

Indian Standard

METHODS OF SAMPLING AND TEST (PHYSICAL AND
CHEMICAL) FOR WATER AND WASTE WATERPART 13 SATURATION INDEX
(WITH RESPECT TO CALCIUM CARBONATE)

(First Revision)

1. Scope — Prescribes a method for determination of saturation index. The method is applicable to all types of water.

2. Principle — Complete analysis data of major ions is required and pH, bicarbonates and calcium contents is determined at the time of sampling.

3. Calculation

3.1 Calculate Ionic strength from the relationship:

$$\text{Ionic strength, } I = \frac{1}{2} \sum_{i=1}^n m_i - z_i^2$$

where

m = molar concentration of the ion, and
 z = charge of the ion.

3.2 Calculate activities of bicarbonate, calcium and hydrogen ions by use of Debye—Huckel equation as given below:

$$\text{Log } r = \frac{-Az^2 \sqrt{I}}{1 + Ba \sqrt{I}}$$

Where, r is activity coefficient, A is a constant relating to the solvent whose value for water at 25°C is 0.508 5, z is the charge of the ion, B is a constant relating to the solvent which for water at 25°C is $0.328 1 \times 10^{-8}$, a is a constant relating to the effective diameter of the ion in solution, and I is the ionic strength. Values of A , B and a for different temperatures and common ions are given in Tables 1 and 2.

**TABLE 1 VALUES OF CONSTANTS FOR USE IN DEBYE — HUCKEL
EQUATION (AQUEOUS SOLUTION)**

Temperature	A	$B (\times 10^{-8})$
(1)	(2)	(3)
°C		
0	0.488 3	0.324 1
5	0.492 1	0.324 9
10	0.496 0	0.325 8
15	0.500 0	0.326 2
20	0.504 2	0.327 3
25	0.508 5	0.328 1
30	0.513 0	0.329 0
35	0.517 5	0.329 7
40	0.522 1	0.330 5
45	0.527 1	0.331 4
50	0.531 9	0.332 1
55	0.537 1	0.332 9
60	0.542 5	0.333 8

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TABLE 2 VALUE OF *a* FOR DIFFERENT IONS IN AQUEOUS SOLUTION
(Clause 3.2)

Ion	<i>a</i> X 10 ⁴
HCO ₃	4.0 - 4.5
Ca ⁺⁺	6
H ⁺	9

3.3 The solubility product of calcite is given at 25°C and atmospheric pressure by the relationship:

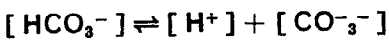


Solubility product for calcite, $K_{sp} = [Ca^{++}] \times [CO_3^{--}] = 10^{-8.37}$

Similarly Ion Activity Product in aqueous phase is

$IAP_{calcite} = [Ca^{++}] \times [CO_3^{--}]$

3.4 As concentrations of CO₃⁻⁻ ions may be difficult to determine for very low values, the activity values may be computed indirectly with the help of following relationship.



$K_{HCO_3} = \frac{[H^+] \times [CO_3^{--}]}{[HCO_3^-]} = 10^{-10.33}$

or $[CO_3^{--}] = \frac{K_{HCO_3} \times [HCO_3^-]}{[H^+]}$

Substituting for [CO₃⁻⁻] in IAP_{calcite}

$IAP_{calcite} = \frac{[Ca^{++}] \times [HCO_3^-] \times K_{HCO_3}}{[H^+]}$

or $\text{Log } IAP_{calcite} = \text{Log } [Ca^{++}] + \text{Log } K_{HCO_3} + \text{Log } [HCO_3^-] + pH \text{ (1)}$

Substituting values in equation (2), (see page 5) saturation index value can be found out.

3.5 For accurate calculations take values of K_{HCO₃} at different temperatures from Table 3.

TABLE 3 VALUES OF K_{HCO₃} AT DIFFERENT TEMPERATURES (HELGESON-1967)

Temperature °C	Log K _{HCO₃}
0	10.63
5	10.56
10	10.49
15	10.43
20	10.38
25	10.33
30	10.29
35	10.25
40	10.22
45	10.20
50	10.17
60	10.15
70	10.13
80	10.13

3.6 Activity coefficients for various ions may also be calculated from Table 4.

TABLE 4 ACTIVITY COEFFICIENTS FOR VARIOUS IONS

Ionic Strength	Cl^- , NO_3^- , K^+ , F^-	Na^+ , HCO_3^-	Mg^{++}	Ca^{++} , Fe^{++}	SO_4^{--}	CO_3^{--}
0.0001	0.99	0.97	0.95	0.95	0.95	0.95
0.0005	0.97	0.97	0.91	0.91	0.91	0.91
0.0010	0.97	0.97	0.87	0.87	0.87	0.87
0.0015	0.96	0.96	0.85	0.86	0.86	0.87
0.0020	0.96	0.95	0.83	0.83	0.82	0.82
0.0050	0.93	0.93	0.76	0.75	0.74	0.75
0.0100	0.90	0.90	0.69	0.68	0.68	0.67
0.0200	0.87	0.86	0.62	0.60	0.58	0.59
0.0500	0.82	0.80	0.52	0.49	0.47	0.48
0.1000	0.77	0.75	0.45	0.41	0.36	0.38
0.2000	0.73	0.73	0.38	0.33	0.24	0.28
0.5000	0.66	0.66	0.31	0.28	0.13	0.20
1.0000	0.60	0.60	0.27	0.24	0.07	0.11

3.7 Equilibrium pH for bicarbonate activities in solution in contact with calcite at 1 atmosphere pressure and 25°C may also be calculated from Fig. 1.

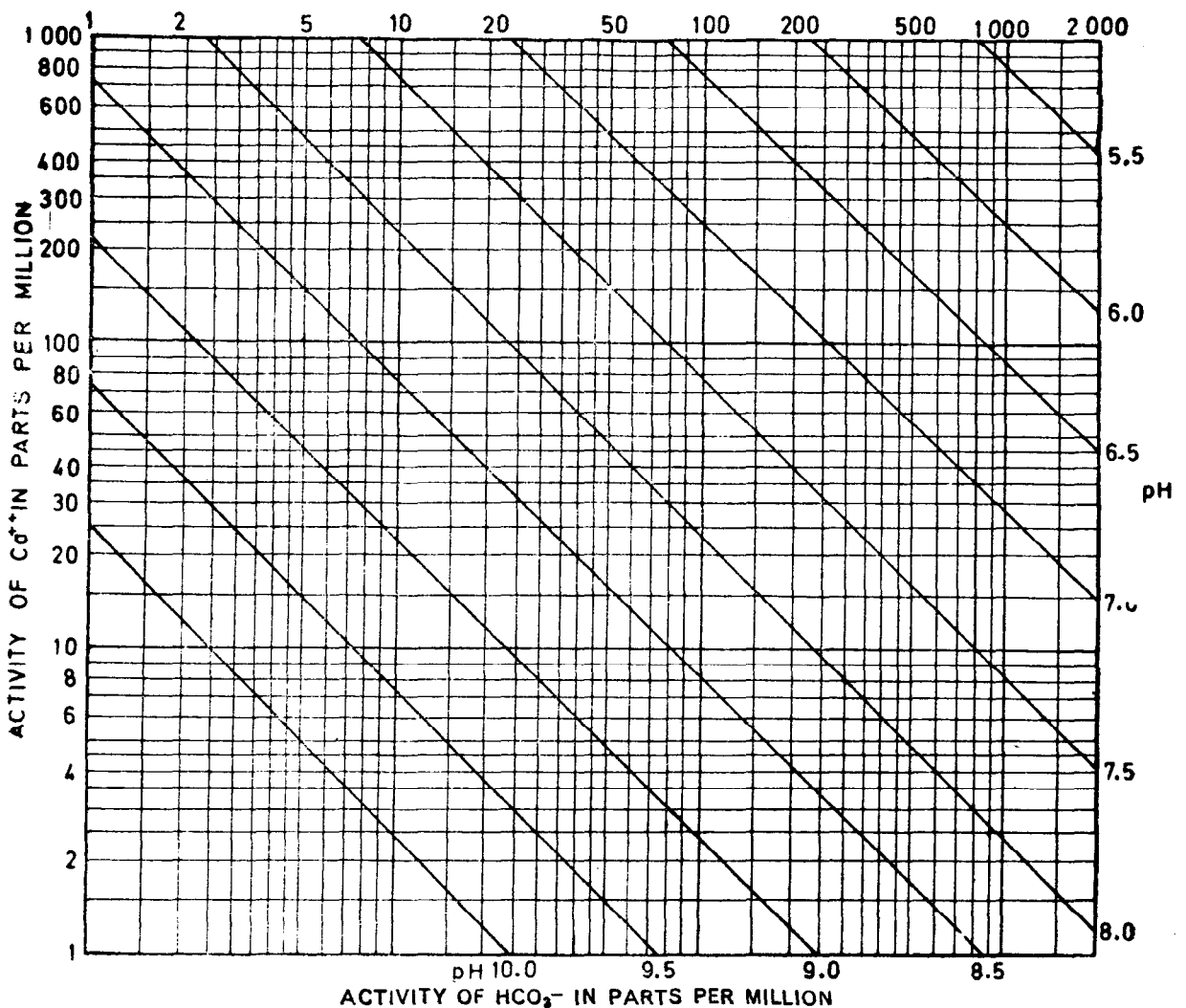


FIG. 1 EQUILIBRIUM pH FOR CALCIUM AND BICARBONATE ACTIVITIES FROM 1 TO 2000 ppm IN SOLUTION IN CONTACT WITH CALCITE, PRESSURE=1 ATMOSPHERE; TEMPERATURE 25°C

3.7.1 Activities of various ions are given by the relationship.

Activity = Activity coefficient×concentration.

For calculation of activity coefficient, ionic strength I is calculated (3.1). For calculation of activity coefficient either Debye-Huckle equation may be used (3.2) or values may be obtained directly as given in Table 4 for different values of ionic strength.

3.7.2 According to the values of activities of calcium and bicarbonate, the point is marked on Fig. 1 and corresponding value of pH is obtained in the ranges given by dotted lines. Saturation index is obtained from the relationship:

Saturation Index = pH measured — pH saturation.

3.8 Degree of saturation or undersaturation is also defined by Langlier Saturation Index as follows:

Langelier Saturation Index = pH_m — pH_s

where

pH_m = experimentally determined value of pH, and

pH_s = equilibrium pH value at saturation.

Negative value of Langelier Saturation Index indicates undersaturation while positive value indicates oversaturation with respect to calcium carbonate and zero value indicates equilibrium.

The value of pH saturation may be calculated from the relationship :

pH_s = C + D — Log (Ca⁺⁺) — Log (Alkalinity)

Where C and D are constants and calcium ion concentration and alkalinity are expressed in terms of mg/1 as CaCO₃ equivalent. Values for the constants and logarithms are given in Tables 5 to 7.

TABLE 5 CONSTANT C AS FUNCTION OF WATER TEMPERATURE

Water Temperature °C	C
0	2.60
4	2.50
8	2.40
12	2.30
16	2.20
20	2.10
25	2.00
30	1.90
40	1.70
50	1.55
60	1.40
70	1.25
80	1.15

TABLE 6 CONSTANT D AS FUNCTION OF TOTAL DISSOLVED RESIDUE

Total Dissolved Residue mg/1	D
0	9.70
100	9.77
200	9.83
400	9.86
800	9.89
1 000	9.90

TABLE 7 LOGARITHMS OF CALCIUM ION AND ALKALINITY CONCENTRATIONS

(Clause 3.8)

Ca⁺⁺ or Alkalinity as CaCO₃ Equivalent,

mg/l	Log
10	1.00
20	1.30
30	1.48
40	1.60
50	1.70
60	1.78
70	1.84
80	1.90
100	2.00
200	2.30
300	2.48
400	2.60
500	2.70
600	2.78
700	2.84
800	2.90
900	2.96
1 000	3.00

EXPLANATORY NOTE

Saturation index with respect to calcite is defined by the relationship:

$$\text{Saturation Index (SI}_{\text{calcite}}) = \text{Log } \frac{\text{IAP}_{\text{calcite}}}{K_{\text{sp calcite}}} \dots\dots\dots(2)$$

Where IAP denotes Ion Activity Product and $K_{\text{sp calcite}}$ denotes solubility product for calcite both being determined at the same temperature. When $\text{SI}_{\text{calcite}}$ is zero, water is in equilibrium with respect to calcite. Negative value of $\text{SI}_{\text{calcite}}$ indicates undersaturation and that the sample is corrosive. Positive value indicates supersaturation with respect to calcite and that the water is having scale-forming property. The concept of saturation index is useful in studies of mineral equilibria of natural waters and scale formation and corrosive properties of water used for different purposes.

Saturation index is also defined in terms of pH as:

$$\text{Saturation Index} = \text{pH actual} - \text{pH}_s$$

Where pH actual is the pH measured at the time of sampling and pH_s is theoretical pH.