Hardness

General Information: Water hardness is commonly defined as the sum of the polyvalent cations dissolved in the water. The most common such cations are calcium and magnesium, although iron, strontium, and manganese may contribute (AWWA, 1990; EPA, 1986). Hardness is usually reported as an equivalent quantity of calcium carbonate ($CaCO_3$). Generally, waters are classified according to degree of hardness as follows (EPA, 1986):

Concentration $CaCO_3$ (mg/l)	Classification
< 75	soft water
75 - 150	moderately hard
150 - 300	hard
> 300	very hard

Hardness is primarily a function of the geology of the area with which the surface water is associated. Waters underlain by limestone are prone to hard water because rainfall, which is naturally acidic because it contains carbon dioxide gas, continually dissolves the rock and carries the dissolved cations to the water system.

Numerical Categories:

Limits:

Designated Use	**Limit (mg/l $CaCO_3$)**

Industry (raw water source) (EPA, 1986)

Textile	120 max concentration
Pulp and paper	475 max concentration
Chemical	1,000 max concentration
Petroleum	900 max concentration

Electric Utilities	5,000 max concentration

Health Effects: Not applicable

Environmental Effects: The effects of hardness on aquatic life is a function of the cations comprising the hardness.

Irrigation Effects: Carbonate deposits may clog pipes and coat the inside of water holding tanks. Extreme hardness may interfere with chemical processes.

Sources:

1. *Nonpoint source:*
    - Natural: The physical weathering of calcium and magnesium strata will contribute cations to surface and ground water.
    - Anthropogenic: Additional sources include discharges of cation-rich waters from operating and abandoned rock quarries (EPA, 1986).
2. *Point source:* Inorganic chemical industry may release dissolved cations in effluent waters (EPA, 1986).

Mode of Transport: Dissolved cations are carried via overland, unsaturated, or saturated flow.

Analytical Techniques:

(APHA, 1992; Nebraska Administrative Code, 1993)

1. **Calculation:** Use following equation to compute hardness from results of separate determinations of Ca and Mg concentrations.

    Hardness, mg equivalent/L $CaCO_3$ = ([Ca,mg/l]*2.497) + ([Mg,mg.l]*4.116)

2. **EDTA Titrimetric Method:** EDTA forms a chelated soluble complex when added to metal cations. Dye added creates a wine-red solution. EDTA added as a titrant complexes with the Ca and Mg. Solution turns blue when all complexed. A pH of 10+/- 0.001 is recommended for sharpest endpoint.
    - *Detection limits:* Varies according to modifications of technique.
    - *Interferences:* Some metal ions interfere: Al, Co, Ni (over 20 mg/l), Cu, and Fe (over 30 mg/l). Suspended or colloidal organic matter may interfere.
