GENERAL INSTRUCTIONS

Introduction

The Cole-Parmer Silver/Sulfide Ion Electrodes are used to quickly, simply, accurately, and economically measure silver and sulfide ions in aqueous solutions. The two ions are virtually never present in solution together, owing to the extreme insolubility of silver sulfide. Indirect measurements of cyanide or measurements of halide ions by titration may be done with this electrode.

Required Equipment

1. A pH/mV meter or an ion meter, either line operated or portable.

2. Semi-logarithmic 4-cycle graph paper for preparing calibration curves when using the meter in the mV mode. Gran's plot paper (10% volume corrected) is recommended for low level chloride measurement.

3. A magnetic stirrer.

4. The Cole-Parmer Silver/Sulfide Ion Combination Glass Electrode, Cat. No. 27502-41, or the Cole-Parmer Silver/Sulfide Ion Combination Epoxy Electrode, Cat. No. 27502-28. Use Cole-Parmer Filling Solution, Cat. No. 27503-75, in both the 27502-41 and 27502-28.

6. Polishing paper or jeweller's rouge to polish dirty or etched electrode membranes.

Required Solutions
Deionized or distilled water for solution and standard preparation. Water used in the preparation of sulfide standards and of SAOB should also be deaerated.

For Silver:

1. Cole-Parmer Ionic Strength Adjuster (ISA), 5M $NaNO_3$, Cat. No. 27503-51. To prepare this solution from your own stock, fill a 1000 ml volumetric flask about half full of distilled water and add 425 grams of reagent grade sodium nitrate. Swirl the flask to dissolve the solid. Fill the flask to the mark with distilled water. Cap the flask

and invert several times to mix the solution.

2. Silver Standard Solution, 0.1M $AgNO_3$, Cat. No. 27503-31. To prepare this solution from your own stock, dry reagent grade, pulverized silver nitrate in a laboratory oven for one hour at $150^{o}C$. Quantitatively transfer 16.99 grams of the dried silver nitrate to a 1 liter flask containing about 500 ml of distilled water. Swirl the flask to dissolve the solid. Fill the flask to the mark with distilled water. Cap the flask and invert several times to mix the solution. Store the solution in a brown bottle, tightly capped, in a dark place.

3. Cole-Parmer Silver Standard Solution, 1000 ppm as Ag^+, Cat. No. 27503-32. To prepare this solution from your own laboratory stock, dry reagent grade, pulverized silver nitrate in a laboratory oven for one hour at $150^{o}C$. Quantitatively transfer 1.57 grams of the dried silver nitrate to a 1 liter volumetric flask containing about 500 ml of distilled water. Swirl the flask to dissolve the solid. Fill the flask to the mark with distilled water. Cap the flask and invert several times to mix the solution. Store the solution in a brown bottle, tightly capped, in a dark place.

3. Chloride Titrant (low level), $2.82 \times 10^{-3}M$ $AgNO_3$. Dry reagent grade, pulverized silver nitrate as described above in Silver Standards. Quantitatively transfer 0.479 grams of dried silver nitrate to a 1 liter volumetric flask about half-full of distilled water. After swirling the flask to dissolve the solid, fill to the mark with distilled water. Cap the flask and invert several times to mix the solution. Store in a brown bottle in a dark place.

For Sulfide:

1. Sulfide Anti-Oxidant Buffer (SAOB). This buffer must be used fresh and will range in color from clear to yellow-brown. It has become oxidized when it turns dark brown and should then be discarded. Store fresh SAOB in a tightly stoppered bottle. To prepare SAOB from your own stock, fill a 1 liter volumetric flask with about 500 ml of distilled, deaerated water, 200 ml of 10M NaOH, 35 grams of ascorbic acid, and 67 grams of disodium EDTA. Swirl the mixture until the solids dissolve and fill to the mark with distilled, deaerated water.

2. Cole-Parmer Lead Perchlorate Solution, 0.1M, Cat. No.27503-18. This solution is used for titration of sulfide standards.

3. Sulfide Standards. To prepare a stock solution of saturated sodium sulfide, add about 100 grams of reagent grade $Na_2S \cdot 9H_2O$ to 100 ml

of distilled, deaerated water. Shake well and let stand overnight, storing in a tightly stoppered bottle in a hood.

Prepare a weekly sulfide standard by adding 500 ml SAOB to a 1 liter volumetric flask, pipetting 10 ml of the stock solution into the flask, and diluting to the mark with distilled, deaerated water.

The exact concentration, C, can be determined by titrating 10 ml of the standard with 0.1M lead perchlorate. Use the silver/sulfide ion electrode (and the reference electrode) to indicate the endpoint.
The calculation is as follows:

$$C = 3206(V_t/V_s)$$

where:

C = concentration as ppm sulfide
V_t = volume of titrant at endpoint
V_s = volume of standard used (10 ml)

Prepare other standards each day by serial dilution of the weekly standard. To do a ten-fold dilution, accurately measure 10 ml of the standard and add it to a 100 ml volumetric flask. Add 45 ml of SAOB and dilute to the mark with distilled, deaerated water.

GENERAL PREPARATION

Electrode Preparation

Remove the rubber cap covering the electrode tip and the rubber insert covering the filling hole of the reference electrode.
Fill the combination electrode with the filling solution shipped with the electrode to a level just below the fill hole. No preparation is required for a sealed reference electrode. Connect the electrode to the proper terminal(s) as recommended by the meter manufacturer.

Electrode Slope Check (with standard pH/mV meter)
(check electrode each day

Using silver standards:
1. To a 150 ml beaker, add 100 ml of distilled water and 2 ml of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution.

2. Using a pipet, add 1 ml of 0.1M or 1000 ppm silver standard to the beaker. When the reading has stabilized, record the millivolt reading.

3. Using a pipet, add 10 ml of the same silver standard used above.

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When the reading has stabilized, record the millivolt reading.

4. Determine the difference between the two readings. A difference of 57 ± 2 mV indicates correct electrode operation, assuming the solution temperature is between 20° and 25^oC. See the **TROUBLESHOOTING** section if the potential change is not within this range.

Using sulfide stock solutions:
1. To a 150 ml beaker, add 50 ml of distilled water and 50 ml of SAOB solution. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution.

2. Using a pipet, add 1 ml of weekly standard sulfide solution to the beaker. When the reading has stabilized, record the millivolt reading.

3. Using a pipet, add 10 ml of weekly standard sulfide to the beaker. When the reading has stabilized, record the millivolt reading.

4. Determine the difference between the two readings. A difference of 26 ± 2 mV indicates correct electrode operation, assuming the solution temperature is between 20° and 25^oC. See the **TROUBLESHOOTING** section if the potential change is not within this range.

Slope is defined as the change in potential observed when the concentration changes by a factor of 10.

Electrode Slope Check (with ion meter)
         (check electrode each day)

Using silver standards:

1. Prepare standard silver solutions whose concentrations vary by tenfold. Use either the 0.1M $AgNO_3$ or the 1000 ppm stock solutions. Use the serial dilution method for this preparation.

2. To a 150 ml beaker, add 100 ml of the lower value standard and 2 ml of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution.

3. Assure that the meter is in the concentration mode.

4. Adjust the meter to the concentration of the standard and fix the

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value in the memory according to the meter manufacturer's instructions.

5. Rinse the electrode with distilled water and blot dry.

6. To a 150 ml beaker, add 100 ml of the higher value standard and 2 ml of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution.

7. Adjust the meter to the concentration of the standard and fix the value in the memory.

8. Read the electrode slope according to the meter manufacturer's instructions. Correct electrode operation is indicated by a slope of 90-100%. See the **TROUBLESHOOTING** section if the potential is not within this range.

Using sulfide stock solutions:

1. Prepare standard sulfide solutions whose concentrations vary by tenfold. Use the serial dilution method and the weekly sulfide standard to prepare these solutions.

2. To a 150 ml beaker, add 50 ml of the lower value standard, 25 ml of SAOB, and 25 ml of distilled water. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution.

3. Assure that the meter is in the concentration mode.

4. Adjust the meter to the concentration of the standard and fix the value in the memory according to the meter manufacturer's instructions.

5. Rinse the electrode with distilled water and blot dry.

6. To a 150 ml beaker, add 50 ml of the higher value standard, 25 ml of SAOB, and 25 ml of distilled water. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. Lower the electrode tip into the solution.

7. Adjust the meter to the concentration of the standard and fix the value in the memory.

8. Read the electrode slope according the meter manufacturer's instructions. Correct electrode operation is indicated by a slope of 90-100%. See the **TROUBLESHOOTING** section if the slope is not within this range.

MEASUREMENT

Measuring Hints

All samples and standards should be at the same temperature for precise measurement. A difference of 1 degrees C in temperature will result in about a 2% measurement error.

Constant, but not violent, stirring is necessary for accurate measurement. Magnetic stirrers can generate sufficient heat to change the solution temperature. To counteract this effect, place a piece of insulating material, such as styrofoam sheet or asbestos sheet, between the stirrer and beaker.

All silver samples and silver standards should be stored away from light.

Always dilute sulfide samples with SAOB (1:1) when they are collected.

Always rinse the electrode with distilled water and blot dry between measurements. Use a clean, dry tissue to prevent cross-contamination.

A slow-responding electrode may point to deposits on the membrane. Use polishing paper to remove such deposits. See the section on **Electrode Response**.

For low level silver measurements, use labware of plastic.

For samples with high ionic strength, prepare standards whose composition is similar to the sample.

Always check to see that the membrane is free from air bubbles after immersion into the standard or sample.

Sample Requirements

All samples must be aqueous and not contain organics which can dissolve the epoxy electrode body and/or cement bonding the sensing crystal to the electrode body. Infrequent measurements in solutions containing methanol, benzene, or acetone are permitted. Please check with your Cole-Parmer distributor before using the electrode in other organic solvents.

The temperature of the sample solution and of the standard solution should be the same and below 80°C.

Samples containing sulfide must be buffered with SAOB to convert HS^{-1} and H_2S to S^{-2}.

Samples containing silver must be below pH 8 to avoid reaction with OH^{-1}. Silver samples should

be acidified with HNO_3(1M), if necessary.

Mercury cannot be present in silver samples. Since HgS and Hg_2S are insoluble, no mercury will be present in sulfide samples. Other interferences should be absent. If they are present, use the procedures found in the **Interferences** and **Electrode Response** sections to remove them.

Units of Measurement

Silver and sulfide concentrations are measured in units of parts per million, equivalents per liter, moles per liter, or any other convenient concentration unit. Table 1 indicates some of these concentration units.

TABLE 1: Concentration Unit Conversion Factors

ppm S^{-2}	ppm Ag^{+1}	$N(S^{-2})$	$M(Ag^{+1})$
321.0	1079.0	2.00×10^{-2}	1.00×10^{-2}
100.0	---	6.23×10^{-3}	3.12×10^{-3}
32.1	108.0	2.00×10^{-3}	1.00×10^{-3}
---	100.0	1.84×10^{-3}	9.27×10^{-4}
3.2	10.8	2.00×10^{-4}	1.00×10^{-4}

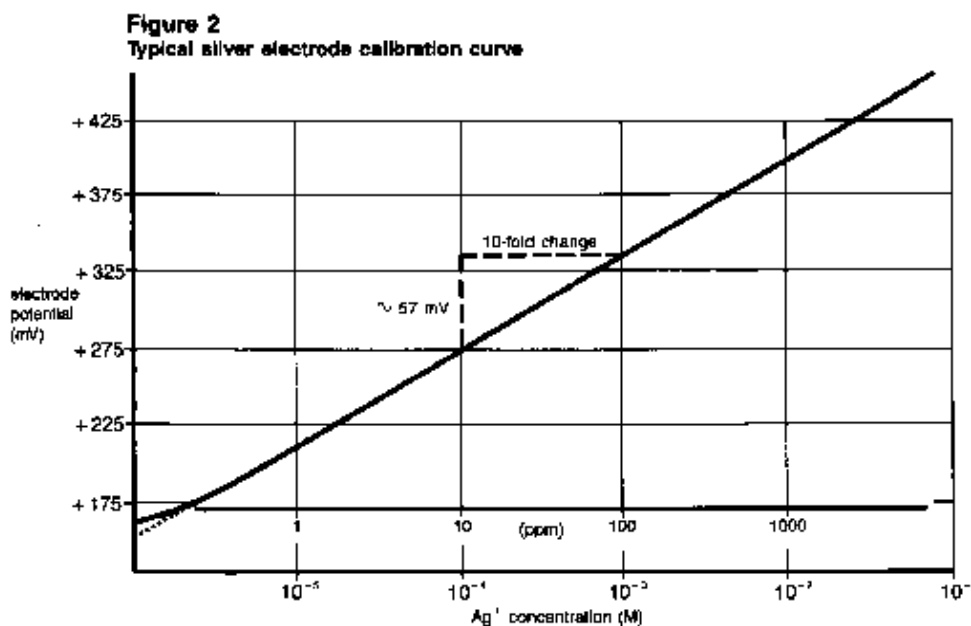## Measurement Procedures

Direct Measurement

A simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The ionic strength of samples and standards should be made the same by adjustment with SAOB for all sulfide solutions and with ISA for all silver solutions. The temperature of both sample solution and standard solution should be the same.

Direct Measurement of Silver (using a standard pH/mV meter)

1. By serial dilution of the 0.1M or 1000 ppm standards, prepare 10^{-2}, 10^{-3}, and 10^{-4}M or 100 and 10 ppm silver standards. Add 2 ml of ISA per 100 ml of standard. Prepare standards with a composition similar to the samples if the samples have an ionic strength above 0.1M.

2. Place the most dilute solution (10^{-4}M or 10 ppm) on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution. When the reading has stabilized, record the millivolt

reading.

3. Place the midrange solution (10^{-3}M or 100 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrode in distilled water, blot dry and immerse the electrode tip in the solution. When the reading has stabilized, record the millivolt reading.

4. Place the most concentrated solution (10^{-2}M or 1000 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrode in distilled water, blot dry and immerse the electrode tip in the solution. When the reading has stabilized, record the millivolt reading.

5. Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against concentration (log axis). Extrapolate the curve down to about 2×10^{-6}M or 0.2 ppm. A typical calibration curve can be found in Figure 2.

Figure 2
Typical silver electrode calibration curve

A calibration curve is constructed on semi-logarithmic paper when using a pH/mV meter in the millivolt mode. The measured electrode potential in mV (linear axis) is plotted against the standard concentration (log axis). In the linear region of the curve, only three standards are necessary to determine a calibration curve. In the non-linear region, additional points must be measured. The direct measurement procedures given are for the linear portion of the curve. The non-linear portion of the curve requires the use of low level procedures.

6. To a clean, dry 150 ml beaker, add 100 ml of sample and 2 ml of ISA. Place the

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beaker on the magnetic stirrer and begin stirring. Place the electrode tip in the solution. When the reading has stabilized, record the millivolt reading. Determine the concentration directly from the calibration curve.

7. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tip in the midrange standard. After the reading has stabilized, compare it to the original reading recorded in Step 3 above. A reading differing by more than 0.5 mV or a change of ambient temperature will necessitate the repetition of Steps 2-5 above. A new calibration curve should be prepared daily.
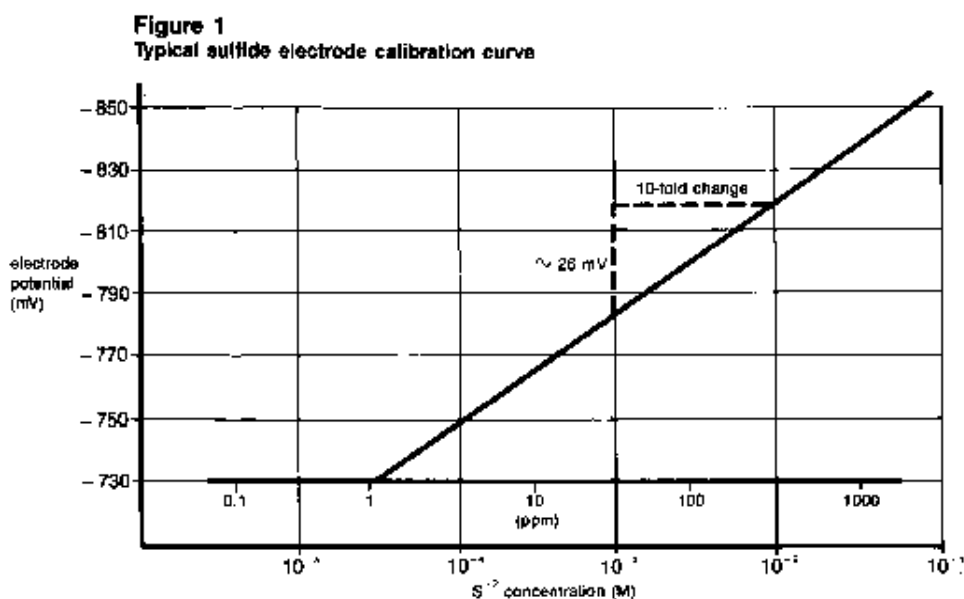
Direct Measurement of Silver (using an ion meter)

1. By serial dilution of the 0.1M or 1000 ppm silver standard, prepare two silver standards whose concentration is near the expected sample concentration. Measure out 100 ml of each standard into individual 150 ml beakers and add 2 ml of ISA to each.

2. Place the more dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode.

3. Lower the electrode tip into the solution.

4. Adjust the meter to the concentration of the silver standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.

5. Rinse the electrode with distilled water and blot dry.

6. Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate.

7. Lower the electrode tip into the solution.

8. Adjust the meter to the concentration of the silver standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.

9. For low level measurements, place the rinsed, dried electrode into a solution containing 100 ml of distilled water and 2 ml of ISA. After stabilization, fix the blank value in the meter according to the meter manufacturer's instructions.

10. Place 100 ml of the sample and 2 ml of ISA in a 150 ml beaker, place it on the magnetic stirrer and begin stirring.

11. Immerse the electrode tip in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.

12.   The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tip in the first silver standard. After the reading has stabilized, compare it to the original reading in Step 4 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of Steps 2-8(9) above. The meter should be re-calibrated daily.

Direct Measurement of Sulfide (using a standard pH/mV meter)

1.   By serial dilution of the weekly standard, prepare three standard sulfide solutions. Measure out 50 ml of each standard into individual 150 ml beakers and add 25 ml of SAOB and 25 ml of distilled water to each.

2.   Place the most dilute solution on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution. When the reading has stabilized, record the millivolt reading.

3.   Place the midrange sulfide standard on the magnetic stirrer and begin stirring. After rinsing the electrode in distilled water, blot dry and immerse the electrode tip in the solution. When the reading has stabilized, record the millivolt reading.

4.   Place the most concentrated sulfide standard on the magnetic stirrer and begin stirring. After rinsing the electrode in distilled water, blot dry and immerse the electrode tip in the solution. When the reading has stabilized, record the millivolt reading.

5.   Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against concentration (log axis). A typical calibration curve can be found in Figure 1.

Figure 1
Typical sulfide electrode calibration curve

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A calibration curve is constructed on semi-logarithmic paper when using a pH/mV meter in the millivolt mode. The measured electrode potential in mV (linear axis) is plotted against the standard concentration (log axis). In the linear region of the curve, only three standards are necessary to determine a calibration curve. In the non-linear region, additional points must be measured. The direct measurement procedures given are for the linear portion of the curve. The non-linear portion of the curve requires the use of low level procedures.

6. To a clean, dry 150 ml beaker, add 50 ml of the sulfide sample, 25 ml of SAOB, and 25 ml of distilled water. Place the beaker on the magnetic stirrer and begin stirring. Place the electrode tip in the solution. When the reading has stabilized, record the millivolt reading. Determine the concentration directly from the calibration curve.

7. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tip in the midrange standard. After the reading has stabilized, compare it to the original reading recorded in Step 3 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of Steps 2-5 above. A new calibration curve should be prepared daily.

Direct Measurement of Sulfide (using an ion meter)

1. By serial dilution of the weekly standard, prepare two sulfide standards whose concentration is near the expected sample concentration. Measure out 50 ml of each standard into individual 150 ml beakers and add 25 ml of SAOB and 25 ml of distilled water to each.

2. Place the more dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode.

3. Lower the electrode tip into the solution.

4. Adjust the meter to the concentration of the sulfide standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.

5. Rinse the electrode with distilled water and blot dry.

6. Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate.

7. Lower the electrode tip into the solution.

8. Adjust the meter to the concentration of the sulfide standard and fix the value in the

memory according to the meter manufacturer's instructions after stabilization of the reading.

9. For low level measurements, place the rinsed, dried electrode into a solution containing 50 ml of SAOB and 50 ml of distilled water. After stabilization, fix the blank value in the meter according to the meter manufacturer's instructions.

10. Place 50 ml of the sample, 25 ml of SAOB, and 25 ml of distilled water in a 150 ml beaker, place it on the magnetic stirrer and begin stirring.

11. Immerse the electrode tip in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.

12. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tip in the first sulfide standard. After the reading has stabilized, compare it to the original reading in Step 4 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of Steps 2-8(9) above. The meter should be re-calibrated daily.

Low Level Silver Determinations (using a standard pH/mV meter)

This procedure is recommended for solutions with ionic strengths less than $1.0X10^{-2}M$. If the solution is high in ionic strength, but low in silver, use the same procedure, but prepare a calibration solution with a composition similar to the samples.

1. Using 1 ml of standard ISA, dilute to 100 ml with distilled water. This low level ISA ($1.0M$ $NaNO_3$) is added at the rate of 1 ml low level ISA to each 100 ml of sample. The background ionic strength will be $1.0X10^{-2}M$.

2. Dilute 1 ml of 0.1M standard to one liter to prepare a $1.0X10^{-4}M$ solution for measurements in moles per liter. Prepare a 10 ppm standard solution by diluting 1 ml of the 1000 ppm standard to 100 ml of solution for measurements in ppm. Standards should be prepared fresh daily.

3. Add 1 ml of low level ISA to a 100 ml volumetric flask and fill to the mark with distilled water. Pour this solution into a 150 ml beaker and place the beaker on the magnetic stirrer. Begin stirring at a constant rate.

4. Place the electrode tip in the solution. Assure that the meter is in the millivolt mode.

5. Add increments of the $1.0X10^{-4}M$ or 10 ppm silver standard as given in Table 2 below.

6. After the reading has stabilized, record the mV reading.

TABLE 2: Stepwise Calibration for Low Level Silver Measurements

Step	Pipet	Added Volume (ml)	Concentration ppm	M
1	A	0.1	0.01	1.0×10^{-7}
2	A	0.1	0.02	2.0×10^{-7}
3	A	0.2	0.04	4.0×10^{-7}
4	A	0.2	0.06	6.0×10^{-7}
5	A	0.4	0.10	9.9×10^{-7}
6	B	2.0	0.29	2.9×10^{-6}
7	B	2.0	0.48	4.8×10^{-6}

Pipet A = 1 ml graduated pipet
Pipet B = 2 ml pipet
Solutions: additions of 10 ppm or 1.0×10^{-4}M
    standard to 100 ml of ISA as
    prepared in Step 3 above.

7.   On semi-logarithmic graph paper, plot the millivolt reading (linear axis) against the concentration (log axis) as in Figure 2.

8.   Rinse the electrode and blot dry.

9.   Measure out 100 ml of the sample into a 150 ml beaker, add 1 ml of low level ISA, and place the beaker on the magnetic stirrer. Begin stirring. Lower the electrode tip into the solution. After the reading has stabilized, record the mV reading and determine the concentration from the low level calibration curve.

10.   Prepare a new low level calibration curve daily. Check the calibration curve every two hours by repeating Steps 2-7.

Titration

A very accurate determination of total sulfide or total silver concentration. This method makes use of the electrode as an endpoint detector. The electrode can also be used to determine halide concentrations.
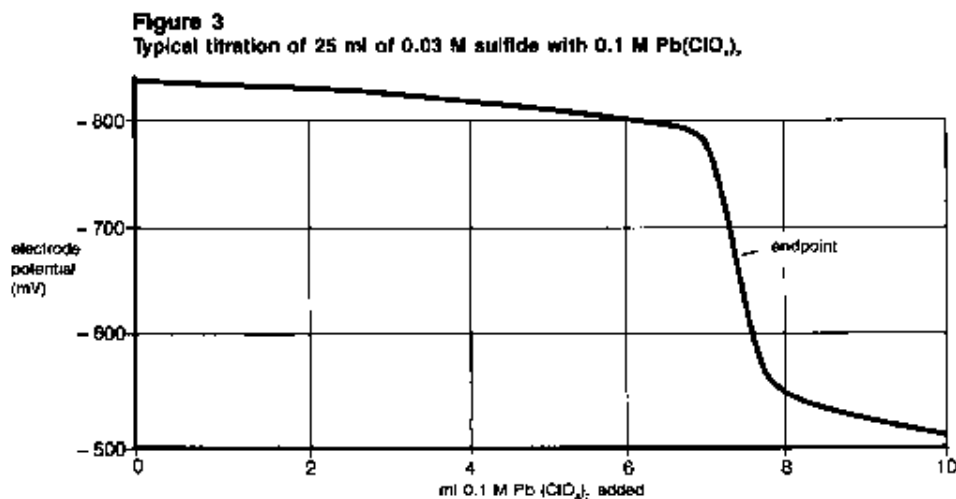
Titration of Sulfide

The minimum sulfide sample concentration for this method is 1.0×10^{-5}M. The titrant to be used is a lead perchlorate standard solution.

1.   Using Cole-Parmer Lead Perchlorate Solution, 0.1M, Cat. No. 27503-18, prepare a lead titrant that is about 10-20 times as concentrated as the expected sample concentration by dilution.

2.   Dilute 25 ml of the sample with 25 ml of SAOB in a 150 ml beaker. Place the

beaker on the magnetic stirrer and begin stirring. Lower the tip of the electrode into the solution.

3. Using a 10 ml burette, add titrant in 0.5-1.0 ml increments. Record the mV reading against the volume of titrant added. As the mV potential change increases, add smaller increments, down to 0.1-0.2 ml increments. Continue to add titrant and record the mV potential against the volume until little change is noted in the mV reading even when adding 0.5-1.0 ml increments.

4. Using linear graph paper, plot the mV readings (y-axis) against the volume (x-axis). The end point is determined at the steepest slope on the titration curve as illustrated in Figure 3.

Figure 3
Typical titration of 25 ml of 0.03 M sulfide with 0.1 M Pb(ClO₄)₂

5. The sample concentration, Cs, is calculated before the dilution with SAOB, as follows:

$$C_s = (V_t/V_s) \, C_t$$

where

V_s = sample volume before dilution (25ml)
V_t = titrant volume at endpoint
C_t = titrant concentration (M)

Titration of Silver

The Cole-Parmer Silver/Sulfide Ion Electrode is a highly sensitive endpoint detector for silver titration with a halide standard solution. It can also be used as an indicator for halide titration with a silver standard solution.

The minimum silver sample concentration for this method is about $1.0 \times 10^{-4} M$. For halides, it is

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1.0×10^{-4}M.

Data gathered by titration of less concentrated samples can be plotted using the Gran's Plot technique. (See the chloride titration that follows.)

1. Using Cole-Parmer Sodium Chloride Solution, 0.1M NaCl, Cat. No. 27503-78, for silver titration, or the 0.1M silver standard for halide titration, prepare a titrant about 10-20 times the expected sample concentration by dilution.

2. Measure out 50 ml of the sample into a 150 ml beaker, place the beaker on the magnetic stirrer, and begin stirring. Place the tip of the electrode in the solution.

3. Using a 10 ml burette, add titrant in 0.5-1.0 ml increments. Record the mV reading against the volume of titrant added. As the mV potential change increases, add smaller increments, down to 0.1-0.2 ml increments. Continue to add titrant and record the mV potential against the volume until little change is noted in the mV reading even when adding 0.5-1.0 ml increments.

4. Using linear graph paper, plot the mV readings (y-axis) against the volume (x-axis). The endpoint is determined at the steepest slope on the titration curve as illustrated in Figure 3.

5. The sample concentration, C_s, is calculated as follows:

$$C_s = (V_t/V_s) \, C_t$$

where
   V_s = sample volume (50 ml)
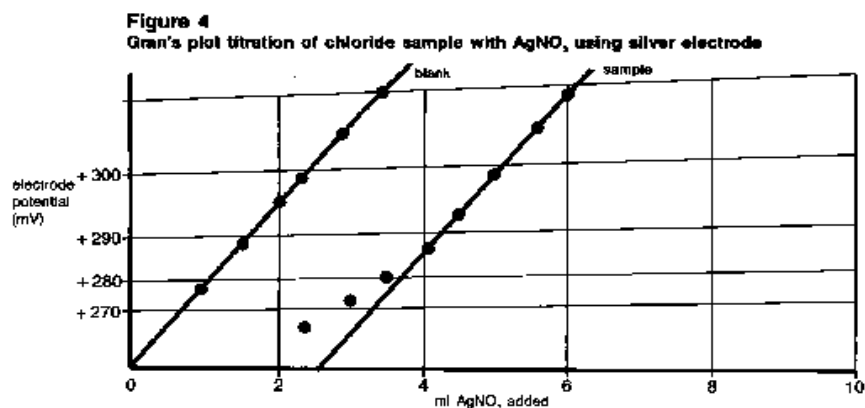 V_t = titrant volume at endpoint
   C_t = titrant concentration (M)

Low Level Chloride Titration

Chloride samples with a concentration below 1.0×10^{-4}M or 5 ppm cannot be titrated in the usual manner since the solubility product of silver chloride is not exceeded.

Using 10% Gran's Plot paper, data from samples down to 4.0×10^{-6}M (0.04 ppm) may be plotted.

1. Using 20 ml of standard ISA, dilute to 100 ml with distilled water. This low level ISA (1.0M $NaNO_3$) is added at the rate of 1 ml low level ISA to each 100 ml of sample. The background ionic strength will be 1.0×10^{-2}M.

2. Measure out 100 ml of distilled water into a 150 ml beaker, add 1 ml of low level ISA, place the beaker on the magnetic stirrer, and begin stirring.

3. Prepare a 10 ml burette with the low level chloride titrant (2.82×10^{-3}M $AgNO_3$) mentioned in the GENERAL INSTRUCTIONS, **Required Solutions.**

4.   Lower the tip of the electrode into the solution.

5.   Add 1 ml of titrant and record the mV reading after stabilization. Repeat this operation four more times.

6.   Using Gran's Plot paper, plot the values as follows:
     a) The horizontal axis is the volume axis. Each major division is equal to 1 ml of titrant used.

     b) The vertical axis is the mV axis. Each major division is equal to 5 mV. The axis should be scaled so that the mV value obtained after 5 ml of titrant added is near the top of the graph.

7.   After drawing a straight line through the points, the line should intersect the horizontal axis at 0 ml. (See Figure 4).

Figure 4
Gran's plot titration of chloride sample with AgNO, using silver electrode

8.   Measure out 100 ml of the sample into a 150 ml beaker, add 1 ml of low level ISA, place the beaker on the magnetic stirrer, and begin stirring.

9.   Prepare a 10 ml burette with the low level chloride titrant mentioned in Step 3 above.

10. Allow the titrant to run slowly into the sample until the mV reading is near the value recorded for the first 1 ml increment added in Step 5 above. Record the mV reading and the total volume added.

11. Add 1 ml increments of titrant and record the mV reading vs the total volume until the mV reading approaches the highest mV reading recorded in Step 5 above.

12. Plot the mV reading vs total volume for all points on the Gran's Plot paper. Draw a straight line through as many points as possible, extending the line to the horizontal axis. The volume intercept value is equal to the chloride concentration in ppm.

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Indicator Titration

A special method for measuring low level cyanide concentration. The silver/sulfide electrode is capable of cyanide measurements down to 0.03 ppm.

ELECTRODE CHARACTERISTICS

Reproducibility

Direct electrode measurements reproducible to ±2% can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuations, drift, and noise limit reproducibility. Reproducibility is independent of concentration within the electrode's operating range.

Interferences

A surface layer of silver metal may be formed by strongly reducing solutions. A layer of silver salt may be deposited on the membrane if high levels of ions forming very insoluble salts are present in the sample. Performance may be restored by polishing. See the section **Electrode Response** for proper polishing procedure.

All silver samples must be free of mercury. Sulfide samples will not have mercury present due to the extreme insolubility of HgS and Hg$_2$S. Biological samples and protein in food interferes with silver measurements, but the protein interference can be removed by acidifying to pH 2-3 with 1M HNO$_3$.

Complexation

Total concentration, C$_t$, whether sulfide or silver ions, consists of free ions, C$_f$, and complexed or bound ions, C$_c$, in solution:

$$C_t = C_f + C_c$$

Since the electrode only responds to free ions, any complexing agent in the solution reduces the measured concentration of ions.

Silver ions complex with many species, notably cyanide, thiosulfate, ammonia and chelants such as EDTA.

Sulfide ions form complexes with hydrogen ions (HS^{-1} and H$_2$S). Sulfide ions also form soluble complexes with elemental sulfur
(S$_2^{-2}$, S$_3^{-2}$, S$_4^{-2}$, etc.) and tin, arsenic, and antimony ions.

Temperature Influences

Samples and standards should be within ±1°C of each other, since electrode potentials are influenced

by changes in temperature. Because of the solubility equilibria on which the electrode depends, the absolute potential of the reference electrode changes slowly with temperature. The slope of the electrode, as indicated by the factor "S" in the Nernst equation, also varies with temperature. Table 3 gives values for the "S" factor in the Nernst equation for each ion.

TABLE 3: **Temperature vs Values for the Electrode Slope**

Temp.(^{o}C)	S^{-2}	Ag^{+1}
0	27.1	54.2
10	28.1	56.2
20	29.1	58.2
25	29.6	59.2
30	30.1	60.1
40	31.1	62.1
50	32.1	64.1

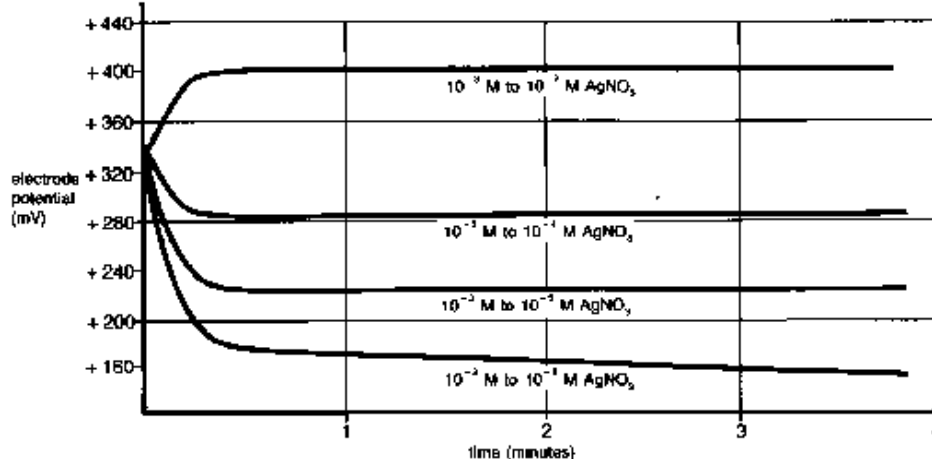If changes in temperature occur, the electrode(s) should be re-calibrated.

The temperature range for the Cole-Parmer Silver/Sulfide Ion Electrode is 0°-80^oC, provided that temperature equilibrium has occurred. If the temperature varies substantially from room temperature, equilibrium times up to one hour are recommended.

Electrode Response

Plotting the electrode mV potential against the silver concentration on semi-logarithmic paper results in a straight line with a slope of about 57 mV per decade. Refer to Figure 2. The sulfide ion also gives a straight line when the electrode mV potential is plotted against the sulfide concentration, but the slope is about 26 mV per decade. See Figure 1.

The time needed to reach 99% of the stable electrode potential reading, the electrode response time, varies from several seconds in highly concentrated solutions to several minutes near the detection limit. Refer to Figure 5.

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Figure 5
Typical electrode time response to step changes in AgNO₃.

A drifting potential reading or a decrease in electrode slope may mean that the electrode membrane needs polishing.

To polish the membrane:

1. If using polishing paper, cut off a 1-2" piece and place it face up on the lab bench.

2. Put a few drops of distilled or deionized water in the center of the paper.

3. Holding the paper (cotton) steady with one hand, bring the membrane of the electrode down perpendicular to the paper and, with a slight swirling motion, gently polish the tip of the electrode against the surface of the polishing paper (cotton) for a few seconds.

4. Rinse the electrode surface with distilled or deionized water and soak the electrode tip in standard solution for about five minutes before use.

5. If using jeweller's rouge, place a cotton ball on the table top and flatten it using the bottom of a beaker.

6. Put 1-2 drops of distilled or deionized water in the center of the cotton pad.

7. Add a small amount of jeweller's rouge to the damp cotton.

8. Continue with Steps 3 and 4 above.

Limits of Detection

The upper limit of detection in pure silver nitrate solutions is 1M. In the presence of other ions, the upper limit of detection is above 1.0×10^{-1}M silver, but two factors influence this upper limit. Both

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the possibility of a liquid junction potential developing at the reference electrode and the salt extraction effect influence this upper limit. Some salts may extract into the electrode membrane at high salt concentrations, causing deviation from the theoretical response. Either dilute samples between 1M and 1.0×10^{-1}M or calibrate the electrode at 4 or 5 intermediate points.

The lower limit of detection is influenced by the slight water solubility of the electrode pellet. Refer to Figure 1 and Figure 2 for a comparison of the theoretical response to the actual response at low levels of sulfide and silver.

pH Effects

Silver reacts with hydroxide ions to form a precipitate of Ag_2O, in ammonia-free basic solutions. By keeping all solutions slightly acidic, this can be avoided. Adjust the pH of silver solutions below 8, if necessary, with 1M HNO_3.

Bisulfide ion (HS^{-1}) and hydrogen sulfide (H_2S) result when hydrogen ion complexes sulfide ion. Larger amounts of sulfide ion are complexed as the pH is lowered. The use of SAOB in all samples containing sulfide maintains a fixed level of S^{-2} ions, since the free sulfide ion (S^{-2}) exists in only very basic solutions. In the acid range, sulfide is chiefly in the form of H_2S, while in the pH range 6-12, almost all the sulfide is in the HS^{-1} form.

Electrode Life

The Cole-Parmer Silver/Sulfide Electrodes will last six months in normal laboratory use. On-line measurements might shorten operational lifetime to several months. In time, the response time will increase and the calibration slope will decrease to the point calibration is difficult and electrode replacement is required.

Electrode Storage

The Cole-Parmer Silver/Sulfide Electrodes may be stored for short periods of time in 1.0×10^{-2} M silver (or sulfide) solution. For longer storage (longer than two weeks), rinse and dry the sensing pellet and cover the membrane tip with any protective cap shipped with the electrode. The reference portion of the combination electrode should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole.

ELECTRODE THEORY

Electrode Operation

The Cole-Parmer Silver/Sulfide Ion Electrode is composed of a silver sulfide crystal membrane bonded into an epoxy or glass body. When an electrode potential develops across the membrane, the membrane is in contact with a solution containing sulfide or silver ions and is capable of measuring free sulfide or silver ions. This electrode potential is measured against a constant reference potential, using a standard pH/mV meter or an ion meter. The level of sulfide or silver ions, corresponding to the measured potential, is described by the Nernst equation:

$$E = E_o + S \log X$$

where

E = measured electrode potential
E_o = reference potential (a constant)
S = electrode slope ($\sim$-27 mV for sulfide; $\sim$+57 mV for silver)
X = level of sulfide or silver in solution

The activity, X, represents the effective concentration of the ions in solution. The activity is related to the free ion concentration, C_f, by the activity coefficient, γ, by:

$$X = \gamma C_f$$

Activity coefficients vary, depending on total ionic strength, I, defined as:

$$I = 1/2 \sum C_x Z_x^2$$

where

C_x = concentration of ion X
Z_x = charge of ion X
$\sum$ = sum of all of the types of ions in the solution.

In the case of high and constant ionic strength relative to the sensed ion concentration, the activity coefficient, γ, is constant and the activity, X, is directly proportional to the concentration.

To adjust the background ionic strength to a high and constant value, ionic strength adjuster is added to samples and standards. The recommended solution for sulfide is SAOB, used to prevent oxidation and free sulfide ion from hydrogen ion, in addition to adjusting the ionic strength. The recommended ISA for silver is $NaNO_3$. Solutions other than these may be used as ionic strength

adjusters as long as ions that they contain do not interfere with the electrode's response to sulfide ions or to silver ions. Samples with high ionic strength (greater than 0.1M) do not need ISA added and standards for these solutions should be prepared with a composition similar to the samples.

The reference electrode must also be considered. When two solutions of different composition are brought into contact with one another, liquid junction potentials arise. Millivolt potentials occur from the interdiffusion of ions in the two solutions. Electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions since ions diffuse at different rates. When making measurements, it is important to remember that this potential be the same when the reference is in the standardizing solution as well as in the sample solution or the change in liquid junction potential will appear as an error in the measured electrode potential.

The composition of the liquid junction filling solution in the reference electrode is most important. The speed with which the positive and negative ions in the filling solutions diffuse into the sample should be as nearly equal as possible, that is, the filling solution should be equitransferent. No junction potential can result if the rate of which positive and negative charge carried into the sample solution is equal.

Strongly acidic (pH = 0-2) and strongly basic (pH = 12-14) solutions are particularly troublesome to measure. The high mobility of hydrogen and hydroxide ions in samples make it impossible to mask their effect on the junction potential with any concentration of an equitransferent salt. One must either calibrate the electrode(s) in the same pH range as the sample or use a known increment method for ion measurement.

TROUBLESHOOTING GUIDE

The goal of troubleshooting is the isolation of a problem through checking each of the system components in turn: the meter, the glassware, the electrode, the standards & reagents, the sample, and the technique.

Meter

The meter may be checked by following the check-out procedure in the instrument instruction manual.

Glassware

Clean glassware is essential for good measurement. Be sure to wash the glassware well with a mild detergent and rinse very well with distilled or deionized water. Clean glassware will drain without leaving water droplets behind.

Electrode

The electrodes may be checked by using the procedure found in the sections entitled **Electrode Slope Check**.

1. Be sure to use distilled or deionized water when following the procedures given in **Electrode Slope Check**.

2. If the electrode fails to respond as expected, see the   sections **Measuring Hints** and **Electrode Response**. Repeat the slope check.

3. If the electrode still fail to respond as expected,   substitute another silver/sulfide ion electrode that is known to be in good working order for the questionable electrode. If the problem persists and you are using an electrode pair, try the same routine with a working reference electrode.

4. If the problem persists, the reagent may be of poor quality, interferences in the sample may be present or the technique may be faulty. (See **Standards & Reagents**, **Sample**, and **Technique** sections below.)

5. If another electrode is not available for test purposes, or if the electrode in use is suspect, review the instruction manual and be sure to:

    - Clean and rinse the electrode thoroughly.
    - Prepare the electrode properly.
    - Use the proper filling solution.
    - Adjust the pH and the ionic strength of the solution by   the use of the proper ISA.
    - Measure correctly and accurately.
    - Review **TROUBLESHOOTING HINTS**.

Standards & Reagents

Whenever problems arise with the measuring procedure that has been used successfully in the past, be sure to check the standard and reagent solutions. If in doubt about the credibility of any of the solutions, prepare them again. Errors may result from contamination of the ISA, incorrect dilution of standards, poor quality distilled/deionized water, or a simple mathematical miscalculation.

Sample

Look for possible interferences, complexing agents, or substances which could affect the response or physically damage the sensing electrode (or the reference electrode) if the electrode(s) work perfectly in the standard, but not in the sample.

Try to determine the composition of the samples prior to testing to eliminate a problem before it starts. (See **Measuring Hints**, **Sample Requirements**, and **Interferences**.)

Technique

Be sure that the electrode's limit of detection has not been exceeded. Be sure that the analysis method is clearly understood and is compatible with the sample.

Refer to the instruction manual again. Reread **GENERAL** **PREPARATION** and **ELECTRODE** **CHARACTERISTICS**.

If trouble still persists, call your Cole-Parmer distributor and ask for the Technical Services Department.

TROUBLESHOOTING HINTS

Symptom	Possible Causes	Next Step
Out of Range Reading	defective meter	check meter with shorting strap `see meter instruction manual)`
	defective electrode	check electrode operation
	electrode not plugged in properly	unplug electrode and reseat
	reference electrode not filled	be sure reference electrode is filled
	air bubble on membrane	remove bubble by re-dipping electrode
	electrode not in solution	put electrode in solution
Noisy or Unstable Readings (readings continuously or rapidly changing)	defective meter	check meter with shorting strap
	air bubble on membrane	remove bubble by re-dipping electrode
	ISA not used	use recommended ISA
	meter or stirrer	ground meter or

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	not grounded	stirrer
	defective electrode	replace electrode
	electrode exposed to interferences	soak electrode in silver or sulfide standard
Drift (reading slowly changing in one direction)	samples and standards at different temperatures	allow solutions to come to room temperature before measurement
	electrode exposed to complexing agents	check section entitled **Complexation**
	incorrect reference filling solution	use recommended filling solution
Low Slope or No Slope	standards contaminated or incorrectly made	prepare fresh standards
	ISA not used	use recommended ISA
	standard used as ISA	use ISA
	electrode exposed to complexing agents	check section entitled **Complexation**
	air bubble on membrane	remove bubble by re-dipping probe
"Incorrect Answer" (but calibration is good)	incorrect scaling of semi-log paper	plot millivolts on the linear axis. On curve the log axis, be sure concentration numbers within each decade are increasing with increasing concentration
	incorrect sign	be sure to note sign

	of millivolt number correctly
incorrect standards	prepare fresh standards
wrong units used	apply correct conversion factor: $10^{-3}M = 32.1$ ppm $S^{-2} = 2 \times 10^{-3}$ N (S^{-2}); $10^{-3}M = 108$ ppm Ag^{+1}
complexing agents in sample	check section entitled **Complexation**

SPECIFICATIONS

Concentration Range: 1M to 1.0×10^{-7}M sulfide(32,000 to 0.003ppm)
                       1M to 1.0×10^{-7}M silver(108,000 to 0.01ppm)

pH Range: 2 to 12

Temperature Range: 0°-80°C

Resistance: <1 Mohm

Reproducibility: +/-2%

Samples: aqueous solutions only;
                  no organic solvents

Size: 110 mm length
                  12 mm diameter
                  1 m cable length

Storage: Store in silver or sulfide solution

ORDERING INFORMATION

P/N   DESCRIPTION

27502-41   Silver/Sulfide Ion Electrode, combination, glass body
27502-28   Silver/Sulfide Ion Electrode, combination, epoxy body

27503-31   Silver Standard, 0.1M $AgNO_3$
27503-32   Silver Standard, 1000 ppm $AgNO_3$

27503-51   Silver Ionic Strength Adjuster (ISA), 5 M $NaNO_3$

27503-75   Reference Electrode Filling Solution, 1M KNO_3, for the 27502-41 and 27502-28 electrodes