IOTRODE™
Ion-Selective Electrode Applications

Bulletin No. 000126

Determination of Water Hardness

INTRODUCTION

Originally the hardness of water was defined as the capacity of water for destroying the lather of soap. The hardness was determined by a titration with a standard soap solution. Metal ions including Ca^{2+}, Mg^{2+}, Al^{3+}, Fe^{2+}, Fe^{3+}, Zn^{2+}, Sr^{2+}, and H^{+} have the ability to cause hardness. However, today water hardness means the total calcium and magnesium ion concentration expressed as calcium carbonate concentration. With the Iotron Divalent electrode the total water hardness (Ca^{2+} and Mg^{2+}) can be determined directly in the range of 1-1000 ppm as calcium carbonate.

EQUIPMENT

Meter:
pH/Millivolt meter. Readability of 1 mV required; 0.1 mV preferred. Specific ion meter will provide direct readout of final answer or concentration factor. Consult manual for millivolt measurement instructions.

Electrodes:
Measuring Electrode: Iotrode AB-460 Divalent Cation ISE.
Reference Electrodes—Double Junction—Refillable
Calomel — RD-101 Removable Sleeve
RD-201 Non-Removable Sleeve
Ag/AgCl — RD-301 Removable Sleeve
RD-401 Non-Removable Sleeve

Glassware:
1. 1 ml, 2 ml, and 10 ml pipets
2. 150 ml beakers
3. 100 ml graduated cylinders
4. 100 ml, 1000 ml volumetric flasks
5. Magnetic stirrer and stirbars or glass stirring rods

REAGENTS

1. **1000 ppm Calcium Standard Solution:** Weigh out 2.499 grams of dried (3-4 hours at 110°C) calcium carbonate into a 400 ml beaker. Add 150 ml of deionized water and exactly 50.0 ml of 1M hydrochloric acid. Stir until reaction is complete. Transfer quantitatively into a one liter volumetric flask and dilute to mark with deionized water. Store in a polyethylene bottle.
2. **Ionic Strength Adjustor (ISA):** Prepare a 0.3 M imidazole buffer by weighing out 20.4 grams of imidazole into a 1 liter beaker. Dissolve in 900 ml of water. Adjust pH of solution to 7.0 with concentrated nitric acid. Add acid dropwise while stirring. Transfer into a one liter volumetric flask. Dilute to mark with deionized water.

ELECTRODE SET-UP

If the electrode is being used for the first time, please follow the instructions of the conditioning procedure of the electrode. Plug the sensing electrode into the G.E. or Glass jack of the meter. Fill the inner and outer chambers of the reference electrode with appropriate solutions. Plug the reference electrode into the REF or Reference jack of the meter. Technique Hints:

1. Stirring: Electrode response is improved if samples and standardizing solutions are stirred at a fixed rate during measurements. If magnetic stirring is not available, stir solution one minute with a clean glass stirring rod before measuring.

2. Temperature: The slope of the sensing electrode and the absolute potential of the reference electrode are temperature dependent. Therefore, samples and standardizing solutions should be at the same temperature.

3. Cleaning Electrodes: Rinse both electrodes with a fresh portion of deionized water and blot dry with tissue between all measurements.

ELECTRODE CALIBRATION

The primary criteria for electrode performance verification is the span test. If 25 millivolts or greater change is observed for a decade change in concentration, the performance is considered satisfactory.

1. Put 90 ml deionized water and 10 ml ISA into a 150 ml beaker. Place the pH meter into the M.V. mode. Place electrodes in the solution to a minimum depth of one inch.

2. Pipet 1 ml of 1000 ppm calcium standard into the solution. Stir thoroughly. Read stable electrode potential in millivolts and record value as E1.

3. Add 10 ml of 1000 ppm calcium standard and stir thoroughly. Read stable electrode potential in millivolts and record as E2. Calculate S by E2 - E1. Assume S value as the slope of the electrode.

NOTE: If the slope value is below 25mV, check electrode set up and recondition sensing electrode.

PROCEDURE

Sample Preparation: Add 10 ml ISA to 100 ml of sample.

Sample Standardization: Add 100 ml of prepared sample solution to a 150 ml beaker. Place electrodes in the solution to a minimum depth of one inch. Read stable electrode potential in millivolts and record as E3.

Standard Addition: Pipet 1 ml of 1000 ppm calcium standard into the solution. Stir thoroughly. Read stable electrode potential in millivolts and record value as E4. Calculate ΔE by E4 - E3.
NOTE: If ΔE is more than 15mV, **dilute standard** 1:10 with deionized water and divide final concentration by 10. If ΔE is less than 5mV, **dilute fresh sample** 1:10 with deionized water and multiply final concentration by 10.

CALCULATIONS

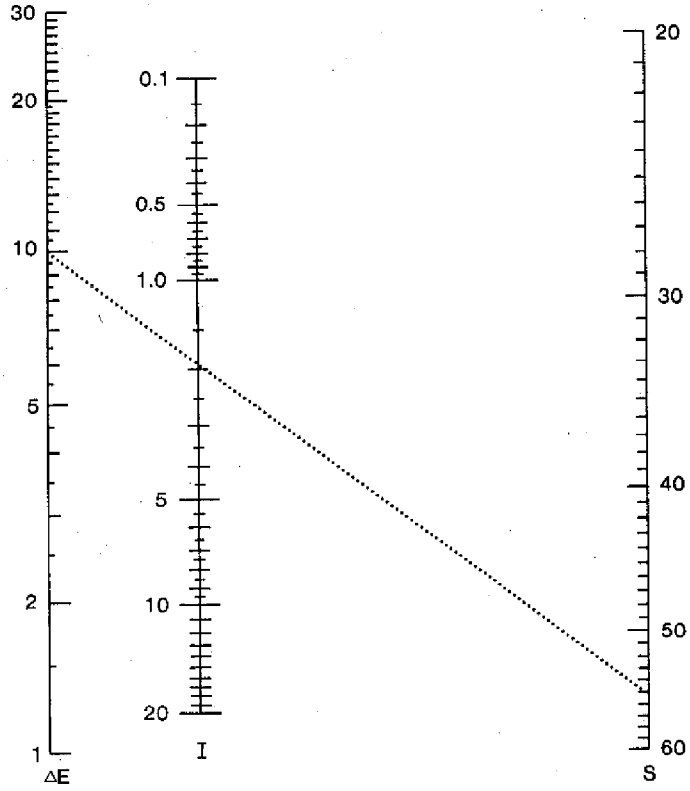
To perform the calculation for standard addition, the following factors are needed:

V_S = Sample Volume
V_a = Volume of standard added
C^* = Concentration of standard
ΔE = Change in potential (see procedure section)
S = Slope of the electrode (see electrode calibration section)

$$\text{Concentration of Sample} = \frac{C^* \left[\frac{V_a}{V_a + V_S} \right]}{\left[\text{antilog} \frac{\Delta E}{S} \right] - \left[\frac{V_S + V_a}{V_S} \right]}$$

Note: If the sample is diluted, multiply sample concentration by appropriate dilution factor.

Standard Addition Nomograph for use with Iotrode™ Electrodes



The standard addition nomograph method of calculation is valid when the increment of standard added to the sample is small compared to the volume. Therefore, if more than 1 ml of standard is added, please utilize the mathematical procedure above.

The following data must be known to utilize the nomograph: (See above for description of factors.)

ΔE, S, C^*, and V_S

Utilizing ΔE and S, draw a straight line to find I on the nomograph.

$$\text{Concentration of Sample} = \frac{(I)\,(C^*)}{V_S}$$

The concentration of Sample will be in the same units of concentration as C^*.

Example: ΔE = 10 mv
S = 55 mv
C^* = 1000 ppm
V_S = 100 ml
I = 2.0 (from Nomograph)

$$\text{Sample Concentration} = \frac{(2.0)\,(1000\ \text{ppm})}{100\ \text{ml}}$$

$$= 20\ \text{ppm}$$