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MColortest™

Carbonate Hardness Test

Acid capacity to pH 4.3 ("SBV", ANC)

1. Definitions

The **hardness** is defined as the content of Ca^{2+} and Mg^{2+} ions ("hardness ions") in a water. A distinction is made between the **carbonate hardness (CH)** and the **non-carbonate hardness (NCH)**, which together form the **total hardness (TH)**:

$$\text{TH} = \text{CH} + \text{NCH}$$

Carbonate hardness ("temporary hardness") is that proportion of hardness ions for which there is an equivalent amount of anions of carbonic acid (hydrogen carbonate, HCO_3^- , and carbonate, CO_3^{2-}). **Non-carbonate hardness** ("permanent hardness") is that proportion of hardness ions for which there is an equivalent amount of other anions (chloride, sulfate, nitrate, phosphate, silicate).

The units for the water hardness relate to calcium or its compounds CaO ($1^\circ\text{d} \triangleq 10 \text{ mg/l CaO}$) or CaCO_3 ($1^\circ\text{e} \triangleq 14.25 \text{ mg/l CaCO}_3$; $1^\circ\text{f} \triangleq 10 \text{ mg/l CaCO}_3$), with the magnesium content being expressed as calcium content and included in the calculation accordingly.

The carbonate hardness is determined by titrating the carbonic acid anions with acid (see below). To be precise, this method measures the **acid capacity to pH 4.3** (" $\text{K}_{\text{S4.3}}$ ") (**acid-binding capacity "SBV"**, **acid-neutralizing capacity ANC**, total alkalinity, m value) in mmol/l H^+ , since in addition to the anions of carbonic acid also all other protonatable anions (e.g. phosphate) react. The presence of the latter, however, is virtually negligible in most natural waters. This is why the **ANC ($\text{K}_{\text{S4.3}}$) is equivalent to the carbonate hardness** (except in the case of "hardness inversion" - see section 8). The concentration ratio between HCO_3^- and CO_3^{2-} is dependent on the pH value. Since carbonate ions play a role only at pH values over about 8, the ANC value of natural waters ($4.3 < \text{pH} < 8.2$) is approximately identical to the concentration of the hydrogen carbonate ions in mmol/l .

2. Method

Titrimetric determination with dropping bottle

Hydrogen carbonate and carbonate ions are titrated with hydrochloric acid against a mixed indicator. At the titration end-point (at pH 4.3) the color changes to red. The carbonate hardness (acid capacity) is determined from the consumption of titration solution.

3. Measuring range and number of determinations

Graduation ¹⁾	Number of determinations ²⁾
1 drop \triangleq 1.25 °e ANC (SBV): 0.36 mmol/l	100 at 12.5 °e at an ANC (SBV) of 3.6 mmol/l

¹⁾ for conversion factors see section 9

²⁾ In the case of carbonate hardness values exceeding 12.5 °e, the maximum number of determinations possible is fewer than 100 (see section 10).

4. Applications

The carbonate hardness (acid capacity to pH 4.3) is an important parameter for the assessment of the buffering effect and the corrosive behavior of water.

Sample material:

Surface water, seawater
Drinking water and mineral water (after degassing)
Aquarium water, waters from aquaculture
Industrial water, process water
Boiler and boiler feed water, cooling water

5. Influence of foreign substances

The determination is interfered with when the water sample contains - in addition to carbonic acid and its salts - compounds that exert a buffering effect at pH 4.3 (e.g. humic acid salts, phosphates), or else when the water sample exhibits an intrinsic coloration or turbidity that makes it difficult to clearly discern any change in color. Acidic precipitating agents produce a false-low carbonate hardness, strong bases a false-high one.

6. Reagents and auxiliaries

Please note the warnings on the packaging materials!

The test reagents are stable up to the date stated on the pack when stored closed at +15 to +25 °C.

Package contents:

1 bottle of reagent CH-1 (indicator solution)
2 bottles of reagent CH-2 (titration solution)
1 graduated 5-ml plastic syringe
1 test vessel
1 card with brief instruction

7. Preparation

Degas strongly carbonic acid-containing waters (e.g. carbonated mineral water) at room temperature by stirring or ultrasound.

8. Procedure

Rinse the test vessel several times with the pretreated sample.		
Pretreated sample (15 - 30 °C)	5 ml	Inject into the test vessel with the syringe.
Reagent CH-1	3 drops ¹⁾	Add and swirl. The solution must turn blue in color. Otherwise no carbonate hardness can be determined.

Holding the reagent bottle **vertically**, **slowly** add reagent CH-2 dropwise to the sample **while swirling** until its color changes from **blue** via **grey** (shortly before the complete color change) to **red**. Shortly before the color changes, wait a few seconds after adding each drop.

Result in °e = number of drops x 1.25

Result as ANC (SBV, $\text{K}_{\text{S4.3}}$) in mmol/l = number of drops x 0.36

¹⁾ Hold the bottle vertically while adding the reagent!

Notes on the measurement:

- In most natural waters $\text{KH} \leq \text{GH}$. On this condition, CH and ANC ($\text{K}_{\text{S4.3}}$) are equivalent, i.e.

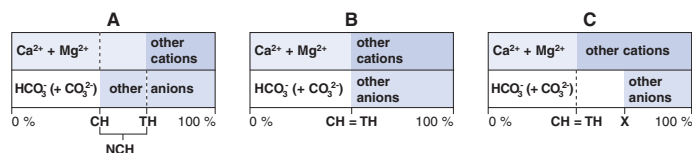
$$\text{CH} [\text{mmol/l Ca}^{2+}] \times 2 = \text{ANC} (\text{K}_{\text{S4.3}}) [\text{mmol/l H}^+ \text{ or } \text{HCO}_3^-]$$

If the carbonate hardness expressed in °e is inserted into this equation with the aid of the table given in section 9, this results in $(\text{CH} [^\circ\text{e}] / 7.02) \times 2 = \text{ANC} (\text{K}_{\text{S4.3}}) [\text{mmol/l}]$ or

$$\text{CH} [^\circ\text{e}] \times 0.285 = \text{ANC} (\text{K}_{\text{S4.3}}) [\text{mmol/l}]$$

- The total hardness should also always be determined in addition to the carbonate hardness. In the event that a carbonate hardness value is found that is apparently higher than that for the total hardness ("hardness inversion"), the value measured for the total hardness must be taken as that for the carbonate hardness actually present: $\text{CH} = \text{TH}$ ($\text{NCH} = 0$). CH and ANC ($\text{K}_{\text{S4.3}}$) are no longer equivalent: $\text{CH} [\text{mmol/l}] \times 2 < \text{ANC}$ or $\text{K}_{\text{S4.3}} [\text{mmol/l}]$

The "hardness inversion" can be explained by the fact that as a rule - in addition to the hardness ions Ca^{2+} and Mg^{2+} - other cations are also dissolved in the water and hence under certain circumstances more equivalents of carbonic acid anions than of hardness ions are present (see Figure C).



Percent composition of aqueous solutions of cation and anion equivalents (X = "apparent carbonate hardness")

9. Conversions

required given	$\text{K}_{\text{S4.3}}$ (ANC) mmol/l	mmol/l CaCO_3 (Ca)	mg/l CaCO_3	mg/l Ca	mg/l HCO_3^-	English degree °e	French degree °f	German degree °d
$\text{K}_{\text{S4.3}}$ (ANC) 1 mmol/l	1	0.5	50.04	20.04	61.02	3.51	5.00	2.80
1 mmol/l CaCO_3 (Ca)	2	1	100.1	40.08	122.0	7.02	10.01	5.61
1 mg/l CaCO_3	0.020	0.010	1	0.400	1.22	0.070	0.100	0.056
1 mg/l Ca	0.050	0.025	2.50	1	3.04	0.175	0.250	0.140
1 mg/l HCO_3^-	0.016	0.008	0.820	0.328	1	0.058	0.082	0.046
1 English degree °e	0.285	0.142	14.25	5.71	17.38	1	1.43	0.799
1 French degree °f	0.200	0.100	10.00	4.00	12.19	0.702	1	0.560
1 German degree °d	0.357	0.178	17.85	7.15	21.76	1.25	1.78	1

10. Notes

- Reclose the reagent bottles immediately after use.
- Rinse the test vessel and the syringe **with distilled water only**.
- In titrimetric determinations the consumption of titration solution is dependent on the concentration of the substance to be determined (here: the hardness ions). The quantities of indicator and titration solution contained in the reagent bottles have been calculated to suffice for 100 determinations each of 12.5 °e. The following applies for other values of the carbonate hardness:

Carbonate hardness °e	Number of determinations	Indicator solution	Titration solution
1.25 - 12.5	100	is used up completely	A remainder is left over.
>12.5	<100	A remainder is left over.	is not sufficient for 100 determinations

- Information on disposal can be obtained at www.disposal-test-kits.com.

Merck KGaA, 64271 Darmstadt, Germany,
Tel. +49(0)6151 72-2440
www.analytical-test-kits.com

EMD Millipore Corporation, 290 Concord Road,
Billerica, MA 01821, USA, Tel. +1-978-715-4321

