Method for Computing Alkalinity Based On Total Inorganic Carbon (TIC) and Related Data

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Summary

Standard Methods (Ref. 1) has a procedure using nomographs for estimating CO_2 concentrations (Method 4500-CO_2 B) based on total alkalinity titrations. The method presented here reverses that process by computing alkalinity based on TIC measurements using infrared technology. These two methods are demonstrated to be compatible, which is not surprising since they use the same stoiciometric relationships.

Inputs

- Total Inorganic Carbon, mgC/l
- Water Temperature, °C (Manual or Automatic)
  - Manual Input of Nominal Temperature Value
  - Automatic Input by Temperature Sensor
- Water pH
- Total Dissolved Solids, mg/l (Manual or Automatic)
  - Manual Input of Nominal TDS value
  - Automatic Ionic Strength Estimate by Conductivity Measurement

Outputs

- Total Alkalinity, mg/l as $CaCO_3$
- Hydroxide Alkalinity, mg/l as $CaCO_3$
- Carbonate Alkalinity, mg/l as $CaCO_3$
- Bicarbonate Alkalinity, mg/l as $CaCO_3$
- Free Carbon Dioxide, mg/l as CO2

Approach

The equilibrium model for CO_2 in water accounts for both ionic and non-ionic species:

$$CO_2 + H_2O \Longleftrightarrow H_2CO_3 \Longleftrightarrow H^+ + HCO_3^- \Longleftrightarrow 2H^+ + CO_3^{-2}$$

$$H_2O \Longleftrightarrow H^+ + OH^-$$

The dissociation constants for these reactions may be corrected for temperature and ionic strength. Equilibrium equations then provide constituent concentrations based on electrical neutrality and mass balance:

$$\textbf{Alkalinity} = [HCO_3^-] + 2[CO_3^{-2}] + [OH^-] - [H^+]$$

$$\textbf{Total Inorganic Carbon} = [H_2CO_3^*] + [HCO_3^-] + [CO_3^{-2}]$$

Based on these relationships specific equations for computing alkalinity values are derived in Appendix A, "Correlation of Alkalinity and TIC".

Results

Figures 1, 2, and 3 illustrate the dependence of alkalinty on the principle variables: TIC, water pH, water temperature, and ionic strength.

Alkalinity is practically linear with TIC at pH below 10, as well as at higher concentrations at higher pH.

Temperature sensitivity increases as pH increases. For pH less than 9.5, the error risk if temperature is ignored is less than 10%, when operating within the range 10 - 30°C.

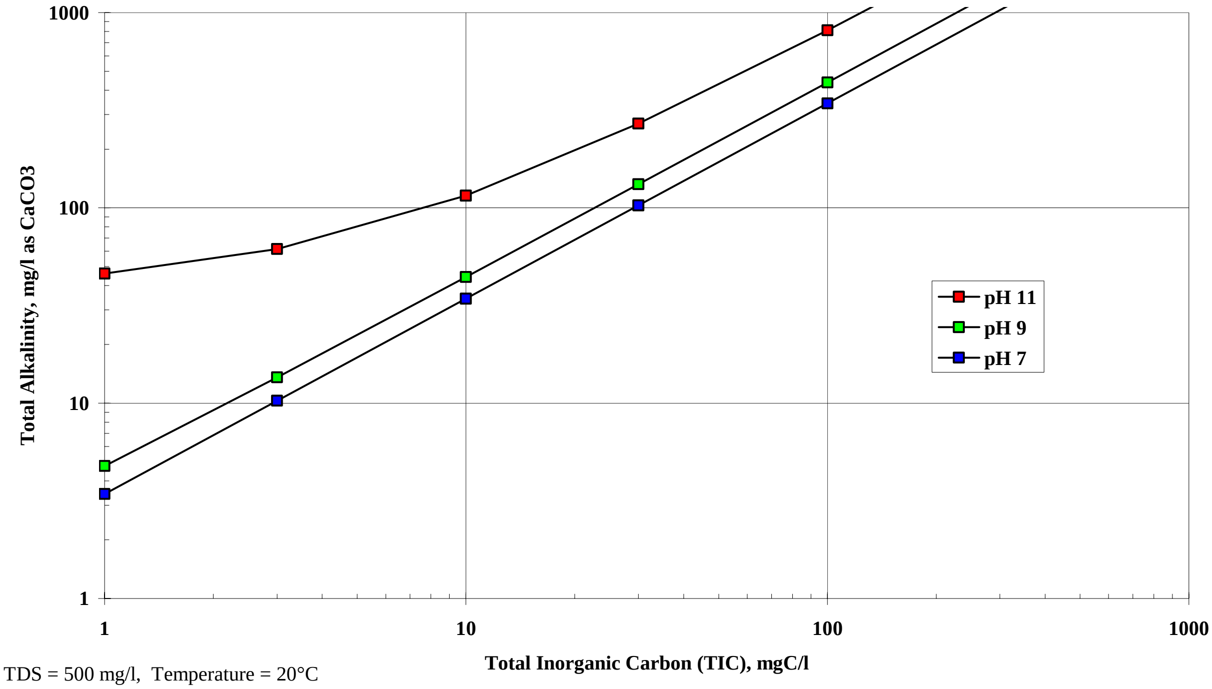
Sensitivity to ionic strength also increases with pH. The error risk if ionic strength is ignored is less than 10%, when operating within the range 0 - 1,000 mg/l Total Dissolved Solids.

Thus, in applications where 10% error is acceptable, nominal temperature and ionic strength values may be used rather than specific values.

Finally, computed alkalinity values using this model are compared in Figure 4 with those obtained using the Standard Methods (Ref. 1) nomographs. Any differences may be attributed to readability of the nomographs. Thus, the model's equations may be used with better precision and convenience.

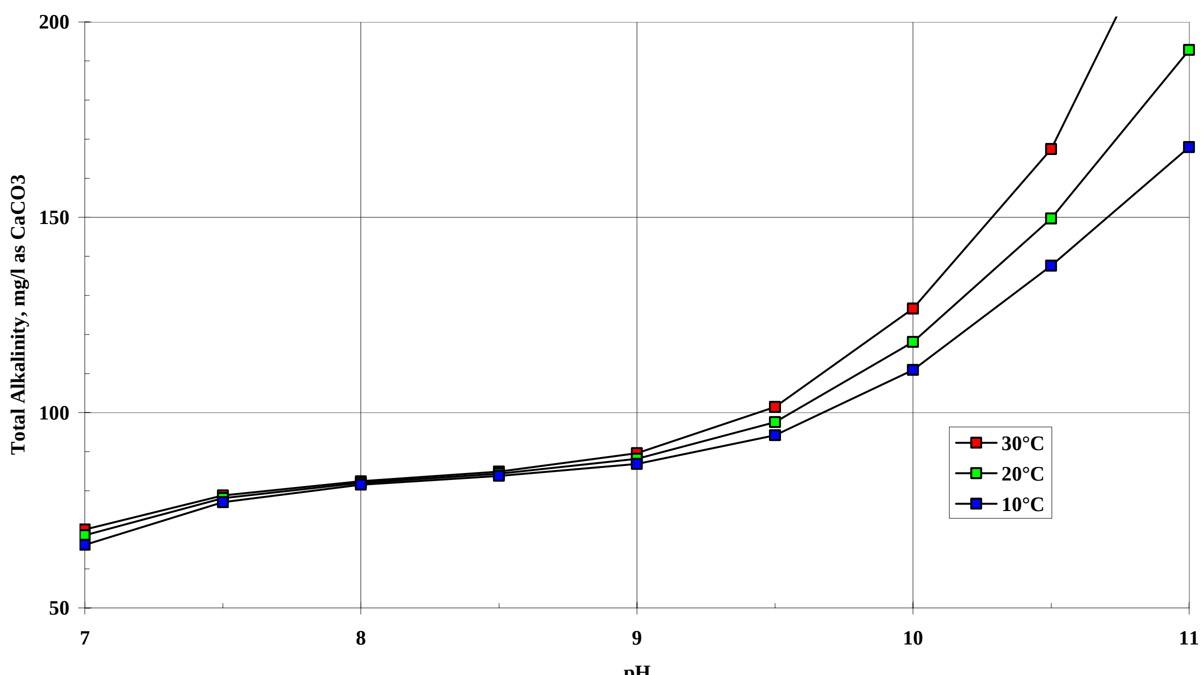
Appendix B presents a computer program in Excel Macro format for computing alkalinity, either on-line or off-line.

Figure 1 - Alkalinity / TIC / pH Relationship



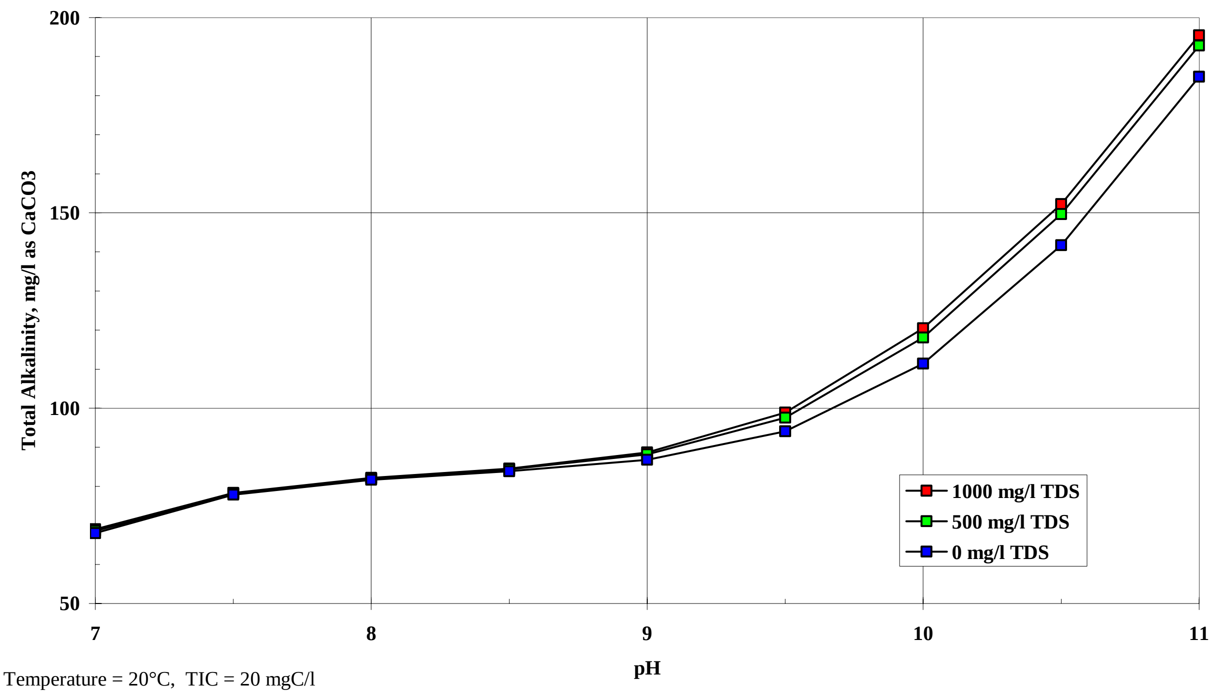
TDS = 500 mg/l, Temperature = 20°C

Figure 2 - Alkalinity / pH / Temperature Relationship



TDS = 500 mg/l, TIC = 20 mgC/l

Figure 3 - Alkalinity / pH / TDS Relationship



Temperature = 20°C, TIC = 20 mgC/l

Figure 4 - Comparison of Results

Total Alkalinity mg/l CaCO3	Temp. °C	TDS mg/l	pH	Hydroxide, mg/l CaCO3 Nomograph	Hydroxide, mg/l CaCO3 Model	Bicarbonate, mg/l CaCO3 Nomograph	Bicarbonate, mg/l CaCO3 Model	Carbonate, mg/l CaCO3 Nomograph	Carbonate, mg/l CaCO3 Model	Free Carbon Dioxide, mg/l Nomograph	Free Carbon Dioxide, mg/l Model
1	10	0	7.0	<0.5	0.00	1	1.00	<0.5	0.00	0.28	0.26
10	10	0	7.0	<0.5	0.00	10	10.00	<0.5	0.01	2.6	2.55
100	10	0	7.0	<0.5	0.00	99	99.94	<0.5	0.07	26	25.52
500	10	0	7.0	<0.5	0.00	490	499.7	<0.5	0.38	130	127.6
1	10	0	9.0	<0.5	0.15	0.9	0.80	<0.5	0.05	<0.1	0.00
10	10	0	9.0	<0.5	0.15	9	9.25	0.55	0.60	<0.1	0.02
100	10	0	9.0	<0.5	0.15	90	93.74	6	6.12	0.25	0.24
500	10	0	9.0	<0.5	0.15	460	469.2	30	30.61	1.4	1.20
10	10	0	7.0	<0.5	0.00	10	10.00	<0.5	0.01	2.6	2.55
10	10	0	8.0	<0.5	0.01	10	9.92	<0.5	0.06	0.28	0.25
50	10	0	9.0	<0.5	0.15	45	46.80	3	3.05	0.13	0.12
50	10	0	10.0	1.5	1.47	28	29.37	19	19.16	<0.1	0.01
500	10	0	11.0	15	14.68	62	64.50	420	420.8	<0.1	0.00
500	10	0	12.0	145	146.8	5	5.33	350	347.9	<0.1	0.00
10	10	400	7.0	<0.5	0.00	10	9.99	<0.5	0.01	2.4	2.27
10	10	400	8.0	<0.5	0.02	9.8	9.89	<0.5	0.09	0.25	0.23
50	10	400	9.0	<0.5	0.16	44	45.63	4	4.20	0.11	0.10
50	10	400	10.0	1.6	1.65	25	25.16	23	23.19	<0.1	0.01
500	10	400	11.0	16	16.47	47	47.33	440	436.2	<0.1	0.00
500	10	400	12.0	160	164.7	3.5	3.60	340	331.7	<0.1	0.00
10	40	0	7.0	<0.5	0.01	10	9.98	<0.5	0.01	1.8	1.74
10	40	0	8.0	<0.5	0.15	9.8	9.74	<0.5	0.12	0.18	0.17
100	40	0	9.0	1.5	1.47	85	87.94	10	10.59	0.16	0.15
100	40	0	10.0	15	14.70	37	38.70	46	46.60	<0.1	0.01
1000	40	0	11.0	150	147.0	60	65.41	800	787.6	<0.1	0.00
2000	40	0	12.0	>800	1,470	4.4	4.36	500	525.3	<0.1	0.00
10	40	400	7.0	<0.5	0.02	10	9.97	<0.5	0.02	1.6	1.55
10	40	400	8.0	<0.5	0.16	9.8	9.67	<0.5	0.16	0.17	0.15
100	40	400	9.0	1.65	1.65	80	84.05	14	14.30	0.13	0.13
100	40	400	10.0	16.5	16.50	30	30.92	60	52.58	<0.1	0.00
1000	40	400	11.0	165	165.0	45	46.37	800	788.7	<0.1	0.00
2000	40	400	12.0	>800	1,650	2.1	2.05	350	348.2	<0.1	0.00