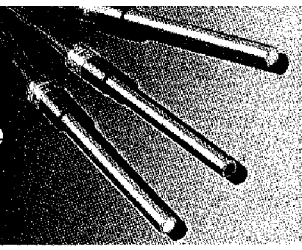
IOTRODE™
Ion-Selective Electrode Applications



Bulletin No. 000104

Silver Ion Analysis In Photographic Fixing Solutions

INTRODUCTION

The total concentration of silver present in fixing solutions may be determined over the range of 1M to 10^{-6}M using the Iotrode Silver Electrode. Fixing solutions usually contain a sulfide-bisulfite buffer and dissolved silver halides. The silver is primarily present in the complexed form as $Ag(S_2O_4)^-$. However, the ratio of free to complexed silver is constant. The standard addition method of analysis allows the original sample concentration of silver to be determined without a calibration curve.

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™ AB170 Silver 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

1. **Ionic Strength Adjustor (ISA):** Prepare 4M KNO_3 by adding 40 grams KNO_3 to a 100 ml volumetric flask. Dissolve in 50 ml deionized water and dilute to the mark.
2. **Outer Junction Reference Filling Solution:** Dilute 10 grams KNO_3 to 100 ml with deionized water.
3. **Silver Nitrate Standard Solution:** The following procedure requires the standard to be approximately ten times the sample concentration. Use the following table to prepare appropriate standard for the sample to be measured.

Fixing Bath Concentration	Concentration of Standard	Grams $AgNO_3$
0.001 — 0.01 oz/gal	1.0 oz/gal	0.75g
0.01 — 1.1 oz/gal	10.0 oz/gal	7.50g
0.1 — 0.1 oz/gal	100.0 oz/gal	75.00g

Preparation of Silver Nitrate Standard: Dry pulverized reagent grade silver nitrate at 150°C for 24 hours. Weigh out appropriate amount into a one liter volumetric flask. Dilute to 1 liter with deionized water. Store in brown polyethylene bottle in a cool dark place.

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 silver nitrate standard into the solution. Stir thoroughly. Read stable electrode potential in millivolts and record value as E_1.

3. Add 10 ml of silver nitrate 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: None.

Sample Standardization: Add 2 ml of ISA and 100 ml of fixing bath 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 E_3.

Standard Addition: Pipet 1 ml of silver nitrate standard into the solution. Stir thoroughly. Read stable electrode potential in millivolts and record value as E_4. Calculate ΔE by E_4-E_3.
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

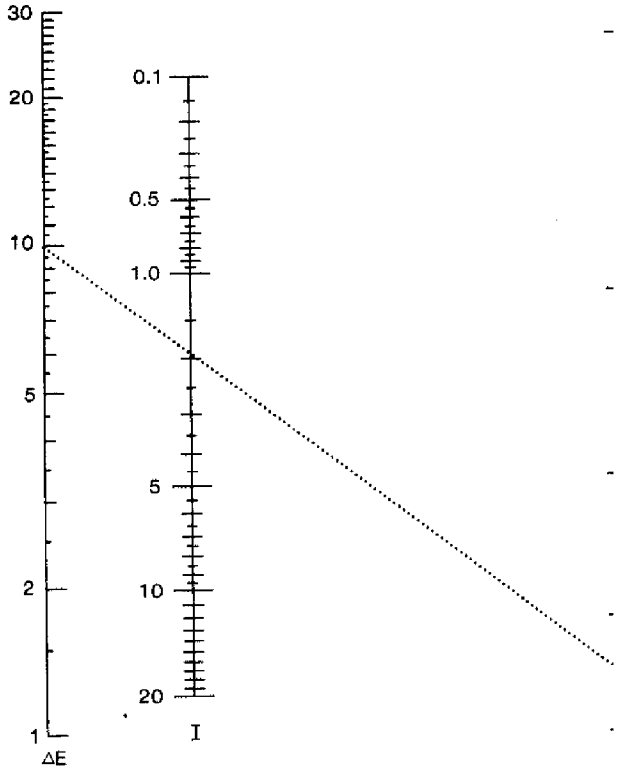
To perform the calculation for standard addition, the following factors are needed:

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.

Standard Addition Nomograph for use with Iotrode™ Electrodes



The standard addition nomograph method of calcula is valid when the increment of standard added to the samp small compared to the volume. Therefore, if more than 1 r standard is added, please utilize the mathematical proce above.

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

ΔE, S, C^*, and V_S

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

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

The concentration of Standard will be in the same uni concentration as C^*.

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

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

$$= 20\text{ ppm}$$