

**SOIL CARBONATES**  
Carbonate Qualitative Test

S - 13.05

### Scope and Application

This method involves tests for the presence of carbonates in soil materials and is also may be known as the "fizz" test. The method is based on the reaction of HCl with soil carbonates and visual observation of gaseous loss of CO<sub>2</sub> from the sample as described by the U.S. Salinity Laboratory Staff (1954). The method is not quantitative. Soils may be categorized as slightly reactive, moderately reactive or highly reactive. The method detection limit is approximately 0.2% CaCO<sub>3</sub> equivalent (on a dry soil basis).

### Equipment

1. 50 mm watchglass.
2. Pipette dispenser, calibrated to 2.0 ± 0.2 mL.

### Reagents

1. Deionized water, ASTM Type I grade.
2. Hydrochloric acid (HCl), 3N. Transfer 250 mL of concentrated HCl to 500 mL of deionized water and dilute to 1.0 L with deionized water.

### Procedure

1. Place 4-6 g of soil on a small watchglass. Using a pipette add sufficient water to saturate the sample (See Comment #1). Using a pipette add a few drops of 3.0 N hydrochloric acid solution. Note any effervescence that occurs. The soil may be classified as slightly, moderately or highly calcareous in accordance to the degree of effervescence.

### Comments

1. Water is added to the sample to displace soil air as to avoid confusion of the loss of soil air with effervescence of lime.

### Literature

Allison L.E. and C.D. Moodie. 1965. Carbonate. P. 1379-1400. *In*: C.A. Black et al. (Ed.) Methods of soil analysis. Part 2. 2nd ed. Agron. Monogr. 9. ASA, CSSA and SSSA, Madison, WI.

Sobeck, A.A., W.A. Schuller, J.R. Freeman, R.M. Smith, 1978 Field and Laboratory Methods to Overburden and Mine soils. U.S. Department of Commerce, National Technical Information Service.

U.S. Salinity Lab. Staff. 1954. Methods for soil characterization. p. 83-147. *In*: Diagnosis and improvement of saline and alkali soils. Agr. Handbook 60, USDA, Washington, D.C.

### Scope and Application

This method involves the quantitative determination of calcium carbonate by gravimetric analysis. The method is based on the reaction of HCl with calcium carbonate and the gravimetric loss of CO<sub>2</sub> from the sample as described by the U.S. Salinity Laboratory Staff (1954). Major sources of error are: evaporation of water and failure to adequately degas CO<sub>2</sub> from the sample. Soil carbonates are measured to determine soil buffering capacity with relation to soil fertility, chemical and pedogenic processes. The method detection limit is approximately 0.2% CaCO<sub>3</sub> equivalent (on a dry soil basis) and is generally reproducible ± 10%.

### Equipment

1. Analytical balance: 100 g capacity, resolution ± 0.1 mg.
2. Repipette dispenser, calibrated to 25.0 ± 0.2 mL.
3. Orbital mechanical shaker, capable of 180 oscillations per minute (opm).
4. Extraction vials, 70 mL with snap-lid having 1 mm holes for gas exchange or 50 mL Erlenmeyer flask with cap (See comment #1).

### Reagents

1. Deionized water, ASTM Type I grade.
2. Hydrochloric acid (HCl), 3M. Transfer 250 mL of concentrated HCl to 500 mL of deionized water and dilute to 1.0 L with deionized water.
3. Calcium carbonate (CaCO<sub>3</sub>), fine ground (100 or 140 mesh sieve, 106-150 μm), reagent grade.

### Procedure

1. Weigh to the nearest 0.1 mg a 70 mL extraction vial containing 10 mL of 3M HCl and record tare weight. Transfer 2.000 to 5.000 g of air-dried soil pulverized to pass 10 mesh sieve (< 2.0 mm) containing 100 to 300 mg of CaCO<sub>3</sub> equivalent, in incremental units to avoid frothing. Accurately record the weight of soil transferred to the nearest 0.1 mg. Include three calcium carbonate standards ranging from 100 to 300 mg. After the effervescence has subsided replace snap-lid and place on orbital shaker for fifteen (15) minutes. Include 3 blanks to determine water vapor loss.
2. After two (2) hours weigh vial to the nearest 0.1 mg and record the mass. (See Comment #3 and #4). Verify recovery of calcium carbonate standards, approximately 100%.

### Calculation

Weight loss of CO<sub>2</sub> (g) = Initial weight (g) - final weight (g) (vial + stopper + acid + soil)

$$\text{CO}_3\text{-C, \%} = \frac{(\text{g CO}_2 \text{ lost}) (0.2727)}{\text{g air-dry soil}} \times 100 \quad [\text{equ. S -13.1-1}]$$

$$\text{CaCO}_3\text{-C, \%} = \frac{(\text{g CO}_2 \text{ lost}) (2.273)}{\text{g air-dry soil}} \times 100 \quad [\text{equ. S -13.1-2}]$$

## Comments

1. Vials snap-lids should be large enough to permit gas exchange of CO<sub>2</sub>, yet small enough to minimize loss of water vapor.
2. Soil weight should be less than 4.0 g for soils with less than 20% CaCO<sub>3</sub>, 2.0 g for soils 20 to 40% CaCO<sub>3</sub>.
3. Use blank subtraction to compensate for water vapor loss. If water vapor loss is > 0.003 g subtract water vapor loss (g) from g CO<sub>2</sub> weight loss.
4. To convert from CaCO<sub>3</sub>-C, % to total inorganic carbon (TIC) multiply value by 0.12 .

## Literature

Allison L.E. and C.D. Moodie. 1965. Carbonate. P. 1379-1400. *In*: C.A. Black et al. (Ed.) Methods of soil analysis. Part 2. 2nd ed. Agron. Monogr. 9. ASA, CSSA and SSSA, Madison, WI.

Loeppert, Richard H. And Donald L. Suarez. 1996. Carbonate and gypsum. p. 437-474. *In*: J.M. Bartel et al. (ed.) Methods of soil analysis: Part 3 Chemical methods. (3rd ed.) ASA and SSSA, Madison, WI. Book Series no. 5

U.S. Salinity Lab. Staff. 1954. Methods for soil characterization. p. 83-147. *In*: Diagnosis and improvement of saline and alkali soils. Agr. Handbook 60, USDA, Washington, D.C.

### Scope and Application

This method involves the quantitative determination of inorganic carbon by volumetric displacement. The method is based on the reaction of HCl with carbonate and the measurement of the loss of CO<sub>2</sub> based on the equations described by Loeppert and Suarez (1996) and by Wagner et al., (1998). The method range is from 0.25 to 100% percent CaCO<sub>3</sub> for a 20 mL serum bottle used as the reaction vessel. The method range for the 100 mL serum vial used as the reaction vessel is 2.0 to 100 percent. Soil inorganic carbon is measured to determine soil buffering capacity with relation to soil fertility, chemical and pedogenic processes and to obtain organic carbon from combustion methods that produce total carbon. The method detection limit is approximately 0.25% CaCO<sub>3</sub> and is reproducible within the ± 5% using the 20 mL serum bottles and 2.0% for the 100 mL serum bottles.

### Equipment

1. Analytical balance: 100 g capacity, resolution ± 0.1 mg.
2. Repipette dispenser, calibrated to 2.0 mL.
3. Reaction vessels, 100 mL capacity wheaton serum bottles.
4. 0.5 dram vials (2.0 mL capacity).
5. Gray butyl rubber stoppers. (See comment #1).
6. Tear-off Aluminum serum bottle seals.
7. Hand-operated crimpers.
8. Power supply (24 volt DC. - 2 amp).
9. Digital voltage meter, capable of reading 0.01 volts resolution.
10. Pressure transducer 0-105 kPa (Setra Model 280E).

### Apparatus

1. The pressure transducer is connected to the power supply with 14 gauge wire with a digital volt meter wired in line to monitor the output.
2. Attached to the base of the pressure transducer is 20 cm of tubing attached to a 18 gauge Luer-loch hypodermic needle with a particle filter in the middle to collect any reflux from reaching the pressure transducer.

### Reagents

1. Deionized water, ASTM Type I grade.
2. Calcium carbonate (CaCO<sub>3</sub>), fine ground (100 mesh sieve, 150 μm), reagent grade.
3. Hydrochloric acid (HCl) 6N with 3% by weight ferrous chloride). Transfer 500 mL of HCl to 400 mL of deionized water and add 30 g of FeCl<sub>2</sub> · 4H<sub>2</sub>O and bring to 1.0 L volume with deionized water.
4. Prepare CaCO<sub>3</sub> standards of 0.25, 0.50, 1, 2, 4, 8, and 15 percent by weight using laboratory sand that has been powder ground and oven dried reagent grade CaCO<sub>3</sub> for 20 mL reaction vessels for the 0-30 percent range. For soils higher than 30% CaCO<sub>3</sub>, use 100 mL reaction vessels with standard concentrations of 10, 20, 30, 40, 50 and 80% CaCO<sub>3</sub>.

## Procedure

1. Weigh 1.00g of soil into a 20 mL Wheaton serum bottle if soil is expected to have less than 30% CaCO<sub>3</sub> or 2.00g of soil into 100 mL Wheaton serum bottle if sample is expected to have more than 30% CaCO<sub>3</sub>. Use soils screened to pass through a 2 mm sieve. Place CaCO<sub>3</sub> appropriate standards into 20 mL or the 100 mL Wheaton serum bottle (See Comment #1).
2. Pipet 2.0 mL of 6.0N HCl reagent into 0.50 dram glass vial. Gently insert acid dram vial into reaction vessel with sample, but do not allow solution to mix with sample. Cap reaction vessel with gray butyl rubber stoppers and crimp with aluminum tear-off seals.
3. Shake reaction vessel vigorously to ensure that acid solution in the dram vial has mixed with the soil. Run three blanks (1.00 g of laboratory sand with acid vial) with each analysis run.
4. Prior to reading the samples on the pressure transducer (15 min), rotate the acid along the sides of the reaction vessel to ensure that soil on the sides is reacting with the acid.
5. After two (2) hours of reaction time with the acid the samples and standards are ready to read on the pressure transducer.
6. Record the voltage output to 2 decimal places. Subtract the average voltage of the blanks from the standards and samples to obtain the change in pressure due to CO<sub>2</sub>.

## Calculation

Using linear regression determine the slope (regression coefficient) and the intercept (b) of the curve of pressure change vs. the dependent variable of percent CaCO<sub>3</sub>. Inorganic carbon can be obtained by dividing the formula weight of CaCO<sub>3</sub> (100) by the formula weight of carbon (12) and multiply this by the % CaCO<sub>3</sub>.

$$\% \text{ CaCO}_3 = (\text{regression coefficient}) \times (\text{delta pressure in volts}) + b.$$

$$\% \text{ Inorganic Carbon} = \% \text{ CaCO}_3 / 8.33 \quad [\text{equ. S -13.3-1}]$$

$$\text{Inorganic carbon g/kg} = 10 \times (\text{Inorganic Carbon percent})$$

## Comments

1. Caution should be used when there is no information available on CaCO<sub>3</sub> content of the soil as vessels may become over pressurized. Use 1.00 g of soil and the 100 mL Wheaton serum bottles as a pre-screen of CaCO<sub>3</sub> content prior to quantitative determination using the appropriate mass and bottle. Sample size may be increased to 2.0 g using the 20 mL Wheaton serum bottle for samples containing less than 15% CaCO<sub>3</sub> to improve method detection and precision.
2. Soils containing dolomite need longer reaction times with acid.
3. Use caution when shaking the reaction vessel (serum bottle containing sample and acid vial) as cracks in the serum bottle can occur with reuse which can weaken the glass if excessive pressure's are encountered.
4. Check 20 and 100 mL serum reaction vessels for irregularities. Discard if irregularities in glass is found.

## Literature

Wagner, S.W., J.D. Hanson, Alan Olness, and W.B. Voorhees. 1998. A volumetric inorganic carbon analysis system. Soil Sci. Soc. Am. J. 62:690-693.

Loeppert, Richard H. and Donald L. Suarez. 1996. Carbonate and gypsum. p. 437-474. In: J.M. Bartels et al. (ed.) Methods of soil analysis: Part 3 Chemical methods. (3rd ed.) ASA and SSSA, Madison, WI. Book series no. 5.