ChemLab Standard Operating Procedure (SOP) for

Preparation of Alkalinity Standards and Calibration of Sulfuric Acid Titrant.

A. Preparation of Alkalinity Standard – Stock Solution:

1. Materials & Reagents:

a. Standard sodium carbonate (Na_2CO_3): Anhydrous Sodium carbonate (Na_2CO_3) certified reference material (CRM) such as; Bharatiya Nirdeshak Dravya (BND) Or United States National Institute of Standards and Technology (NIST) traceable material.

b. Molar mass of Na_2CO_3: 105.988 g/mol ≈ 1.06 g/mol

c. Equivalent weight of Na_2CO_3: 52.994 g/eq ≈ 53g/eq

d. Anhydrous form of Na_2CO_3 usually forms monohydrate when absorbing a moderate amount (up to 10% by weight) of water to become sodium carbonate monohydrate (Na_2CO_3 H_2O).

e. Double Distilled/Deionised (DD) Water, i.e., IS1070:2023 Reagent Grade-2 Water.

f. 1L volumetric flask with ground glass stopper for preparation of stock solution.

g. 1L HDPE or Polypropylene bottle with air-tight screw cap for storage of stock solution.

2. Alkalinity Standard Stock Solution:

a. Take about 1.2g of standard i.e., certified reference material (CRM) sodium carbonate (Na_2CO_3) in a tared porcelain crucible or glass weighing dish. [We are taking a little extra amount of sodium carbonate to allow for loss of mass due to evaporation of water molecules, if any, during drying.]

b. Place crucible with Na_2CO_3 in hot air oven at 250°C for 4 hours.

c. Transfer the heated vessel (using crucible tongs) to desiccator to cool to room temperature without absorbing moisture from ambient air.

d. In the mean while boil or heat the double distilled water before preparing alkalinity stock solution to remove dissolved carbon dioxide which forms carbonic acid and makes the water slightly acidic, interfering with accurate alkalinity measurements. Boiling drives off the CO_2, restoring the water's pH closer to neutral, ensuring the measured alkalinity comes solely from the added Na_2CO_3.

e. Remove cooled crucible containing Na_2CO_3 from the desiccator and retain exactly 1.06g by removing excess Na_2CO_3, if required.

f. Dissolve 1.06 g of anhydrous sodium carbonate in double distilled water and dilute to 1000 mL. 1.0 mL stock solution ≈ 1.00 mg $CaCO_3$.

g. Normality of Na_2CO_3 stock solution: 0.02N.

$$Normality\ (N) of\ Na2CO3\ Stock\ Soln. = \frac{1.06\ g}{53\ g\ (Equivalent\ Wt\ of\ Na2CO3) \times 1\ L} = 0.02\ N$$

h. Store stock solution in 1-L Polypropylene bottle with air-tight screw.

   i. *For alkalinity stock solutions, high-density polyethylene (HDPE) or polypropylene (PP) bottles are preferred over glass or PET due to their excellent chemical resistance to bases, durability, and non-leaching properties, preventing contamination and ensuring sample stability. Glass bottles are not preferred because strongly alkaline solutions (high* *pH) react with the silica in glass tend to leach silicates other impurities into the solution, altering its chemical composition and compromising analytical accuracy. Moreover, when stored in glass-stoppered bottles, alkaline solutions can react at the glass-to-glass interface, forming sodium silicate that effectively freezes the stopper shut (frozen stoppers).*

ii. *Airtight screw cap is necessary to minimise absorption of atmospheric CO_2.*

iii. *Exact size storage bottle is necessary to minimise the headspace in the container. Too much headspace would give scope for CO_2 exchange, which may affect alkalinity of the stored stock solution.*

iv. *Store in a cool dry place below 24°C.*

v. *Recommended shelf life of stock solution; one week.*

B. Calibration of Sulfuric Acid Titrant:

1. It's hard to make exact normality of sulfuric acid because highest stable concentration of sulfuric acid is about 98.3%. Reagent grade concentrated sulfuric acid is usually about of 98% but the exact concentration can vary from 95+% to 98%. Strength of most reagent grade concentrated sulfuric acid varies slightly between 97-98%. Moreover, the extreme heat generated during the process of dilution requires careful, slow addition to water to prevent spattering and hazards. The risk of adverse events makes precise volume measurement challenging. Hence, an approximate dilution of sulfuric acid targeting for required normality is prepared initially. This preparation is then calibrated by titration against standard Na_2CO_3 to calculate the actual normality of the sulfuric acid titrant.
2. Calibration procedure:
   a. First prepare approximately ≈0.2N sulfuric acid solution by diluting 5.6 ml of concentrated sulfuric acid (relative density 1.84) to 1 Litre double distilled (IS 1070: Reagent Grade-2) water. Then prepare required volume of uncalibrated ≈0.02N sulfuric acid (H_2SO_4) solution by diluting 100 ml of ≈0.2N H_2SO_4 to 1L double distilled (DD) water. Calculate required volume according to workload for one month or less, as shelf life of calibrations should not extend beyond one month.
   b. Take 100 ml of 0.02 N Sodium Carbonate (Na_2CO_3) (Alkalinity standard stock solution prepared as is A.2 above) in a beaker. Add two drops of methyl orange indicator. Titrate with the near-0.02N sulfuric acid (H_2SO_4) till endpoint (yellow changes to red). Record volume of acid (titrant) consumed.
   c. Calibrated Normality (N_c) of Sulfuric Acid Solution:

$$N_c = \frac{g\ of\ Na2CO3\ used\ to\ prepare\ 1L\ stock\ solution \times Vol.of\ Na2CO3\ stock\ soln\ titrated}{53.00 \times Volume\ of\ titrant\ (dilute\ sulfuric\ acid)\ consumed.}$$

In the specific case of 100 ml of 0.02 N Sodium Carbonate (Na_2CO_3) prepared as per A.2 above titrated with dilute sulfuric acid prepared as per B.2.a above, the formula at B.2.c above reduces to the following:

$$N_c = \frac{1.06 \times 100}{53 \times C} = \left(\frac{1.06 \times 100}{53}\right) \times \frac{1}{C} = \left(\frac{106}{53}\right) \times \frac{1}{C} = \frac{2}{C}$$

Where;

N_c = Calibrated Normality of the dilute sulfuric acid; and

C= Volume of Sulfuric Acid consumed till titration end-point.

C. Preparation of Working Standards / Spiked Samples for Method Verification:

1. The following ready reckoner table is to facilitate preparation of working standard alkalinity solutions as may be required for verification of standard-alkalinity method. There is no need to prepare all of the working solutions listed in the following table. Use the ready reckoner to prepare working standards that are needed for method verification.

For example; in order to verify accuracy and precision of standard alkalinity method you have selected low-point = 20 mg/L as $CaCO_3$, mid-point= 200mg/L as $CaCO_3$ and high-point = 500 mg/L as $CaCO_3$. For each level, you will need 60 to 100 ml of spiked alkalinity sample for 3 to 5 trials at each trial. Hence, prepare 100 ml of low-point alkalinity sample following the volumes specified in row-2, then prepare 100 ml of mid-point alkalinity sample using volumes specified in row-8 and finally prepare 100 ml of high-point alkalinity sample using volumes specified in row-12.

Table 1: Ready reckoner for preparation of low-, mid- and high-point spiked samples for standard alkalinity method verification.

Row	Alkalinity as mg/L $CaCO_3$	Initial Vol. DD Water	Volume & Normality of Stock Solution	Makeup (Final) Vol. of Working Standard.	Normality (N) of Na_2CO_3
1	10	50 ml	1 ml of 0.02N Na_2CO_3	100 ml	0.0002 N
2	20	50 ml	2 ml of 0.02N Na_2CO_3	100 ml	0.0004 N
3	40	50 ml	4 ml of 0.02N Na_2CO_3	100 ml	0.0008 N
4	60	50 ml	6 ml of 0.02N Na_2CO_3	100 ml	0.0012 N
5	80	50 ml	8 ml of 0.02N Na_2CO_3	100 ml	0.0016 N
6	100	50 ml	10 ml of 0.02N Na_2CO_3	100 ml	0.002 N
7	180	50 ml	18 ml of 0.02N Na_2CO_3	100 ml	0.0036 N
8	200	50 ml	20 ml of 0.02N Na_2CO_3	100 ml	0.004 N
9	250	50 ml	25 ml of 0.02N Na_2CO_3	100 ml	0.005 N
10	300	50 ml	30 ml of 0.02N Na_2CO_3	100 ml	0.006 N
11	400	50 ml	40 ml of 0.02N Na_2CO_3	100 ml	0.008 N
12	500	50 ml	50 ml of 0.02N Na_2CO_3	100 ml	0.01 N
13	600	50 ml	60 ml of 0.02N Na_2CO_3	100 ml	0.012 N

2. The following ready reckoner table is to facilitate preparation of working standard alkalinity solutions as may be required for method verification of low-alkalinity method. There is no need to prepare all of the working solutions listed in the following table. Use the ready reckoner to prepare working standards that are needed for method verification.

For example; in order to estimate LOD of low-alkalinity method you have decided to perform trials using pike concentration of 4 ppm alkalinity as $CaCO_3$. For 8 trials you will need at least 800 ml spiked sample at 4 ppm concentration. Hence, prepare 1000 ml of 4ppm spiked alkalinity solution following the volumes specified in row-4. Thereafter, you want to estimate accuracy and precision of low-alkalinity method at mid-point of say 10ppm. Then prepare 1000 ml of 10 ppm spiked alkalinity solution using volumes specified in row-10. You may use about 300 to 500 ml depending on the number of trials. The remaining can be stored for subsequent use or be discarded after its shelf life is over.

Table 2: Ready reckoner for preparation of spiked samples for low-alkalinity method verification to estimate LOD, accuracy & precision.

Row	Alkalinity as mg/L $CaCO_3$	Initial Vol. DD Water	Volume & Normality of Stock Solution	Makeup (Final) Vol. of Working Standard.	Normality (N) of Na_2CO_3
1	1	500 ml	1 ml of 0.02N Na_2CO_3	1000 ml	0.00002 N
2	2	500 ml	2 ml of 0.02N Na_2CO_3	1000 ml	0.00004 N
3	3	500 ml	3 ml of 0.02N Na_2CO_3	1000 ml	0.00006 N
4	4	500 ml	4 ml of 0.02N Na_2CO_3	1000 ml	0.00008 N
5	5	500 ml	5 ml of 0.02N Na_2CO_3	1000 ml	0.0001 N
6	6	500 ml	6 ml of 0.02N Na_2CO_3	1000 ml	0.00012 N
7	7	500 ml	7 ml of 0.02N Na_2CO_3	1000 ml	0.00014 N
8	8	500 ml	8 ml of 0.02N Na_2CO_3	1000 ml	0.00016 N
9	9	500 ml	9 ml of 0.02N Na_2CO_3	1000 ml	0.00018 N
10	10	500 ml	10 ml of 0.02N Na_2CO_3	1000 ml	0.0002 N
11	15	500 ml	15 ml of 0.02N Na_2CO_3	1000 ml	0.0003 N
12	19	500 ml	19 ml of 0.02N Na_2CO_3	1000 ml	0.00038 N

D. Explanatory Notes:

1. Why Alkalinity is expressed as $CaCO_3$?

Calcium carbonate (CaCO3) is used as the standardized basis for measuring factors like calcium hardness and total alkalinity because of its molar weight. $CaCO_3$ is 100.09 g/mole ≈ 100g/mole, and water is 1000 g/Liter. This makes for relatively easy math when calculating mg/L, which is the metric equivalent to parts-per-million (ppm).

2. Equivalent weight of CaCO3:

Molar weight of $CaCO_3$ = 100.09 g; Valence of $CaCO_3$=2

Equivalent weight of $CaCO_3 = \frac{100.09\ g/mol}{2} = 50.045\ g/eq$

3. Why Na_2CO_3 is used to prepare alkalinity standard instead of $CaCO_3$?

Sodium carbonate (Na_2CO_3) is preferred over calcium carbonate ($CaCO_3$) for alkalinity standards because it's more soluble, readily dissolves to form a stable alkaline solution, has a consistent composition when dried (low hygroscopicity), and provides a well-defined, stoichiometric reaction with acid, making it a superior primary standard for accurately determining unknown alkalinity, unlike $CaCO_3$ which has limited solubility and can introduce calcium ions, affecting water chemistry.

4. Conversion Factor; $CaCO_3$ to Na_2CO_3 :

$$CaCO_3 \text{ to } Na_2CO_3 = \frac{\text{Na2} \quad g/eq}{\text{CaC} \quad g/eq} = \frac{52.994}{50.045} = 1.051 \approx 1.06$$

The USEPA, Method 310.2 for verification of Alkalinity (Colorimetric, Automated, Methyl Orange) by Autoanalyzer (USEPA, 1974) adopted the $CaCO_3$ to Na_2CO_3 factor of 1.06. The same figure is adopted in this SOP.

In other words;

50.045 g $CaCO_3$ is equivalent to 52.994 Na_2CO_3;

1 g of $CaCO_3$ is equivalent to $= \frac{52.994}{50.045} = 1.051 \approx 1.06\ g$

1 g of $CaCO_3$ in 1L (1000ml) is equivalent to 1.06 g Na_2CO_3 in 1L (1000ml)

Converting 1g = 1000mg and 1L = 1000 ml

1 ml of (1.06 g Na_2CO_3 in 1L) solution is equivalent to 1mg $CaCO_3$.

5. Why heat reference material grade anhydrous sodium carbonate before preparing alkalinity standard solution?

Even reference grade anhydrous Na_2CO_3 can absorb moisture during the course of handling. It can also absorb atmospheric carbon dioxide forming sodium bicarbonate ($NaHCO_3$) the atmosphere. Absorbed water changes actual mass and hence can affect the standard solutions true concentration. As heating decomposes sodium bicarbonate and sodium carbonate, evaporates absorbed water and releases carbon dioxide, we get a precise mass of pure Na_2CO_3 for preparation of alkalinity stock solution.

References:

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