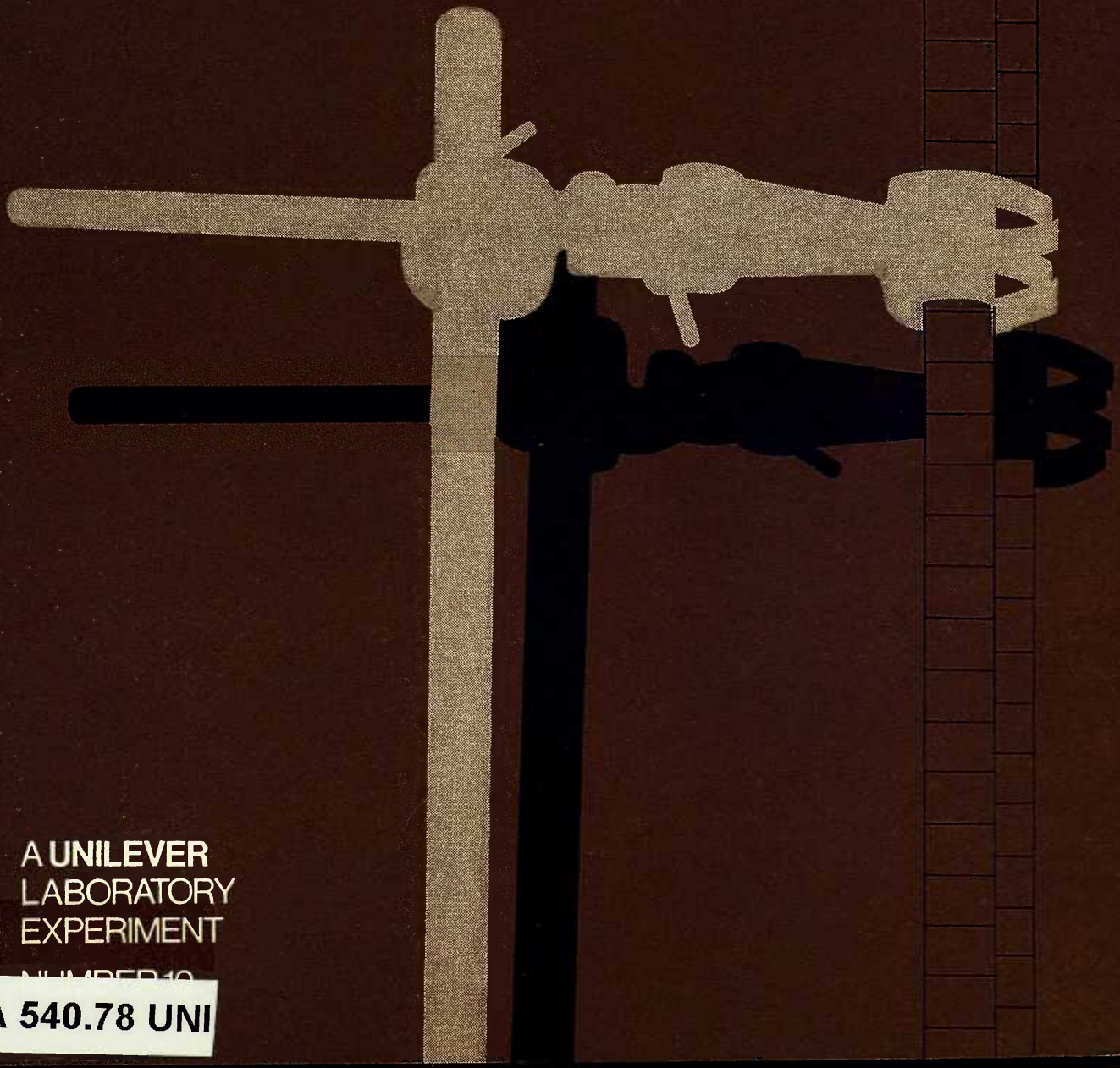
Determination of the total hardness of water



A **UNILEVER**
LABORATORY
EXPERIMENT

NUMBER 10

Determination of the total hardness of water

The experiment described in this leaflet is the widely used method developed by Diehl, Goetz and Hach published in 1950. This uses the disodium salt of ethylene diamine tetracetic acid (EDTA) as titrant with Eriochrome Black T as indicator. With alkaline earth metals, this dye yields highly coloured complexes in solution buffered to pH=10. In the presence of free magnesium ions, a wine red colour is observed. However, these metals form more stable complexes with EDTA and as a result, when EDTA is added, the metal ions complex with the titrant preferentially, first the free calcium ions and then, when these have been completely removed by the disodium EDTA, free magnesium ions. At the end point, the disodium EDTA has extracted the magnesium ions from the dye complex, and the colour changes to blue. (Note 1).

Chemicals

A.R. calcium carbonate
Dilute hydrochloric acid (approx. 1 in 5 dilution)
A.R. disodium EDTA (BDH)
Magnesium chloride ($MgCl_2.6H_2O$)
Ammonium chloride
Ammonium hydroxide solution (SG 0·880)
Eriochrome Black T indicator solutions (Note 2)

Apparatus

Standard volumetric equipment
250 ml pyrex conical flasks
White tile as a background for observing colour changes

Procedure

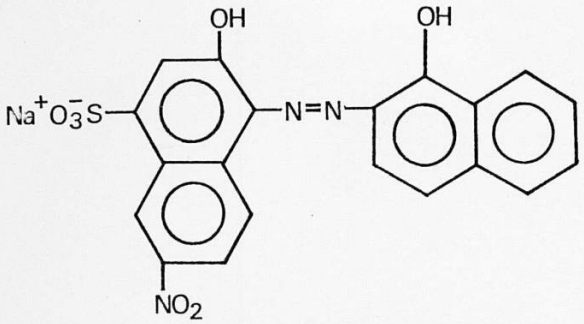
Prepare pH=10 buffer solution by dissolving 67·5 g of ammonium chloride in 570 ml of ammonium hydroxide solution (SG 0·880) and diluting to one litre with distilled water.
Prepare disodium EDTA solution by dissolving 4 g of analytical grade disodium EDTA and 0·1 g of magnesium chloride ($MgCl_2.6H_2O$) in water, and making the solution up to 1 litre. (Note 3). This solution is then standardized with calcium carbonate using the following method.
A standard solution of calcium ions is made up by dissolving an accurately known weight (about 1 g) of Anala R calcium carbonate in the minimum volume of dilute hydrochloric acid and diluting the resulting solution to 1 litre with distilled water. Transfer exactly 25 ml of this solution to a 250 ml pyrex conical flask and add 1 ml of buffer and 4 drops of indicator A. The solution is swirled continuously and carefully titrated with disodium EDTA solution, the colour changing from wine red to a pure blue. The end point is taken when the last of the reddish tinge disappears. (Note 4). From the titration figures obtained and the weight of calcium carbonate taken, the number of mg of calcium carbonate equivalent to 1 ml of disodium EDTA solution may be computed.
To estimate the total hardness of a sample of water as ppm calcium carbonate, transfer 50 ml of sample to a 250 ml pyrex conical flask, add 1 ml of buffer solution followed by 4 drops of indicator A. Whilst swirling the flask and contents, titrate with standard disodium EDTA solution.
Knowing the titre used, compute the number of mg of calcium carbonate in the sample and hence, multiplying by a factor of 20 (Note 5) calculate the total hardness as calcium carbonate in parts per million (ppm) i.e. mg of calcium carbonate per 1000 ml of sample.
To ensure that reproducible results are obtained, all titrations must be done in duplicate.

Alternative procedures

If the water sample taken contains copper or iron or manganese, these ions can interfere with the end point if they are in sufficient quantity, and an alternative method must be used.
The alternative method is to use a mixed indicator system, 4 drops of indicator A and 4 drops of indicator B, the rest of the experiment being as previously described.
For samples of low total hardness, it may be necessary to use a larger aliquot of sample to obtain a more accurate result.

Note 1

Eriochrome Black T (BDH)
Sodium 1- (1-hydroxy-2-naphthylazo)-6-nitro-2-naphthol-4-sulphonate



This acts as an acid-base indicator.
Representing it as H_2In^-, i.e. a tribasic acid in its mono-sodium form,

$$H_2In^- \rightleftharpoons HIn^{2-} \rightleftharpoons In^{3-}$$
pH=6·3 pH=11·5
Blue Orange

At pH=10 (buffer solution)

$$Mg^{++} + HIn^{2-} \rightleftharpoons MgIn^- + H^+$$
Blue Wine red

This reaction goes to completion since the proton is removed by the alkaline buffer solution as soon as it is formed.

Note 2

Indicator A
0·5 g Eriochrome Black T+4·5 g hydroxylamine hydrochloride dissolved in 100 ml alcohol.
(Alternatives are to use the solution above, without the hydroxylamine hydrochloride or to use 0·5 g Eriochrome Black T dissolved in 100 ml distilled water. The latter has poor keeping qualities).
Indicator B
0·5 g Eriochrome Black T+4·5 g dry sodium diethyldithiocarbamate dissolved in 100 ml alcohol.

Note 3

Since magnesium ions are required to function with the indicator, it is normal to add magnesium ions to the disodium EDTA solution *before* standardization. This eliminates the need for a "blank" correction to be applied to all the titrations.

Note 4

As the end point is approached, shown by the first blue tint, run in the disodium EDTA slowly, swirling continuously between each addition. Care is needed to prevent the titration from overshooting since the reaction between disodium EDTA and heavy metal ions is fairly slow, and must be allowed to go to completion before adding further volumes of titrant.

Note 5

As described, 1 ml of disodium EDTA will be found to be equivalent to a quantity of x mg of calcium carbonate by standardization of the titrant with a known weight of Anala R calcium carbonate.
When estimating the total hardness of a water sample, a 50 ml aliquot is normally used. When titrated, this aliquot will be found to require v ml of standard disodium EDTA.
∴ Weight of calcium carbonate present in a 50 ml aliquot of water $= [x \times v]$ mg
∴ Weight of calcium carbonate present in 1 ml of sample $= \frac{[x \times v]}{50}$ mg
Now ppm calcium carbonate is given by weight of calcium carbonate in grams per million ml of solution
∴ Weight of calcium carbonate (expressed as grams, 1 g $= 10^3$ mg) present in 10^6 ml of sample is given by:

$$\frac{[x \times v] \times 1{,}000\,000}{50 \times 1000} \text{ g}$$

$$= [x \times v] \times 20 \text{ g}$$

i.e.
$[x \times v] \times 20$ ppm calcium carbonate for a 50 ml aliquot of sample

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The properties and behaviour of water and its interaction with other substances are important to many of Unilever's activities, for example, to the detergent process, to food processing, to toilet preparations and indeed, to every piece of machinery with which water comes into contact.

Unilever Laboratory Experiment
Number 10
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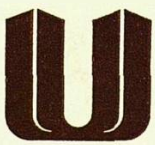

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