



ALKALINITY

Acidity is one measure of alkalinity that is indicated by pH. However, the nature and amount of other ions such as carbonate or bicarbonate can also affect mud filtrates alkalinity. For fresh water mud systems these ions can be indicative of the rheological stability of such mud systems. Concentrations of either ion can result in high, low shear rate viscosity (yield point) and high, progressive gel strengths. Three methods can be employed for the determination of carbonate and bicarbonate concentration. The very common Pf/Mf method is restricted to mud systems having a low organic content whereas the P1/P2 method or the Garrett Gas Train may be used for better, more quantitative analysis, especially in the systems with high organic content.

PF / MF METHOD

Equipment		Product Code
1.	Phenolphthalein	EY1120
2.	Bromocresol Green Indicator	EY1010
3.	Distilled Water	EY1060
4.	Sulfuric Acid N/50	EY1220
5.	Titration Dish	E10173
6.	Stirring Rod	E10339
7.	Pipette (1 mL)	EN5900
8.	Pipette Safety Bulb	E83102

TEST PROCEDURES

- Using a 1 mL pipette, measure 1 mL of filtrate into a titration dish.
- Add 2 to 3 drops of phenolphthalein indicator
 - if no color change occurs, then Pf = 0.0, continue to step 4
 - if a pink or red color develops, Pf > 0.0, continue to step 3
- Using a pipette, add N/50 sulfuric acid continuously while swirling or stirring until the sample changes from red to colorless, (or original filtrate tint). the number of mL of N/50 sulfuric acid required to reach this point is recorded as the Pf value.
- To the sample, which has been titrated to the Pf end point, add 2-3 drops of bromocresol indicator to obtain a light blue color. Continue titrating with swirling (or stirring) until the color changes from light blue to apple green, (pH = 4.0-4.5). This end point, which includes the number of mL required to obtain the Pf end point is recorded as the Mf end point.

ALKALINITY

CALCULATIONS

Use the following table to estimate the carbonate, (CO₃), bicarbonate (HCO₃), or hydroxyl (OH), present in the mud filtrate.

Pf/Mf Relation	Bicarbonate (mg/L HCO ₃)	Carbonate (mg/L CO ₃)	Hydroxyl (mg/L OH)
Pf = 0	1220 x Mf	0	0
Pf = Mf	0	0	340 x Mf
2Pf = Mf	0	1200 x Pf	0
2Pf > Mf	0	1200(Mf - Pf)	340(2Pf - Mf)
2Pf < Mf	1220 (Mf - 2Pf)	1200 x Pf	0

P1 / P2 METHOD

Inorganic ions such as borate, silicate, sulfide, and phosphate ions can have a real effect on drilling mud alkalinity. Additionally, organic compounds (e.g., anionic organic thinners, fluid loss additives, or other polymers) and their degradation by-products may also affect the determination of the relative amounts of carbonate, bicarbonate, or hydroxyl ions in solution. The P1/P2 method eliminates these effects.

Equipment		Product Code
1.	Sodium Hydroxide (0.2N)	EY1170
2.	Barium Chloride	EY1000
3.	Phenolphthalein	EY1120
4.	Sulfuric Acid (N/50)	EY1220
5.	Titration Dish	E10173
6.	Stirring Rod	E10339
7.	Pipette (1 mL)	EN5900
8.	Pipette Safety Bulb	E83102

TEST PROCEDURE

1. Determine the Pf end point as outlined in step 1-3 of the Pf/Mf method. If the Pf = 0.0 there are no carbonates present.
2. Place 1 mL of filtrate in a white titration dish and add 24 mL of distilled water.
3. Add a measured 2 mL of 0.1N sodium hydroxide solution to convert all bicarbonates to carbonates. Check the pH, if it is less than 11.5, continue to add 0.1N sodium hydroxide in 1-2 mL increments until the pH exceeds 11.5. Make a record of the total amount of sodium hydroxide added in this step.
4. Add a measured amount of barium chloride to precipitate all the possible carbonates. Add 2-4 drops of phenolphthalein solution with stirring.
5. Using a 1 mL pipette, titrate immediately to the end point with N/50 sulfuric acid. Record the number of mL's of N/50 sulfuric acid added as the P1 end point.
6. Place exactly the same amounts of 0.1N sodium hydroxide, barium chloride, and indicator into 25 mL of distilled water and titrate to the end point using N/50 sulfuric acid and record this as the P2 end point.

ALKALINITY

CALCULATIONS

$P_f = 0.0$, there are no carbonates present.

$P_1 > P_2$:

mg/l $\text{HCO}_3 = 0.0$

mg/l $\text{CO}_3 = 1200 [P_f - (P_1 - P_2)]$

mg/l OH = 340 (P1 - P2)

$P_2 > P_1$:

mg/l OH = 0.0

mg/l $\text{CO}_3 = 1200 \times P_f$

mg/l $\text{HCO}_3 = 1220(P_2 - P_1)$

WARNING: The reagents may be hazardous to the health and safety of the user if inappropriately handled.

GARRETT GAS TRAIN METHOD

Either of the methods above is still subject to some error and certain situations may require yet another method. The Garrett Gas Train separates gas from liquid, thereby preventing contamination of the CO_2 detecting Dräger tube by the liquid phase.

The CO_2 Dräger tube responds to the CO_2 passing through it by progressively staining (purple) along its length as the hydrazine chemical and the CO_2 react causing a methyl violet indicator to turn purple. The stain length is dependent on the amount of CO_2 present and the total gas volume that passed through the tube.

Consequently, for accurate results, the gas exiting the train must first be captured in a one-liter gasbag to allow the CO_2 to mix uniformly with the carrier gas. Then the contents of the bag are drawn through the tube using 10 strokes of the Dräger hand pump. This will draw exactly one (1) liter of gas through the tube.

TEST PROCEDURE

1. Be sure the gas train is clean, dry and on a level surface.
2. With the regulator T-handle backed off, install and puncture a N_2 gas cartridge.
3. Add 20 mL distilled water to chamber No. 1. (The chambers are numbered beginning at the regulator).
4. Add 5 drops of octanol defoamer to chamber No. 1.
5. Install the top on the gas train and evenly hand tighten to seal all O-rings.
6. Attach the flexible tubing from the regulator onto the dispersion tube of chamber No. 1.
7. Inject with syringe, an accurately measured sample of filtrate into chamber No. 1. See table on the next page.

ALKALINITY

Dräger Tube Identification			
Carbonate Range mg/L	Sample Volume cm ³	Dräger Tube Identification	Tube Factor
25 - 750	1.0	CO ₂ 100/a	2.5*
50 - 1500	5.0		
250 - 7500	2.5		
60 - 1020	10.0	CO ₂ 0.2% o/a	0.12*
120 - 2040			
240 - 4080			

*Tube factor applies to new tubes, CO₂ 100/a with scale 100 to 3000. Old tubes use the tube factor 25,000.

- Flow carrier gas through the gas train for one minute to purge the system of air. Stop gas flow.
- Install one end of a piece of flexible tubing onto the stopcock, which is fitted directly into the gasbag. Have the gasbag fully collapsed. Fit the other end of the tubing onto the outlet tube of chamber No. 3.
- Slowly inject 10 ml sulfuric acid solution into chamber No. 1 through the septum using the syringe and needle. Gently shake gas train to mix acid with sample in chamber No. 1.
- Open the stopcock on the gasbag. Restart nitrogen flow gently and allow the gasbag to fill. When the bag is full, (DO NOT burst it) shut off and close the stopcock. Immediately proceed to the next step.
- Remove the tubing from chamber No. 3 outlet tube and re-install it onto upstream end of the CO₂ 0.01%/A Dräger tube. (Observe that the arrow indicates gas flow direction) Attach Dräger hand pump to other end of Dräger tube.
- Open stopcock on bag. With a steady hand pressure fully depress the hand pump, then release so that the gas flows out of the bag and through the Dräger tube. Operate pump ten times. This should essentially empty the bag.
- Observe a purple stain on the Dräger tube if CO₂ is present. Record the stain length in the units marked on the Dräger tube.

CALCULATIONS

mg/L CO₃ = 25,000 x Tube stain length / mL sample volume

CARE AND CLEANING

To clean the gas train, remove the flexible tubing and gas train top. Wash out the chambers using a brush with warm water and mild detergent. Use a pipe cleaner to clean the passages between the chambers.

Wash, rinse and then blow out the dispersion tube with air or nitrogen gas. Rinse the unit with distilled water and allow to drain dry.