Determination of Calcium Carbonate Equivalence

1. Scope:

This procedure is used to determine calcium carbonate equivalence in hydrated or burnt lime, limestone, dolomite and marl type products. The neutralizing value is reported as equivalence of calcium carbonate for limestone, dolomite, and marl and as calcium carbonate ($CaCO_3$) (or calcium oxide (CaO) for lime).

2. Principle:

Samples are acidified to release carbonates as carbon dioxide (CO_2). The samples are then neutralized with sodium hydroxide. The amounts of acid and base are used in a calculation to determine the equivalent amount of calcium carbonate.

Samples are prepared according to RA-SP-SMPL-PREP.

3. Safety:

Read SDS for all materials before using.

Always wear personal protective equipment (safety glasses/face protection, gloves, etc.) when handling dangerous materials.

Hydrochloric acid (HCl) can cause severe skin burns, eye damage, and may cause respiratory irritation. Use extreme caution and always use in a fume hood.

Sodium hydroxide (NaOH) can cause severe skin burns and serious eye damage. Do not breathe vapors. Use extreme caution and always use in a fume hood.

Phenolphthalein can cause dizziness or drowsiness and severe eye irritation and is highly flammable (both liquid and vapor). Use in a fume hood away from sources of ignition

Potassium hydrogen phthalate (KHP) may cause serious skin, eye, and respiratory irritation. Use in a fume hood.

4. Reagents and Supplies (equivalents are acceptable):

4.1 Sodium hydroxide pellets (Fisher cat# S318-500) or prepared 0.25N sodium hydroxide solution (Fisher cat# SS272)
4.2 Hydrochloric acid, concentrated (12.1N) (Fisher cat# SA55) or prepared 0.25N HCl solution (Fisher cat# 18-610-871)
4.3 Phenolphthalein (Fisher cat# P79-500)
4.4 Potassium hydrogen phthalate (KHP) (Sigma Aldrich cat# P1088)
4.5 Calcium carbonate ($CaCO_3$), reagent grade (Fisher cat# AC423515000)
4.6 Analytical balance capable of measuring to 0.0001g

4.7 Erlenmeyer flask, 250mL
4.8 Watch glass

5. Preparation and Standardization of Reagents:

5.1 Prepare 1% phenolphthalein in 50% ethanol by weighing 1.0g phenolphthalein into a 1000mL flask. Add 50mL each ethanol and DI water swirl to dissolve. Fill to the mark with 50/50 ethanol/DI water.

5.2 If using prepared 0.25N NaOH, skip this step and proceed with step 5.3. Prepare ~0.25N sodium hydroxide solution by weighing 10g of NaOH into a 1000mL flask. Dissolve in DI water and allow to cool. Dilute to the mark with water. Skip this step if using prepared 0.25N NaOH.

5.3 Standardize the NaOH solution by weighing 1-2g KHP into a 250mL Erlenmeyer flask (record the weight).

5.4 Add ~50mL water to the flask to dissolve the KHP.

5.5 Add 3-4 drops of 1% phenolphthalein solution and titrate with 0.25N NaOH to a persistent endpoint (faint pink color), recording the initial and final volume of NaOH used.

5.6 Calculate the normality of the NaOH solution:

$$N_{NaOH} = \frac{M_{KHP}}{V_{NaOH}}$$

Where N_{NaOH} = Normality of NaOH solution
M_{KHP} = Moles of KHP (grams of KHP/204.2 g/mol)
V_{NaOH} = Volume of NaOH used (L)

5.7 Repeat steps 5.3 – 5.6 a total of 3 times and average the results. The standard deviation of the values must be ± 10%. If they are not, repeat steps 5.3 – 5.6 until this criterion is met.

5.8 If using prepared 0.25N HCl, skip this step and proceed with step 6.1. Prepare ~0.25N HCl solution by pipetting 20.7mL of concentrated HCl into a 1000mL flask. Add ~200mL DI water, mix well, and dilute to mark.

5.9 Pipette 25.0mL of 0.25N HCl into a 250mL Erlenmeyer flask. Add 3-4 drops of 1% phenolphthalein solution and titrate with the standardized 0.25N NaOH solution prepared above to a persistent endpoint (faint pink color), recording the initial and final volume of HCl used

5.10 Calculate the normality of the HCl solution:

$$N_{HCl} = \frac{N_{NaOH} * V_{NaOH}}{V_{HCl}}$$

Where N_{HCl} = Normality of HCl solution
N_{NaOH} = Normality of NaOH solution from step 5.5
V_{NaOH} = Volume of NaOH used (mL)
V_{HCl} = Volume of HCl used (mL)

5.11 Repeat steps 5.9 – 5.10 a total of 3 times and average the results. The standard deviation of the values must be ± 10%. If they are not, repeat steps 5.9 – 5.10

6. Sample Preparation & Analysis:

6.1 Mix samples thoroughly before weighing.

6.2 Verify the analytical balance.

6.3 Reagent grade $CaCO_3$ is used as a laboratory control sample (LCS) and should be prepared and analyzed in the same manner as the samples.

6.4 Weigh 0.4000 – 1.0000g of sample based on the guarantee (record weight) and place in an Erlenmeyer flask.

6.5 Add 50.0mL HCl and cover with a watch glass.

6.6 Place flask on a hot plate and gently boil for ~5 minutes.

6.7 Add 2-3 drops of phenolphthalein solution. If any solid material remains or solution turns pink from the phenolphthalein, add an additional 25.0mL HCl and boil for ~5 more minutes.

6.8 Cool then titrate with NaOH. Phenolphthalein is used to determine the endpoint which is the first permanent pink color.

7. QA/QC:

The results of the LCS shall be with 2% of the true value. If it falls outside this range, restandardize the NaOH and/or HCl solution(s). See section 5 for determining the normality of the NaOH and HCl solutions.

8. Calculations:

$$\%\text{Calcium Carbonate Equivalence} = \frac{(V_{HCl} * N_{HCl}) - (V_{NaOH} * N_{NaOH})}{W} * 5.004$$

Where V_{HCl} = Volume of HCl used (mL)
N_{HCl} = Normality of HCl solution
V_{NaOH} = Volume of NaOH used (mL)
N_{NaOH} = Normality of NaOH solution
W = Weight of sample (g)

$$\%\text{Calcium Oxide Equivalence} = \frac{(V_{HCl} * N_{HCl}) - (V_{NaOH} * N_{NaOH})}{W} * 2.8$$

Where V_{HCl} = Volume of HCl used (mL)
N_{HCl} = Normality of HCl solution
V_{NaOH} = Volume of NaOH used (mL)
N_{NaOH} = Normality of NaOH solution
W = Weight of sample (g)

9. References:

AOAC Official Methods of Analysis, Methods 1.1.04, 16th Edition, 1995.

Approvals:

Written By:

Stacy Aylesworth — 3/19/21
Stacy Aylesworth — Date
Senior Environmental Scientist

Approved By:

Maryam Khosravifard — 3/19/21
Maryam Khosravifard — Date
Environmental Program Manager I

Sarva Balachandra — 4/13/21
Sarva Balachandra — Date
Quality Assurance Officer

Revision Log:

Date	What was Revised? Why?