

## Hardness

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### EQUIPMENT

Digital titrator

Tetrasodium EDTA titrator cartridge

Delivery tube

Cal-Ver packet

Buffer solution (8 N potassium hydroxide). **NOTE:** potassium hydroxide is very caustic.

Magnetic stir plate

Stir bar

Gloves, goggles, lab coat

### METHOD SUMMARY

The Hach method for hardness measurement involves titration of a sample with tetrasodium EDTA in the presence of potassium hydroxide and a color indicator. The endpoint is a color change from pink to purple. The method measures calcium hardness in mg/L CaCO<sub>3</sub>.

Two EDTA titrator cartridges are available: 0.800 and 0.0800 N EDTA. The **0.800 N** cartridge is for hardness measurements between 100 and 400 mg/L CaCO<sub>3</sub>, which is considered the typical analysis for most samples. If the sample is determined to be out of this range, see the Hach Digital Titrator manual, page 83, for correct sample volumes and cartridge selection.

### SAMPLE HANDLING

Samples should be brought to room temperature and measured as soon as possible. Samples may be held at 4°C for 7 days if acidified with concentrated nitric acid (1.5 ml per liter of sample). Neutralize to pH 7 with ammonium hydroxide before testing.

Typically, 100 ml of sample is required for measurement. However, because sample hardness cannot be predicted, extra sample (at least 25 ml) should be available for repeat analyses.

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### MEASUREMENT OF HARDNESS

1. Check for freshness of reagents (should not be older than expiration date).
2. Check for date of last Quality Control check (in Calibration Log)—if > 3 months, check again (see Quality Control section).
3. Place correct titrator cartridge into digital titrator (typically 0.800 N). Place correct delivery tube into syringe (tip only) and turn delivery knob until fluid comes out of tube. Wipe tube.
4. Measure appropriate volume (typically 100 ml) of sample into 250-ml plastic tri-pour beaker.
5. Place stir bar in sample; set sample on stir plate.
6. Add contents of one Cal-Ver 2 packet (solution turns blue).
7. Add 2 droppers of Buffer Solution (8 N potassium hydroxide). Fill dropper to 1-ml mark each time. Solution turns pink. Lower digital titrator until tube is approximately 1 cm below the surface of sample.
8. Zero the titrator, and begin slowly adding Tetrasodium EDTA with delivery knob until color change is noted (from pink to purple).
9. Read the number on titrator. When measuring 100 to 400 mg/L, this number equals the actual mg/L  $\text{CaCO}_3$  present in the sample. For other measurement ranges, see manual for the appropriate digit multiplier.
10. Record the actual mg/L  $\text{CaCO}_3$ .
11. Zero titrator and rinse stir bar before each subsequent sample.

### QUALITY CONTROL

Check for method and titrator accuracy quarterly. Measure 100 ml of sample in the 100-400 mg/L hardness range into 250-ml plastic tri-pour beaker. Titrate to color change as described above. Snap the neck off of a Hardness Voluette Ampule, 10,000 mg/L as  $\text{CaCO}_3$ . Add 100  $\mu\text{L}$  to the titrated sample, and titrate back to the endpoint. Ten titrator digits should be used to return to the endpoint. Do this standard addition three times. Record additions in Calibration Log book on the Hach Alkalinity and Hardness QA Log. Titration should be within 10% (one digit) of 10.