by evaporation of a solution of *tri*sodium phosphate with a molar ratio $Na^+ : PO_4^{3-}$ of 3 : 1 contain mainly *di*sodium hydrogen phosphate and that the supernatant liquor contains some free sodium hydroxide. If the molar ratio of $Na^+ : PO_4^{3-}$ is kept at 2.6 : 1, or just below, no free sodium hydroxide is formed in the supernatant liquor (see Figure 3).

High localized concentrations of sodium hydroxide can thus be avoided by adjusting the required boiler water pH value in relation to the sodium phosphate level, so that even if complete evaporation occurs at the metal surface, no free sodium hydroxide is formed. In marine practice this is best achieved using *di*sodium hydrogen phosphate and sodium hydroxide. By maintaining the pH value and phosphate levels at or just below the upper limit in Figure 3 a molar ratio of $Na^+ : PO_4^{3-}$ of less than 2.6 : 1 is achieved and free sodium hydroxide does not form.

28.5.2 *Initial treatment.* Whenever a boiler is filled, suitable premixed quantities of *di*sodium hydrogen phosphate and sodium hydroxide should be added.

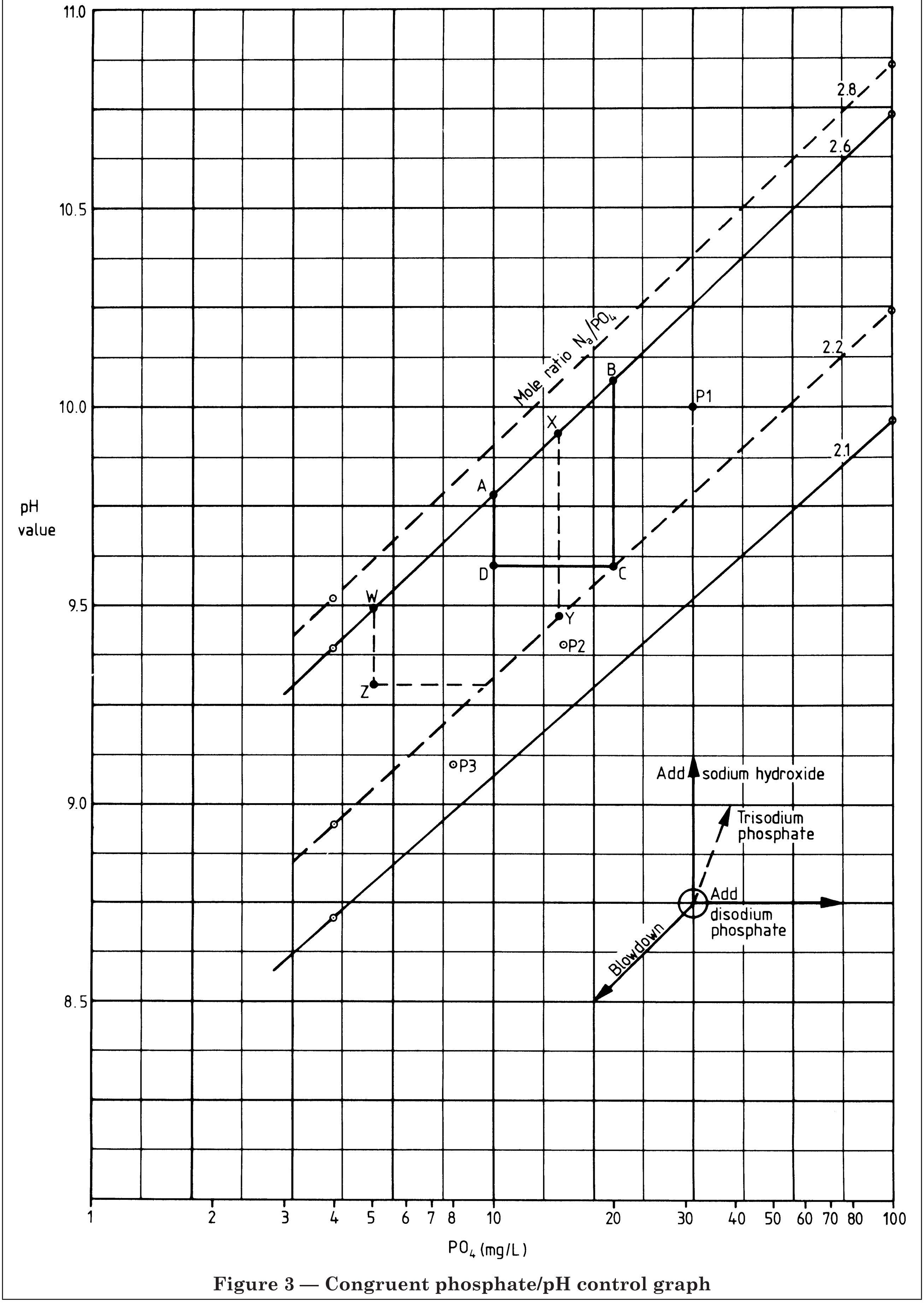

Figure 3 — Congruent phosphate/pH control graph

28.5.3 *Subsequent treatment during steaming*. During steaming the chemicals should be added to the boiler water as described in **28.5.4**, if required, following the routine control tests and in the amounts indicated by the results of these tests. The usual control tests and the frequency of making them are stated in Table 6 a) which, together with Figure 3, gives the characteristics to be maintained in a correctly treated boiler water.

28.5.4 *Methods of applying chemicals*. The various chemicals in the amounts required following each series of daily and weekly control tests should be dissolved in warm water (of the same quality as the extra feed) contained in a stainless steel tank and the whole of the solution should be added over a period of approximately 30 min direct to the boiler, using a suitable chemical pump. To make the solution use about 10 L of water for each 100 g of chemical, adding the latter slowly to the water (not vice versa) with constant stirring until solution is complete. See Appendix C for precautions to be taken in handling chemicals.

When the chemical solution has been injected to the boiler, the chemical dosing unit should be flushed through with water to make sure that the interior of the unit, the chemical line and the chemical injection fitting are left in a clean condition.

It should be noted, however, that any substantial deviation from the limits stated in Table 5 is a clear indication of condenser leakage or other defect requiring remedial action other than the addition of chemicals. In such circumstances, the frequency of testing should increase beyond the twice daily routine indicated in **28.5.5**, in order to check that the faulty condition has been remedied as soon as possible.

28.5.5 *Sampling and control tests*. Samples should be taken from each boiler twice every day and tested as soon as possible, preferably within 30 min. If tests cannot be carried out within this time, samples should be stored in completely filled and sealed bottles until required. Details of control tests are given in Appendix D.

Accurate testing is required for congruent control. Test results should be reported to the nearest 0.1 pH unit and a pH meter accurate to better than this value should therefore be used. Continuous sampling and recording is recommended for pH.

NOTE For sampling arrangements and equipment, see clause **22**.

28.5.6 *Adjustment of chemical treatment*. Measure the pH and phosphate levels in the boiler water and plot the result on Figure 3. For boilers operating between 80 bar and 100 bar, the point should be within the area marked ABCD and, for boilers operating between 100 bar and 130 bar, within the area marked WXYZ.

If the point lies outside the appropriate area, take the necessary corrective action(s), as shown in the bottom righthand corner of Figure 3, to bring the point within this area. For example, consider a boiler operating between 80 bar and 100 bar, so that the area ABCD is applicable. For point P1 on the graph it would be necessary to blowdown the boiler, for point P2 to add sodium hydroxide and for point P3 to add *di*sodium phosphate and sodium hydroxide or, alternatively, *tri*sodium phosphate only.

The recommended quantities of chemicals to be added are as follows.

a) *Disodium phosphate*. If the phosphate test (see **D.14**) shows less than the recommended mean level of sodium phosphate as PO_4, add the appropriate amount of disodium hydrogen phosphate to give a phosphate reserve of midway between the recommended limits. Approximately 2 g of *di*sodium phosphate dihydrate are required per 1 000 kg of water in the boiler to achieve an increase of 1 mg/L in the phosphate reserve. If the phosphate test result is above the maximum level, blowdown the boiler until the phosphate as PO_4 is within the recommended limits.

b) *Sodium hydroxide*. After first correcting the phosphate level to within the recommended limits, check the pH value of the boiler water. From Figure 3, determine the pH value of the boiler water corresponding to the phosphate level.

If the pH value of the boiler water is within the recommended limits, no addition of sodium hydroxide is required.

If the pH value is below the minimum recommended limit, add sufficient sodium hydroxide to restore the pH value to within the recommended limits according to the graph.

If the pH value is above the upper recommended limit, blowdown the boiler until the pH value falls to within the recommended limits.

c) *Hydrazine*. If hydrazine is used to remove the last traces of oxygen, it should be added continuously, by means of a suitable metering pump, to the feed system immediately after the deaerator or, as is sometimes recommended, into the cross-over pipe between the high-pressure and low-pressure turbines. When injecting into the cross-over pipe, provision for continuous injection into the feed system immediately after the deaerator is also required, for use when the turbines is shut down. Only cold feed water should be used for dilution.

The amount used should be sufficient to remove all oxygen in the feed water and to maintain a reserve in the boiler water of 0.05 mg/L to 0.1 mg/L as N_2H_4 for boilers operating at pressures up to 100 bar.

For boilers operating at higher pressures, hydrazine addition should be based on twice the oxygen level in the feed water.

CAUTION. Hydrazine is toxic and suitable precautions for its handling should be observed (see **C.4**).

28.5.7 *Protection of steam and condensate systems*

NOTE Attention is drawn to any regulations governing the use of volatile treatment chemicals in relation to the end use of steam.

If corrosion in steam and condensate systems is a serious problem neutralizing amines can be used to counteract such an attack.

Neutralizing amines may be continuously or intermittently added as a solution to the feed system at any suitable point before the main boiler feed pump. Control of the treatment should be exercised by maintaining the pH value of the condensate continuously within the range 9.0 to 9.5 as determined by a continuously recording pH meter. Only cold feed water should be used for dilution.

If the hydrazine is injected into the turbine cross-over pipe, a separate chemical dosing unit is required for a continuous application of the amine to the feed water after the deaerator. Both chemicals can be added at this point when the turbine is shut down.

28.5.8 *Silica in boiler water*. Silica concentration should be as low as possible for steam turbines, generally less than 0.02 mg/L of silica in steam. Figure 4 shows the maximum concentrations of silica in boiler water for a range of conditions to ensure that this limit is not exceeded. It should be noted that the maximum acceptable silica concentration is not only dependent on the boiler pressure, but also on the pH level maintained in the boiler water.

28.6 Treatment using a low solids non-phosphate treatment

28.6.1 *Principle*. By ensuring that the make-up feed is free from all hardness salts and that there is no contamination of the feed water or condensate, the need for phosphate treatment is avoided. This is carried out by maintaining the quality of the feed water, make-up feed and condensate such that the dissolved solids in the boiler are kept below 20 mg/L with a maximum chloride of 10 mg/L as NaCl for boilers operating up to 100 bar, and a maximum of 5 mg/L as NaCl for boilers operating between 100 bar and 130 bar.

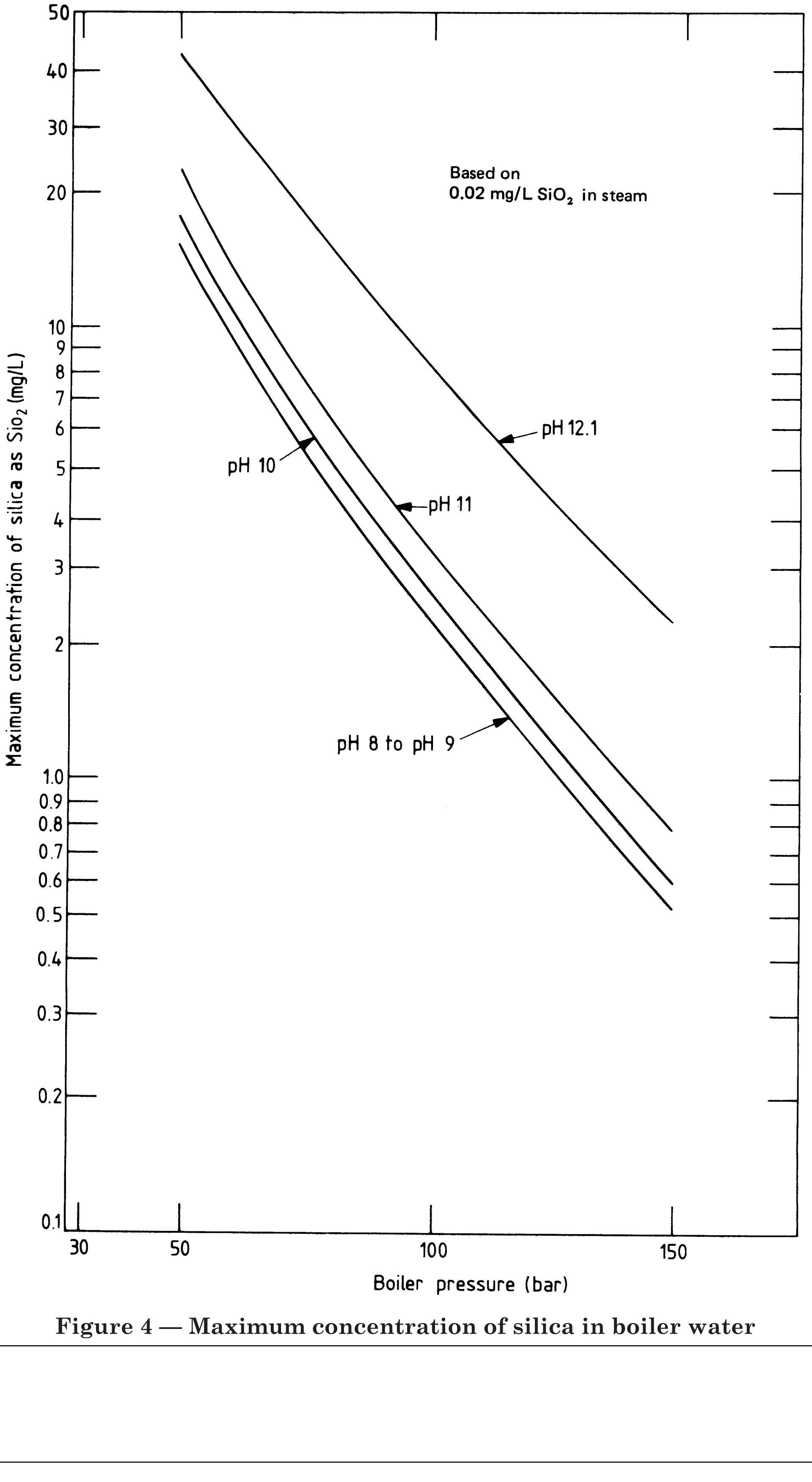

Figure 4 — Maximum concentration of silica in boiler water

In practice sufficient sodium hydroxide is added to the boilers to maintain an alkalinity to phenolphthalein (in terms of $CaCO_3$) of between 5 mg/L and 10 mg/L for boilers operating up to 100 bar, and between 2 mg/L and 5 mg/L for boilers operating between 100 bar and 130 bar.

28.6.2 *Initial treatment.* Whenever a boiler is filled, a suitable quantity of sodium hydroxide should be added.

28.6.3 *Subsequent treatment during steaming.* During steaming the chemicals should be added to the boiler water as described in **28.6.4**, if required, following the routine control tests and in the amounts indicated by the results of these tests. The usual control tests and the frequency of making them are stated in Table 6 b) which, together with Figure 4, gives the recommended characteristics to be maintained in a correctly treated boiler water.

28.6.4 *Method of applying chemicals.* The sodium hydroxide should normally be applied as a solution as and when required. The amount of solid for each application should be dissolved in water (of the same quality as the make-up water) contained in a stainless steel tank of suitable capacity, and the whole of the solution should be added over a period of approximately 30 min direct to the boiler, using a suitable pump. To make the solution use about 10 L of cold water for each 100 g of sodium hydroxide, adding the latter slowly to the water (not vice versa) with constant stirring until the solution is complete. See Appendix C for precautions to be taken in handling chemicals.

When the chemical solution has been injected into the boiler, the chemical dosing unit should be flushed through with water to make sure that the interior of the unit, the chemical line and the chemical injection fittings are left in a clean condition.

28.6.5 *Sampling and control tests.* Samples should be taken from each boiler twice every day and tested as soon as possible, preferably within 30 min. If tests cannot be carried out within this time, samples should be stored in completely filled and sealed bottles until required. Details of control tests are given in Appendix D.

NOTE For sampling arrangements and equipment, see clause **22**.

28.6.6 *Adjustment of chemical treatment.* The recommended quantities of chemicals to be added are as follows.

a) *Sodium hydroxide.* If the alkalinity to phenolphthalein in the boiler is less than the recommended mean value in Table 6 b), 0.8 g of sodium hydroxide per 1 000 kg of water in the boiler should be added for every 1 mg/L of alkalinity deficiency.

If the alkalinity is in excess of the upper limit given in the table, blowdown the boiler until the alkalinity is within the recommended limits.

b) *Hydrazine.* If hydrazine is used to remove the last traces of oxygen, it should be added continuously by means of a suitable metering pump to the feed system immediately after the deaerator or, as is sometimes recommended, into the cross-over pipe between the high and low pressure turbines. When injecting into the cross-over pipe, provision for continuous injection to the feed system immediately after the deaerator is also required, for use when the turbine is shut down. Only cold feed water should be used.

The amount used should be sufficient to remove all oxygen in the feed water and to maintain a reserve in the boiler water of 0.05 mg/L to 0.1 mg/L as N_2H_4 for boilers operating at pressures up to 100 bar. For boilers operating at higher pressures, hydrazine addition should be based on twice the oxygen level in the feed water.

CAUTION. Hydrazine is toxic and suitable precautions for its handling should be observed (see **C.4**).

28.6.7 *Protection of steam and condensate systems*

NOTE Attention is drawn to any regulations governing the use of volatile treatment chemicals in relation to the end use of steam.

If corrosion in steam and condensate systems is a serious problem, neutralizing amines can be used to counteract such attack.

Neutralizing amines may be continuously or intermittently added as a solution to the feed system at any suitable point before the main boiler feed pump. Control of the treatment should be exercised by maintaining the pH value of the condensate continuously within the range 9.0 to 9.5 as determined by a continuously recording pH meter. Only cold feed water should be used for dilution.

If the hydrazine is injected to the turbine cross-over pipe, a separate chemical dosing unit is required for a continuous application of the amine to the feed water after the deaerator. Both chemicals can be added at this point when the turbine is shut down.

28.6.8 *Silica in boiler water*. Silica concentrations should be as low as possible for steam turbines, generally less than 0.02 mg/L of silica in steam. Figure 4 shows the maximum concentrations of silica in boiler water for a range of conditions to ensure that this limit is not exceeded. It should be noted that the maximum acceptable silica concentration is not only dependent on the boiler pressure, but also on the pH level maintained in the boiler water.

28.7 Boiler water, feed water and condensate characteristics. For recommended boiler water characteristics, see Table 6 and recommended feed water and condensate characteristics, see Table 7.

Section 7. Preservation of idle boilers

29 Long term storage

The following methods are suitable for the storage of boilers for up to 12 months provided conditions are checked at regular two-monthly intervals.

a) Drying out the boiler by gentle heat and aferwards inserting trays of silica gel or calcium oxide (quicklime) before sealing up the boiler.

b) Drying out the boiler by gentle heat and introducing a vapour phase inhibitor e.g. cyclohexylamine, before sealing up the boiler.

CAUTION. The fumes are toxic. Precautions recommended by the supplier should be observed before any person is allowed to enter a boiler that has not been filled with water following an idle period during which the boiler was protected by a vapour phase inhibitor.

c) Drying out the boiler by gentle heat and afterwards inserting electrical heaters to prevent condensation in the boiler. In this method the manholes are left open.

Table 6 — Boiler water characteristics for group 6 boilers (80 bar to 130 bar)

a) Congruent phosphate/pH treatment

Boiler pressure	**Frequency of test**					
	Twice daily	**Continuously using a meter**	**Twice daily**	**Continuously using a meter**	**Daily**	**Weekly**
	Sodium phosphate	**pH value**	**Hydrazine**	**Conductivity at 25 °C (max.)**	**Chlorides (max.)**	**Silica (max.)**
bar	mg/L as PO_4		mg/L as N_2H_4	µS/cm[a]	mg/L as NaCl	mg/L as SiO_2
80 to 100	10 to 20	9.6 to 10.0	0.05 to 0.1	150	10	See Figure 4
100 to 130	5 to 15	9.3 to 9.9	See note	100	5	See Figure 4

b) Low solids/non-phosphate treatment

Boiler pressure	**Frequency of test**				
	Twice daily	**Twice daily**	**Continuously using a meter**	**Twice daily**	**Weekly**
	Alkalinity to phenolphthalein	**Hydrazine**	**Conductivity at 25 °C (max.)**	**Chlorides (max.)**	**Silica (max.)**
bar	mg/L as $CaCO_3$	mg/L as N_2H_4	µS/cm[a]	mg/L as NaCl	mg/L as SiO_2
80 to 100	5 to 10	0.05 to 0.1	50	10	See Figure 4
100 to 130	2 to 5	See note	25	5	See Figure 4

NOTE At pressures above 100 bar it may not be possible to maintain measurable hydrazine reserves in the boiler. The daily additions of hydrazine should be calculated for the oxygen content of the feed water after the deaerator. Use twice the theoretical quantity of hydrazine required to react with the oxygen, bearing in mind that hydrazine is normally supplied as a 15 % or 35 % solution in water.

[a] Microsiemens per centimetre.

Table 7 — Feed water and condensate characteristics for group 6 boilers (80 bar to 130 bar)

Test sample	**Frequency of test**				
	Continuously using oxygen meter	**Continuously using a pH meter**	**Continuously using a sodium monitor**	**Weekly (laboratory check every 2 months)**	
	Dissolved oxygen after deaeration (max.)	**pH value**	**Sodium ion (max.)**	**Copper (max.)**	**Iron (max.)**
	mg/L as O_2		mg/L as Na^+	mg/L as Cu	mg/L as Fe
Feed water (after physical deaeration)	0.005	—	0.005	0.005	0.01
Condensate (immediately after condenser extraction pump)	—	9.0 to 9.5	0.005	—	—

NOTE Figures for copper and iron concentrations represent average steady load values (see **17.6**).

d) Using a mixture of corrosion inhibitors. In this case the boiler is filled completely with water correctly treated with the appropriate amounts of corrosion inhibitors. A head tank should be fitted to the highest point to allow for expansion/contraction with temperature fluctuations. A suitable corrosion inhibitor is a mixture of sodium nitrite and sodium borate at a concentration of 3 000 mg/L of each chemical. When bringing the boiler back into service, wash out thoroughly before refilling the boiler with water that has been correctly treated for steam raising. Provision should be made for disposing of the inhibitor mixture to the satisfaction of local authorities. This method cannot be used if the boiler is exposed to temperatures below freezing point.

e) When using the methods described in items a), b) or c), it is essential to ensure that all the valves on the boiler are closed and do not leak, otherwise, steam, feed water or blowdown could enter the boiler and vitiate the precautions.

Protection for the external surfaces is also required. First remove all external deposits of vanadium pentoxide, sodium bisulphate and sodium sulphate using the appropriate cleaning techniques. If heat is available to prevent moisture condensing on the metal surfaces, then further action may be unnecessary. However, additional insurance may be provided by spraying the tubes with a protective film of a film-forming corrosion inhibitor.

30 Short term storage

30.1 Boilers in groups 1 and 2. The boiler should be completely filled with alkaline water containing sufficient sodium sulphite to combine with the dissolved oxygen and leave an excess of 200 mg/L of Na_2SO_3. After closing but before sealing the boiler, the water should be raised to boiling point to induce mixing by circulation and to complete the chemical reaction. A head tank should be fitted to the highest point to allow for expansion or contraction with temperature fluctuations.

30.2 Boilers in groups 3, 4, 5 and 6. The boiler should be completely filled with alkaline water containing sufficient hydrazine to combine with the dissolved oxygen and to leave an excess of about 100 mg/L of hydrazine. After closing but before sealing the boiler, the water should be raised to boiling point to induce mixing by circulation and to complete the chemical reaction. A head tank should be fitted to the highest point to allow for expansion or contraction with temperature fluctuations.

30.3 Boilers in all groups. When using the methods described in **30.1** or **30.2** the alkalinity should be maintained at the recommended value for the boiler. These methods cannot be used if the boiler is exposed to temperatures below freezing point.

Appendix A Explanation of terms (for information only, see also clause 3)

NOTE Terms given in italic typescript are explained in this appendix.

acidity. The concentration of acidic salts or acids present when measured by titration with a standard alkali to a selected pH endpoint. (See Appendix B.)

alkaline hardness. *Hardness* in water caused by the presence of bicarbonates, and carbonates and hydroxides of calcium and magnesium, but in most natural water supplies present as bicarbonates (It was formerly known as “temporary” or “carbonate” hardness.) (See *non-alkaline hardness*.)

alkalinity. The concentration of alkaline salts or bases present when measured by titration with a standard acid to a selected pH endpoint. (See *bicarbonate alkalinity, caustic alkalinity, total alkalinity* and Appendix B.)

amines. Organic derivatives of ammonia. (See *volatile amines*.)

anhydrous. This means literally “without water”. It is a term applied to a salt that does not contain water of crystallization.

anion. A negative *ion* formed in an *electrolyte* by dissociation.

antifoam. A substance added to boiler water to prevent *foaming*.

attemperator. A device normally installed between a primary and a secondary superheater to control steam temperature. The “spray type” involves spraying water of suitable quality into the steam; the “surface type” is an indirect heat exchanger using feed water or boiler water as the cooling medium.

bar. A unit of pressure. $1 \text{ bar} = 10^5 \text{ N/m}^2 = 100 \text{ kPa}$; atmospheric pressure is approximately 1 bar (1 atm = 1.01325 bar).

NOTE It is realized that many older boilers are fitted with instruments graduated in pounds-force per square inch and for the purposes of this standard, it is often sufficient to use the conversions $1\,000 \text{ lbf/in}^2 = 69 \text{ bar}$ and $10 \text{ bar} = 145 \text{ lbf/in}^2$.

base exchange softening. See *sodium ion exchange softening*.

bicarbonate alkalinity. The *alkalinity* caused by the presence of bicarbonates. It is measured by titration with a standard acid to endpoints against both methyl orange and phenolphthalein and calculated as described in BS 1427.

blowdown. Water removed from a boiler in order that feed water may be added to reduce the concentrations of dissolved substances, or in order that sediment may be carried to waste. It is also the process of removing this water.

calcium hardness. *Hardness* caused by calcium salts.

carbonate alkalinity. The *alkalinity* caused by the presence of carbonates. It is calculated from measurements by titration with a standard acid after the addition first of the indicator phenolphthalein, then of the indicator methyl orange; or, as the difference between *total alkalinity* and *caustic alkalinity*. (See BS 1427.)

carbonate control. The maintenance of a controlled reserve of carbonate *ions* in a boiler water as a means of preventing scale formation.

carry-over. Water and solids carried out of a boiler or evaporator with the steam, especially at times of *foaming* or *priming*.

cation. A positive *ion* formed in an electrolyte by dissociation.

caustic alkalinity. The *alkalinity* caused by the presence of hydroxides. It is measured by titration with a standard acid following the addition of a neutralized solution of barium chloride and the indicator phenolphthalein (see BS 1427.) It is often known as the “0 reading”.

caustic cracking. The intergranular cracking of steel under high tensile stress in the presence of a solution of a caustic alkali having a concentration in excess of 5 % (*m*/*m*).

caustic embrittlement. A term previously used for caustic cracking.

coagulant. A substance used to reduce the electrical surface charge on suspended particles so as to enable them to flocculate. See also *colloids and flocculation*.

colloids. Particles (normally within the size range 1 nm to 100 nm) that, due to their size and electrical surface charge, tend to remain in stable suspension and do not settle under the effect of gravity.

condensate. Water formed by condensation of steam from the boiler.

condensate polishing. A method of improving the quality of *condensate* by filtration and/or *ion exchange*.

conditioning. The addition of chemicals, either to the feed water before its entry into the boiler or to the water in the boiler, to prevent corrosion or scale formation. The make-up water has usually received *external treatment*.

conductivity. The ability of a solution to pass an electric current. Its measurement is used to determine the amount of ionized substances in water.

congruent phosphate conditioning. The control of phosphate and pH value in boiler water in such a manner that the ratio of alkali to phosphate corresponds to a mixture of *di*sodium phosphate and *tri*sodium phosphate.

continuous blowdown. The continuous removal of water from a boiler to waste in order to maintain the *dissolved solids* or some other parameters at a set maximum concentration.

coordinated phosphate conditioning. The control of phosphate and pH value in boiler water so that the alkali present in relation to the phosphate corresponds to *tri*sodium phosphate.

corrosion fatigue. The transgranular cracking of a metal in a corrosive environment under a cyclic stress.

deaeration. The removal of dissolved gases, particularly oxygen, from feed water, achieved by thermal, mechanical or chemical methods.

dealkalization. The removal of bicarbonates by *ion exchange*.

deionization. See *demineralization*.

demineralization. The partial or virtually complete removal of *dissolved solids* by a process that uses both anion and cation exchange.

dissolved solids. The solids in solution in water that would be left if all the water were evaporated.

distillate. Water formed by condensation of vapour from an evaporator.

EDTA. Ethylenediamine-tetracetic acid or its sodium salts, which are used for estimating the hardness of water and in water treatment.

electrolyte. A substance giving rise to *ions* in solution.

external treatment. The treatment of water for removal of *hardness* or other impurities before the water enters the boiler.

filming amines. *See volatile amines.*

filtrate. Liquid that has passed through a filter for the purpose of removing suspended matter.

flocculation. The formation of large particles by aggregation of small particles as a result of relative movement.

foaming. The formation at the water surface of a stable mass of bubbles that may fill the whole steam space in a boiler and lead to *carry-over*.

hardness. A term originally used to denote that a water has the property of destroying soap lather. It is also used to denote that certain impurities are present (see *alkaline hardness* and *non-alkaline hardness*).

hardness salts. Generally accepted as the calcium and magnesium salts in water (see *hardness*).

heat flux density. The quantity of heat passing through unit surface area in unit time.

hideout. Apparent loss from the boiler water of normally soluble salts when the load on the boiler is increased.

internal treatment. The addition of chemicals to the feed water or direct to the boiler in order to prevent scale and/or corrosion. The reaction between the treatment chemicals and the impurities in the water take place in the boiler.

ion. An electrically charged atom or group of atoms. Molecules of certain dissolved substances are dissociated into ions (see Appendix B).

ion exchange. The replacement of ions in a liquid by ions present in an exchanger by passing the liquid through the exchanger.

low solids treatment. A treatment that employs demineralized make-up water so that the dissolved solids in the boiler water are derived almost entirely from chemicals used for *conditioning* the boiler water.

magnesium hardness. *Hardness* caused by magnesium salts.

milligrams per litre (mg/L). A unit of concentration in dilute solutions. If the solvent is water, it is numerically equivalent to *parts per million* (p.p.m.).

M reading. This is the *alkalinity* of a solution to methyl orange (see *total alkalinity*).

neutralizing amines. See *volatile amines*.

non-alkaline hardness. *Hardness* in water caused mainly by the chlorides, sulphates and nitrates of calcium and magnesium. (It was formerly known as “permanent” or “non-carbonate” hardness.) (See *alkaline hardness*).

organic matter. Vegetable and animal matter that is present in some water.

parts per million (p.p.m.). A means of expressing concentration (see *milligrams per litre*).

permanent hardness. See *non-alkaline hardness*.

phosphate control. The maintenance, by *internal treatment,* of a controlled reserve of phosphate *ions* in a boiler water as a means of preventing scale formation.

pH value. A point on a numerical scale designed to show the degree of *acidity* or *alkalinity* of a solution. Alkaline solutions have pH values between 7 and 14 and acid solutions have pH values less than 7 (see Appendix B).

polishing. See *condensate polishing*.

polyelectrolytes. Organic or inorganic polymers having ionized groups and capable of coagulating or flocculating or dispersing suspended solids. They are used in clarification treatment, scale prevention and to assist mobility of sludge in the boiler.

P reading. This is the *alkalinity* of a solution to phenolphthalein (see BS 1427).

precipitate. An insoluble solid formed by the interaction of substances dissolved in water or formed by the action of heat on solutions of some substances.

priming. The ejection of relatively large quantities of boiler water from the boiler with the steam (as *carry-over*).

reserve. An excess of *conditioning* chemicals maintained in a boiler water.

resin capacity. The quantity of exchangeable material capable of being taken up by an *ion exchange* resin. It is usually expressed in terms of kg $CaCO_3/m_3$ of resin.

s.a.c. resin. Strong acid *cation* exchange resin. (See **17.4**.)

s.b.a. resin. Strong base *anion* exchange resin. (See **17.4**.)

shot dose. See *slug addition*.

sludge conditioner. Material added to boiler water for the purpose of making sludge more amenable to removal by *blowdown*.

slug addition. The intermittent addition of a solution of treatment chemicals over short periods at regular intervals.

sodium ion exchange softening. The substitution of calcium and magnesium *ions* by sodium *ions* using *ion exchange* treatment. It was previously known as *base exchange softening*. (See **17.4**.)

softening. The removal of *hardness* salts from water.

steam blanketing. The formation of a pocket or blanket of steam in contact with the internal surface of a boiler tube.

stress corrosion. A type of corrosion where stress in metal in a corrosive medium has initiated corrosion or accelerated its rate. It is usually applied to the corrosion of stainless steel in media containing chloride *ions* or alkali.

suspended matter. Matter contained in water that may be removed by filtration, coagulation or sedimentation.

temporary hardness. See *alkaline hardness*.

total alkalinity. The combined concentrations of bicarbonates and carbonates or of carbonates and hydroxides expressed in a common form, usually in terms of calcium carbonate. It is often known as the *M reading* (see BS 1427).

volatile amines. *Amines* that are volatile in steam; cyclohexylamine and morpholine, for example, are used to neutralize carbon dioxide in *condensate*. They are also used to increase the *pH value* of feed water or boiler water in order to prevent corrosion. Octadecylamine is used to protect *condensate* lines by forming a protective film.

zero solids treatment. Treatment that employs complete *demineralization* of the make-up water and only volatile chemicals for *conditioning* the boiler water.

Appendix B pH value, acidity and alkalinity

NOTE The following explanation of pH value is a simplified one; more precise explanation is given in BS 1647.

In its broadest sense the pH value is a measure of the acidity or alkalinity of water, high values indicating alkaline solutions and low values acid solutions. It should be understood that pH is not a constituent or impurity of the water, but merely a figure representing the concentration of hydrogen ions in the water produced by various chemicals dissolved in it. Water itself contains hydrogen ions (H^+) and hydroxyl ions (OH^-) from the dissociation of the water molecules as follows:

$$H_2O \rightleftharpoons H^+ + OH^-$$

In pure water, the concentration of hydrogen ions is approximately 0.000 000 1 g/L of water; in other words, 10^{-7} g/L of H^+ and this is exactly balanced by an equal number of hydroxyl ions; such water is said to be neutral, i.e. neither acidic nor alkaline. The product of the concentrations of hydrogen ions and hydroxyl ions is constant at any fixed temperature.

If an acid such as hydrochloric acid (HCl) is dissolved in pure water, it dissociates into H^+ and Cl^- ions and there will be an overall increase in the concentration of hydrogen ions. If, as a result, the concentration increases tenfold, it will become 0.000 001 g/L of H^+ or 10^{-6} g/L of H^+.

For simplicity, the base 10 and the negative sign are omitted, so that the hydrogen ion concentration of pure water is reported as a pH value of 7.0 and of acidified water as a pH value of 6.0. A further tenfold increase in the concentration of hydrogen ions, obtained by the addition of more acid, would lower the pH value to 5.0 and so on as shown in Figure 5.

If a strong alkali, such as sodium hydroxide ($NaOH$), is dissolved in pure water, it dissociates into sodium ions (Na^+) and hydroxyl ions (OH^-). There is, in consequence, an increase in the concentration of hydroxyl ions and the original balance between hydrogen ions and hydroxyl ions is upset. An increase in hydroxyl ions decreases the concentration of hydrogen ions (H^+). A tenfold increase in the hydroxyl ion concentration is equivalent to a tenfold decrease in hydrogen ion concentration from 0.000 000 1 g/L to 0.000 000 01 g/L; in other words from 10^{-7} g/L of H^+ (or pH 7.0) to 10^{-8} g/L of H^+ (or pH 8.0).

If a neutral salt, such as sodium chloride ($NaCl$), is dissolved in water, it dissociates into Na^+ ions and Cl^- ions. As there is neither an increase nor a decrease of hydrogen ion (H^+) or hydroxyl ion (OH^-) concentrations, the pH value does not change.

Appendix C Chemicals used in marine boiler water treatment

NOTE The following general precautions should be included in the instructions issued to all personnel engaged in handling chemicals, and appropriate notices should be displayed in or near the boiler room.

Specific precautions relevant to a particular chemical are given where appropriate. Warnings to the same effect are usually included in the container labelling for the chemicals concerned.

C.1 Safe handling of chemicals

C.1.1 *General.* All chemicals used in water treatment and analysis should be handled with care and the precautions listed in **C.1.2** should be observed. These are given here in general terms only and it is recommended that the appropriate British Standards and/or manufacturer's literature are consulted for more detailed information.

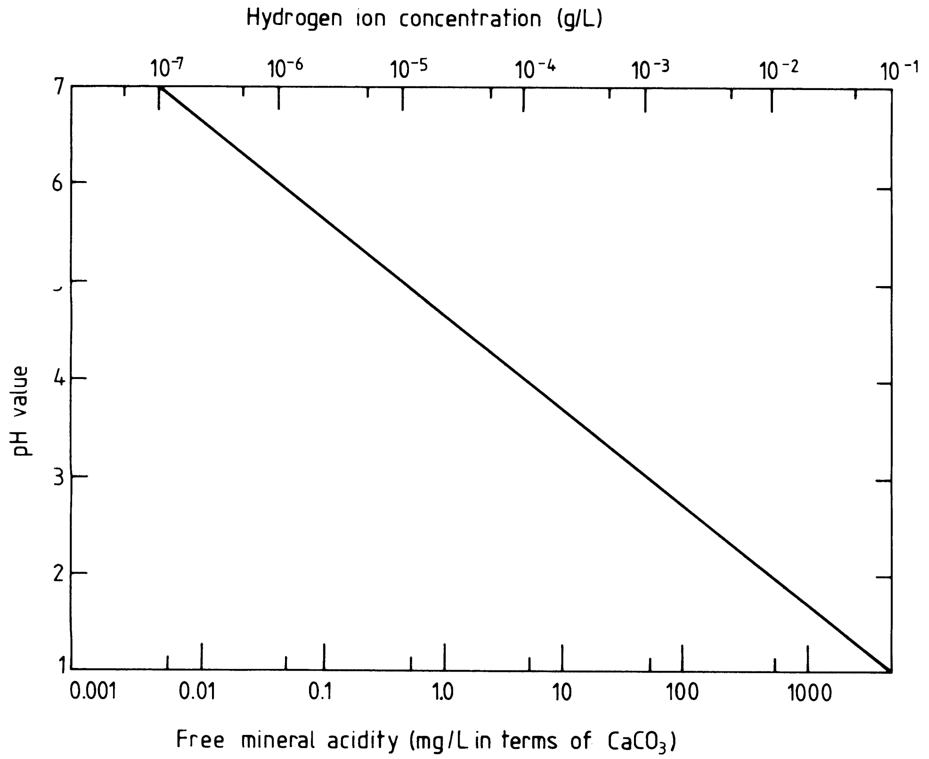

Figure 5 — Effect of mineral acidity on pH value

C.1.2 *Personal precautions.* The following precautions should be observed.

a) Treat all materials as harmful.

b) Ensure secure storage especially on board ship.

c) Ventilate the storage area.

d) Do not smoke or use naked lights in the storage and handling area.

e) First aid equipment should be available and warning notices displayed.

f) Ensure safety of others by warnings.

g) Make sure you know the nature of the chemicals to be handled, read the appropriate safety instructions and take the proper precautions to deal with them.

h) Wear protective clothing and equipment, i.e. goggles, gloves, apron, safety cap, overalls and the appropriate respirator for dusty, fuming or volatile chemicals.

i) Dissolve chemicals in the order specified in the instructions.

j) Follow specific instructions carefully.

k) Do not touch chemicals or residues with bare hands. Wash away accidental contact immediately.

l) Wash after handling chemicals. Do not eat, drink or smoke until you have.

m) Never transfer traces of chemicals from your hands to your eyes, mouth or face.

n) Keep yourself and your clothing clean. Remove, wash and/or destroy contaminated clothing.

o) Neutralize and wash away any accidental spillage of chemicals or solutions. Do not allow spillage to dry out.

p) Do not attempt to empty containers by applying pressure.

q) Do not reuse-drums or other containers.

r) Wash out drums or other containers before disposal.

s) Record all chemical accidents and medical attention.

C.1.3 *First aid.* In all cases of contact with chemicals, speed is essential to prevent injury. Remove the patient from the danger area immediately, then proceed as follows.

a) *Eyes.* Wash out the eyes thoroughly for at least 15 min with water or eyewash solution provided, whichever is quicker to obtain. Obtain medical attention or advice as soon as possible.

b) *Lungs.* Remove the patient from exposure to vapour or dust. Rest and keep warm. Obtain medical attention or advice as soon as possible.

c) *Skin.* Drench the skin with plenty of water. Remove contaminated clothing. In severe cases obtain medical attention or advice as soon as possible.

d) *Mouth.* Wash out the mouth thoroughly with water and then give plenty of water to drink. For acids give milk of magnesia; for alkalis give vinegar or 1 % acetic acid. Obtain medical attention as soon as possible.

C.2 Amines

C.2.1 *General.* Amines are organic compounds containing nitrogen which are chemically related to ammonia. Amines are used to combat corrosion in steam and condensate lines caused by dissolved carbon dioxide that passes over the lines with the steam.

Two types of amines are employed, neutralizing amines and filming amines (see **C.2.2** and **C.2.3**).

C.2.2 ***Neutralizing amines***

NOTE Attention is drawn to any regulations governing the use of volatile treatment chemicals in relation to the end use of the steam.

Neutralizing amines include cyclohexylamine and morpholine. These compounds are colourless, volatile liquids which are miscible with water and have an ammoniacal odour. They are supplied commercially as solutions, e.g. 40 % (*m*/*m*) solution of cyclohexylamine. Solutions to be used for boiler water treatment should be kept in closed containers in a cool place.

> CAUTION. Neutralizing amines are strongly alkaline and volatile, giving off vapour that is toxic and has a smell similar to ammonia but not so pungent. Although the intensity of the effects is reduced by dilution, the solutions all require careful handling and the exercise of proper safety precautions. Skin contamination should be washed off immediately with plenty of soap and water, and eyes washed thoroughly with water alone or boric acid solution. For protection, it is advisable to wear rubber gloves and goggles or a face shield when dispensing even small quantities. It is essential that full protective clothing is worn if large quantities of the concentrated solutions are involved, e.g. because of large spillages.
>
> Protection should also be given against the inhalation of amine vapour and good ventilation in all work areas is essential. An ammonia-type gas mask should be worn if amine vapour can be smelt, or if it is necessary to work in an atmosphere containing the vapour. In spite of all precautions, certain individuals may be allergic to amines and develop dermatitis after prolonged or repeated contact; in such cases the individual should be removed immediately from all contact with the amines. Water that has been treated with neutralizing amines, or steam from such water, should not be allowed to contact foodstuffs or products intended for internal consumption.

The advice of a water treatment specialist should be sought before a volatile amine treatment is applied to a boiler installation where live steam is used for process purposes.

C.2.3 *Filming amines.* The most commonly used filming amine is octadecylamine ($C_{18}H_{37}NH_2$) which is an odour-less, waxy solid, insoluble in water at room temperature and volatile in steam.

To facilitate additions to the boiler system, it is supplied as a dispersion having the appearance of a viscous, milky fluid.

Filming amines inhibit corrosion by forming a protective adsorbed layer on metal surfaces, this layer acting as a barrier between the metal and any water droplets.

C.3 Antifoams

Antifoams are complex organic compounds of high molecular weight including certain polyoxides and polyamides. They are used to control foaming in the boiler drum thus preventing carry-over.

When a chemical mixture is used for the boiler water treatment, an antifoam is usually incorporated and further additions should not be necessary.

C.4 Hydrazine

NOTE Attention is drawn to any regulations governing the use of volatile treatment chemicals in relation to the end use of steam.

A compound of nitrogen and hydrogen (N_2H_4), which when pure is a colourless, volatile liquid possessing a pungent, ammoniacal odour. It forms a hydrate, $N_2H_4 \cdot H_2O$, and is completely miscible with water.

Hydrazine is a strong reducing agent which reacts with oxygen in alkaline solutions. It is commercially available in aqueous solutions of various concentrations. Solutions to be used for boiler water treatment should be kept in closed containers in a cool place.

> CAUTION. Hydrazine solutions are strongly alkaline and volatile, giving off hydrazine vapour which is very toxic and has a smell similar to ammonia but not so pungent. This vapour can be absorbed through the skin. Although the intensity of the effects is reduced by dilution, the solutions all require careful handling and the exercise of proper safety precautions. If, nevertheless, skin contamination occurs, this should be washed off immediately with plenty of soap and water; eyes should be washed thoroughly with water alone or boric acid solution.
>
> For protection, it is essential to wear rubber gloves and goggles or a face shield when dispensing even small quantities. It is essential that full protective clothing is worn if large quantities of the concentrated solutions are involved, e.g. because of large spillages.
>
> Protection should also be given against the inhalation of hydrazine vapour and good ventilation in all work areas is essential. An ammonia-type gas mask should be worn if hydrazine can be smelt, or if it is necessary to work in an atmosphere containing hydrazine vapour. In spite of all precautions, certain individuals may be allergic to hydrazine; in such cases the individual should be removed immediately from all exposure to hydrazine.
>
> Hydrazine solutions should be stored away from strong acids, supporters of combustion and oxidizing agents.
>
> Water that has been treated with hydrazine, or steam from such water, should not be allowed to contact foodstuffs or products intended for internal consumption.

C.5 Potassium hydroxide (KOH, caustic potash)

Potassium hydroxide is a strong alkali, solid at room temperature, which readily absorbs moisture and carbon dioxide from the atmosphere. It should therefore be stored in a cool, dry place and the container closed as tightly as possible. Because of its great affinity for moisture and carbon dioxide it cannot easily be supplied as a component of a chemical mixture, such as described in **20.8**.

> CAUTION. Great care should be taken to prevent inhalation of the dust and to prevent the material coming into contact with the skin or eyes. On adding to water heat is evolved and therefore the solid should always be added to water slowly and progressively with stirring so as not to cause excessive temperature rise and local boiling of the solution. It is imperative that water is never added to the solid or to a concentrated solution. It is essential that buckets and containers of enamel or stainless steel, not of plastics or glass, are used for mixing potassium hydroxide solutions.

C.6 Sludge conditioning agents

C.6.1 *General.* These agents disperse the sludge formed by treatment of waters, converting it to a form that does not adhere to heat transfer surfaces. In this way sludge may be removed by periodic blowdown. Several materials are used, including starch and certain polyelectrolytes, sodium aluminate, and tannins.

C.6.2 *Organic polymers (polyelectrolytes).* The synthetic organic polymers used in boiler water treatment are normally based on acrylic acid $CH_2 \cdot CH(COOH)n$.

The polymerized versions of acrylic acid are called polyacrylate acid salts ($CH_2 \cdot CH \cdot COONa)n$, where n can be any value up to several thousand. The relative molecular mass of the organic polymers used in water treatment aboard ship are normally within the range 1 500 to 15 000.

In practice, the polyacrylates are marketed as solutions in water of various strengths.

C.6.3 *Starch.* The starch used should be pure, refined, finely pulverized corn starch containing not more than 13 % of moisture and not more than 0.2 % of ash.

C.6.4 *Tannins.* Many types and grades of tannins are used for water treatment, e.g. chestnut, quebracho, cutch and mimosa. The type used should be soluble in cold or luke-warm water (solution of certain tannins is accelerated by adding a small amount of alkali, e.g. sodium carbonate, to the water) and should not contain any impurities that might adversely affect a boiler or any component thereof.

C.7 Sodium carbonate (soda ash)

The usual commercial form of this alkali is a fine, white powder containing at least 98 % of pure sodium carbonate (Na_2CO_3). It should be stored in a cool dry place and the containers should be closed as tightly as possible. If this precaution is not taken, the sodium carbonate may absorb moisture and carbon dioxide from the atmosphere and so become converted to hydrated forms of sodium carbonate or to sodium bicarbonate. In either case a greater mass will be required to maintain a specified alkalinity in boiler water.

C.8 Sodium hydroxide (NaOH, caustic soda)

Sodium hydroxide is a strong alkali, solid at room temperature, which readily absorbs moisture and carbon dioxide from the atmosphere. It should therefore be stored in a cool, dry place and the container closed as tightly as possible. Because of its great affinity for moisture and carbon dioxide, it cannot easily be supplied as a component of a chemical mixture, such as described in **20.8**.

Sodium hydroxide is also available commercially as a solution containing about 47 % by mass of the solid, supplied in steel drums. It is essential to keep the solution at a temperature of 10 °C or above, otherwise it starts to solidify.

> CAUTION. Great care should be taken to prevent inhalation of the dust and to prevent the material coming into contact with the skin or eyes. On adding to water heat is evolved and therefore the solid should always be added to water slowly and progressively with stirring so as not to cause excessive temperature rise and local boiling of the solution. It is imperative that water is never added to the solid or to a concentrated solution. It is essential that buckets and containers of enamel or stainless steel, not of plastics or glass, are used for mixing sodium hydroxide solutions.

C.9 Sodium nitrate

Sodium nitrate is a white, deliquescent solid, readily soluble in water. It is used to prevent caustic cracking in boilers and is available commercially in a purity greater than 98 % of $NaNO_3$. As it absorbs moisture from the atmosphere it should be stored in sealed containers.

C.10 Sodium phosphate

C.10.1 *General.* Phosphates are used primarily to prevent the formation of scale in boilers, the value of any one form compared with that of any other being directly proportional to the amount of phosphate (PO_4) each contains. Sodium phosphate is available in several forms (see **C.10.2** to **C.10.4**).

C.10.2 Di*sodium phosphate. Di*sodium phosphate is available in three states of hydration, as follows:

a) anhydrous salt containing approximately 67 % of PO_4;

b) crystalline dodecahydrate containing approximately 26.5 % of PO_4;

c) crystalline dihydrate containing approximately 53 % of PO_4.

1 kg of the anhydrous salt is equivalent to 2.5 kg of the dodecahydrate or 1.25 kg of the dihydrate.

C.10.3 Tri*sodium phosphate. Tri*sodium phosphate is available in two states of hydration as follows:

a) anhydrous salt containing approximately 58 % of PO_4;

b) commercial hydrate corresponding approximately to the hydrate $Na_3PO_4 \cdot 12H_2O$ and containing approximately 25 % of PO_4.

1 kg of the anhydrous salt is equivalent to 2.3 kg of the hydrate.

C.10.4 *Glassy sodium phosphate* (sodium metaphosphate or Graham's salt). Glassy sodium phosphate is available in the form of glass-like chips or powder containing approximately 93 % of PO_4.

C.11 Chemical mixture

The chemical mixture described in **20.8** is a simple and convenient material for use in boiler water treatment. The mixture is available in many parts of the world and it consists essentially of anhydrous sodium carbonate (soda ash), anhydrous *di*sodium phosphate, and organic sludge conditioning agents in the approximate proportions of 3 : 4 : 1 by mass respectively.

C.12 Sodium sulphate

Sodium sulphate is available in two forms as follows:

a) anhydrous salt containing approximately 98 % of Na_2SO_4;

b) crystalline decahydrate (also known as Glauber's salt) containing approximately 44 % of Na_2SO_4.

1 kg of the anhydrous salt is equivalent to 2.25 kg of the crystalline decahydrate.

C.13 Sodium sulphite

Sodium sulphite is available in two forms as follows:

a) anhydrous salt containing approximately 50 % of available SO_2;

b) crystalline heptahydrate ($Na_2SO_3 \cdot 7H_2O$) containing approximately 25 % of available SO_2.

Sodium sulphite marketed as a water treatment chemical is usually catalysed by the addition of small amounts of certain metals, e.g. cobalt, to increase the speed of reaction in combining with oxygen.

1 kg of the anhydrous salt is equivalent to 2 kg of the crystalline heptahydrate.

C.14 Sulphamic acid ($NH_2SO_3 \cdot H$, aminosulphonic acid)

Sulphamic acid, available as a water-soluble, pure crystalline solid, is a strong acid when dissolved in water. It is used as a convenient solid substitute for sulphuric acid.

> CAUTION. Care should be taken to prevent the material coming into contact with the skin or eyes. Addition to water produces a solution with similar properties to sulphuric acid.

C.15 Sulphuric acid (H_2SO_4)

Sulphuric acid is a strong acid, available commercially as a liquid usually of 98 % (*m*/*m*) concentration.

> CAUTION. Great care should be taken to prevent the material coming into contact with the skin or eyes.
>
> **It is imperative that water is never added to the concentrated acid.** On adding to water, heat is evolved and therefore the acid should always be added to water slowly and progressively with stirring so as not to cause excessive temperature rise and local boiling of the solution. It is essential that buckets and containers of enamel or stainless steel, not plastics or glass, are used for diluting concentrated sulphuric acid. The dilute acid is corrosive to unprotected metal surfaces and when cool is best stored in strong plastics or glass containers.

Appendix D Methods of test

NOTE 1 Only test methods for the control of boiler water treatment are given in this clause. For other test methods reference should be made to BS 1427 or BS 2690 as appropriate. Information and equipment for alternative proprietary test methods may be available from specialist water treatment suppliers.

NOTE 2 The test for nitrate is not one that can conveniently be made on board ship. If the information is required, a sample of water should be sent to a qualified analytical chemist or water treatment adviser.

NOTE 3 Attention is drawn to the sampling recommendations given in BS 1328 and BS 3285.

D.1 General instructions

CAUTION. A number of the reagents used are corrosive or toxic and therefore all the reagents should be handled with care (see **C.1**).

D.1.1 Except where otherwise stated in a particular method, carry out the tests on a clear sample of the boiler water obtained, if necessary, by preliminary filtration through a good quality filter paper. If the amount of suspended matter is sufficient to delay the filtering unduly, most of it may be allowed to settle to the bottom of the sample container before decanting the partly clear sample through the filter paper.

D.1.2 Apparatus complying with the following British Standards should be used for carrying out the tests:

> BS 604, BS 612, BS 700, BS 718, BS 846, BS 1583, BS 1704, BS 1792, BS 1923, BS 2586, BS 3145, BS 3218 and BS 5404.

D.1.3 Use burettes graduated in 0.1 mL divisions except where otherwise stated in a particular method. Automatic burettes are recommended for most routine work unless a non-automatic type is stated.

D.1.4 Use reagents of analytical reagent quality where available. Use deionized water for all analytical procedures in this appendix except for the determination of soluble silica (see **D.15**) for which it is essential to use silica-free water (see **E.50**).

Water for all other analytical purposes on board ship should be prepared by passing good quality evaporated water through a deionizing cartridge. To ensure a long life for the deionizing resin the evaporated water should have a conductivity less than 500 µS/m at 20 °C.

The deionized water should be collected and stored in polyethylene bottles reserved exclusively for the purpose. It should have a conductivity less than 100 µS/m at 20 °C when freshly prepared.

D.1.5 Prepare indicators and standard volumetric solutions in the manner described in Appendix E.

D.1.6 Apparatus in frequent use often becomes greasy and soapless detergents are recommended to clean it.

D.1.7 Wash all apparatus with deionized water before use. Rinse all apparatus to be used for measuring with a small portion of the liquid to be measured.

D.1.8 If desired, 0.02N nitric acid solution may be used in place of 0.02N sulphuric acid solution.

D.1.9 Some of the reagents used are corrosive or toxic and therefore, in the interests of safety, pipettes should not be filled by sucking with the mouth. Various types of graduated dispenser (e.g. droppers) are commercially available.

D.1.10 In some cases colour comparison by means of a disc[2)] is required. For use on board ship, apparatus in which the discs are used should be provided with an appropriate specially-designed source of artificial illumination.

Only in the event of a failure of the source should the colorimetric apparatus be used with daylight. In that case the manufacturer's instructions should be followed, bearing in mind that where "north daylight" is specified, the instruction relates to use of the apparatus in the northern hemisphere.

D.2 Determination of alkalinity to phenolphthalein

D.2.1 *Principle.* A few drops of the indicator, phenolphthalein, are added to a measured volume of sample. The colourless indicator becomes pink in the presence of alkali in the sample. Sulphuric acid of known strength is then added until the pink colour just disappears. The volume of acid required to make this change is a direct measurement of the amount of alkali in the sample.

D.2.2 ***Reagents***

D.2.2.1 *Phenolphthalein indicator solution* (see **E.28**).

D.2.2.2 *Sulphuric acid,* 0.02N solution (see **E.46**).

D.2.3 ***Apparatus***

D.2.3.1 *Graduated measuring cylinder,* 100 mL.

D.2.3.2 *White, flat-bottomed casserole or a porcelain basin,* approximately 200 mL.

D.2.3.3 *Dropping bottle,* for phenolphthalein indicator.

D.2.3.4 *Burette,* 20 mL.

D.2.3.5 *Glass stirring rod*

D.2.4 *Procedure.* Measure 100 mL of the sample and transfer it to the porcelain basin. Add 1 mL of phenolphthalein indicator solution and if the sample turns pink, run in from the burette the 0.02N sulphuric acid solution, whilst slowly stirring with the glass rod, until the colour just disappears.

If the quantity of 0.02N sulphuric acid solution required is more than 20 mL, repeat the test using a 50 mL or 25 mL water sample.

D.2.5 *Calculation of result.* The alkalinity to phenolphthalein (in mg/L as $CaCO_3$) is equal to the volume of acid (in mL) multiplied by 10.

If a 50 mL or 25 mL water sample is used, multiply the result by 20 or 40 instead of 10 as is the case when a 100 mL sample is used.

NOTE The solution remaining at the end of this test may be used for the determination of chloride (see **D.5**).

D.3 Determination of caustic alkalinity

D.3.1 *Principle.* The main difference between this determination and that of alkalinity to phenolphthalein (**D.2**) is in the use of sufficient barium chloride to precipitate from the boiler water sample any carbonate and phosphates that may be present. If the sample contains caustic alkalinity, a pink colour is produced when the phenolphthalein indicator is added and the amount of caustic alkalinity is measured by running in a solution of sulphuric acid of known strength until the pink colour just disappears. The operation is conducted fairly quickly and is ended immediately the colour disappears. The colour may return after a few seconds but is then ignored.

D.3.2 ***Reagents***

D.3.2.1 *Sulphuric acid,* 0.02N solution (see **E.46**).

D.3.2.2 *Phenolphthalein indicator solution* (see **E.28**).

[2)] Suitable discs and apparatus are obtainable from The Tintometer Ltd., Salisbury.

D.3.2.3 *Barium chloride,* either solid (see **E.5**) or in solution (see **E.6**).

D.3.3 ***Apparatus***

D.3.3.1 *Graduated measuring cylinder,* 100 mL.

D.3.3.2 *White, flat-bottomed casserole or a porcelain basin,* approximately 200 mL.

D.3.3.3 *Dropping bottle,* for phenolphthalein indicator.

D.3.3.4 *Burette,* 25 mL.

D.3.3.5 *Measuring cylinder,* 10 mL.

D.3.3.6 *Glass stirring rod*

D.3.4 *Procedure.* Measure 100 mL of the sample and transfer it to the porcelain basin. Add 1 mL of phenolphthalein indicator followed by 10 mL of barium chloride solution or 1 g of solid barium chloride. Stir well for 2 min and then run in from the burette sulphuric acid until the pink colour just disappears. Disregard any reappearance of the pink colour.

If the quantity of sulphuric acid used in the titration is more than 20 mL, repeat the test using a 50 mL or 25 mL water sample.

D.3.5 *Calculation of result.* The caustic alkalinity (in mg/L as $CaCO_3$) is equal to the volume of acid (in mL) multiplied by 10.

If a 50 mL or 25 mL water sample is used, multiply the result by 20 or 40 instead of 10 as is the case when a 100 mL sample is used.

D.4 Determination of ammonia

D.4.1 *Range.* The range of the determination is 0.02 mg/L to 2.0 mg/L as NH_3.

D.4.2 *Principle.* This method depends upon the reddish brown colour that ammonia in solution produces with Nessler's reagent. This colour is compared with a series of coloured discs, suitably calibrated against known quantities of ammonia. The determination is made as soon as possible after sampling.

D.4.3 ***Reagents***

D.4.3.1 *Nessler's reagent* (see **E.25**).

D.4.3.2 *Potassium sodium tartrate solution* (see **E.37**).

D.4.4 ***Apparatus***

D.4.4.1 *Two droppers,* 1 mL and 2 mL.

D.4.4.2 *Two Nessler cylinders,* 50 mL.

D.4.4.3 *Nessleriser discs,* NAA, NAB, NAC and NAD covering the ranges 0.02 to 0.2, 0.2 to 0.52, 0.56 to 1.2 and 1.2 to 2.0 mg/L as NH_3 respectively.

D.4.4.4 *Nessleriser*[3)]

D.4.5 *Procedure.* Fill two Nessler cylinders to the 50 mL mark with the clear sample and to each add 1 mL of potassium sodium tartrate to prevent turbidity developing.

To one of the cylinders add 2 mL of Nessler's reagent using the dropper. Allow both samples to stand for 10 min for the colour to develop, then place in the appropriate compartment of the Nessleriser with the untreated sample in the other compartment. Match the colour produced against the appropriate disc.

D.4.6 *Calculation of result.* The ammonia content (in mg/L as NH_3) is equal to

$x/50$,

where x is the disk reading (in μg).

D.5 Determination of chloride

D.5.1 *Introduction.* Two methods are given for the determination of chloride. The method using silver nitrate is suitable for waters containing the higher concentrations of chloride and having high dissolved solids contents. It is therefore recommended for samples taken from boilers in groups 1 to 5 inclusive. The method using mercuric nitrate is more suitable for waters containing the lower concentrations of chloride and having low dissolved solids contents. It is therefore recommended for samples taken from boilers in group 6 and for samples of feed water and of condensate taken from boilers in all groups.

[3)] A BDH Lovibond Nessleriser, Mark 3 is suitable. It is available from The Tintometer Ltd., Salisbury.

D.5.2 ***Determination of chloride using silver nitrate***

D.5.2.1 *Range.* The range of the determination is 5 mg/L to 500 mg/L as Cl^-.

D.5.2.2 *Principle.* Chloride is determined by titrating a neutral or slightly acid solution with silver nitrate solution in the presence of potassium chromate indicator. White silver chloride is precipitated. The end point is indicated by the formation of red silver chromate. Sulphite interference is removed by the addition of 1 g of potassium persulphate.

D.5.2.3 *Reagents*

D.5.2.3.1 *Phenolphthalein indicator solution* (see **E.28**).

D.5.2.3.2 *Potassium chromate indicator solution* (see **E.32**).

D.5.2.3.3 *Silver nitrate,* 0.02 mol/L solution (see **E.38**).

D.5.2.3.4 *Potassium persulphate* (solid) (see **E.36**).

D.5.2.3.5 *Sulphuric acid,* 0.02N solution (see **E.46**).

D.5.2.4 *Apparatus*

D.5.2.4.1 *Graduated measuring cylinder,* 100 mL.

D.5.2.4.2 *White, flat-bottomed casserole or a porcelain basin,* approximately 200 mL.

D.5.2.4.3 *Stirring rod*

D.5.2.4.4 *Burette* of amber glass, 20 mL.

D.5.2.4.5 *Burette,* 25 mL.

D.5.2.4.6 *Dropping bottles,* for indicator solutions.

D.5.2.5 *Procedure*

NOTE If an alkalinity to phenolphthalein test (see **D.2**) has been made, the same sample may be used instead of using a fresh sample, but if it contains a large quantity of chloride a large amount of silver nitrate will be required.

Measure 100 mL of a filtered sample, transfer it to the porcelain basin and then add 1 g of potassium persulphate. Add 10 drops of phenolphthalein indicator solution and run in from the burette (**D.5.2.4.5**) the sulphuric acid until the pink colour disappears.

Add a further 4 mL of sulphuric acid, followed by 10 drops of potassium chromate indicator solution.

Run in from the burette (**D.5.2.4.4**) the silver nitrate solution, stirring well the whole time, until the yellow colour just acquires a reddish-brown tinge which indicates the end point.

If more than 20 mL of silver nitrate is used before the end point is reached, repeat the test using a smaller volume of sample, e.g. 25 mL.

D.5.2.6 *Calculation of result.* The chloride content (in mg/L as NaCl) is equal to

$$11.7\,V,$$

where

V is the volume of the silver nitrate solution (in mL).

If a 25 mL sample is used, the chloride content is equal to $4 \times 11.7V$.

D.5.3 ***Determination of chloride using mercuric nitrate***

D.5.3.1 *Range.* The range of this determination is 0.1 mg/L to 10 mg/L as Cl^-.

D.5.3.2 *Principle.* Chloride is determined by titration of a water sample with standard mercuric nitrate solution in the presence of diphenylcarbazone as indicator. Before the titration with mercuric nitrate is commenced, the acidity of the sample is adjusted by the addition of dilute nitric acid in the presence of bromophenol blue, which indicates the pH of the solution. In practice the two indicators are prepared as a single solution in *iso*propyl alcohol (see **E.10**) which is added to the sample before the acidity is adjusted. Sulphite and hydrazine interference is removed by adding hydrogen peroxide solution.

D.5.3.3 *Reagents*

D.5.3.3.1 *Hydrogen peroxide,* approximately 300 g/L solution (see **E.18**).

D.5.3.3.2 *Mercuric nitrate,* 0.00564N solution (see **E.23**).

D.5.3.3.3 *Chloride mixed indicator solution* (see **E.10**).

NOTE The mixed indicator solution does not keep for longer than two months. Consequently it should be prepared on board ship using a pre-weighed quantity of the mixed solid indicators.

D.5.3.3.4 *Nitric acid,* 0.05N solution (see **E.26**).

D.5.3.4 *Apparatus*

D.5.3.4.1 *White, flat-bottomed casserole or a porcelain basin,* approximately 450 mL.

D.5.3.4.2 *Graduated cylinders,* 5 mL and 250 mL.

D.5.3.4.3 *Burette,* 10 mL, graduated in 0.02 mL divisions.

D.5.3.4.4 *Brown glass dropping bottle,* for chloride mixed indicator solution.

D.5.3.4.5 *Glass dropping bottle,* with dropper marked at 2 mL for 0.05N nitric acid solution.

D.5.3.4.6 *Glass mixing rod*

D.5.3.5 *Procedure.* Do not filter the water sample; if cloudy allow it to stand and then use the clear liquid.

Measure 200 mL of unfiltered sample into the porcelain basin. Add 4 mL of hydrogen peroxide solution, stir with the glass rod and wait for 2 min. Add ten drops of chloride mixed indicator solution and mix again. Add the nitric acid drop by drop, stirring the liquid in the basin with the glass rod, until the colour of the liquid just changes to a pale yellow, then add a further 2 mL of the nitric acid.

Titrate the liquid with the mercuric nitrate solution contained in the burette until a blue-violet colour persists throughout. Record the volume of mercuric nitrate solution used.

Carry out a blank determination at the same time, following the same procedure but using 200 mL of deionized water in place of the sample. Record the volume of mercuric nitrate solution required for the blank titration.

D.5.3.6 *Calculation of result.* Subtract the volume of mercuric nitrate solution required for the blank titration from the volume required for titration of the sample; this gives the net volume of mercuric nitrate solution for the water sample.

The chloride concentration in the sample (in mg/L as NaCl) is equal to

$1.65\,V$,

where

V is the net volume of mercuric nitrate solution.

D.6 Determination of copper

D.6.1 *Range.* The range of the determination is 0.0125 mg/L to 0.25 mg/L as Cu.

NOTE This range applies when the method is applied directly to a sample of water. If the method is used to determine copper in a solution prepared from a sample of suspended solids as described in **D.18**, the concentrating process described in that subclause enhances the sensitivity of this analytical method by a factor of 100, so that the range for suspended copper is 0.000125 mg/L to 0.0025 mg/L, i.e. 0.125 µg/L to 2.5 µg/L as copper.

D.6.2 *Principle.* Sodium diethyldithiocarbamate forms a yellow compound when it is added to alkaline solutions containing traces of copper. The yellow compound is soluble in methylchloroform and the intensity of the yellow colour in this solvent is proportional to the quantity of copper in the water. The extraction of the yellow compound is performed in situ in a special cell and the measurement of the depth of the yellow colour is made by comparison with a series of permanent glass standards in a Lovibond comparator.

D.6.3 ***Reagents***

D.6.3.1 *Copper buffer agent* (see **E.11**).

D.6.3.2 *1,1,1-trichloroethane* (methylchloroform) (see **E.22**).

D.6.4 ***Apparatus***

D.6.4.1 *Lovibond comparator*[4], fitted with disc 3/109 covering the range 0.0125 mg/L to 0.25 mg/L as copper in a sample taken directly from source and 0.000125 mg/L to 0.0025 mg/L as copper suspended in the sample if the test solution is prepared as described in **D.18**. The comparator is used with a special extraction cell (capacity 105 mL) in which the yellow compound is both formed in aqueous solution and extracted into 1,1,1-trichloroethane.

D.6.4.2 *Graduated cylinder,* 10 mL.

D.6.4.3 *Test tube to fit comparator,* with a graduation line at 10 mL.

D.6.4.4 *Rubber bung*

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[4] Available from The Tintometer Ltd., Salisbury.

D.6.4.5 *Polyethylene squares*

D.6.4.6 *Polyethylene funnel*

D.6.5 *Procedure.* Ensure that all apparatus is clean and dry before the determination is begun.

Measure 5 mL of 1,1,1-trichloroethane into the extraction cell and add the solution to be tested to bring the liquid level up to the 105 mL mark. Introduce 2 g to 3 g of copper buffer reagent into the cell through the funnel. Ensure that the funnel is dry and does not touch the liquid in the cell. Tap the funnel gently to make sure that all the reagent passes into the cell. Withdraw the funnel and stopper the cell. Shake the cell until the reagent has dissolved completely and allow to stand for 5 min.

NOTE The comparator may be used as a stand.

Whilst allowing the cell to stand, measure 5 mL of 1,1,1-trichloroethane into the test tube and add 2 g to 3 g of copper buffer reagent through the funnel. Withdraw the funnel and add deionized water up to the 10 mL mark. Cover the rubber bung with a fresh square of polyethylene film and stopper the test tube. Shake the test tube to dissolve the reagent and allow to stand.

After standing for at least 5 min, shake both the extraction cell and the test tube for 3 min to extract the yellow colour into the lower (1,1,1-trichloroethane) layer. "Bubbles" of water in this layer may be cleared by gently rotating the tubes.

Place the test tube in the left-hand compartment of the comparator and the extraction cell in the right-hand compartment. Match the depth of colour in the extraction cell against the glass standards in the disc, using the source of light provided with the instrument or, failing this, daylight (see **D.1.10**).

If the colour is deeper than that of the glass standard marked 0.25 mg/L, repeat the determination using a more dilute solution prepared by adding deionized water or some of the 30 mL of solution remaining after the determination of suspended iron if the procedure described in **D.18** has been used. Alternatively, the sampling of suspended solids described in **D.18** may be repeated, passing a smaller volume of sample through the cellulose filter, but this method is less sensitive because this is only a small concentration in the first instance.

D.6.6 *Calculation of result.* For a sample prepared as described in **D.18**, the content of suspended copper in feed water (in mg/L as Cu) is equal to 0.01 times the disc reading.

For a sample taken directly from source, the copper content is shown by the disc reading (in mg/L as Cu).

D.7 Determination of dissolved oxygen

D.7.1 *Range.* The range of this determination is 0.007 mg/L to 0.17 mg/L as O_2.

D.7.2 *Principle.* Dissolved oxygen is determined by comparing the colour produced with indigo-carmine, which has been reduced with glucose, with a series of standard colours. These range through orange, pink and mauve to blue with increasing oxygen content. The sample is collected in a modified Nessler cylinder (see Figure 6). The cylinder fits into a Nessleriser enabling the developed colour to be matched against standard colours on a calibrated disc.

D.7.3 ***Reagents***

D.7.3.1 *Indigo-carmine solution* (see **E.20**).

D.7.3.2 *Potassium hydroxide,* 8N solution (see **E.34**).

D.7.4 ***Apparatus***

D.7.4.1 *Nessleriser*[5)]

D.7.4.2 *Two modified Nessler cylinders,* with ground-glass stoppers (see Figure 6).

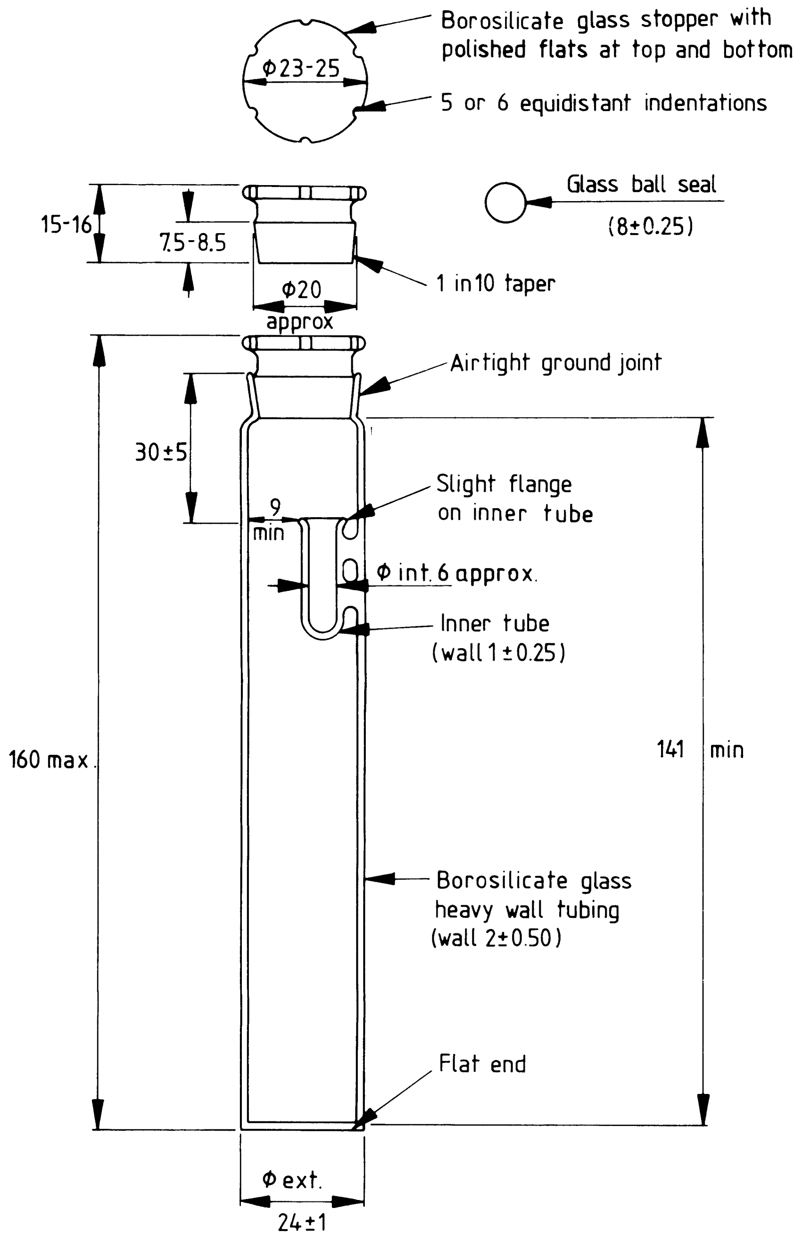
D.7.4.3 *Nessleriser disc,* NOE covering the range 0 mL/L to 0.12 mL/L (0 mg/L to 0.17 mg/L) as O_2.

D.7.4.4 *Reagent bottle,* 30 g.

D.7.4.5 *Graduated pipette,* 10 mL, with orifice approximately 2 mm.

NOTE The 2 mm orifice is required because the solution to be pipetted is very viscous.

[5)] A BDH Lovibond Nessleriser Mark 3 is suitable. It is available from The Tintometer Ltd., Salisbury.



All dimensions are in millimetres.

NOTE The ratio of the capacity of the inner tube to that of the stopper cylinder is to be between 1 : 70 and 1 : 75.

Figure 6 — Modified Nessler cylinder

D.7.4.6 *Safety pipette,* 2 mL.

D.7.4.7 *Dropping pipette,* graduated at 1 mL and 2 mL.

D.7.4.8 *Glass tubing,* 75 mm long × 8.5 mm internal diameter.

D.7.4.9 *Glass balls,* 7 mm to 8 mm diameter.

D.7.5 *Sampling.* Fit an efficient stainless steel or nickel-copper cooling coil to the sampling cock so that the temperature of the water when sampled is not above the ambient temperature. Fit a rigid vertical exit tube (about 250 mm long and 5.8 mm in external diameter) pointing downwards on to the end of the cooling coil. Butt the exit tube on to the end of the cooling coil. Do not use any connecting plastics tubing that might retain minute air bubbles on the interior surface.

D.7.6 *Procedure.* Pipette 8 mL of the indigo-carmine solution into the dry 30 g reagent bottle using the graduated pipette (**D.7.4.5**). Wipe the outside of the pipette to avoid more than 8 mL being added to the bottle. Next add 2 mL of the potassium hydroxide solution to the bottle by means of the safety pipette. Stopper the bottle and mix well. Keep undisturbed in the dark at a temperature of not less than 15 °C until the initial dark red colour changes to lemon yellow.

NOTE This should take approximately 30 min.

This reduced indigo-carmine, hereinafter referred to as the "leuco reagent", is prepared fresh each day.

Remove the glass stopper from the modified Nessler cylinder. Clean and dry the inner tube and glass ball and then fill the small inner tube with the leuco reagent. This is done by taking up about 1 mL of the leuco reagent into the dropping pipette and then slowly forcing the reagent into the inner tube, avoiding as far as possible the introduction of any air bubbles. Wait until any minute air bubbles have risen to the surface, then hold nearly vertically a length of clean, dry glass tubing over the top surface of the inner tube and roll the glass ball down inside the glass tubing so that it alights on the surface of the leuco reagent. Make certain that no air bubbles have been trapped.

Take the modified Nessler cylinder to the cooling coil and with the water running at a rate of about 200 mL/min raise the cylinder slowly until the bottom of the exit tube is close to the bottom of the vessel. Allow the water to flow until the sampling line and cylinder have been thoroughly flushed and a true sample is being obtained. In the meantime ensure that the glass stopper from the modified Nessler cylinder is clean and wet from the water being sampled. Slowly lower the modified Nessler cylinder, with the water still flowing, until it is just free of the sampling line, and then immediately slide the clean, freshly wetted glass stopper across and into the top of the cylinder. Make certain that no air bubbles have been trapped.

With the forefinger over the glass stopper, invert the Nessler cylinder so that the glass ball falls off the inner tube and the leuco reagent flows into the water. Invert the Nessler cylinder several times until it is clear from observation that there is no leuco reagent left in the inner tube.

Allow 5 min from when the cylinder was first inverted, then place it in the appropriate compartment of a Nessleriser and in the other compartment place a second modified Nessler cylinder filled with the sample.

Rotate the disc until a colour match is obtained.

D.7.7 *Calculation of result.* The oxygen content is shown by the disc reading in millilitres per litre. This figure may be converted to milligrams per litre by multiplying by 1.4.

D.8 Determination of dissolved solids

D.8.1 *Introduction.* The direct determination of dissolved solids requires laboratory facilities and thus falls outside the scope of this standard. However, the electrical conductivity and density of water are related to the amounts of solids dissolved in the water, therefore it is possible to obtain the approximate dissolved solids content of a sample from either the electrical conductivity or the density, the former being preferred.

The total amount of dissolved solids in a boiler water may be ascertained with sufficient accuracy for all normal control purposes by one of the following two methods.

a) Calculation from the measurement of electrical conductivity at a known temperature.

NOTE This method is the only one that can conveniently be used on board ship if the amount of dissolved solids is less than 2 000 mg/L.

b) Calculation from the density at a known temperature.

NOTE This method is not sufficiently accurate if less than 2 000 mg/L of solids are present, and is therefore not suitable for the control of water-tube boilers.

D.8.2 *Determination of dissolved solids from measurement of electrical conductivity*

D.8.2.1 *Principle.* The basis of this determination is the fact that the electrical conductance of a water sample is proportional to the quantity and the nature of the substances dissolved in it.

If practically all the soluble matter in a water consists either of neutral salts (e.g. sodium chloride, sodium sulphate or magnesium sulphate) or only slightly alkaline compounds (e.g. the bicarbonates of calcium, magnesium or sodium) and the remainder consists of relatively small amounts of organic matter, an approximate measure of the total quantity of dissolved solids, S, (in mg/L) is given by

$$S = 0.67\ C$$

where

C is the conductivity (in µS/cm) at 25 °C.

If a water contains highly alkaline compounds, especially sodium hydroxide and sodium carbonate, in addition to neutral salts and organic matter, this simple relationship does not apply because the conductivity of a highly alkaline solution differs considerably from that of a neutral or even slightly alkaline solution of the same concentration. A correctly treated boiler water is essentially a mixture of weak solutions of strong and mild alkalis, neutral salts and, usually, some organic matter. Before the formula given above can be used in connection with a boiler water to convert conductivity measurements into mg/L, the strong alkali has to be neutralized. If the neutralizing is done carefully, and the volume of boiler water sample is not increased by more than 2 % or 3 % in the process, the errors so introduced may be ignored so far as normal routine control work is concerned.

D.8.2.2 *Reagents*

D.8.2.2.1 *Phenolphthalein indicator solution* (see **E.28**).

D.8.2.2.2 *Acetic acid,* 5 mol/L solution (see **E.1**).

D.8.2.3 *Apparatus*

D.8.2.3.1 *Conductivity meter,* with the following components.

a) Conductivity cells containing a pair of electrodes. Each cell is labelled with the value of the cell constant expressed in reciprocal centimetres at 25 °C.

b) An instrument for measuring the electrical conductance (or resistance, which is the inverse of conductance) of the sample in contact with the electrodes of the cell.

c) A thermometer or means for compensating automatically for the temperature of the sample in the cell.

NOTE There are several satisfactory commercial models and operators would be well advised to purchase a ready-made instrument.

D.8.2.4 *Procedure.* Cool the sample, exposing it to a clean atmosphere, until its temperature lies between 15 °C and 30 °C. Add a few drops of phenolphthalein indicator solution and then add carefully the acetic acid, drop by drop, until the pink colour just disappears. Shake the sample after each addition. Use some of the sample to wash out the conductivity cell thoroughly, then fill the conductivity cell. Proceed as follows according to the type of measuring instrument used.

a) *Instruments reading directly in conductivity units and fitted with a temperature-compensating device.* Read the temperature in the cell, set the compensator to correspond with it and measure the conductivity in accordance with the manufacturer's instructions.

b) *Instruments reading directly in conductivity units but not fitted with a temperature-compensating device.* Measure the conductivity in accordance with the manufacturer's instructions. Read the temperature in the cell and apply a temperature correction in the manner described in **D.8.2.5**.

c) *Instruments reading directly conductance or resistance*

1) *Conductance.* Measure the conductance in microsiemens. Multiply the conductance by the cell constant to obtain the conductivity (in μS/cm) at the temperature of measurement.

2) *Resistance.* Measure the resistance in megohms. Divide the cell constant by the resistance to obtain the conductivity (in μS/cm) at the temperature of measurement.

In both cases apply the temperature correction in the manner described in **D.8.2.5**.

D.8.2.5 *Temperature correction.* Conductivities can be compared with one another only when they are corrected to the same temperature. In Great Britain the temperature adopted for this purpose is 25 °C, and in these methods this is regarded as the reference temperature.

For accurate work, it is necessary to adjust the temperature of the solution at the time of measurement. For all routine testing, it is sufficient to measure the conductivity at any convenient temperature and apply a correction, remembering that the more the temperature at the time of measurement diverges from 25 °C the less accurate the correction will be.

In order to apply the correction, multiply the measured conductivity by

$$\frac{1}{1 - 0.022\ (25 - t)}$$

where

t is the temperature of the solution in degrees Celsius at the time of measurement.

D.8.2.6 *Calculation of result.* Express the conductivity in microsiemens per centimetre at 25 °C, exposed to atmosphere and neutralized to phenolphthalein.

Calculate the approximate dissolved solid content as described in **D.8.2.1**.

D.8.3 ***Determination of dissolved solids from measurement of density***

D.8.3.1 *Principle.* The basis of this determination is, first, that when a solid is dissolved in water, the density of the resulting solution is a function of the solid, its amount in relation to the amount of water employed and the temperature of the solution at the time and, secondly, that when two or more solutions are mixed together in equal volumes, the resulting density of the mixture is usually the mean of the individual densities. If the density of a solution (e.g. a boiler water) at 20 °C is known, the value may be multiplied by a factor to obtain an approximate estimate of the total amount of dissolved solids.

D.8.3.2 *Apparatus*

D.8.3.2.1 *Hydrometer,* series 0.0005 × 100 with nominal range either 0.950 g/mL to 1.000 g/mL or 1.000 g/mL to 1.050 g/mL, complying with BS 718.

NOTE 1 Other hydrometers and salinometers are in use for special purposes and may be used if desired. If an alternative to the standard hydrometer is used, this should be stated in the report.

NOTE 2 Care is necessary to ensure that metal hydrometers are undamaged, as the slightest dent would invalidate the result.

D.8.3.2.2 *Hydrometer jar,* of minimum internal diameter 50 mm and minimum internal depth 400 mm.

D.8.3.2.3 *Thermometer,* capable of measuring temperatures in the range – 10 °C to + 105 °C.

D.8.3.2.4 *Filter funnel, filter papers, filter stand*

D.8.3.3 *Procedure.* Clean both the hydrometer and the jar before use, particularly to remove all traces of grease. After cleaning, handle the hydrometer only by the top of the stem, taking care that the fingers only touch the stem above the graduated scale.

It is more convenient to take readings at approximately room temperature than to bring the boiler water to a specified temperature and maintain it there. The density of the water at any specified temperature can readily be calculated from its density at any known temperature.

Pour the filtered sample of boiler water down the side of the hydrometer jar, taking care to avoid the formation of air bubbles. Add three drops of alkylbenzene sulphonate wetting agent.

Insert the hydrometer carefully into the sample, holding it by the top of the stem and releasing it when approximately in its position of equilibrium.

NOTE With a little experience an operator can appreciate when the hydrometer is approaching equilibrium and can release it in such a position that it rises or falls only by a small amount.

When the hydrometer has been released, note the reading and then, by pressing down on top of the stem, immerse the hydrometer to two or three subdivisions (about 3 mm to 5 mm) beyond the position of equilibrium and release again. Observe the meniscus surrounding the hydrometer stem while the hydrometer is settling down to its final position. If the stem of the hydrometer and the surface of the sample are clean, the meniscus remains unchanged as the hydrometer rises and falls. If the meniscus is distorted by the motion of the hydrometer, the hydrometer needs to be cleaned.

When the hydrometer has settled down to its position of equilibrium, note tha scale reading corresponding to the plane of intersection of the level liquid surface and the stem. Do not allow the hydrometer to touch the side of the vessel when the reading is being taken.

In general, it is sufficient to observe the temperature of the sample immediately after taking the hydrometer reading.

D.8.3.4 *Calculation of results.* If the density of a sample is determined at a temperature t (in °C) other than 20 °C, then a correction is necessary to obtain the density of the water at 20 °C. The correction is 0.0002 g/(mL·°C) and the density is given by the following formula:

$$\rho_{20} = \rho_t + 0.0002\,(t - 20)$$

where

ρ_{20} is the density (in g/mL) at 20 °C;

ρ_t is the density (in g/mL) at t °C.

The quantity of dissolved solids, S, (in mg/L) is given by

$$S = \rho_{20} - 0.9982 \times 1.1 \times 10^6$$

Example:

If

$$\rho_{26} = 1.0022 \text{ g/mL}$$

$$\rho_{20} = 1.0022 + (6 \times 0.0002) = 1.0034 \text{ g/mL}$$

Therefore

$$S = (1.0034 - 0.9982) \times 1.1 \times 10^6 = 5\,720 \text{ mg/L}$$

D.9 Determination of electrical conductivity

D.9.1 *Principle.* The conductance of a column of the sample is measured under standardized conditions, the instrument being so calibrated as to give the result in terms of conductivity.

D.9.2 ***Apparatus***

D.9.2.1 *Conductivity meter,* consisting of a conductivity cell and an instrument to measure the conductance and indicate the result as conductivity when used with the appropriate cell.

NOTE Several types of portable conductivity meter are available. The various types of meter use different methods to correct for the temperature of the sample, to apply the cell constant, and to vary the range.

Flow cells, which measure the conductivity of a flowing sample and thus avoid atmospheric contamination, are available for use with water of very low conductivity.

D.9.3 ***Procedure***

D.9.3.1 *High purity water.* Connect a flow cell to the sampling point or cooling coil with plastics tubing and allow the water to run slowly through the cell for 5 min. Determine the conductivity in accordance with the manufacturer's instructions.

Express the result in microsiemens per centimetre at 25 °C.

NOTE If the instrument used does not compensate for the temperature of the sample, correct the conductivity obtained by multiplying by:

$$\frac{1}{1 - 0.022\ (25 - t)}$$

where

t is the temperature (in °C).

D.9.3.2 *Water other than high purity water.* Adjust the temperature of the sample to between 15 °C and 30 °C, avoiding atmospheric contamination.

With part of the sample wash out the electrode system and drain off the washings. Fill the electrode vessel with the sample. Ensure that no bubbles adhere to the electrodes and proceed according to the manufacturer's instructions.

Express the result in microsiemens per centimetre at 25 °C.

NOTE If the conductivity of the sample exceeds the range of the instrument and dilution is necessary, record the result obtained on the diluted sample as "electrical conductivity of diluted sample (diluted *x* times)".

D.10 Hardness

D.10.1 *Introduction.* Originally the hardness of a water was regarded as its power to destroy the lather formed by soap. This property is primarily due to the presence of compounds of calcium and magnesium. Salts of other metals, such as iron, aluminium, manganese and barium, behave in a similar manner but these seldom occur in natural waters in sufficient quantities to affect the test. The presence of free acid, even carbonic acid, will also destroy the lather from sodium and potassium soaps by precipitating the free fatty acid.

The Wanklyn soap method, formerly used for determining hardness, was not a precise test and has been superseded by tests that accurately determine the calcium and magnesium content of a water. For this reason and because in the majority of cases the hardness is entirely due to the calcium and magnesium salts present, it has become customary to regard the hardness as a measure of the total calcium and magnesium in a water.

D.10.2 *Range.* The range of the determination is 0 mg/L to 250 mg/L in terms of $CaCO_3$.

D.10.3 *Principle.* Hardness is determined by titrating a sample at the correct pH value with *di*sodium dihydrogen ethylenediamine *NNN′N′* tetra-acetate dihydrate (EDTA) using Mordant Black 11 as indicator, which has a red colour in the presence of an alkaline solution of calcium and magnesium salts. On the addition of EDTA to the red coloured solution, the calcium and magnesium are converted to their EDTA complexes and, when this process is complete, the colour of the indicator reverts to blue.

D.10.4 ***Reagents***

D.10.4.1 *EDTA,* 0.01 mol/L standard solution (see **E.13**).

D.10.4.2 *Ammonia buffer solution* (see **E.4**).

D.10.4.3 *Mordant Black 11 indicator* (see **E.24**).

D.10.5 ***Apparatus***

D.10.5.1 *Filter funnel,* of diameter 90 mm.

D.10.5.2 *Filter papers*[6], of diameter 150 mm.

D.10.5.3 *Graduated cylinder*, 100 mL.

D.10.5.4 *White, flat-bottomed casserole or a porcelain basin,* approximately 200 mL.

D.10.5.5 *Two pipettes,* 2 mL.

NOTE Ostwald-Folin type or dropping pipettes with rubber teats are suitable.

D.10.5.6 *Burette,* 10 mL.

D.10.5.7 *Glass stirring rod,* with flattened end.

D.10.6 *Procedure.* Measure 100 mL of the filtered sample in the graduated cylinder and transfer it to the porcelain basin. Add approximately 2 mL of ammonia buffer solution and 0.2 g of Mordant Black 11 indicator (or one tablet). If a tablet is used, crush it immediately with the flattened end of the stirring rod. Stir vigorously until dissolved. If hardness salts are present, the solution turns wine-red.

Immediately titrate with the EDTA solution, stirring continuously with the glass rod until the colour begins to change from wine-red to purple. Then add the EDTA solution drop by drop, stirring continuously until all traces of red colour have disappeared; the end point has now been reached. The final colour at the end point is usually pure blue, but with some waters a greyish-coloured end point is obtained.

D.10.7 *Calculation of result.* The total hardness of the water (in mg/L as $CaCO_3$) is equal to

$$10\,V$$

where

V is the volume of EDTA solution (in mL).

D.11 Determination of hydrazine

D.11.1 *Principle.* Hydrazine is determined by comparing the colour produced with 4-dimethylaminobenzaldehyde with a series of standard colours. The final colours are a range of yellows.

D.11.2 *Sampling.* Since hydrazine in alkaline or neutral solutions tends to be destroyed in contact with air it is essential to use the following method of sampling.

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[6] Whatman no. 1 papers are suitable.

Insert the outlet tube from an efficient stainless steel cooling coil to the bottom of a 250 mL bottle. Allow the water to flow until a representative sample is obtained, at a temperature of between 17 °C and 30 °C. Withdraw the outlet tube slowly and immediately stopper the bottle, avoiding trapping any air bubbles.

D.11.3 ***Reagents***

D.11.3.1 *4-dimethylaminobenzaldehyde solution* (see **E.12**).

D.11.3.2 *Hydrochloric acid,* approximately 0.5N solution (see **E.16**).

D.11.4 ***Apparatus***

D.11.4.1 *Nessleriser*[7].

D.11.4.2 *Two Nessler cylinders,* 50 mL.

D.11.4.3 *Nessleriser disc,* NOH covering the range 0 mg to 10 mg as hydrazine.

D.11.4.4 *Two measuring cylinders,* 10 mL.

D.11.4.5 *Measuring cylinder,* 25 mL.

D.11.5 *Procedure.* Carry out the test immediately after the sample has been taken.

Into a Nessler cylinder containing 10 mL of the 0.5N hydrochloric acid solution, add 10 mL of the sample, diluted as necessary to give a reading within the range of the disk. Add 10 mL of 4-dimethylaminobenzaldehyde solution, mix and make the total volume up to 50 mL with deionized water. Mix again and allow to stand for 10 min.

Whilst allowing the mixture to stand, place 10 mL of hydrochloric acid into a second Nessler cylinder, then add 10 mL of the 4-dimethylaminobenzaldehyde solution and enough deionized water to give a total volume of 50 mL. This cylinder serves as a blank.

At the end of the 10 min, place the treated sample in the appropriate compartment of a Nessleriser and the blank in the other compartment. Match the sample against the colours of the disc.

D.11.6 *Calculation of result.* The hydrazine concentration (in mg/L as N_2H_4) is equal to

$$D/10$$

where D is the disc reading (in µg).

If the sample has been diluted (see **D.11.5**) multiply the disk reading by the corresponding factor.

D.12 Determination of iron

D.12.1 *Range.* The range of the determination is 0.05 mg/L to 1.0 mg/L as Fe.

NOTE This range applies when the method is applied directly to a sample of water. If the method is used to determine iron in a solution prepared from a sample of suspended solids as described in **D.18**, the concentrating process described there enhances the sensitivity of this analytical method by a factor of 100, so that the range for suspended iron is 0.0005 mg/L to 0.01 mg/L as Fe.

D.12.2 *Principle.* Ferrous iron forms a coloured complex with *ortho*-phenanthroline. To determine the total iron content, the ferric iron in the solution is reduced with hydroxylammonium chloride. The depth of colour due to the red complex is proportional to the amount of iron in the solution once it has all been reduced and is determined by comparison with permanent glass standards in a Lovibond comparator.

D.12.3 ***Reagents***

D.12.3.1 *Buffer solution* (see **E.21**).

D.12.3.2 *Hydroxylammonium chloride solution* (see **E.19**).

D.12.3.3 *Ortho-phenanthroline solution* (see **E.27**).

D.12.4 ***Apparatus***

D.12.4.1 *Lovibond comparator*[8], fitted with adaptor for 40 mm cells and with disc 3/88 covering the range 0.05 mg/L to 1.0 mg/L as Fe.

D.12.4.2 *Two comparator cells,* 40 mm.

D.12.4.3 *Two plastics beakers,* 100 mL.

D.12.4.4 *Two graduated measuring cylinders,* 50 mL.

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[7] A BDH Lovibond Nessleriser Mark 3 is suitable. It is available from The Tintometer Ltd., Salisbury.

[8] Available from The Tintometer Ltd., Salisbury.

D.12.5 *Procedure.* Measure 20 mL of the sample into one of the plastics beakers and measure 20 mL of deionized water into the other. To each beaker add in succession 2 mL of buffer solution, 1 mL of hydroxylammonium chloride solution and 2 mL of *ortho*-phenanthroline solution. Mix the solution in each beaker thoroughly. Allow the solutions in the two beakers to stand for 15 min. Transfer the solution in the first beaker to one of the comparator cells and place the cell in the right-hand compartment of the comparator. Transfer the solution in the second beaker to the other cell and place the cell in the left-hand compartment.

Match the depth of colour in the right-hand cell against that of the glass standards in the disc, using the source of light provided with the instrument (see **D.1.10**). If the colour is deeper than that of the disc marked 1 mg/L, dilute the sample with deionized water and repeat the determination. Allow for the dilution factor when calculating the iron concentration.

If sufficient solution is not available from the procedure described in **D.18**, repeat the procedure described therein, passing a smaller volume of water through the cellulose filter and allowing for this in calculating the iron concentration after determining the iron content of that solution.

D.12.6 *Calculation of results.* For a sample prepared as described in **D.18**, the content of suspended iron in feed water (in mg/L as Fe) is equal to 0.01 times the disc reading.

For a sample taken directly from source, the iron content is shown by the disc reading (in mg/L as Fe).

D.13 Determination of pH value

D.13.1 *Introduction.* The pH value of a solution can be determined either colorimetrically or potentiometrically by use of a pH meter. In the colorimetric method, the colour produced by a pH indicator varies according to the indicator chosen and the pH value of the sample.

The colorimetric method is unsuitable if the sample is highly coloured, strongly alkaline or of high purity. The potentiometric method is used in these cases.

D.13.2 *Colorimetric method*

D.13.2.1 *Range.* The range of the determination covers the following pH ranges, according to the specific indicator used:

a) bromocresol purple	5.2 to 6.8;
b) bromothymol blue	6.0 to 7.6;
c) phenol red	6.8 to 8.4;
d) thymol blue	8.0 to 9.6.

D.13.2.2 *Reagents*

D.13.2.2.1 *Bromocresol purple indicator solution* (see **E.8**).

D.13.2.2.2 *Bromothymol blue indicator solution* (see **E.9**).

D.13.2.2.3 *Phenol red indicator solution* (see **E.29**).

D.13.2.2.4 *Thymol blue indicator solution* (see **E.48**).

D.13.2.2.5 *Universal pH indicator solution* (see **E.30**).

D.13.2.3 *Apparatus*

D.13.2.3.1 *Graduated measuring cylinder,* 10 mL.

D.13.2.3.2 *Two test tubes,* 25 mL.

D.13.2.3.3 *Two Ostwald-Folin pipettes,* 0.2 mL.

D.13.2.3.4 *Glass stirring rod*

D.13.2.4 *Procedure.* Allow the sample bottle to stand until any suspended solids have settled. Open the bottle and immediately decant 10 mL of the sample into each of two test tubes. To the first tube add 0.2 mL of the universal pH indicator and mix with a clean glass rod.

Compare the colour produced with that shown on the manufacturer's colour scale for the particular indicator.

NOTE This pH value is a rough guide only. The test may be liable to considerable error if the sample bottle was incompletely filled or left open to the atmosphere.

Depending on the pH range indicated by the universal indicator, add 0.2 mL of one of the indicators listed in **D.13.2.1**. Compare the colour produced with the appropriate scale as follows:

a) bromocresol purple, colour change from yellow to bluish-violet over the pH range 5.2 to 6.8;

b) bromothymol blue, colour change from yellow to blue over the pH range 6.0 to 7.6;

c) phenol red, colour change from yellow to red over the pH range 6.8 to 8.4;

d) thymol blue, colour change from yellow to violet-blue over the pH range 8.0 to 9.6.

D.13.3 ***Potentiometric method***

D.13.3.1 *Range,* the range of this determination is 0.0 pH to 14.0 pH.

D.13.3.2 *Principle.* A wide range glass electrode and a reference electrode are put in the sample. A variable electrical potential dependent on the pH value of the sample is developed between the sample and the glass electrode. This potential, relative to the standard potential of the reference electrode, is measured on a pH meter.

D.13.3.3 *Reagents*

D.18.3.3.1 *Potassium chloride,* saturated solution (see **E.31**).

D.13.3.3.2 *Potassium hydrogen phthalate,* buffer solution (see **E.33**).

D.13.3.3.3 *Sodium tetraborate,* buffer solution (see **E.39**).

D.13.3.4 *Apparatus*

D.13.3.4.1 *pH meter,* portable, with glass electrode.

D.13.3.5 *Procedure*

D.13.3.5.1 *Precautions.* Carefully follow the manufacturer's operating instructions. Handle the glass electrode with care, ensuring that it does not touch the sides of the electrode assembly beaker. At certain intervals make adjustments to the pH meter, as given in the manufacturer's instructions.

NOTE These adjustments are usually referred to as a setting-up operation, and buffer solutions of a known pH value are required for this purpose.

D.13.3.5.2 *Setting up.* Assemble the pH meter in accordance with the manufacturer's instructions.

Take freshly prepared potassium hydrogen phthalate buffer solution which is at a temperature of between 20 °C and 25 °C and place enough in the electrode assembly beaker to cover the end of the reference electrode and the bulb of the glass electrode. Adjust the instrument in the manner laid down by the manufacturer so that it reads pH 4.00. Discard the buffer solution and replace with fresh buffer solution, re-adjusting if necessary so that the meter again reads pH 4.00.

Wash the electrode assembly beaker and the electrodes with deionized water until two consecutive readings of the pH value of the water are within 0.1 pH unit. Fill the electrode assembly beaker with sodium tetraborate buffer solution at a temperature of 25 ± 1 °C, take a reading, empty and refill with buffer solution, and continue until a constant reading is obtained to within 0.1 pH unit. This reading should be 9.18 ± 0.10. If it is outside this value, repeat the whole standardization operation with fresh buffer solutions and if the same result occurs, check the electrode by substitution. If the correct figure is still not obtained, consult the manufacturers.

Wash the electrode assembly beaker and the electrodes with deionized water as before and leave the electrodes as recommended by the manufacturer.

D.13.3.5.3 *pH of other than high purity waters.* Fill and empty the electrode assembly beaker with the unfiltered sample at between 20 °C and 25 °C until two consecutive readings agree. Record this figure as the pH value. Wash the electrode assembly beaker and the electrodes with deionized water after use.

D.13.3.5.4 *pH of high purity waters.* Use a flow cell for the electrode assembly which permits the pH of the sample to be determined out of contact with air. Set up the pH meter as described in **D.13.3.5.2** and then connect the flow cell with its electrodes to the sample point by means of plastics tubing. Ensure that the temperature of the running sample is between 20 °C and 25 °C, if necessary, by use of a stainless steel cooling coil. Allow the sample to run slowly through the cell for 5 min and then record the pH value.

D.14 Determination of phosphate (orthophosphate)

D.14.1 *Introduction.* Two methods are given for the determination of phosphate. The method using vanadomolybdate reagent (see **D.14.2**) is suitable for the majority of boilers, but for those in group 6 operating at pressures above 100 bar with congruent phosphate control, the more sensitive method described in **D.14.3** is preferred. For uniformity of procedure, it is recommended that the same method should be used for auxiliary boilers as for main boilers on any one ship and therefore the method described in **D.14.3** includes directions for the dilution of auxiliary boiler water samples to allow for the higher phosphate concentrations found there.

D.14.2 ***Determination of phosphate using vanadomolybdate reagent***

D.14.2.1 *Range.* The range of this determination is 10 mg/L to 100 mg/L of phosphate as PO_4.

D.14.2.2 *Principle.* In the presence of vanadates, phosphates react with molybdates to form yellow molybdophosphovanadate. The intensity of this yellow colour, which is proportional to the amount of phosphate present, is determined by comparison with a series of Lovibond permanent glass standards. If the boiler water is coloured by the presence of organic matter, this is removed by means of potassium persulphate before the test.

D.14.2.3 *Reagents*

D.14.2.3.1 *Vanadomolybdate reagent* (see **E.49**).

D.14.2.3.2 *Potassium persulphate* (solid) (see **E.36**).

D.14.2.4 *Apparatus*

D.14.2.4.1 *Lovibond comparator*[9] fitted with lighting cabinet and disc 3/60 covering the range 10 mg/L to 100 mg/L of phosphate as PO_4.

NOTE For control of small low-pressure boilers where accurate determination of phosphate reserve is not required, a simplified Lovibond block comparator is available, containing two colour standards only. These correspond to 30 mg/L (low) and 80 mg/L (high) of phosphate respectively.

D.14.2.4.2 *Two comparator tubes or cells,* 13.5 mm.

D.14.2.4.3 *Graduated measuring cylinder with stopper,* 50 mL.

D.14.2.4.4 *Filter papers, funnel and stand*

D.14.2.4.5 *Beaker,* 150 mL.

D.14.2.5 *Procedure.* Filter the water through a fine filter paper into the 50 mL stoppered graduated cylinder. Ensure that after filtration the sample is clear. Use the first few millilitres of filtrate to rinse out the cylinder. Filter between 20 mL and 25 mL of sample, and then add an equal volume of the vanadomolybdate reagent. Stopper the cylinder and mix the contents. Rinse one of the 13.5 mm comparator tubes or cells with this solution, then fill it and place it in the right-hand compartment of the comparator. In the left-hand compartment place a blank prepared by mixing equal volumes of the vanadomolybdate reagent and deionized water. Allow the colour to develop for at least 3 min and then match the colour of the sample tube against that of the standards in the disc. If the colour is deeper than the 100 mg/L colour standard, dilute the solution with deionized water and repeat the comparison, making due allowance for the degree of dilution.

If the original water sample is coloured, measure 50 mL into a 150 mL beaker and add 1 g to 2 g of potassium persulphate. Boil the sample until colourless, cool and make up to 50 mL with deionized water, then proceed as before.

D.14.3 ***Determination of phosphate using Palin tablets***

D.14.3.1 *Range.* The range of application of this method is determined by the boiler group.

The intrinsic sensitivity of the method is such that the Nessleriser disk covers the range 1 mg/L to 10 mg/L of phosphate as PO_4. When applied to analysis of marine boiler water samples, these should be diluted by a factor that depends on the group to which the boiler belongs, so that the effective range of the method is as given in Table 8.

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[9] Available from The Tintometer Ltd., Salisbury.

Table 8 — Dilutions for phosphate determination

Boiler group	Dilution factor	Effective range
		mg/L of PO_4
1, 2	10	10 to 100
3, 4, 5	5	5 to 50
6	2	2 to 20

D.14.3.2 *Reagent*

D.14.3.2.1 *Palin phosphate tablets* (Nessleriser type)[10] (see **E.51**).

NOTE Before use, a check should be made that the useful life of the tablets (as dated on the bottle) has not been exceeded.

D.14.3.3 *Apparatus*

D.14.3.3.1 *BDH Lovibond comparator*[11], fitted with lighting cabinet and disc NOX, covering the range 1 mg/L to 10 mg/L as PO_4 in steps of 1 mg/L, omitting 9 mg/L.

NOTE The disc may be labelled in p.p.m. (parts per million) which is numerically equal to mg/L.

D.14.3.3.2 *Two Nessler cylinders,* 50 mL.

D.14.3.3.3 *Graduated measuring cylinder,* 250 mL.

D.14.3.3.4 *Filter funnel and filter papers*

D.14.3.3.5 *Two glass rods,* each with one end flattened.

D.14.3.4 *Procedure*

D.14.3.4.1 Prepare a blank by filling one of the Nessler cylinders to the 50 mL mark with deionized water then add one Palin phosphate tablet. Dissolve the tablet by a combination of crushing, using the flat end of a glass rod and vigorous stirring until the tablet has completely dissolved. Place this cylinder in the left-hand compartment of the Nessleriser.

D.14.3.4.2 Proceed as follows according to the group to which the boiler under test belongs.

a) For boilers in groups 1 and 2 maintaining a phosphate reserve of 30 mg/L to 70 mg/L as PO_4, filter cold boiler water sample into the measuring cylinder to the 25 mL mark, remove the filter funnel and add deionized water to the 250 mL mark. Mix well.

b) For boilers in groups 3, 4 and 5 maintaining a phosphate reserve of 30 mg/L to 50 mg/L or 20 mg/L to 30 mg/L as PO_4, filter cold boiler water sample into the measuring cylinder to the 25 mL mark, remove the filter funnel and add deionized water to the 125 mL mark. Mix well.

c) For boilers in group 6 maintaining a phosphate reserve of 10 mg/L to 20 mg/L or 5 mg/L to 15 mg/L as PO_4, filter cold boiler water sample into the measuring cylinder to the 60 mL mark, remove the filter funnel and add deionized water to the 120 mL mark. Mix well.

D.14.3.4.3 Add the diluted sample prepared by the appropriate method described in **D.14.3.4.2** to the second Nessler cylinder to the 50 mL mark, then add one Palin phosphate tablet. Dissolve the tablet by a combination of crushing, using the flat end of the second glass rod and vigorous stirring until the tablet has completely dissolved. Place this cylinder in the right-hand compartment of the Nessleriser. Allow to stand for 10 min.

Match the depth of colour in the sample against that of the standards in the disc.

D.14.3.5 *Calculation of results.* For boilers in groups 1 and 2 the phosphate reserve (in mg/L as PO_4) is equal to 10 times the disc reading.

For boilers in groups 3, 4 and 5, the phosphate reserve (in mg/L as PO_4) is equal to five times the disc reading.

For boilers in group 6, the phosphate reserve (in mg/L as PO_4) is equal to twice the disc reading.

D.15 Determination of silica

D.15.1 *Range.* The range of the determination is 0.5 mg/L to 2.5 mg/L of silica as SiO_2.

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[10] These tablets are available from The Tintometer Ltd., Salisbury, or Houseman (Burnham) Ltd., Slough, Bucks.

[11] Available from The Tintometer Ltd., Salisbury.

D.15.2 *Principle.* Soluble silica reacts with ammonium molybdate in acid solution to form molybdosilicate, which is reduced with 4-amino-3-hydroxynaphthalene-1-sulphonic acid to produce molybdenum blue. The intensity of the blue colour is proportional to the amount of soluble silica present and is determined by comparison with a series of permanent glass standards in a Lovibond Nessleriser. Phosphate interference is suppressed by the addition of tartaric acid.

D.15.3 *Precautions.* It is very important to keep the temperature of the solutions within the range 20 °C to 30 °C and to use polyethylene bottles for storage of the reagents. All water used for the dilution of samples, for the blank determination and for the preparation of reagent solutions on board ship should be silica-free water supplied specially for the purpose. Deionized water is unlikely to be suitable despite its low conductivity.

D.15.4 ***Reagents***

D.15.4.1 *Acid ammonium molybdate solution* (see **E.2**).

D.15.4.2 *Tartaric acid solution* (see **E.47**).

D.15.4.3 *4-amino-3-hydroxynaphthalene-1-sulphonic acid solution* (see **E.3**).

D.15.4.4 *Silica-free water* (see **E.50**).

D.15.5 ***Apparatus***

D.15.5.1 *Lovibond comparator*[12)], fitted with lighting cabinet and disc NV covering the range 0.2 mg/L to 1.0 mg/L of silica as SiO_2, in steps of 0.1 mg/L.

D.15.5.2 *Two Nessler cylinders,* 50 mL.

D.15.5.3 *Bulb pipette,* 20 mL.

D.15.5.4 *Thermometer,* capable of measuring the temperature range – 10 °C to + 110 °C.

D.15.5.5 *Filter papers, filter funnel and stand*

D.15.6 *Procedure.* As the 4-amino-3-hydroxynaphthalene-1-sulphonic acid solution and the tartaric acid solution do not keep indefinitely, first check that they are less than two months old. If either is not, make up a fresh supply.

Check that the temperatures of the sample and all reagents lie within the range 20 °C to 30 °C and adjust if necessary. Filter not less than 50 mL of the sample into a clean container.

Measure 20 mL of the filtered sample into each Nessler cylinder then add silica-free water to each cylinder to bring the liquid up to the 50 mL mark. Place one cylinder in the left-hand compartment of the Nessleriser; to the other cylinder add 2 mL of the acid ammonium molybdate solution and mix. After 5 min add 4 mL of the tartaric acid solution and 1 mL of the 4-amino-3-hydroxynaphthalene-1-sulphonic acid solution, mix and allow to stand for 20 min, making quite certain that the temperature of the solution remains within the range of 20 °C to 30 °C. Place the cylinder in the right-hand compartment of the Nessleriser. Match the depth of colour of the sample against that of the glass standards in the disc. If the colour is deeper than that of the standard labelled 1 mg/L, repeat the determination using a smaller volume of filtered sample in each cylinder and allow for this in the calculation of the silica concentration.

D.15.7 *Calculation of results.* The silica content (in mg/L as SiO_2) is equal to 2.5 times the disc reading.

D.16 Determination of sulphate

D.16.1 *Range.* The range of the determination is 150 mg/L to 2 000 mg/L as Na_2SO_4.

D.16.2 *Principle.* Sulphate is precipitated as barium sulphate by the addition of a known amount of barium chloride to an acidified solution. The excess barium chloride is then determined by titrating with *dis*odium dihydrogen ethylenediamine-*NNN′N′*-tetra-acetate dihydrate (EDTA), using Mordant Black 11 as indicator. The test is not applicable to waters containing appreciable amounts of calcium and magnesium salts as these are also titratable with EDTA. The test is generally applicable to boiler waters of hardness less than 20 mg/L in terms of $CaCO_3$. In these circumstances the error caused by hardness salts can be ignored.

D.16.3 ***Reagents***

D.16.3.1 *Barium chloride,* 0.02 mol/L solution (see **E.7**).

D.16.3.2 *EDTA solution,* 0.01 mol/L standard solution (see **E.13**).

[12)] Available from The Tintometer Ltd., Salisbury.

D.16.3.3 *Hydrochloric acid,* approximately 0.5N solution (see **E.16**).

D.16.3.4 *Mordant Black 11 indicator* (see **E.24**).

D.16.3.5 *Sulphate buffer solution* (see **E.41**).

D.16.4 ***Apparatus***

D.16.4.1 *Pipettes,* 3 mL and 10 mL.

D.16.4.2 *Two burettes,* 10 mL.

D.16.4.3 *White, flat-bottomed casserole or a porcelain basin,* approximately 200 mL.

D.16.4.4 *Glass stirring rod,* with flattened end.

D.16.4.5 *Beaker,* 10 mL.

D.16.5 *Procedure.* Pipette 10 mL of the sample into the porcelain basin and acidify it with 1 mL of the 0.5N hydrochloric acid solution. Add exactly 10 mL of the 0.04N barium chloride solution by means of a burette and stir well.

Pipette into the beaker 3 mL of the sulphate buffer solution and add to it 0.2 g of the Mordant Black 11 indicator (or one tablet). If a tablet is used, crush it immediately with the flattened end of the stirring rod. Stir vigorously until dissolved, mix well and pour into the basin containing the sample.

Slowly titrate the contents of the basin with the EDTA solution, stirring continuously with the glass rod until the colour begins to change from wine-red to purple. Add the EDTA solution, drop by drop, stirring continuously until all traces of red colour have disappeared. The end point has now been reached. The final colour at the end point is usually pure blue, but with some waters a greyishcoloured end point is obtained.

D.16.6 *Calculation of result.* The sulphate content (in mg/L as Na_2SO_4) is given by:

$$\left(10 - \frac{V_2}{2}\right) \frac{2840}{V_1}$$

where

V_1 is the volume of the sample (in mL);

V_2 is the volume of EDTA solution (in mL).

To convert mg/L as Na_2SO_4 to mg/L as SO_4 multiply by 0.68.

D.17 Determination of sulphite

D.17.1 *Range.* The range of the determination is 15 mg/L to 300 mg/L as Na_2SO_3.

D.17.2 *Principle.* Sulphite is determined by titrating an acidified solution with potassium iodate-iodide solution in the presence of a starch-type indicator (powder or solution) that responds to iodine. Sulphite is oxidized to sulphate in contact with the potassium iodate-iodide solution. When all the sulphite has been oxidized and free iodine is present, the solution turns blue.

D.17.3 *Sampling.* Since sulphite tends to be oxidized by contact with air, it is essential to use the following method of sampling.

Insert the outlet tube from a stainless steel or nickel-copper cooling coil to the bottom of a 250 mL bottle to give a sample at a temperature below 30 °C. Allow the water to flow until at least five changes have occurred. Withdraw the outlet tube slowly and immediately stopper the bottle, avoiding trapping any air bubbles. Analyse the sample immediately.

D.17.4 ***Reagents***

D.17.4.1 *Starch indicator solution* (see **E.40**).

D.17.4.2 *Potassium iodate-iodide,* 0.02N solution (see **E.35**).

D.17.4.3 *Sulphuric acid,* 2.35N solution (see **E.43**).

D.17.5 ***Apparatus***

D.17.5.1 *Graduated measuring cylinders,* 5 mL and 100 mL.

D.17.5.2 *Burette,* 10 mL.

D.17.5.3 *White, flat-bottomed casserole or a porcelain basin,* approximately 200 mL.

D.17.6 *Procedure.* Carry out the test immediately after the sample has been taken.

Measure 4 mL of the sulphuric acid into the porcelain basin and add 100 mL of the unfiltered sample and about 1 mL of starch indicator solution. Titrate with the potassium iodate-iodide solution, stirring continuously until a permanent faint blue colour is obtained.

D.17.7 *Calculation of result.* The sulphate content (in mg/L as Na_2SO_3) is given by

$$\frac{V_2 \times 1260}{V_1}$$

where

V_1 is the volume of the sample (in mL);

V_2 is the volume of the iodate-iodide solution (in mL).

To convert mg/L as Na_2SO_3 to mg/L as SO_3 multiply by 0.64.

D.18 Suspended solids

D.18.1 *Principle.* A 10 L sample is passed through a high-pressure filter (pore size 0.45 µm), and the filter disc therein is removed and treated with hydrochloric acid to extract iron and copper compounds. The extract is then analysed for iron as described in **D.12** and for copper as described in **D.6**.

D.18.2 ***Reagent***

D.18.2.1 *Hydrochloric acid, concentrated,* 36 % (*m*/*m*) (11N) (see **E.14**).

D.18.3 ***Apparatus***

D.18.3.1 *Two graduated measuring cylinders,* 100 mL.

D.18.3.2 *Glass beaker,* 250 mL.

D.18.3.3 *Clock glass*

D.18.3.4 *High-pressure filter holder*[13), 47 mm diameter.

D.18.3.5 *Cellulose filters*[13), 47 mm diameter, 0.45 µm pore size.

D.18.3.6 *Non-serrated filter forceps*[13)

D.18.3.7 *Hydraulic pipework,* complying with the following. (See also Figure 7.)

The pipework is attached to the sample take-off point by a high-pressure coupling. It leads from this point to a two-way valve which allows water to flow either to waste or to the high-pressure filter holder. The outlet side of the filter is provided with a pressure gauge and a fine-control metering valve which is used to control the rate of flow through the filter as indicated on the rotameter-type flowmeter. The water is collected in a polyethylene bottle graduated at 10 L. The working pressure of all components of the hydraulic system up to and including the metering valve is at least equal to the maximum boiler pressure. This section of the pipework is made of stainless steel.

Low-pressure fittings may be used downstream of the metering valve.

NOTE To aid dismantling of the filter holder in order to insert or remove a filter disk the connection between the metering valve outlet and the flowmeter may be made with flexible hose or tubing.

D.18.4 ***Procedure***

D.18.4.1 Ensure that the part of the hydraulic system that lies upstream from the filter disk is scrupulously clean before each determination. Connect the system to the sampling outlet point. With the two-way valve arranged for direct discharge of water to waste, open the sample control valve and allow water to flow for a sufficient time to flush out the sampling line (see clause **22**). Meanwhile, open the filter holder and, using the special forceps, install a clean dry filter disk. Reassemble the filter holder taking care not to contaminate the internal surfaces upstream of the disk. Make sure that the metering valve is fully closed.

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13) For information on the availability of suitable filter kits, apply to Central Enquiries Section, BSI, 2 Park Street, London W1A 2BS, enclosing a stamped addressed envelope for reply.

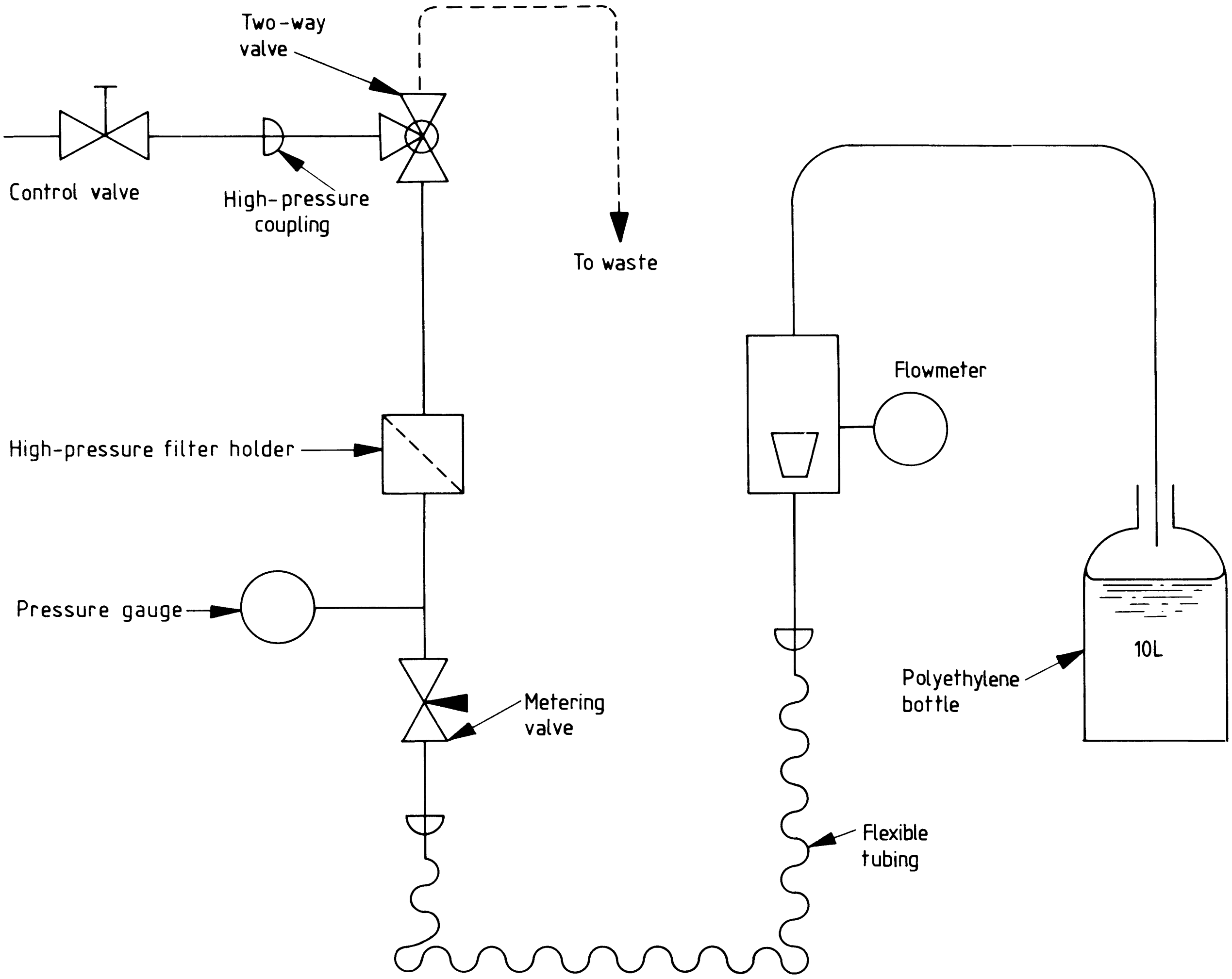

Figure 7 — Hydraulic system for sampling suspended solids

D.18.4.2 When the sampling line has been flushed out, close the control valve and adjust the two-way valve to allow water to pass to the filter holder. Open the control valve slowly to admit pressure to the system. When the pressure at the outlet side of the filter has reached a steady value as shown by the pressure gauge, open the metering valve sufficiently to establish the desired flowrate of about 300 mL/min as indicated on the flowmeter. Allow water to pass at this rate into the bottle until a volume of 10 L has collected. Close the control valve and wait for the pressure in the filter holder to fall to zero. Open the metering valve fully and adjust the two-way valve so that the sampling outlet is connected directly to waste.

D.18.4.3 Dismantle the filter holder and, holding the filter disk at the edge by the special forceps, transfer the disk to the beaker so that it rests on the bottom with the upstream side uppermost. Allow 2 mL of hydrochloric acid to flow over the disc. Cover the beaker with the clock glass, and allow to stand for 15 min. Remove the clock glass and carefully add 20 mL of water to the beaker. Swirl the liquid in the beaker to hasten the mixing and then transfer the liquid to one of the 100 mL graduated cylinders. Add a second portion of 20 mL of water to the beaker to wash the filter disc. Transfer the liquid to the same 100 mL graduated cylinder, add water to raise the level to the 100 mL mark, and mix.

D.18.4.4 Transfer 50 mL of this solution to a second 100 mL graduated cylinder and add water to bring the level to the 100 mL mark. This solution is to be used for the determination of copper as described in **D.6**.

D.18.4.5 The 50 mL of solution remaining in the first cylinder is to be used for the determination of iron as described in **D.12**.

D.18.5 ***Procedure for higher contents of suspended solids***

D.18.5.1 In certain circumstances the iron content of the feed water due to suspended solids may greatly exceed the limits given in Table 4, Table 5 and Table 6, e.g. as a result of the operation of cargo pumps on tankers. This results in a massive burst of corrosion products coming from the return lines from those pumps. The presence of an exceptionally large quantity of suspended solids is indicated by the unusually deep colour of the filter disc. A proportionally greater volume of hydrochloric acid is needed for their dissolution. It is also necessary to dilute the acid extract produced in **D.18.4.3** in order not to exceed the ranges of concentration specified for the determination of iron and copper in **D.12** and **D.6** respectively. Make allowance for the dilution factor when calculating the concentrations of suspended iron and copper in the sampled water as described in **D.6** and **D.12**.

D.18.5.2 An alternative method for dealing with an exceptionally high content of suspended solids is to take a general sample, but reducing the volume passed through the filter below the 10 L prescribed in **D.18.4.2**, provided that it is certain that the temporarily high value of suspended solids is still in being when the second sampling is made.

NOTE This method of varying the sensitivity of the determination is less flexible than diluting the acid extract.

Appendix E Preparation of reagents

E.0 Introduction

It is essential that all reagents are of recognized analytical reagent quality. Deionized water should be used wherever water is required; this should have a conductivity less than 100 µS/m at 20 °C when freshly prepared. For the determination of soluble silica (see **D.15**), specially supplied silica-free water (**E.50**) is to be used exclusively.

Deionized water should be collected and stored in polyethylene bottles to prevent its contamination by traces of silica and metals.

On board ship the deionizing apparatus should be fed by evaporated water. To ensure a long life for the deionizing resin, the evaporated water should have a conductivity less than 500 µS/m at 20 °C.

E.1 Acetic acid

5 mol/L solution. Measure 30 mL of glacial acetic acid and make up to 100 mL with water.

E.2 Acid ammonium molybdate solution

To 75 g of ammonium molybdate, $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$, dissolved in silica-free water (**E.50**), add 332 mL of 10N sulphuric acid solution (**E.44**) and make up to 1 L. Store this solution in a polyethylene bottle provided with a dropper marked to deliver 2 mL.

E.3 4-amino-3-hydroxynaphthalene-1-sulphonic acid solution.

This solution does not keep indefinitely, and therefore should be made up when required, from the following:

a) a dry mixture of *di*sodium disulphite $Na_2S_2O_5$ (sodium metabisulphite) (9 g) and sodium sulphite heptahydrate (1.4 g) pre-weighed in a sachet.

b) 150 mg of 4-amino-3-hydroxynaphthalene-1-sulphonic acid pre-weighed in a sachet.

Measure 90 mL of silica-free water (**E.50**) in a 100 mL measuring cylinder. Add the contents of the first sachet, mix until dissolved, then add the contents of the second sachet and mix until dissolved. Make up the volume of the solution to 100 mL with silica-free water (**E.50**). Store the solution in a polyethylene bottle labelled with the date the solution was made. The bottle should be provided with a dropper marked to deliver 1 mL. Discard any solution remaining after two months.

E.4 Ammonia buffer solution

Measure 570 mL of concentrated ammonia solution 25 % (*m*/*m*) (13.5N) into a 2 L beaker and add 67.5 g of ammonium chloride. Dilute the solution to 950 mL with water. Dissolve 0.616 g of magnesium sulphate, $MgSO_4 \cdot 7H_2O$ in 50 mL of water and add 0.93 g of *di*sodium dihydrogen ethylenediamine-*NNN′N′*-tetra-acetate dihydrate (EDTA). When this is dissolved, add the solution to the ammonium hydroxide/ammonium chloride mixture.

E.5 Barium chloride

$BaCl_2 \cdot 2H_2O$ (solid).

E.6 Barium chloride

100 g/L. Dissolve 10 g of solid barium chloride (**E.5**) in water and dilute to 100 mL.

E.7 Barium chloride

0.02 mol/L solution. Dissolve 4.886 g of solid barium chloride (**E.5**) in water and make-up to the mark in a 1 L one-mark volumetric flask.

E.8 Bromocresol purple indicator solution

Warm 0.1 g of bromocresol purple with 5 mL of 95 % (*V*/*V*) ethanol until dissolved. Add 20 mL of 95 % (*V*/*V*) ethanol and 3.7 mL of 0.05N sodium hydroxide solution. Mix, add 30 mL of 95 % (*V*/*V*) ethanol and dilute to 250 mL with water.

E.9 Bromothymol blue indicator solution

Warm 0.1 g of bromothymol blue with 3.2 mL of 0.05N sodium hydroxide solution and 5 mL of 95 % (*V*/*V*) ethanol. After solution is effected, add 50 mL of 95 % (*V*/*V*) ethanol and dilute to 250 mL with water.

E.10 Chloride mixed indicator solution

The indicator is supplied as a mixture of solid diphenylcarbazone (250 mg) and solid bromophenol blue (25 mg) in capsules or sachets.

To make the solution dissolve the contents of one sachet in 50 mL of isopropyl alcohol (**E.52**). Keep the solution in a brown glass dropping bottle bearing the date on which the solution was made. Discard any solution remaining after two months.

E.11 Copper buffer reagent

Grind together the following reagents in the proportions indicated, by weight, until the mixture is homogeneous:

ammonium chloride, 15 parts

sodium carbonate Na_2SO_3, 15 parts

*tri*ammonium citrate $(NH_4)_3C_6H_5O_7$, copper-free, 30 parts

sodium diethyldithiocarbamate, 0.4 parts

Store the mixture in a brown glass screw-cap bottle.

NOTE A suitable size is one having a screw-cap which, when used as a measure, holds between 2 g and 3 g of reagent.

E.12 4-dimethylaminobenzaldehyde solution

Dissolve 4.0 g of 4-dimethylaminobenzaldehyde (special grade for hydrazine determination) in a mixture of 200 mL of methanol and 20 mL of concentrated hydrochloric acid (**E.14**).

E.13 *Di*sodium dihydrogen ethylenediamine- *NNN′N′*tetra-acetate dihydrate (EDTA), 0.01 mol/L standard solution.

Dissolve 3.72 g of *di*sodium dihydrogen ethylenediamine-*NNN′N′*-tetra-acetate dihydrate, $[CH_2 \cdot N(CH_2 \cdot COOH)CH_2 \cdot COONa]_2 \cdot 2H_2O$, in water and make up in a 1 L one-mark volumetric flask.

E.14 Hydrochloric acid, concentrated

36 % (*m*/*m*) (11N). Concentrated hydrochloric acid is required for the dissolution of suspended solids sampled by high-pressure filtration (**D.18**). The iron and heavy metal contents of the acid should be as low as possible, in order to cause minimal interference with the determination of iron and copper described in **D.12** and **D.6** respectively. The use of an ultra-pure (electronic) grade acid is therefore recommended for this application. The acid should be supplied in a bottle provided with a dropper marked to deliver 2 mL.

E.15 Hydrochloric acid

0.02N solution. Measure, by means of a measuring cylinder, 18 mL of concentrated hydrochloric acid (**E.14**). Pour this into about 500 mL of water and dilute to 1 L in a measuring cylinder. Mix well.

Standardize this solution and adjust it to exactly 0.2N as follows:

a) *Standardization.* Weigh out accurately two portions, each between 0.24 g and 0.28 g, of anhydrous sodium carbonate. Transfer each portion carefully to a wide-necked 250 mL conical flask containing about 50 mL of water and swirl gently until dissolved.

Add 3 drops of methyl orange indicator solution and titrate with the 0.2N hydrochloric acid solution until the colour changes from yellow to orange.

b) *Calculation of factor*. For each of the two portions of sodium carbonate originally weighed out, calculate an acid concentration factor (F_1).

$$F_1 = \frac{m}{0.0106 \times V_1}$$

where

m is the mass of sodium carbonate (in g);

V_1 is the volume of hydrochloric acid (in mL).

The two values of F_1 should be in close agreement. Divide the sum of these two values of the factor (F_1) by two to give the mean factor (F).

c) *Adjustment*. Note the volume (in mL) of 0.2N hydrochloric acid solution left in the 1 L measuring cylinder (V_2). Add V_2 ($F - 1$) mL of water to it, mix well and repeat the standardization. The final factor (F) should be 1.00 ± 0.005.

E.16 Hydrochloric acid

Approximately 0.5N solution. Measure, by means of a measuring cylinder, 45 mL of concentrated hydrochloric acid (**E.14**). Pour this into about 500 mL of water and make up to 1 L in a measuring cylinder. Mix well.

E.17 Hydrochloric acid

0.02N solution. Dilute 100 mL of 0.2N hydrochloric acid solution (**E.15**) to the mark in a 1 L one-mark volumetric flask.

E.18 Hydrogen peroxide solution

This will contain approximately 30 g of hydrogen peroxide per 100 mL.

E.19 Hydroxylammonium chloride solution

Dissolve 20 g of hydroxylammonium chloride, NH_3OHCl, in 100 mL of deionized water.

NOTE The solution should be supplied in a bottle provided with a dropper marked to deliver 1 mL.

E.20 Indigo-carmine solution

Place one indigo-carmine/glucose tablet into a dry 100 mL measuring cylinder and add 5 mL of water from a pipette. Crush the tablet with the flattened end of a long glass rod and swirl the cylinder until the tablet has completely dissolved.

NOTE This needs a few minutes and as the solution is deep blue, careful observation is necessary to ensure that no particles of the tablet remain undissolved.

Add glycerol to the measuring cylinder to give a total volume of 80 mL and mix the contents thoroughly with the glass rod. This solution is stable for one month if kept cool and in the dark.

E.21 Buffer solution for determination of iron

Dissolve 40 g of ammonium acetate and 50 mL of glacial acetic acid in water and make up to 100 mL.

NOTE The solution should be supplied in a bottle provided with a dropper marked to deliver 2 mL.

E.22 1,1,1-trichloroethane (methylchloroform)

Laboratory reagent quality is satisfactory.

E.23 Mercuric nitrate

0.00564N solution. Dissolve 0.9680 g of mercury (II) nitrate monohydrate, $Hg(NO_3)_2 \cdot H_2O$, in 25 mL of water acidified with 2.5 mL of concentrated nitric acid, 70 % (*m*/*m*) (16N) solution. Dilute the acidified mercuric nitrate solution with water to 1 L. Filter if necessary, and standardize against standard 0.025N sodium chloride solution using the procedure described in **D.5.3**.

E.24 Mordant Black 11 indicator[14]

Triturate 0.2 g of Mordant Black 11 with 100 g of sodium chloride to a fine powder.

NOTE The prepared indicator is available commercially as “total hardness indicator tablets” in tablets weighing 0.2 g.

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[14] Available commercially under various trade names, e.g. Eriochrome Black-T and Solochrome Black WDFA.

E.25 Nessler's reagent

Dissolve 35 g of potassium iodide and 12.5 of mercuric chloride in 800 mL of water and add a cold saturated solution of mercuric chloride until, after repeated shaking, a slight red precipitate remains; then add 120 g of sodium hydroxide and shake until dissolved. Add sufficient saturated mercuric chloride solution to ensure a permanent precipitate and dilute to 1 000 mL. Shake occasionally during several days, allow to stand, and use the clear supernatant liquid for the tests.

E.26 Nitric acid

0.05N solution. Add 3 mL of concentrated nitric acid, 70 % (*m*/*m*) (16N) solution, to about 500 mL of water in a 1 L measuring cylinder. Add water to bring the volume to 1 L and mix well.

E.27 1,10-phenanthroline solution

Dissolve 0.5 g of 1,10-phenanthroline hydrochloride in 100 mL of deionized water.

NOTE The solution should be supplied in a bottle provided with a dropper marked to deliver 2 mL.

E.28 Phenolphthalein indicator solution

Dissolve 2.5 g of phenolphthalein in 250 mL of 95 % (*V*/*V*) ethanol.

E.29 Phenol red indicator solution

Warm 0.05 g of phenol red with 2.85 mL of 0.05N sodium hydroxide solution and 5 mL of 95 % (*V*/*V*) ethanol. After solution is effected, add 50 mL of 95 % (*V*/*V*) ethanol and dilute to 250 mL with water.

E.30 pH indicator solution

Universal.

E.31 Potassium chloride

Saturated solution.

E.32 Potassium chromate indicator solution

Dissolve 5 g of potassium chromate in 100 mL of water.

E.33 Potassium hydrogen phthalate

0.05N solution. Dissolve 10.211 g of potassium hydrogen phthalate in freshly deionized water and make up to the mark in a 1 L one-mark volumetric flask. Alternatively, make up the buffer solution on board ship using pH 4.0 buffer tablets and deionized water, following the directions given on the bottle of tablets.

E.34 Potassium hydroxide solution

8N solution. Dissolve 37.5 g of potassium hydroxide in 62.5 mL of water.

E.35 Potassium iodate/iodide

0.02N solution. Dissolve 0.713 g of potassium iodate in 200 mL of water, then add 7 g of potassium iodide and 0.5 g of sodium hydrogen carbonate. When dissolved, make up to the mark with water in a 1 L one-mark volumetric flask.

E.36 Potassium persulphate

Crystalline solid.

E.37 Potassium sodium tartrate solution

Dissolve 500 g of potassium sodium tartrate in 1 L of water. Boil off 200 mL of water or until free from ammonia. Cool and dilute to 1 000 mL with ammonia-free water.

E.38 Silver nitrate

0.02 mol/L solution. Dissolve 3.398 g of silver nitrate in water and make up to the mark in a 1 L one-mark volumetric flask. Store the solution in the dark.

E.39 Sodium borate, buffer solution

Dissolve 19.07 g of *di*sodium tetraborate, $Na_2B_4O_7 \cdot 10H_2O$, in freshly deionized water and make up to the mark in a 1 L one-mark volumetric flask. Alternatively, make up the buffer solution on board ship using pH 9.18 buffer tablets and deionized water, following the directions given on the bottle of tablets.

E.40 Starch indicator solution

Triturate 0.5 g of soluble starch with 5 mL of water and add this, with constant stirring, to sufficient boiling water to produce about 100 mL. Boil for a few minutes and cool.

E.41 Sulphate buffer solution

To 56.5 mL of concentrated ammonia solution, 35 % (*m*/*m*) (18N), add 4.125 g of ammonium chloride and make up to 500 mL with water. Add 3.72 g of *di*sodium dihydrogen ethylenediamine-tetra-acetate dihydrate (EDTA), mix and then add 2.03 g of magnesium chloride, $MgCl_2 \cdot 6H_2O$.

E.42 Sulphuric acid, concentrated

98 % (*m*/*m*) (36N).

E.43 Sulphuric acid

2.35N solution. Carefully add 6.5 mL of concentrated sulphuric acid (**E.42**) to water, with constant stirring, and dilute to 100 mL.

E.44 Sulphuric acid

10N solution. Measure, by means of a measuring cylinder, 280 mL of concentrated sulphuric acid (**E.42**) and add very carefully and slowly, with stirring, to about 600 mL of silica-free water (**E.50**) in a 2 L beaker. Partially immerse the beaker in cold water during the addition of the acid. When the diluted acid is cool, dilute to 950 mL with silica-free water in a measuring cylinder and mix well. Allow any extra heat generated to dissipate before finally making up the volume to 1 L with silica-free water. For the determination of soluble silica (**D.15**), it is not necessary to standardize the 10N acid.

E.45 Sulphuric acid

2N solution. Measure, by means of a measuring cylinder, 56 mL of concentrated sulphuric acid and add it very carefully and slowly to about 600 mL of water contained in a 1 L beaker. Partially immerse the beaker in cold water during the addition of the sulphuric acid. When the diluted acid is cool, dilute to 1 000 mL in a measuring cylinder and mix well.

Standardize this solution and adjust it to exactly 2N as follows:

a) *Standardization.* Pipette 50 mL of the diluted acid into a 500 mL one-mark volumetric flask and make up to the mark with water. This solution is approximately 0.2N sulphuric acid.

Weigh out accurately two portions, each between 0.24 g and 0.28 g, of anhydrous sodium carbonate. Transfer each portion carefully to a wide-necked 250 mL conical flask containing about 100 mL of water and swirl gently until dissolved. Add 3 drops of methyl orange indicator solution and titrate with the 0.2N sulphuric acid solution until the colour changes from yellow to orange.

b) *Calculation of factor.* For each of the two portions of sodium carbonate originally weighed out, calculate an acid concentration factor (F_1).

$$F_1 = \frac{m}{0.0106 \times V_1}$$

where

m is the mass of sodium carbonate (in g);

V_1 is the volume of sulphuric acid (in mL).

Divide the sum of these two values of the factor (F_1) by two to give the mean factor (F).

c) *Adjustment.* Note the volume of 2N sulphuric acid solution left in the 1 L measuring cylinder (V_2 mL). Add $V_2(F - 1)$ mL of water to it, mix well and repeat the standardization. The final factor (F) should be 1.00 ± 0.005.

E.46 Sulphuric acid

0.02N solution. Pipette 5 mL of the 2N sulphuric acid solution into a 500 mL one-mark volumetric flask and dilute to the mark with water. Mix well.

E.47 Tartaric acid solution

Dissolve the contents of one sachet (10 g) of tartaric acid in 100 mL of silica-free water (**E.50**). Store the solution in a polyethylene bottle bearing the date the solution was prepared. The bottle should be provided with a dropper marked to deliver 4 mL. Discard any remaining solution after two months.

E.48 Thymol blue indicator solution

Warm 0.1 g of thymol blue with 4.3 mL of 0.05N sodium hydroxide solution and 5 mL of 95 % (*V*/*V*) ethanol. After solution is effected, add 50 mL of 95 % (*V*/*V*) ethanol and dilute to 250 mL with water.

E.49 Vanadomolybdate reagent

Make up two solutions as follows:

Solution A. Dissolve 20 g of ammonium molybdate tetrahydrate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in 250 mL of deionized water.

Solution B. Dissolve 1 g of ammonium metavanadate, NH_4VO_3, in a mixture of 40 mL of concentrated nitric acid and 200 mL of water.

Mix solutions A and B, add 100 mL of concentrated nitric acid, 70 % (*m*/*m*) (16N) solution, and dilute to 1 000 mL with water.

E.50 Silica-free water

Water to be used for the determination of soluble silica (**D.15**) should be certified by the supplier as containing not more than 50 µg of soluble silica per litre, and should be supplied in polyethylene bottles.

E.51 Palin phosphate tablets (Nessleriser type)

These tablets should be supplied in bottles bearing the date after which they are no longer fit for use.

E.52 ***Iso*****propyl alcohol** (propan-2-ol)

This is required for the preparation of chloride mixed indicator solution (**E.10**) on board ship.

CAUTION. This solvent is highly flammable.

Appendix F On-line instrumentation and automation

NOTE There are companies that can provide, install and commission complete sampling stations, on-line instruments and automatic chemical control systems. However, the following is a guide to the analytical requirements and to the most suitable instrumentation currently available.

F.1 Boiler water analysis

F.1.1 *Introduction.* For congruent phosphate pH control in a high-pressure boiler (group 6), pH value would be in the range 9.3 to 10.0 and phosphate in the range 5 mg/L to 20 mg/L. Reducing conditions would be maintained in the boiler by the addition of hydrazine and not sulphite.

F.1.2 *pH value.* This is measured using a pH meter and there are numerous suitable on-line instruments available on the market.

NOTE Automation is more difficult when using the conventional phosphate treatment because, with the pH value maintained in the region of 11.2 or higher, the pH glass electrode is subject to inaccuracies and has only a short operating life.

F.1.3 *Hydrazine.* The preferred instrument is based on the electrochemical cell; the hydrazine is oxidized at the anode and the current derived from the oxidation process is proportional to the hydrazine concentration in the sample.

NOTE Colorimetric instruments are also available.

F.1.4 *Total dissolved solids.* An approximate measurement of the total dissolved solids is obtained by using a conductivity meter and converting the conductivity to total dissolved solids by applying an appropriate factor.

F.2 Feed water analysis

F.2.1 *Introduction.* The location of sampling points in the condensate and feed system depends very much on system design but some duplication of the instrumentation given in **F.2.2** to **F.2.5** may be necessary.

F.2.2 *pH value.* This is measured using a pH meter. However, there may be difficulties with the measurement of pH value in high purity feed water and it is important to ensure that both the electrode system and the pH meter are suitable for the measurement of pH value in very low conductivity samples.

F.2.3 *Hydrazine.* For measurement of hydrazine, see **F.1.3**.

F.2.4 *Oxygen.* The preferred instruments for measuring feed water oxygen levels are based on the semi-permeable membrane electrode system.

NOTE Instruments based on thallium electrodes and also on the current or voltage produced across an electrode system may also be used with some success though the former have the disadvantage of producing toxic effluent.

F.2.5 *Chloride.* There are instruments for monitoring chloride in the feed water but in order to achieve the necessary sensitivity to sea water ingress, the instruments currently available are large, complex, very sensitive to both sample and environmental conditions and are thus not suitable for marine use. However, chloride can be measured indirectly in one of two ways as follows.

a) *Sodium ion monitor*. This instrument uses sodium-specific ion electrodes and is the more sensitive and the more suitable for monitoring the feed water for impurities and, in particular, traces of sea water ingress.

b) *Cation conductivity meter*. This instrument measures the conductivity of the feed water after passing it through a cation ion exchange column in the hydrogen form. Instruments are available that differentiate between the increase in conductivity produced when a sea water ingress occurs and that produced when the cation ion exchange column has become exhausted by ammonia.

F.3 Automatic control

In addition to the local indication on the instruments all the appropriate high-level and low-level alarms can be located on a panel in the control room. Control can be fully automated by signals being fed direct from the instruments to the chemical control equipment. Alternatively, the control system can be semi-automatic, being initiated by remote manual operation when the instrument alarms indicate that corrective action is required.

Details of the control equipment are not discussed in this standard but can be obtained from suppliers of such equipment.

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Publications referred to

BS 604, *Graduated measuring cylinders.*
BS 612, *Nessler cylinders.*
BS 700, *Specification for graduated pipettes (including blowout pipettes).*
BS 718, *Specification for density hydrometers.*
BS 846, *Specification for burettes.*
BS 1328, *Methods of sampling water used in industry.*
BS 1427, *Routine control methods of testing water used in industry.*
BS 1583, *One-mark pipettes.*
BS 1704, *General purpose thermometers.*
BS 1792, *One-mark volumetric flasks.*
BS 1923, *Glass filter funnels.*
BS 2486, *Recommendations for treatment of water for land boilers.*
BS 2586, *Specification for glass and reference electrodes for the measurement of pH.*
BS 2690, *Methods of testing water used in industry.*
BS 3145, *Specification for laboratory pH meters.*
BS 3218, *Test tubes and boiling tubes.*
BS 3285, *Method of sampling superheated steam from steam generating units.*
BS 5404, *Specification for plastics laboratory ware.*

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