

Methods of

Sampling and examining deposits from boilers and associated industrial plant —

Part 1: Water-side deposits

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Co-operating organizations

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Association of Public Passenger Transport Operators	Institute of Iron and Steel Wire Manufacturers
British Non-ferrous Metals Federation	London Transport Board
British Plastics Federation	National Coal Board

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Foreword

This British Standard was first published in 1954 with the title “*Sampling and testing boiler water deposits*” in order to provide a series of standard methods for the sampling and testing of deposits formed on the water-side or steam-side surfaces of any industrial plant involving heat transfer. The object was to make possible a direct comparison between the findings of different workers.

Since the first publication of this British Standard the increase in boiler operating pressures has made a more rigorous examination of boiler water deposits necessary and there have been substantial improvements in methods of analysis.

The instructions for sampling deposits have been simplified as experience has shown that it is not possible to specify a scheme for sampling that will cover all conditions. A few general principles, which should govern the taking of any sample, have been laid down but their detailed application has been left to the discretion of the skilled and responsible person who should be in charge of the taking of any sample for examination.

In addition to methods given in the first edition for the determination of a number of elements and radicals, methods have been included in this edition for the determination of material insoluble in acid, ferrous iron, potassium, zinc, and manganese.

The determination of nickel and chromium, which are more usually found in fire-side than in water-side deposits, will be included in Part 2 of this British Standard, which will cover methods for sampling and examining fire-side or gas-side deposits associated with industrial plant.

This Part of this British Standard is confined to a description of methods suitable for the more general problems encountered and does not necessarily cater for special cases; the methods have been chosen to give reliable results of an accuracy adequate both for routine purposes and for cases of disputes; they have been deliberately selected from those not requiring expensive instrumental equipment. Some analysts experienced in the examination of this type of material may favour the use of the many modern instrumental analytical techniques now available. Atomic absorption spectrophotometry is particularly useful for the determination of metals in solution and could with advantage be used in place of certain methods given in this Part of this British Standard. In particular, zinc is more reliably determined by atomic absorption than by the colorimetric zincon method included here and a suitable method will be described in Part 2.

It is appreciated that the quantity of sample recommended for analysis may not always be available. In such cases, the mass of the test portion will need to be scaled down, which may impose limitations on the scope and precision of the analyses. The report of the results should then include mention of the mass of test portion used.

A British Standard does not purport to include all the necessary provisions of a contract. Users of British Standards are responsible for their correct application.

Compliance with a British Standard does not of itself confer immunity from legal obligations.

Summary of pages

This document comprises a front cover, an inside front cover, pages i and ii, pages 1 to 22, 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.

1 Scope

This Part of this British Standard is concerned with deposits that form on the surfaces of industrial plant normally in contact with steam and/or water. The methods of sampling and analysis described in this standard are intended to cover a complete investigation of deposits in cooling systems, boilers, condensers, turbines and heat exchangers.

Deposits can occur on the water- or steam-side of any industrial plant involving heat transfer, for example:

- 1) Water-tube boilers: steam-generating tubes, superheater and reheater tubes, steam and water drums, headers, connecting boxes, de-superheaters.
- 2) Shell type boilers: furnace tubes, smoke tubes, boiler shells and plates.
- 3) Feed water systems: heaters, economizers, pumps, pipework.
- 4) Steam turbines: blades, casings, steam strainers.
- 5) Condensers: tubes and plates, piping to and from condensers, condensate return lines, extraction pumps.
- 6) Cooling systems.

Deposits that are found during routine examination should be assessed with a view to preventing their excessive build-up and possible plant failure. Deposits should also be examined in connection with special investigations subsequent to malfunction or plant failure.

It is not obligatory that for any particular investigation the complete procedure should be adopted. The amount and position of sampling and the extent of photography and analysis shall be at the discretion of, and by agreement between, the parties concerned.

NOTE The titles of the British Standards referred to in this standard are listed on the inside back cover.

2 Definitions

For the purposes of this Part of this British Standard, the following definitions apply:

2.1 deposit

any adventitious material that occurs on the plant surfaces in the water or steam spaces

2.2 sludge

a suspension in water of solid material that may form a deposit

2.3 scale

a coherent deposit that adheres to, or has adhered to and subsequently broken away from, the surface on which it formed

2.4 corrosion product

a deposit arising from the action of steam, water or dissolved substances on a metal

NOTE A corrosion product may have a characteristic colour which may be modified by admixture with deposits from other sources.

3 Apparatus, water and reagents

3.1 Apparatus. The following British Standards relate to apparatus used for carrying out the tests in this British Standard: BS 846, BS 1583, BS 1752, BS 1792, BS 2021, BS 2071, BS 2461, BS 2734, BS 3218, BS 3787, and BS 4244.

3.2 Water. Subject to the special requirements of certain methods, pure water, having a conductivity of less than 50 $\mu\text{S}/\text{m}$ at 20 °C when freshly prepared and measured out of contact with air, shall be used whenever water is required. This degree of purity can be achieved by treating water with the correct grades of ion exchange resins.

3.3 Reagents. All reagents shall be of a recognized analytical reagent quality. The reagents referred to in each test method are, as far as possible, those recommended in BS 4245 and the preparation of any other reagent mentioned is described in Appendix A.

4 Sampling

4.1 General principles

4.1.1 Responsibility for sampling. Proper sampling is as necessary as the subsequent examination and shall not be delegated to unskilled personnel. The person taking the sample shall have a clear understanding of the purpose for which it is required, and of the relevant factors involved in operating the plant.

4.1.2 Sampling locations. Because of the wide variety of types of plant and operating conditions it is not possible to specify exactly the sampling locations. The position from which samples are taken shall be consistent with the aims of either routine examination or of diagnosing the cause of malfunction and subsequently applying corrective measures. If required, photographs should be taken before disturbing the deposits.

Vital information can often be obtained by examining areas of the plant not adjacent to the point of immediate interest.

If practicable, a portion of the affected part of the plant shall be removed and sent to the laboratory intact.

4.1.3 Sample information. Provide the laboratory with full details of the samples, as described in 4.4.

4.1.4 Transport of sample. Transfer immediately all samples into chemically inert airtight containers and send them to the laboratory as soon as possible.

4.2 Methods of sampling deposits

4.2.1 General. It is not possible to put forward any standard procedure applicable in all the circumstances met with in practice, and no single tool is suitable for obtaining samples of all kinds of deposits. Sampling, especially from boilers, can be extremely difficult due to inaccessibility.

Where a tube has suffered metal failure or serious damage, a section should be removed, if practicable, by cutting at positions about 30 cm from the damaged area, and sent to the laboratory intact, avoiding contamination during cutting and transport.

4.2.2 Adherent deposits and scale. Adherent deposits and scale vary widely in chemical composition, crystalline structure and texture. These qualities depend not only on the composition of the water used, but also on the method of operation of the plant. Consequently, if a condition such as temperature differs appreciably from point to point in a section of the plant, no sample of scale from a single location will be representative of that in the plant as a whole.

In some instances, scale that adheres initially to a surface breaks and becomes partially or wholly detached from it. Such scale is often found mixed with sludge. Frequently the metal surface laid bare by the breaking of the scale acquires a fresh deposit and when samples of partly detached scale are collected such newly formed deposits shall also be sampled separately. Pieces of scale that have fallen to the bottom of the vessel may not only acquire adherent deposits on their surfaces, but may also undergo changes in composition by reaction with the water, especially if the method or extent of water treatment has been varied during the period of build up of the deposit. Such scale may offer valuable evidence of the effectiveness of the water treatment.

The patch of deposit to be sampled shall be marked off from the unwanted portion around it and removed, using a suitable tool, in pieces as large as possible preferably removing the total thickness down to the bare metal. Contamination of the sample by the surrounding material may be avoided by cleaning a band about 25 mm wide around the selected area and brushing away loose material. Removal of the scale is best achieved by using a light-weight hammer and a thin sharp chisel with a wooden handle. If the deposit tends to split into layers, portions of such layers shall be retained separately. Detailed observation of the physical nature of the deposit shall be made during its removal, e.g. hardness, colour, texture, homogeneity, thickness and adherence to metal; close-up photographs may be taken if desired.

If the deposit contains corrosion products these should be removed from the main bulk of the material and examined separately. The location and nature of corrosion pits associated with the deposits shall be recorded.

4.2.3 Soft accumulated deposits. Soft accumulated deposits are formed from sludge, which can settle at rates dependent not only on the size, shape and density of the sludge particles, but also on the movement of water in the vessel. They remain on the bottom of the vessel, particularly in boiler drums. Remove them in such a way as to represent the total thickness of the deposit. If a sample is too large, reduce it by quartering to obtain a smaller representative laboratory sample.

If it is necessary to flush a sample from an inaccessible place some of the deposit may dissolve. In such a case, collect all the solid and solution and subsequently separate them in the laboratory. Analyse the solids by the methods described in this British Standard and the solution by the methods in BS 1427 or BS 2690, making allowance for the composition of the water used for flushing; if practicable, pure water (see 3.2) should be used.

4.3 Labelling of sample after collection. The following information shall be written on the label accompanying the sample:

- 1) Identification of the plant from which the sample was taken;
- 2) Exact position from which the sample was taken;
- 3) Identification code of sample;
- 4) Date and time of sampling.

4.4 Detailed information about sample. The following detailed information shall be recorded:

- 1) Identification of the plant and name and address of the owner;
- 2) Exact position from which the sample was taken, giving details of the section or sub-section of plant;
- 3) Identification code of the sample;
- 4) Date and time of sampling;
- 5) Purpose of investigation;
- 6) Detailed method of sampling;
- 7) Date of previous inspection of the plant, and subsequent operational history, if known;
- 8) Description of the deposit;
- 9) Particulars of any photograph taken;
- 10) Identity of responsible sampler.

5 Preparation of test sample

5.1 Visual examination. The preparation of each test sample shall be regarded as a separate problem depending on its nature and the method adopted shall be recorded.

Deposits from the water-side of industrial plant may reach the laboratory in a variety of forms and conditions. They may be wet, dry or oily and may show inclusions of old scale in a new matrix or laminations built up at different times in the history of the plant. Make a thorough visual examination of the sample using a hand lens or microscope and record the observations. Remove as much as possible of any obvious metallic contamination. If it is thought helpful to the investigation the deposit should be photographed and a portion of the sample retained in its original form for future reference.

Deposits may be received still attached to parts of the plant or already detached from the supporting surfaces. In either case it is often necessary to use appropriate tools to separate and break the deposit so as to minimize contamination by other material. If samples are laminated, or contain inclusions or appreciable quantities of magnetic material, each fraction shall be examined individually, if practicable, and the components shall be separated as a first step in the preparation.

If it is evident at any stage in the preparation of the test sample that oil is present in an amount likely to interfere with the process of preparation or subsequent analysis, the sample shall at that stage be treated as described in 5.2 and Clause 9 for the drying, extraction and estimation of the oil. A correction will be needed to all the results of the quantitative analysis to allow for this preliminary removal of the oil.

5.2 Preparation for analysis. The analytical investigation of solids shall be carried out on a dry test sample. If the laboratory sample contains appreciable quantities of free water, as in a sludge, it shall be filtered and the filtrate analysed separately. All solid laboratory samples shall be dried in an oven at 105 °C to 110 °C; if desired, the resulting percentage loss in mass of the sample should be recorded.

Break and crush the laboratory sample or its component fractions into pieces of a size suitable for grinding in a mortar and then, if necessary, quarter each of them to yield a mass of not more than 20 g. Grind the crushed and quartered sample to pass through a test sieve with 250 µm nominal aperture size (see BS 410).

Bottle each test sample, or fraction, separately and label the container with a description of the contents.

6 Instrumental examination

A deposit may consist of crystals of different compositions and a knowledge of the nature and form of the various constituents present can frequently be of considerable value in diagnosing the conditions that have existed in the section of plant from which the sample was taken. The compounds present in a deposit usually cannot be identified by chemical analysis alone.

Microscopic examination can identify some of the substances present in the deposit but a more generally useful technique is X-ray powder diffraction analysis. In this a diffraction pattern is obtained which is made up of patterns corresponding to the crystalline constituents present; identification can be made by comparison with reference patterns of pure substances or known mixtures. It is not possible to identify cryptocrystalline material using the microscope, or amorphous material by either technique.

Other physical methods of analysis which can be applied with advantage to the examination of deposits are atomic absorption spectrophotometry and X-ray fluorescence spectroscopy. Atomic absorption has already been mentioned with respect to the determination of zinc (see Foreword), and some laboratories may well find it useful to apply the technique to the determination of some or all of the metals present. X-ray fluorescence spectroscopy, where available, may readily replace part of the qualitative examination (see Clause 7).

7 Qualitative analysis

7.1 General. In these methods for qualitative analysis the masses and volumes of samples and reagents are approximate. The test sample (see 5.2) shall be used for the tests described in 7.3 to 7.9.

7.2 Inspection for magnetic material. Place each separated fraction of the laboratory sample on a sheet of clean smooth paper or synthetic polymer film. Move a strong magnet to and fro under the support near the sample material, and observe whether any material is separated.

7.3 Organic matter and oil, preliminary test. Heat to red heat a piece of clean platinum foil or nickel foil or porcelain, between 250 mm² and 1 000 mm² in area, and allow it to cool out of contact with any organic material.

Place 0.5 g of the test sample on this support and heat it gently at first, then to red heat. Keep the residue for the tests described in 7.6, 7.7 and 7.9. Charring, the evolution of smoke, swelling and/or eventual glowing during the heating indicate the presence of organic matter. The evolution of oily vapours may indicate the presence of oil, which can be confirmed by the procedure described in 7.4.

7.4 Oil, confirmatory test

7.4.1 Reagents. The following reagents are required:

- 1) *Hydrochloric acid*, 5N reagent solution.
- 2) *Petroleum spirit*, boiling range 40 °C to 60 °C.

7.4.2 Procedure. To 0.5 g of the test sample in a glass vessel add about 10 ml of the hydrochloric acid and heat the mixture to boiling point for 5 min. Cool the solution and filter through a sintered glass crucible of porosity grade No. 4 (see BS 1752) using gentle suction. Rinse the vessel with 10 ml of the petroleum spirit and wash any residue and the filter with this, combining the filtrates.

Transfer the combined filtrates to a separating funnel, stopper and shake it and then carefully release any pressure. Run off the aqueous layer, wash the petroleum spirit layer by shaking with 10 ml of water, remove and discard these washings and pour the petroleum spirit solution into a small basin. Heat the basin and contents gently on a water bath in a fume cupboard, away from any source of ignition. An appreciable residue indicates the presence of oil in the sample.

7.5 Carbonate

7.5.1 Reagents. The following reagents are required:

- 1) *Hydrochloric acid*, 5N reagent solution.
- 2) *Barium hydroxide*, 30 g/l reagent solution (see A.6).

7.5.2 Procedure. To 0.1 g of the test sample in a small glass test tube add 1 ml of water and 0.5 ml of the hydrochloric acid. If effervescence occurs, test the evolved gases with the barium hydroxide solution; a white precipitate in this indicates the presence of carbonate.

7.6 Phosphate

7.6.1 Reagents. The following reagents are required:

- 1) *Ammonium nitrate*.
- 2) *Ammonium nitromolybdate* reagent solution (see A.5).
- 3) *Nitric acid*, 5N reagent solution.

7.6.2 Procedure. Transfer 0.1 g of the residue from the test for organic matter (see 7.3) to a test tube and add 5 ml of the nitric acid. Heat the mixture to boiling point, filter if necessary and cool. Add 0.5 g of the ammonium nitrate and then 5 ml of the ammonium nitromolybdate solution. Warm to a temperature not above 70 °C; a canary yellow precipitate indicates the presence of phosphate.

7.7 Sulphate

7.7.1 Reagents. The following reagents are required:

- 1) *Barium chloride*, 100 g/l reagent solution.
- 2) *Hydrochloric acid*, 5N reagent solution.

7.7.2 Procedure. Transfer 0.1 g of the residue from the test for organic matter (see 7.3) to a test tube and add 2 ml of the hydrochloric acid. Heat the mixture to boiling point and filter. Dilute the filtrate with about twice its volume of water and heat to near boiling point. Add 1 ml of the barium chloride solution; a white precipitate indicates the presence of sulphate.

7.8 Chloride

7.8.1 Reagents. The following reagents are required:

- 1) *Nitric acid*, 5N reagent solution.
- 2) *Silver nitrate*, 20 g/l reagent solution.

7.8.2 Procedure. Transfer 0.1 g of the test sample to a test tube and add 5 ml of the nitric acid. Shake for about 1 min and filter. To the filtrate add 2 ml of the silver nitrate solution; a white precipitate indicates the presence of chloride.

7.9 Iron, copper and nickel

7.9.1 Reagents. The following reagents are required:

- 1) *Ammonia solution*, concentrated, 25 % (m/m) (13.5N).
- 2) *Dimethylglyoxime*, 10 g/l ethanol solution.
- 3) *Hydrochloric acid*, 5N reagent solution.

7.9.2 Procedure. Transfer 0.1 g of the residue from the test for organic matter (see 7.3) to a test tube and add 2 ml of the hydrochloric acid. Heat the mixture to boiling point and filter. Add to the filtrate an equal volume of water, mix and add ammonia solution until the pH value is greater than 11 when determined by using a test paper. Allow any precipitate to settle.

A brown precipitate indicates the presence of iron, and a blue coloration in the clear solution, when viewed against a white background, indicates the presence of copper or nickel.

Filter the ammoniacal solution and to the filtrate add 1 ml of the dimethylglyoxime solution. If nickel is present the solution will turn red or a carmine red precipitate will form. If there is only a change to brown without any trace of red, nickel is absent.

8 Scheme for quantitative analysis

8.1 A knowledge of the major constituents of the deposit will usually indicate the cause of the corrosion or deposit formation. To this end the quantitative analysis can be guided by the results of the qualitative analysis. In general an analysis accounting for 90 % of the constituents is sufficient. However, a comprehensive list of methods is included so that the analysis may be as complete as desired.

The order in which the determinations are performed and the size of aliquot portion taken depends on the nature of the deposit; general guidance is given by the order of appearance in the analytical scheme in Figure 1. If the mass specified in an individual method is not available a smaller quantity may be taken with a reduction in the quantity of reagents where appropriate. Any large deviation from the recommended mass of test portion shall be stated in the report of the results.

8.2 Ranges. The range of amounts of the substance being determined is stated at the beginning of each test method and given in either micrograms (μg) or milligrams (mg). The procedures described for the various tests cover the stated ranges; they may in certain circumstances be modified by taking a smaller aliquot portion of the sample solution.

8.3 Interferences. Although the methods given will be applicable in almost all cases occasionally some substance may be present that will render a method unsuitable. Details of known significant interferences are referred to in the methods.

8.4 Colorimetric methods. The spectrophotometer used for colorimetric determinations should have a bandwidth not exceeding 1 % of the wavelength at which the measurement is made.

The temperatures at which optical density measurements are made, of both the sample solution and the calibration solutions, should be within 1 °C, and preferably within the range 20 °C to 25 °C.

The compensating optical cell shall be filled with water. A blank solution shall be included with each batch of calibration solutions or sample solutions and the value for the blank solution shall be deducted from the other values obtained before calibration or calculation. If the sample solution is significantly coloured a correction shall be applied as described in the individual methods.

Measurements at wavelengths of 350 nm and over will usually be made using optical cells of glass; for shorter wavelengths, optical cells of silica shall be used. Unless the same optical cell is used for all calibration and sample solutions in any determination, the optical densities of the individual cells filled with water shall be measured and appropriate cell corrections applied.

9 Oil

9.1 Range. 2 mg upwards of oil.

9.2 Principle. The material soluble in petroleum spirit at its boiling temperature (40 °C to 60 °C) is weighed.

9.3 Reagent. The following reagent is required:
Petroleum spirit, boiling range 40 °C to 60 °C.

9.4 Procedure. Accurately weigh about 2 g of the dried test sample into a paper extraction thimble¹⁾ and plug the thimble with cotton wool.

Extract the oil with the petroleum spirit in a Soxhlet extractor at a rate of about 20 cycles/hour for 4 h.

Distil most of the solvent from the extraction flask on a hot water bath. Transfer the residual solution to a small weighed vessel. Wash the extraction flask with several small quantities of the petroleum spirit and transfer the washings to the weighed vessel.

Evaporate the solvent and dry the vessel and contents in an oven at 105 °C to 110 °C for 1 h. Cool in a desiccator for 30 min and weigh.

¹⁾ Whatman, single, seamless, fat-free thimbles are suitable.