Determination of total Hardness

Equipment
1 Bulb pipette 100 ml
1 Bulb pipette 50 ml
1 Bulb pipette 5 ml
1 Bulb pipette 4 ml
3 Measuring pipette 10 ml
2 Erlenmeyer flasks 300 ml
1 Beaker 600 ml
1 Beaker 250 ml
1 Volumetric flask 500 ml
1 Watch glass disc
Piston burette
Magnetic Stirrer
Magnetic follower

The sample solution has a hardness of approximately 9 French degrees

Subject
Titrimetric method for the determination of the total hardness and the calcium and magnesium ion content of water.

Area of application
Can be applied to all kinds of water with a total hardness of at least 5 µmol/L, a calcium content of at 1east 1 mg/L and a magnesium content of at least 1 mg/L. As a rule, the determination is not suitable for waste water.

Remark
More than 5 mg magnesium ions in the analysis sample interfere with the calcium determination. Other bivalent metals which are determined together under the conditions of the method of procedure and are calculated in the total hardness do not generally occur in interfering amounts, except in waste water. Large amounts of carbonate and hydrogen carbonate ions (with a total of more than 10 meq/L) do interfere with the determination but can be removed. More than 1.5 mg iron ions in the analysis sample does interfere with the determination but this interference can be stopped. Possible small amounts of lead and zinc are not determined when using this method of procedure.

Definition
Total hardness = the sum of the concentrations of the calcium and magnesium ions expressed in mmol/L.

Principle
The total hardness is determined by titration with ethylenediamine-tetraacetic acid,

disodium salt dihydrate (From now on referred to as Na_2EDTA). Na_2EDTA forms few dissociated complexes using a particular pH with calcium and magnesium ions. During titration, the Na_2EDTA complex the free calcium ions first, followed by the free magnesium ions and finally the magnesium which forms a compound with the small amount of added indicator. The colour changes as a result of the release of the indicator. Eriochrome black T is used as indicator which gives complex red compounds with the ions of the alkaline earth metals. Under the conditions of the determination, the free eriochrome black T is coloured blue so that the end of the titration is marked because the last trace of red disappears from the blue colour. Because the calcium complex with eriochrome black T is less stable than the magnesium complex and furthennore, in many kinds of water, there is only a very small amount of magnesium ions present, the end point of the titration is marked more clearly by adding a small amount of magnesium EDT A beforehand. The titration is carried out in a solution buffered by a pH between 10.0 and 10.5 and which has a temperature between 20 and 40 ^{o}C. In a stronger alkaline solution and by using calconcarboxylic acid as indicator, only the calcium ion content is determined. The difference between the two titrations is a measure of the magnesium ion content.

Reagents and additives

Na_2EDTA 0.025 mol/L SOLUTION (molar concentration c_1)

Na_2EDTA 0.005 mol/L SOLUTION (molar concentration c_2): Transfer 50 ml Na_2EDTA 0.025 mol/L solution in a 250 ml volumetric flask (use a bulb pipette), fill up to the graduation mark and mix. The molar concentration $c_2 = 0.2\ c_1$.

STANDARD CALCIUM SOLUTION: Dissolve approximately 500 mg calcium carbonate (=*a*) in 50 ml hydrochloric acid 0.5 mol/L, boil the solution and dilute after cooling to 500 ml in a volumetric flask.

Indicators

Indicators for the determination of hardness:

0.lg eriochrome black T with 30 g potassium chloride

0.lg eriochrome black T and 0.04g methyl red with 30g potassium chloride.

Indicator for the determination of calcium: 0.l g calconcarboxylic acid with 30g potassium chloride

Remark

The choice of the indicator for the determination of hardness is determined by the colour sensitivity of the researcher. Using the indicator 1 (eriochrome black T), the colour changes from red (or violet) to blue, using indicator 2 (0.lg eriochrome black T and 0.04g methyl red with 30g potassium chloride), from orange (or grey) to green. For determination of the Na_2EDTA titer solution, the same indicator must always be used as used for the determination procedure.

Buffer solution pH 10.3 - 10.5*:* per litre 75g glycine and 100 ml potassium hydroxide solution

Triethanolamine solution 100 mI/1

Potassium hydroxide solution: 50g potassium hydroxide in 100 ml water.

Magnesium EDTA solution 3 g/L

Content determination of the Na_2EDTA 0.025 mol/L solution

Transfer 50 ml of the calcium solution in a 250 ml conical flask, (use a bulb pipette) dilute to 100 ml, add 5 ml buffer solution, 5ml triethanolamine solution (5.6), 5ml magnesium

EDTA solution, and sufficient indicator, the solution should be clearly coloured. Titrate slowly with the Na_2EDTA solution (5./) until, the blue, respectively green colour does not change any more (the volume used = *V).*
Calculate the molar concentration c_1

$$c_1 = \frac{a}{10 M_{CaCO_3} \cdot V}$$

in which:

M_{CaCO_3} is the molar mass of calcium carbonate (= 100.1 g/mol)

c_1 is the molar concentration of the Na_2EDTA solution in mol/L;

a is the weighed amount of calcium carbonate, in mg;

V is the volume of Na_2EDTA solution used in ml

Transfer 50 ml of the calcium solution in a 250 ml conical flask, (use a bulb pipette), dilute to 100 ml, add 5ml triethanolamine solution, 4 ml potassium hydroxide solution and a sufficient amount of indicator.

The liquid should have a clear red colour. Titrate with the Na_2EDTA solution until, this time, the blue colour does not change anymore (the volume used = *V).*

Calculate the molar concentration c_1' of the Na_2EDTA solution: *a*

$$c_1' = \frac{a}{10 M_{CaCO_3} \cdot V'}$$

in which:

M_{CaCO_3} is the molar mass of calcium carbonate (= 100.1 g/mol);

c_1' is the molar concentration of the Na_2EDTA solution in mol/L;

a is the weighed amount of calcium carbonate, in mg;

V' is the amount of Na_2EDTA solution used in ml.

The values c_1 and c_1' should correspond within the boundaries for dual determinations. If this is not the case, then the reason for the difference must be found and limited by means of systematic research of the reagents used. The use of different titres for hardness, respectively calcium determination must be advised against.

Analysis sample

Choose the volume of sample to be used and the molar concentration of the Na_2EDTA solution using the following table:

expected hardness		expected calcium concentration	maximum volume of water	molar concentration Na_2EDTA-solution
mmol/L	meq/L	mg/L	ml	mol/L
-	-	< 20	100	0.005

0.005 - 0.15	0.01 – 0.3	> 20	500	0.005
0.15 - 0.75	0.3 – 1.5	> 20	200	0.025
> 0.75	> 1.5	> 20	100	0.025

Neutralize the water if it shows an acid reaction in relation to methyl red.

Procedure

The determination of hardness

Place the sample (W_1) in a conical flask and if necessary, dilute with distilled water to 100 ml. Add 5ml buffer solution, 5 ml triethanolamine solution, 5 ml magnesium EDTA solution, and a sufficient amount of indicator, the solution should have a clear colour. Mix after each addition. Titrate with Na_2EDTA solution until the blue, respectively green colour, does not change (volume used = V_1).

Determination of calcium

Place the analysis sample (W_2) in a conical flask and if necessary, dilute with distilled water to 100 ml. Add 5mL triethanolamine solution, 4 ml potassium hydroxide solution, and after 5 minutes, a sufficient amount of indicator, so that the solution is clearly coloured red or violet. Mix after each addition. Titrate with Na_2EDTA solution until, the blue colour does not change (volume used = V_2).

Calculation of the total hardness

$$H_t = \frac{1000\, V_1 c}{W_1}$$

which:
H_t is the total hardness, in mmol/L;
V_1 is the amount of Na_2EDTA solution used during the determination of hardness in ml;
c is the molar concentration of the Na_2EDTA solution (c_1 resp. c'_1), in mol/L;
W_1 is the amount of water used for the determination of hardness, in ml.

Calculate the calcium ion content

$$C_{Ca^{2+}} = \frac{1000\, V_2 c}{W_2}$$

in which:
$C_{Ca^{2+}}$ is the calcium ion content, in mmol/L;
V_2 is the amount of Na_2EDTA solution used during the
c is the molar concentration of die Na_2EDTA solution (c_1 resp. c'_1), in mol/L;
W_2 is the amount of water used for determination of calcium, in ml.

Calculate the magnesium ion content

$$C_{Mg^{2+}} = H_t - C_{Ca^{2+}}$$

in which: $C_{Mg^{2+}}$ is the magnesium ion content, in mmol/L.

For the conversion of calcium, respectively magnesium content of mmol/L to meq/L, the following applies:
1 mmol calcium = 2 meq calcium = 40.08 mg
1 mmol magnesium = 2 meq magnesium = 24.32mg.

Prevention of interferences

If the water contains more than 10 meq carbonate and/or hydrogencarbonate ions per liter, remove the interfering amounts by acidification, by boiling for a short time and by neutralising again on methyl red.

If the analysis sample contains more than 1.5 mg iron ions, then the amount of triethanolamine solution added is not sufficient to stop the interference. In that case, per 2 mg iron ions, add another 5 ml triethanolamine solution.

Remarks

°D; 1 German degree of hardness corresponds to 10 mg CaO per liter.
°F; 1 French degree of hardness corresponds to 10 mg $CaCO_3$ per liter.
°E; 1 English degree of hardness corresponds to 1 grain $CaCO_3$ per UK. gal.

For the conversion factors for these units, see the table

	meq/l	mmol/L	°D	°F	°E	mg $CaCO_3$/L
mmol/L	2.00	1.00	5.60	10.00	7.02	100.0
meq/L	1.00	0.50	2.80	5.00	3.51	50.0
°D	0.357	0.17	1.00	1.78	1.25	17.8
°F	0.200	0.10	0.56	1.00	0.70	10.0
°E	0.285	0.14	0.80	1.43	1.00	14.3
mg $CaCO_3$/L	0.020	0.01	0.056	0.10	0.07	1.00