Hardness, Issue 4, page 1 of 3



# THE DETERMINATION OF HARDNESS

Using Eriochrome Powder

# **INTRODUCTION**

The hardness of water is a measure of its soap-consuming capacity; in practice it corresponds to the calcium and magnesium ion content. The soap test originally used for its estimation has now been superseded by complexometric methods using dyes such as Eriochrome Black T, developed by Biedermann and Schwarzenbach<sup>1</sup>. A modification has been made to the titrimetric method to allow a gradual colour change with increasing hardness, so permitting the use of a simple colorimetric procedure.

To overcome the deterioration in storage associated with solutions of Eriochrome Black T, the indicator is incorporated in the test powder formulation, which, as an additional advantage, provides much greater convenience in practice.

#### PRINCIPLE OF THE METHOD

At a suitable pH a solution of Eriochrome Black T has a blue colour. In the presence of calcium and magnesium ions the colour changes to wine-red. The addition of the indicator to the water sample thus produces a colour, which enables the hardness to be determined by comparison with a series of Lovibond permanent colour glass standards.

#### **REAGENTS REQUIRED**

- 1. Lovibond Hardness (Eriochrome) Powder
- 2. Lovibond Supplementary Buffer Powder (for highly alkaline boiler water). See Note 4.

#### THE STANDARD LOVIBOND COMPARATOR DISC 4/38

This disc covers the range 0 - 60 mg./1. of hardness, calculated as CaCO<sub>3</sub>, in steps of: -0, 5, 10, 15, 20, 25, 30, 40, 60 mg./l. and is used with a 13.5 mm./10 ml. moulded cell.

By five-times dilution of sample the range may be extended to 300mg./l. so enabling waters to be placed in the officially adopted classification.

## **TECHNIQUE**

- 1. Fill a 13.5mm./10ml. moulded cell to the 10ml. mark with sample.
- 2. Unscrew and remove the cap from the tube of Hardness Eriochrome Powder. The amount of powder required per test is <u>exactly</u> one level spoonful. Tip this quantity into the cell taking care not to wet the spoon, which is then returned into the tube of powder and the cap screwed on firmly.
- 3. The contents of the cell are mixed thoroughly until the powder has dissolved and then allowed to stand for 1 minute.
- 4. The cell is then placed in the right hand compartment of the Comparator. In the left hand compartment is placed a similar cell containing the sample only, to act as a blank. Match against the standards in the disc using a standard source of white light such as the Lovibond Daylight 2000 Unit (not fluorescent lighting) or failing this North daylight and rotating the disc until the nearest colour match is obtained. See Note 6.

# Lovibond

To extend the range of the disc by dilution proceed as follows:

- 1. Place 2ml. (or other appropriate quantity) of sample in the cell and makeup to the 10ml. mark with deionised water. Add one spoonful of reagent powder as before, mix to dissolve and allow to stand for 1 minute.
- 2. Prepare a blank cell by dilution of the same quantity of sample to 10ml. with deionised water and place it in the left hand compartment of the Comparator. (If the original sample is colourless, use deionised water in the blank cell). Match against the disc as before, finally multiplying the observed reading by the dilution factor (5 in the example quoted, where 2ml. of sample was taken).

#### NOTES

- 1. Samples such as boiler water, which may be coloured or turbid, should first be filtered through a Whatman No. 1 paper. Discard the first runnings so as to obtain as clear a filtrate as possible for testing.
- 2. The following classification is officially adopted<sup>2</sup> for waters of varying hardness.

Hardness mg./.l. (as CaCO3)	Description of water	
0 - 50	Soft	
50 - 100	Moderately soft	
100 - 150	Slightly hard	
150 - 200	Moderately hard	
200 - 300	Hard	
over 300	Very hard	

3. The following recommendations are made<sup>3</sup> for the hardness of boiler water and boiler feed-water.

Low pressure boilers	5 mg./l. or less (carbonate treated)
	2 mg./l. or less (phosphate treated)
	Feed water under 20mg./l.
Medium pressure boilers	2 mg./l. or less
	Feed water under 10mg./l.
High pressure boilers	2 mg./l. or less
	Feed water under 1mg./l.

When internal alkali treatment is used, the boiler water hardness should be under 10 and preferably under 5mg./l. When phosphate is used for internal treatment, the desired boiler water hardness is 2mg. /l. or less.

- 4. In testing boiler waters of high caustic alkalinity, there may be interference with the test due to the colours produced being too red. To check this add a small quantity of supplementary buffer powder (about 0.2g) to the sample cell and mix vigorously until there is no further change of colour. Allow undissolved crystals to settle and match against the disc as before.
- 5. If result is required in grains per gallon, the conversion is 7 gpg = 100mg./l. In the German system of Degrees of Hardness,  $1^{\circ}$ DH = 10mg./l. CaO. Therefore, to convert mg/l CaCO<sub>3</sub> to  $^{\circ}$ DH, multiply by 0.056.
- 6. A reading at the limit of the disc scale (60) should always be checked by repeating with a sample diluted with deionised water, to make certain that the true value is not higher. This may not be apparent from the colour produced in the first test. Always dilute until a reading below the figure of 60 is obtained, and then multiply by the appropriate factor.



# **REFERENCES**

- 1. W. Biedermann and G. Schwarzenbach, Chimia, 1948, 2, 56.
- 2. Ministry of Health "Water Softening", H.M. Stationery Office, London 1949
- 3. P. Halmer, J.Jackson and E.F. Thurston "Industrial Water Treatment Practice", Imperial Chemical Industries Ltd., London 1961.

## **REVISION HISTORY**

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