



IOTRODE™
Ion-Selective Electrode
Applications

Bulletin No. 000108

**Chloride Determination
In Copper-Sulfuric Acid
Plating Bath**

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:

1. Iotrode™ AB110 Chloride Electrode with polishing kit.
2. Reference electrode (Double Junction Type)
Iotrode AB450 (Ag/AgCl internal) or
Iotrode AB455 (Calomel Internal)

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

Ionic Strength Adjustor (ISA): Weigh out 101 grams KNO_3 into a one liter volumetric flask. Dilute to mark with deionized water.

Reference Electrode Outer Junction Filling Solution: Dilute ISA (1:1) with deionized water. Add two drops of concentrated H_2SO_4 per 10 ml of filling solution.

3000 ppm Chloride Standard: Weigh out 4,947 grams NaCl (dried at 150°C for 4 hours) 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 for polishing the membrane surface. 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 55 millivolts or greater change is observed for a decade change in concentration, the performance is considered satisfactory.

1. Put 100 ml deionized water and 2 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 3000 ppm chloride standard into the solution. Stir thoroughly. Read stable electrode potential in millivolts and record value as E_1 .
3. Add 10 ml of 3000 ppm chloride standard and stir thoroughly. Read stable electrode potential in millivolts and record as E_2 . Calculate S by $E_2 - E_1$. Assume S value as the slope of the electrode.

PROCEDURE

Sample Preparation: If electrode potential is not stable during sample standardization, dilute 1:1 with deionized water. (Dilution factor = 2)

Sample Standardization: Add 100 ml of sample solution and 2 ml ISA 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 3000 ppm chloride 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 30mV, **dilute standard** 1:10 with deionized water and divide final concentration by 10. If ΔE is less than 8mV, **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)

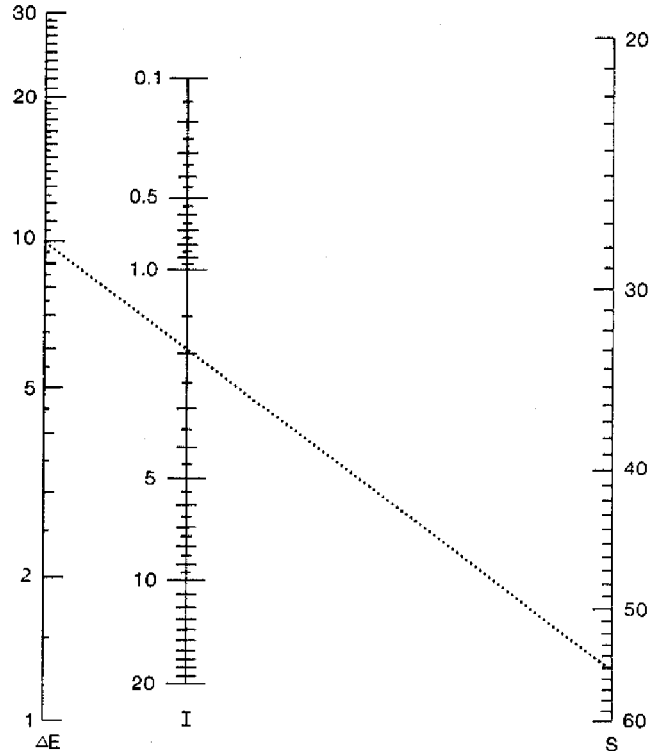
$$\text{Concentration of Sample} = \frac{C^* \left[\frac{V_a}{V_a + V_s} \right]}{\left[\text{antilog} \frac{\Delta E}{S} \right] - \left[\frac{V_s + V_a}{V_s} \right]}$$

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

REFERENCES:

Frant, M.S., Application of Selection Electrodes to Electroplating Analyses, Plating, p. 686 (July 1971).

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.

$$\text{Concentration of Standard} = \frac{(I) (C^*)}{V_s}$$

The concentration of Standard 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)

$$\text{Sample Concentration} = \frac{(2.0) (1000 \text{ ppm})}{100 \text{ ml}} = 20 \text{ ppm}$$