perfectION™ Guidebook

perfectION™
Combination Silver/Sulfide Electrode
Successful Ion Measurement

METTLER TOLEDO
perfectION™

METTLER TOLEDO

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1. Introduction

This user guide contains information on the preparation, operation and maintenance for the silver/sulfide ion selective electrode (ISE). General analytical procedures, electrode characteristics and electrode theory are also included in this user guide. The silver/sulfide electrode measures free silver ions or sulfide ions in aqueous solutions quickly, simply, accurately and economically. Silver sulfide (Ag_2S) is extremely insoluble, so silver and sulfide ions are virtually never present in the same solution. The silver/sulfide electrode can also be used to perform low-level cyanide and halide titrations.

perfectION™ Combination Silver/Sulfide Electrode

The reference and sensing electrodes are built into one electrode, which decreases the amount of required solution and reduces waste. The built-in Click & Clear™ reference junction prevents clogging of the diaphragm and provides fast and stable readings.

The perfectION™ Combination Silver/Sulfide Electrode is available with a BNC connector (P/N 51344700) and a Lemo connector (P/N 51344800) for METTLER TOLEDO titrators.

2. Required Equipment

1. METTLER TOLEDO ISE meter, such as the SevenMulti™ benchtop meter or the SevenGo pro™ portable meter, or a METTLER TOLEDO titrator, such as the Tx (T50, T70, T90) Excellence or G20 Compact titrators.

   METTLER TOLEDO combined ISEs can be used on any ISE meter with a BNC connection.

2. perfectION™ combined silver/sulfide ion selective electrode

3. Stirrer

4. Volumetric flasks, graduated cylinders, beakers and pipettes. Plastic labware is required for low-level silver analysis.

5. Distilled or deionized water

6. Silver/sulfide reference filling solution:
   Use Ion Electrolyte B Reference filling solution (P/N 51344751). Ion Electrolyte B Reference filling solution is supplied with the electrode and can be used for most silver or sulfide measurements and titrations. It is designed to reduce junction potentials and minimize silver or sulfide ion contamination of the sample.

   Ion Electrolyte C Reference filling solution (P/N 51344752) is recommended for precise silver measurements.
   Ion Electrolyte A Reference filling solution (P/N 51344750) is recommended for precise sulfide measurements.
   Ion Electrolyte A and C Reference filling solution provide an optimum temperature and time response when sample temperatures vary.

7. Calibration standards and ISA solutions

Silver Calibration Standards and ISA Solution:

Silver standard solution 1000 mg/L (P/N 51344770).

Ionic Strength Adjuster (ISA) for Solid State Ion Selective Electrodes (P/N 51344760). To adjust ionic strength of samples and standards.

Preparation note:

- **0.1 mol/L silver nitrate (AgNO$_3$) standard** – Prepare reagent-grade silver nitrate by pulverizing and then drying it in an oven at 150 °C for one hour. Place 16.99 g of the dried silver nitrate into a 1 L volumetric flask. Dissolve the solid and dilute to volume with distilled water. Store the solution in an opaque bottle in a dark location.

- **1000 mg/L as silver standard** – Prepare reagent-grade silver nitrate by pulverizing and then drying it in an oven at 150 °C for one hour. Place 1.57 g of the dried silver nitrate into a 1 L volumetric flask. Dissolve the solid and dilute to volume with distilled water. Store the solution in an opaque bottle in a dark location.

- **Low-level chloride titrant, 2.82 x 10^{-3} mol/L AgNO$_3$ equivalent to 100 mg/L as chloride** – Prepare reagent-grade silver nitrate by pulverizing and then drying it in an oven at 150 °C for one hour. Place 0.479 g of the dried silver nitrate into a 1 L volumetric flask. Dissolve the solid and dilute to volume with distilled water. Store the solution in an opaque bottle in a dark location.

Sulfide anti-oxidant buffer, Titration Solution and Calibration Standards:

Note: All water must be deaerated to prevent oxidation.

Sulfide anti-oxidant buffer

Sulfide standard solution 1000 mg/L (P/N 51344781)

0.1 mol/L lead perchlorate solution for titrations of sulfide standard solutions

Preparation note:

- Sulfide anti-oxidant buffer - Add 17 g of reagent-grade Ascorbic Acid (C6H8O6) to a 500 mL volumetric flask. Add 475 mL of 2 mol/L Sodium Hydroxide (NaOH) with EDTA and mix the solution thoroughly until the solids are dissolved.

- Prepare a stock solution of saturated sodium sulfide by dissolving approximately 100 g of reagent-grade $Na_2S \bullet 9H_2O$ in 100 mL of distilled, deaerated water. Shake the solution well and let it stand overnight. Store the solution in a tightly stoppered bottle in a fume hood.

- Prepare a sulfide standard weekly by pipetting 10 mL of the stock solution into a 1 L volumetric flask. Add 500 mL of Sulfide anti-oxidant buffer and dilute to the mark on the flask with distilled, deaerated water. Determine the exact concentration, C, by titrating 10 mL of the standard with 0.1 mol/L lead perchlorate, using the silver/sulfide electrode as the endpoint indicator and calculating:

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

where
- C = concentration, mg/L as sulfide
- V_t = volume of titrant at endpoint
- V_s = volume of standard (10 mL)

- Prepare lower concentration sulfide standards daily by serial dilution of the weekly standard. To do a ten-fold dilution, pipette 10 mL of the standard into a 100 mL volumetric flask, add 45 mL Sulfide anti-oxidant buffer and dilute to volume with distilled, deaerated water.

3. Electrode and Measurement Setup

Electrode Preparation

Remove the protective shipping cap from the sensing element and save the cap for storage. Fill the electrode with Ion Electrolyte B Reference filling solution or another Reference filling solution that is specially formulated for the application.

- Ion Electrolyte B Reference filling solution is supplied with the electrode and can be used for most silver or sulfide measurements and titrations. It is designed to reduce junction potentials and minimize silver and - sulfide ion contamination of the sample.

- Ion Electrolyte C Reference filling solution is recommended for precise silver measurements. It provides an optimum temperature and time response when sample temperatures vary.

- Ion Electrolyte A Reference filling solution is recommended for precise sulfide measurements. It provides an optimum temperature and time response when sample temperatures vary.

Electrode Filling Instructions:

1. Install the flip spout cap on the filling solution bottle and lift the flip spout on the bottle to a vertical position.

2. Insert the spout into the fill hole on the outer body of the electrode and add a small amount of filling solution to the reference chamber. Invert the electrode to moisten the O-ring and return the electrode to the upright position.

3. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.

4. Release the electrode cap. If the sleeve does not return to its original position, see if the O-ring is moist and repeat steps 2 through 4 until the sleeve returns to the original position.

5. Add filling solution to the electrode up to the filling hole.

Note: *Add filling solution each day before using the electrode. The filling solution level should be at least 2.5 cm above the level of sample in the beaker to ensure a proper flow rate. The fill hole should always be open during measurements.*
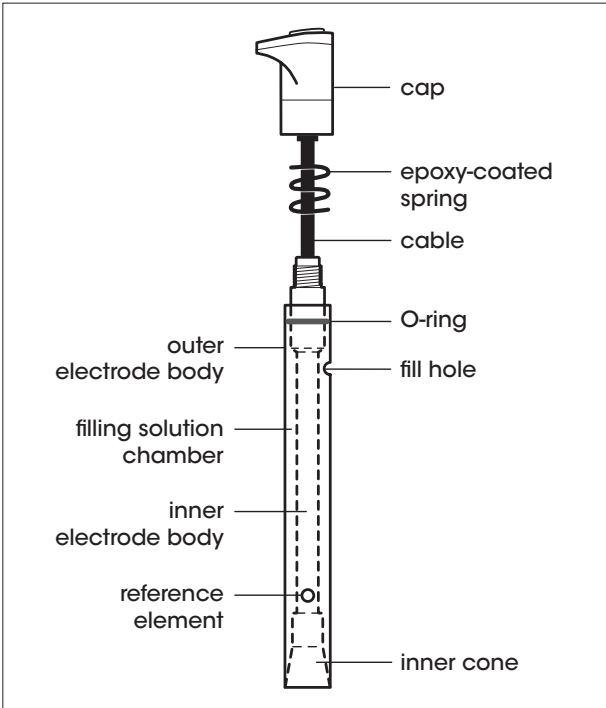

Figure 1 – *perfectION™ Silver/Sulfide combination electrode*

Checking Electrode Operation (Slope)

These are general instructions that can be used with most meters to check the electrode operation.

This procedure measures the electrode slope. Slope is defined as the change in millivolts observed with every tenfold change in concentration. The slope value provides the best means for checking the electrode operation.

1. If the electrode has been stored dry, prepare the electrode as described in the **Electrode Preparation** section.
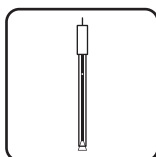
2. Connect the electrode to the meter. Set the meter to the mV mode.
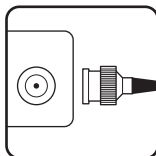
3. For silver analysis – Place 100 mL of distilled water and 2 mL of silver ISA into a 150 mL beaker. Stir the solution thoroughly. Use a 0.1 mol/L or 1000 mg/L silver standard in the following steps.
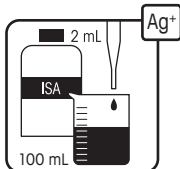
   For sulfide analysis – Place 50 mL of distilled water and 50 mL of Sulfide anti-oxidant buffer into a 150 mL beaker. Stir the solution thoroughly. Use a 100 mg/L sulfide standard in the following steps.
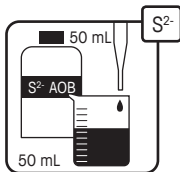
4. Rinse the electrode with distilled water, blot it dry and place the electrode into the solution prepared in step 3.
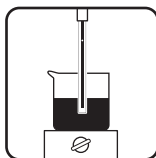
5. Select the appropriate standard. Pipette 1 mL of the standard into the beaker and stir thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.

6. Pipette 10 mL of the same standard into the same beaker and stir thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.
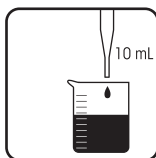
7. For silver analysis – There should be a 54 to 60 mV difference between the two millivolt readings when the solution temperature is between 20 to 25 ˚C.
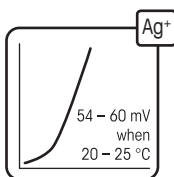
    For sulfide analysis – There should be a 25 to 30 mV difference between the two millivolt readings when the solution temperature is between 20 to 25 ˚C.

    If the millivolt potential is not within this range, refer to the **Troubleshooting** section.

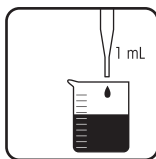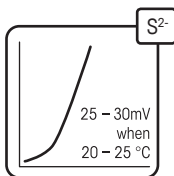## Sample Requirements

The epoxy body of the silver/sulfide electrode is resistant to damage by inorganic solutions. The electrode may be used intermittently in solutions that contain methanol or ethanol.

Samples and standards should be at the same temperature. The solution temperature must be less than 100 °C.

Silver samples must be acidified to below pH 8 with 1 mol/L HNO_3 to avoid a reaction with hydroxide ions. Sulfide samples must be buffered above pH 12 with Sulfide anti-oxidant buffer so HS^- and H_2S compounds are converted to S^{2-}.

Dissolved mercury compounds must be absent from silver samples. Because of the insolubility of HgS and Hg_2S, no dissolved mercury ions will be present in sulfide samples.

Measuring Hints

Concentration can be measured in moles per liter (mol/L), milligrams per liter (mg/L) or any convenient concentration unit.

Table 1 – *Silver Concentration Unit Conversion Factors*

mol/L	mg/L Silver (Ag⁺)
1.0	107900
10^{-1}	10790
10^{-2}	1079
10^{-3}	107.9
9.27×10^{-6}	1

Table 2 – *Sulfide Concentration Unit Conversion Factors*

mol/L	mg/L Sulfide (S²⁻)
1.0	32060
10^{-1}	3206
10^{-2}	320.6
10^{-3}	32.06
3.12×10^{-5}	1

- Stir all standards and samples at a uniform rate.

- Always use fresh standards for calibration.

- Always rinse the electrode with distilled water between measurements and shake the electrode to remove the water and prevent sample carryover. Do not wipe or rub the electrode sensing element.

- Allow all standards and samples to come to the same temperature for precise measurements.

- Place a piece of insulating material, such as Styrofoam or cardboard, between the magnetic stirrer and beaker to prevent measurement errors from the transfer of heat to the sample.

- Verify the electrode calibration every two hours by placing the electrode in a fresh aliquot of the least concentrated standard used for calibration. If the value has changed by more than 2% for silver measurements or 4% for sulfide measurements, recalibrate the electrode.

- After immersing the electrode in a solution, check the electrode sensing surface for air bubbles and remove air bubbles by reimmersing the electrode in the solution.

- For high ionic strength samples, prepare standards with a background composition similar to the sample.

- Concentrated samples (greater than 1 mol/L silver or sulfide) should be diluted before measurement.

- Remove the filling hole cover during measurements to ensure a uniform flow of reference filling solution.

- If the electrode is used in dirty or viscous samples or the electrode response becomes sluggish, empty the electrode completely, hold the junction open and flush the junction with distilled water. Empty any water from the electrode and refill it with fresh filling solution. Press down on the electrode cap to let a few drops of the filling solution flow out of the electrode and then replenish any lost solution.

- Start the calibration or measurement with the lowest concentrated standard or sample.

Electrode Storage and Maintenance

Electrode Storage

For storage between measurements and up to one week, store the electrode in distilled water with a few drops of filling solution. The filling solution inside the electrode should not be allowed to evaporate, as crystallization will result.

For storage longer than one week, drain the electrode, flush the chamber with distilled water and store the electrode dry with the protective shipping cap covering the sensing element.

Polishing the Sensing Surface of the Silver/Sulfide Combination Electrode

The sensing surface of solid state electrodes can wear over time, which causes drift, poor reproducibility and loss of response in low-level samples. The electrode can be restored by polishing the sensing surface with polishing strips. The polishing strip can also be used if the sensing surface has been etched or chemically poisoned.

1. Cut off an 2.5 cm length of the polishing strip.

2. Hold the electrode with the sensing surface facing up.

3. Place a few drops of distilled water on the sensing surface.

4. With the frosted side of the polishing strip facing down, use light finger pressure to place the polishing strip on top of the sensing surface.

5. Rotate the electrode for about 30 seconds.

6. Rinse the electrode with distilled water and then soak the electrode in a 1 mg/L or 10^{-5} mol/L silver standard for about two minutes.

Flushing the Silver/Sulfide Combination Electrode

If the area between the electrode sleeve and inner cone becomes clogged with sample or precipitate, flush the area with filling solution or distilled water.

1. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to drain the chamber. Push down on the cap until all the filling solution is drained from the chamber.

2. Fill the electrode with distilled water and then push down on the cap until all the water is drained from the chamber.

3. Fill the electrode with fresh filling solution up to the fill hole. Push down on the cap to allow a few drops of filling solution to drain out of the electrode and then refill any lost filling solution.

Disassembling the Silver/Sulfide Combination Electrode

Note: Disassembly is usually not required and should not be done unless a thorough cleaning is required.

1. Tip the electrode so the filling solution moistens the O-ring on the electrode body. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to drain the chamber.

2. Unscrew the cap counter clock-wise and then slide the cap and the spring up the cable.

3. Hold the outer sleeve with one hand and firmly push down on the threaded portion with the thumb and forefinger to separate the inner body from the sleeve.

4. Grasp the cone with a clean, lint-free tissue and withdraw the body from the sleeve using a gentle twisting motion. Do not touch the pellet above the cone, it will damage the pellet. Rinse the outside of the electrode body and the entire sleeve with distilled water. Allow it to air dry.

Reassembling the Silver/Sulfide Combination Electrode

1. Moisten the O-ring on the electrode body with a drop of filling solution. Insert the screw-thread end of the electrode body into the tapered, ground end of the sleeve.

2. Push the body into the sleeve using a gentle twisting motion until the bottom surface of the inner cone is flush with the tapered end of the sleeve.

3. Place the spring onto the electrode body and screw on the cap. Refill the electrode with filling solution.

Serial Dilutions

Serial dilution is the best method for the preparation of standards. Serial dilution means that an initial standard is diluted, using volumetric glassware, to prepare a second standard solution. The second standard is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.

1. **To prepare a 100 mg/L silver standard** – Pipette 10 mL of the 1000 mg/L standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

2. **To prepare a 10 mg/L standard** – Pipette 10 mL of the 100 mg/L standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

3. **To prepare a 1 mg/L standard** – Pipette 10 mL of the 10 mg/L standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

To prepare standards with a different concentration use the following formula:

$$C_1 * V_1 = C_2 * V_2$$

C_1 = concentration of original standard
V_1 = volume of original standard
C_2 = concentration of standard after dilution
V_2 = volume of standard after dilution

For example, to prepare 100 mL of a 1 mg/L silver standard from a 100 mg/L silver standard:

C_1 = 100 mg/L silver
V_1 = unknown
C_2 = 1 mg/L silver
V_2 = 100 mL
100 mg/L * V_1 = 1 mg/L * 100 mL
V_1 = (1 mg/L * 100 mL) / 100 mg/L = 1 mL

To prepare the 1 mg/L silver standard, pipette 1 mL of the 100 mg/L silver standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

4. Analytical Techniques

A variety of analytical techniques are available to the analyst. The following is a description of these techniques.

Direct Calibration is a simple procedure for measuring a large number of samples. Only one meter reading is required for each sample. Calibration is performed using a series of standards. The concentration of the samples is determined by comparison to the standards. ISA or Sulfide anti-oxidant buffer is added to all solutions to ensure that samples and standards have similar ionic strength.

Incremental Techniques provide a useful method for measuring samples, since calibration is not required. As in direct calibration, any convenient concentration unit can be used. The different incremental techniques are described below. They can be used to measure the total concentration of a specific ion in the presence of a large (50-100 times) excess of complexing agents.

- **Known Addition** is useful for measuring dilute samples, checking the results of direct calibration (when no complexing agents are present), or measuring the total concentration of an ion in the presence of an excess complexing agent.
  The electrode is immersed in the sample solution and an aliquot of a standard solution containing the measured species is added to the sample. From the change in potential before and after the addition, the original sample concentration is determined.

- **Known Subtraction** is useful as a quick version of a titration, or for measuring species for which stable standards do not exist. It is necessary to know the stoichiometric ratio between standard and sample. For known subtraction, an electrode sensing the sample species is used. Stable standards of a species reacting completely with the sample in a reaction of known stoichiometry are necessary.

- **Analyte Addition** is often used to measure soluble solid samples, viscous samples, small or very concentrated samples, to diminish the effects of complex sample matrices, or to diminish the effects of varying sample temperatures. This method is not suitable for dilute or low concentration samples. Total concentration is measured even in the presence of complexing agents. The electrode is immersed in a standard solution containing the ion to be measured and an aliquot of the sample is added to the standard. The original sample concentration is determined from the change in potential before and after the addition.

- **Analyte Subtraction** is used in the measurement of ions for which no ion-selective electrode exists. The electrode is immersed in a reagent solution that contains a species that the electrode senses, and that reacts with the sample. It is useful when sample size is small, or samples for which a stable standard is difficult to prepare, and for viscous or very concentrated samples. The method is not suited for very dilute samples. It is also necessary to know the stoichiometric ratio between standard and sample.

Titrations are quantitative analytical techniques for measuring the concentration of a species by incremental addition of a reagent (titrant) that reacts with the sample species. Sensing electrodes can be used for determination of the titration end point. Ion selective electrodes are useful as end point detectors, because they are unaffected by sample color or turbidity. Titrations are approximately 10 times more precise than direct calibration.

Indicator Titrations are useful for measuring ionic species when an ion-specific electrode does not exist. With this method, the electrode senses a reagent species that has been added to the sample before titration. A procedure for measuring low levels of cyanide ions down to 0.03 mg/L using the silver/sulfide electrode is described in the Low-Level Cyanide Indicator Method section.

Silver Analytical Procedures

Direct Calibration

The following procedure is recommended for mid-level and high-level measurements. All samples must be in the linear range of the electrode; samples must have a concentration greater than 0.5 mg/L as silver (4.6×10^{-6} mol/L $AgNO_3$).

Setup

1. Prepare the electrode as described in the **Electrode Preparation** section

2. Connect the electrode to the meter.

3. Prepare at least two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. See the **Serial Dilution** section for instructions on how to prepare standards. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to the **Temperature Effects** section.

   For samples that have an ionic strength of 0.1 mol/L or greater, prepare standards with a background composition similar to that of the samples.

   Store all silver samples and standards away from light.

Typical Silver Calibration Curve

In the direct calibration procedure, a calibration curve is constructed either in the meter memory or on semi-logarithmic paper. Electrode potentials of standard solutions are measured and plotted on the linear axis against their concentrations on the log axis. In the linear regions of the curves, only two standards are needed to determine a calibration curve. In non-linear regions, more points must be taken.
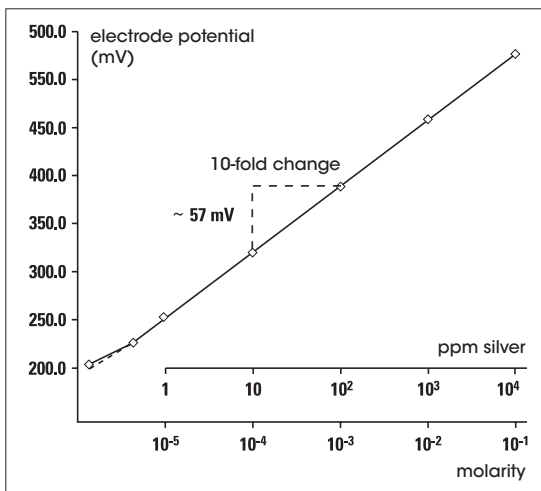
Figure 2 – *Typical Silver Calibration Curve*

Direct Calibration Using a Meter with an ISE Mode

Note: *See the meter user guide for more specific information.*

1. Measure 100 mL of the less concentrated standard and 2 mL of ISA and pour the solutions into a 150 mL beaker. Stir the solution thoroughly.

2. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the less concentrated standard. Wait for a stable reading and then adjust the meter to display the value of the standard, as described in the meter user guide.

3. Measure 100 mL of the more concentrated standard and 2 mL of ISA and pour the solutions into a second 150 mL beaker. Stir the solution thoroughly.

4. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the more concentrated standard. Wait for a stable reading and then adjust the meter to display the value of the second standard, as described in the meter user guide.

5. Record the resulting slope value. The slope should be between 54 to 60 mV when the standards are between 20 to 25 °C.

6. Measure 100 mL of the sample and 2 mL of ISA and pour the solutions into a clean 150 mL beaker. Stir the solution thoroughly.

7. Rinse the electrode with distilled water, blot it dry and place the electrode into the sample. The concentration of the sample will be displayed on the meter.

Note: *Smaller volumes of solutions may be used as long as the ratio of standard or sample to ISA does not change.*
For example, 50 mL of standard or sample requires the addition of 1 mL of ISA.

Direct Calibration Using a Meter with a Millivolt Mode

1. Adjust the meter to measure mV.

2. Measure 100 mL of the less concentrated standard and 2 mL of ISA and pour the solutions into a 150 mL beaker. Stir the solution thoroughly.

3. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the less concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.

4. Measure 100 mL of the more concentrated standard and 2 mL of ISA and pour the solutions into a second 150 mL beaker. Stir the solution thoroughly.

5. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the more concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.

6. Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis.

7. Measure 100 mL of the sample and 2 mL of ISA and pour the solutions into a clean 150 mL beaker. Stir the solution thoroughly.

8. Rinse the electrode with distilled water, blot it dry and place the electrode into the sample. When a stable reading is displayed, record the mV value.

9. Use the calibration curve prepared in step 6 in order to determine the unknown concentration of the sample.

Note: Smaller volumes of solutions may be used as long as the ratio of standard or sample to ISA does not change. For example, 50 mL of standard or sample requires the addition of 1 mL of ISA.

Low-Level Measurements

These procedures are for solutions that have a silver concentration of less than 0.5 mg/L silver (4.6×10^{-6} mol/L silver). For solutions low in silver but high in total ionic strength, perform the same procedure by preparing a calibrating solution with a composition similar to the sample. Accurate measurement requires that the following conditions be met:

- Prepare at least three calibration standards that bracket the expected sample concentration.

- Always use low-level ISA for standards and samples.

- Plastic labware must be used for all low-level silver measurements.

- Adequate time must be allowed for electrode stabilization. Longer response time will be needed at low-level measurements.

- Stir all standards and samples at a uniform rate.

Low-Level Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.

2. Connect the electrode to the meter. Set the meter to the mV mode.

3. Prepare the low-level ISA by pipette 20 mL of the ISA into a 100 mL volumetric flask and diluting to the mark with distilled water. Use low-level ISA for low-level measurements only.

4. Use either a 10 mg/L silver standard or a 10^{-4} mol/L silver standard.

Low-Level Calibration and Measurement

1. Measure 100 mL of distilled water and 1 mL of low-level ISA and pour the solutions into a 150 mL beaker.

2. Rinse the electrode with distilled water and place into beaker. Stir the solution thoroughly.

3. Add increments of a 10 mg/L or 10^{-4} mol/L silver standard mixed with low-level ISA to the beaker using the steps outlined in **Table 3**. Record the stable millivolt reading after each increment.

4. On semi-logarithmic paper, plot the concentration (log axis) against the millivolt potential (linear axis). Prepare a new calibration curve with fresh standards each day.

5. Measure 100 mL of sample and 1 mL of low-level ISA and pour the solutions into a clean 150 mL beaker. Rinse the electrode with distilled water, blot it dry and place the electrode into the sample.

6. Stir the solution thoroughly. When a stable reading is displayed, record the mV value.

7. Determine the sample concentration corresponding to the measured potential from the low-level calibration curve.

Table 3 – Calibration Curve For Low-Level Measurements

*Additions of standard (with low-level ISA) to 100 mL distilled water and 1 mL low-level ISA solutio*n

Step	Pipette Size	Volume Added	Concentration mg/L	mol/L
1	1 mL	0.1 mL	0.01	1.0×10^{-7}
2	1 mL	0.3 mL	0.04	4.0×10^{-7}
3	1 mL	0.6 mL	0.10	1.0×10^{-6}
4	2 mL	2.0 mL	0.30	3.0×10^{-6}

Known Addition

Known addition is a convenient technique for measuring samples in the linear range of the electrode (greater than 0.5 mg/L silver) because no calibration curve is required. It can be used to verify the results of a direct calibration or to measure the total concentration of an ion in the presence of a large excess of a complexing agent. The sample potential is measured before and after addition of a standard solution. Accurate measurement requires that the following conditions be met:

- Concentration should approximately double as a result of the addition.

- Sample concentration should be known to within a factor of three.

- Either no complexing agent or a large excess of the complexing agent may be present.

- The ratio of the uncomplexed ion to complexed ion must not be changed by addition of the standard.

- All samples and standards should be at the same temperature.

Known Addition Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.

2. Connect the electrode to the meter.

3. Prepare a standard solution that will cause the silver concentration of the sample to double when added to the sample solution. Refer to **Table 4** for guidelines.

4. Determine the electrode slope by performing the procedure in the **Checking Electrode Operation (Slope)** section.

5. Rinse the electrode with distilled water.

Table 4 – *Guideline For Known Addition*

Volume of Addition	Concentration of Standard
1 mL	100 times sample concentration
5 mL	20 times sample concentration
10 mL*	10 times sample concentration

* Most convenient volume to use

Known Addition Using a Meter with a Known Addition Mode

Note: *See the meter user guide for more specific information.*

1. Set the meter to measure in the known addition mode.

2. Measure 100 mL of the sample and 2 mL of ISA and pour the solutions into a beaker. Rinse the electrode with distilled water and place it into the sample solution. Stir the solution thoroughly.

3. When a stable reading is displayed, set the meter as described in the meter user guide, if required.

4. Pipette the appropriate amount of the standard solution into the beaker. Stir the solution thoroughly.

5. When a stable reading is displayed, record the sample concentration.

Known Addition Using a Meter with a Millivolt Mode

1. Set the meter to the relative millivolt mode. If a relative millivolt mode is not available, use the millivolt mode.

2. Measure 100 mL of sample and 2 mL of ISA and pour the solutions into a 150 mL beaker. Stir the solution thoroughly.

3. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker. When a stable reading is displayed, record the actual mV value.

4. Pipette the appropriate amount of standard solution into the beaker. Stir the solution thoroughly.

5. When a stable reading is displayed, record the mV value. Subtract the first reading from the second reading to calculate ΔE.

6. Use **Table 5** to find the Q value that corresponds to the change in potential, ΔE. To determine the original sample concentration, multiply Q by the concentration of the added standard:

$$C_{sample} = Q * C_{standard}$$

where
$C_{standard}$ = standard concentration
C_{sample} = sample concentration
Q   = value from **Table 5**

The table of Q values is calculated for a 10% volume change. The equation for the calculation of Q for different slopes and volume changes is given below.

$$Q = (p * r) / [(1 + p) * 10^{\Delta E/S}] - 1$$

where
Q   = value from **Table 5**
ΔE = $E_2 - E_1$
S   = slope of the electrode
p   = volume of standard / volume of sample and ISA
r   = volume of sample and ISA / volume of sample

Table 5 – Q Values for a 10% Volume Change

ΔE	Q Concentration Ratio by Slope			
	57.2	58.2	59.2	60.1
5.0	0.2917	0.2957	0.2996	0.3031
5.2	0.2827	0.2867	0.2906	0.2940
5.4	0.2742	0.2781	0.2820	0.2854
5.6	0.2662	0.2700	0.2738	0.2772
5.8	0.2585	0.2623	0.2660	0.2693
6.0	0.2512	0.2550	0.2586	0.2619
6.2	0.2443	0.2480	0.2516	0.2548
6.4	0.2377	0.2413	0.2449	0.2480
6.6	0.2314	0.2349	0.2384	0.2416
6.8	0.2253	0.2288	0.2323	0.2354
7.0	0.2196	0.2230	0.2264	0.2295
7.2	0.2140	0.2174	0.2208	0.2238
7.4	0.2087	0.2121	0.2154	0.2184
7.6	0.2037	0.2070	0.2102	0.2131
7.8	0.1988	0.2020	0.2052	0.2081
8.0	0.1941	0.1973	0.2005	0.2033
8.2	0.1896	0.1927	0.1959	0.1987
8.4	0.1852	0.1884	0.1914	0.1942
8.6	0.1811	0.1841	0.1872	0.1899
8.8	0.1770	0.1801	0.1831	0.1858
9.0	0.1732	0.1762	0.1791	0.1818
9.2	0.1694	0.1724	0.1753	0.1779
9.4	0.1658	0.1687	0.1716	0.1742
9.6	0.1623	0.1652	0.1680	0.1706
9.8	0.1590	0.1618	0.1646	0.1671
10.0	0.1557	0.1585	0.1613	0.1638
10.2	0.1525	0.1553	0.1580	0.1605
10.4	0.1495	0.1522	0.1549	0.1573
10.6	0.1465	0.1492	0.1519	0.1543
10.8	0.1437	0.1463	0.1490	0.1513
11.0	0.1409	0.1435	0.1461	0.1485
11.2	0.1382	0.1408	0.1434	0.1457
11.4	0.1356	0.1382	0.1407	0.1430
11.6	0.1331	0.1356	0.1381	0.1404
11.8	0.1306	0.1331	0.1356	0.1378
12.0	0.1282	0.1307	0.1331	0.1353
12.2	0.1259	0.1283	0.1308	0.1329
12.4	0.1236	0.1260	0.1284	0.1306
12.6	0.1214	0.1238	0.1262	0.1283
12.8	0.1193	0.1217	0.1240	0.1261
13.0	0.1172	0.1195	0.1219	0.1239
13.2	0.1152	0.1175	0.1198	0.1218
13.4	0.1132	0.1155	0.1178	0.1198
13.6	0.1113	0.1136	0.1158	0.1178
13.8	0.1094	0.1117	0.1139	0.1159
14.0	0.1076	0.1098	0.1120	0.1140
14.2	0.1058	0.1080	0.1102	0.1121
14.4	0.1041	0.1063	0.1084	0.1103
14.6	0.1024	0.1045	0.1067	0.1086
14.8	0.1008	0.1029	0.1050	0.1069
15.0	0.0992	0.1012	0.1033	0.1052
15.5	0.0953	0.0973	0.0994	0.1012
16.0	0.0917	0.0936	0.0956	0.0974
16.5	0.0882	0.0902	0.0921	0.0938
17.0	0.0850	0.0869	0.0887	0.0904
17.5	0.0819	0.0837	0.0856	0.0872
18.0	0.0790	0.0808	0.0825	0.0841
18.5	0.0762	0.0779	0.0797	0.0813
19.0	0.0736	0.0753	0.0770	0.0785
19.5	0.0711	0.0727	0.0744	0.0759
20.0	0.0687	0.0703	0.0719	0.0734
20.5	0.0664	0.0680	0.0696	0.0710
21.0	0.0642	0.0658	0.0673	0.0687
21.5	0.0621	0.0637	0.0652	0.0666
22.0	0.0602	0.0617	0.0631	0.0645

ΔE	Q Concentration Ratio by Slope			
	57.2	58.2	59.2	60.1
22.5	0.0583	0.0597	0.0612	0.0625
23.0	0.0564	0.0579	0.0593	0.0606
23.5	0.0547	0.0561	0.0575	0.0588
24.0	0.0530	0.0544	0.0558	0.0570
24.5	0.0514	0.0528	0.0541	0.0553
25.0	0.0499	0.0512	0.0525	0.0537
25.5	0.0484	0.0497	0.0510	0.0522
26.0	0.0470	0.0483	0.0495	0.0507
26.5	0.0456	0.0469	0.0481	0.0492
27.0	0.0443	0.0455	0.0468	0.0479
27.5	0.0431	0.0443	0.0455	0.0465
28.0	0.0419	0.0430	0.0442	0.0452
28.5	0.0407	0.0418	0.0430	0.0440
29.0	0.0395	0.0407	0.0418	0.0428
29.5	0.0385	0.0396	0.0407	0.0417
30.0	0.0374	0.0385	0.0396	0.0406
30.5	0.0364	0.0375	0.0385	0.0395
31.0	0.0354	0.0365	0.0375	0.0384
31.5	0.0345	0.0355	0.0365	0.0374
32.0	0.0335	0.0345	0.0356	0.0365
32.5	0.0327	0.0336	0.0346	0.0355
33.0	0.0318	0.0328	0.0337	0.0346
33.5	0.0310	0.0319	0.0329	0.0337
34.0	0.0302	0.0311	0.0320	0.0329
34.5	0.0294	0.0303	0.0312	0.0321
35.0	0.0286	0.0295	0.0305	0.0313
35.5	0.0279	0.0288	0.0297	0.0305
36.0	0.0272	0.0281	0.0290	0.0298
36.5	0.0265	0.0274	0.0282	0.0290
37.0	0.0258	0.0267	0.0275	0.0283
37.5	0.0252	0.0260	0.0269	0.0276
38.0	0.0246	0.0254	0.0262	0.0270
38.5	0.0240	0.0248	0.0256	0.0263
39.0	0.0234	0.0242	0.0250	0.0257
39.5	0.0228	0.0236	0.0244	0.0251
40.0	0.0223	0.0230	0.0238	0.0245
40.5	0.0217	0.0225	0.0232	0.0239
41.0	0.0212	0.0219	0.0227	0.0234
41.5	0.0207	0.0214	0.0221	0.0228
42.0	0.0202	0.0209	0.0216	0.0223
42.5	0.0197	0.0204	0.0211	0.0218
43.0	0.0192	0.0199	0.0206	0.0213
43.5	0.0188	0.0195	0.0202	0.0208
44.0	0.0183	0.0190	0.0197	0.0203
44.5	0.0179	0.0186	0.0192	0.0198
45.0	0.0175	0.0181	0.0188	0.0194
45.5	0.0171	0.0177	0.0184	0.0190
46.0	0.0167	0.0173	0.0179	0.0185
46.5	0.0163	0.0169	0.0175	0.0181
47.0	0.0159	0.0165	0.0171	0.0177
47.5	0.0156	0.0162	0.0168	0.0173
48.0	0.0152	0.0158	0.0164	0.0169
48.5	0.0148	0.0154	0.0160	0.0166
49.0	0.0145	0.0151	0.0157	0.0162
50.0	0.0139	0.0144	0.0150	0.0155
51.0	0.0132	0.0138	0.0143	0.0148
52.0	0.0126	0.0132	0.0137	0.0142
53.0	0.0121	0.0126	0.0131	0.0136
54.0	0.0116	0.0120	0.0125	0.0130
55.0	0.0110	0.0115	0.0120	0.0125
56.0	0.0106	0.0110	0.0115	0.0119
57.0	0.0101	0.0106	0.0110	0.0114
58.0	0.0097	0.0101	0.0105	0.0110
59.0	0.0093	0.0097	0.0101	0.0105
60.0	0.0089	0.0093	0.0097	0.0101

Low-Level Chloride Titration

The silver/sulfide electrode is a highly sensitive endpoint detector for titrations of silver samples with a halide standard and halide samples with a silver standard. The low-level chloride titration is an example of this type of measurement. With careful technique, titrations can be performed that are accurate to ± 0.1% of the total chloride ion concentration of the sample.
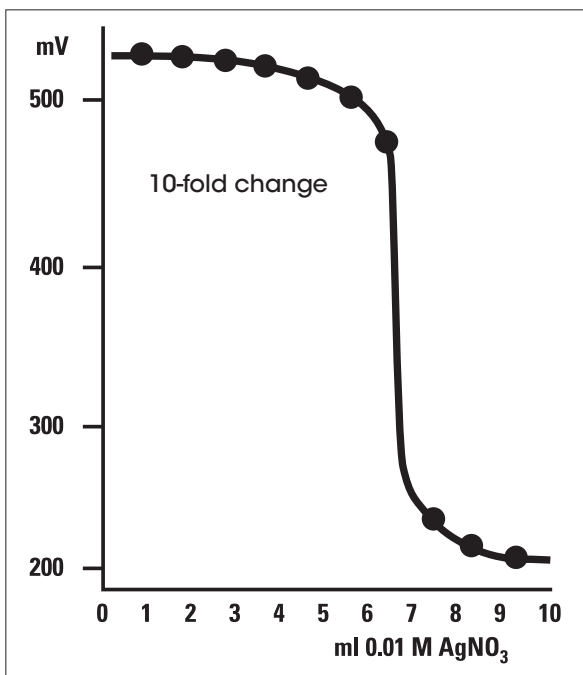
Figure 3 – Typical Titration of 25 mL of 0.001 mol/L Chloride Sample (Before Dilution) with 0.01 mol/L $AgNO_3$

Setup

1. Prepare the electrode as described in the Electrode Preparation section.

2. Connect the electrode to the meter.

3. Prepare a titrant solution that is 10 to 20 times more concentrated than the sample by diluting the 0.1 mol/L silver standard solution

Titration

1. Place 50 mL of sample into a 150 mL beaker. Place the electrode into the sample. Stir the solution thoroughly.

2. Perform an equivalence point titration using a standard EQP (equivalence point) titration method template available in the Tx Excellence and G20 Compact titrators. The EQP of the titration is the point of the greatest slope (inflection point). See **Figure 3**.

3. The concentration of the sample solution is calculated using the following equation:

$R \ (mol/L) = Q*C/m$

where
Q = VEQ*c*TITER
VEQ = Volume at the EQP
c = nominal concentration of the silver titrant
$TITER$ = Titer of the silver titrant
C = $1/z, \ z=1$ (equivalent number of the silver titrant)
m = volume of the sample solution

Low-Level Cyanide Indicator Method

The silver/sulfide electrode can be used for cyanide measurements down to 0.03 mg/L as CN^-. A small amount of $KAg(CN)_2$ is added to the solution as an indicator. The $Ag(CN)_2^-$ dissociates to form some silver and cyanide ions and the electrode measures the silver concentration. The degree of ion dissociation depends on the free cyanide concentration, so measurement of the silver concentration is an indirect measure of the cyanide concentration. Sulfide is an interference for this method, but can be removed by precipitation with cadmium. Cyanide complexed by copper, nickel, cobalt or iron cannot be measured directly with this method. These complexes may be broken by distillation per ASTM Method D 2036, Section 12.2.

Setup

1. Prepare the electrode as described in the **Electrode Preparation** section. Connect the electrode to the meter.

2. Prepare the following solutions:
   Ethylenediamine – anhydrous (98% purity or better) for the removal of formaldehyde.

   Silver nitrate titrant (– 1 mL = 1 mg CN^-) Crush about 5 g of reagent-grade silver nitrate ($AgNO_3$) crystals and dry at 150 °C for 1 hour. Add 3.265 g of the dried silver nitrate to a 1 L volumetric flask, dilute to the mark with distilled water and mix the solution well.

   NaOH diluent (for diluting cyanide standard solutions) – Add 25 g of reagent-grade sodium hydroxide (NaOH) to a 1 L volumetric flask, dilute to the mark with distilled water and mix the solution well.

   Silver potassium cyanide [$KAg(CN)_2$] – Reagent-grade or equivalent, available from electroplating chemical suppliers.

   Indicator/buffer – Add 33 g of reagent-grade disodium hydrogen phosphate ($Na_2HPO_4 \cdot 7H_2O$) and 80 mL of distilled water to a 100 mL volumetric flask. Stir the solution for 30 minutes. Add 2.2 g of reagent-grade sodium hydroxide (NaOH), 0.1 g of silver potassium cyanide [$KAg(CN)_2$] and 3.4 mL of ethylenediamine to the flask and dissolve the solids by thorough mixing the solution. Dilute to the mark with distilled water and mix the solution well. Check the solution before use for precipitation and discard it if precipitate appears.

Potassium cyanide (– 1000 mg/L stock solution, 1 mL = approximately 1 mg CN^-) Dissolve approximately 2 g of reagent-grade sodium hydroxide (NaOH) and 2.51 g of reagent-grade potassium cyanide (KCN) in 1 L of distilled water.

Caution: KCN is highly toxic. Avoid contact or inhalation.

Standardization of KCN Stock Solution

1. Standardize the KCN stock solution by performing a titration with the silver nitrate titrant. Pipette 20 mL of the KCN stock solution into a 150 mL beaker. Immerse the silver/sulfide electrode in the solution and gently stir the solution.

2. Modify a the titration template 'EQP' available in the Tx Excellence or G20 Compact titrator and perform an equivalence point (EQP) titration. The equivalence point is the point of the greatest slope in the titration curve. The volume to this point is labeled as VEQ.

3. Prepare a blank solution by dissolving 2 g of reagent-grade NaOH in 1 L of distilled water. Titrate 20 mL of the blank solution using the titration template 'Blank with EQP' available in the Tx Excellence or G20 Compact titrator. The result is stored as the Blank value in the setup of the respective titrator.

4. Calculate the cyanide concentration of the stock solution as follows:

   CN^- (mg/L) = (A - B) * 1000 / C

   where
   - A = VEQ in mL obtained from the titration of the cyanide solution
   - B = Blank value in mL obtained from the titration of the blank solution
   - C = mL of cyanide stock solution used for the titration

5. Standardize the stock solution each week because the solution loses strength gradually.

6. Prepare a 100 mg/L cyanide standard daily by diluting the stock solution with the NaOH diluent. The 100 mg/L solution is prepared by pipetting a volume, V, into a 100 mL volumetric flask. The volume, V, is calculated using the following formula where D is equal to the concentration (mg/L) of cyanide stock solution.

   V = 10000 / D

7. Prepare 10 mg/L and 1 mg/L standards daily by serial dilution with the NaOH diluent. For lower levels of cyanide, prepare 0.1 mg/L and 0.01 mg/L standards as well.

Sample Measurement Setup

1. Prepare the electrode as described in the **Electrode Preparation** section. Connect the electrode to the meter.

2. Use the two standards prepared in step 7. Standards should be at the same temperature as the samples.

Indicator Method Procedure Using a Meter with an ISE Mode

Note: *See the meter user guide for more specific information.*

1. Measure 100 mL of each standard and sample into separate 150 mL beakers. Add 2 mL of the indicator/buffer to each beaker. Stir the solutions thoroughly.

2. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the least concentrated standard. Wait for a stable reading and then adjust the meter to display the value of the standard, as described in the meter user guide.

3. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the next standard. Wait for a stable reading and then adjust the meter to display the value of the standard, as described in the meter user guide.

4. Repeat step 3 for all standards, working from the least concentrated to most concentrated standard. The slope should be between 58 to 61 mV/decade.

5. Rinse the electrode with distilled water, blot it dry and place the electrode into the sample. The concentration of the sample will be displayed on the meter.

Indicator Method Procedure Using a Meter with a mV Mode

1. Measure 100 mL of each standard and sample into separate 150 mL beakers. Add 2 mL of the indicator/buffer to each beaker. Stir the solutions thoroughly.

2. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the least concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.

3. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the next standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.

4. Repeat step 3 for all standards, working from the least concentrated to most concentrated standard.

5. Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis. See **Figure 2.**

6. Rinse the electrode with distilled water, blot it dry and place the electrode into the sample. When a stable reading is displayed, record the mV value.

7. Using the calibration curve prepared in step 5, determine the unknown sample concentration.

Sulfide Analytical Procedures

Direct Calibration

The following procedure is recommended for high-level sulfide measurements. All samples must be in the linear range of the electrode; samples must have a concentration greater than 0.32 mg/L as sulfide (1×10^{-5} mol/L).

Setup

1. Prepare the electrode as described in the Electrode Preparation section.

2. Connect the electrode to the meter.

3. Prepare at least two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement.

   All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to the Temperature Effects section.

   For samples that have an ionic strength of 0.1 mol/L or greater, prepare standards with a background composition similar to that of the samples.

   Always use deaerated water when preparing sulfide standards to prevent the oxidation of sulfide.

   Always dilute samples and standards using a 1:1 ratio with the Sulfide anti-oxidant buffer. For example, combine 25 mL of sample and 25 mL of Sulfide anti-oxidant buffer.

   Dilute sulfide samples 1:1 with Sulfide anti-oxidant buffer as they are collected, except when using the analyte subtraction measurement technique.

Note: If samples have been preserved with Sulfide anti-oxidant buffer, do not add more Sulfide anti-oxidant buffer before measuring the samples.

Typical Sulfide Calibration Curve

In the direct calibration procedure, a calibration curve is constructed either in the meter memory or on semi-logarithmic paper. Electrode potentials of standard solutions are measured and plotted on the linear axis against their concentrations on the log axis. In the linear regions of the curves, only two standards are needed to determine a calibration curve. In non-linear regions, more points must be taken.
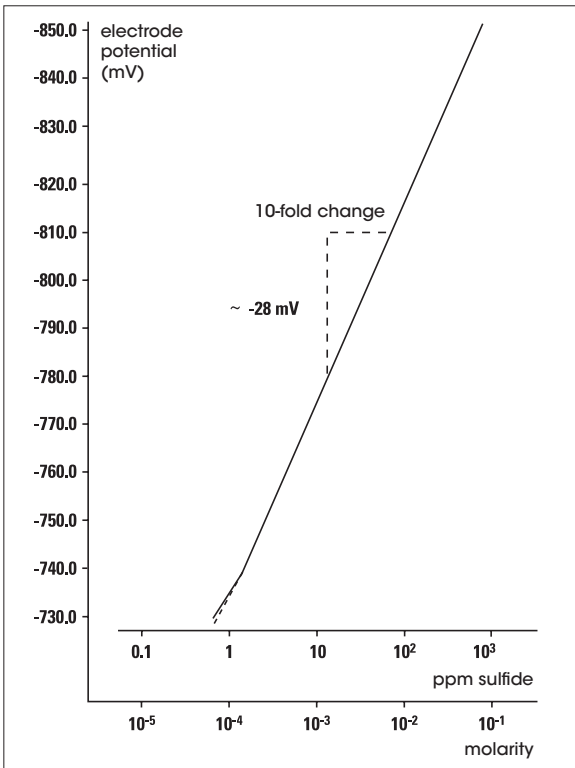
Figure 4 – *Typical Sulfide Calibration Curve*

Direct Calibration Using a Meter with an ISE Mode

Note: See the meter user guide for more specific information.

1. Measure 25 mL of the less concentrated standard and 25 mL of Sulfide anti-oxidant buffer and pour the solutions into a 150 mL beaker. Stir the solution thoroughly.

2. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the less concentrated standard. Wait for a stable reading and then adjust the meter to display the value of the standard, as described in the meter user guide.

3. Measure 25 mL of the more concentrated standard and 25 mL of Sulfide anti-oxidant buffer and pour the solutions into a second 150 mL beaker. Stir the solution thoroughly.

4. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the more concentrated standard. Wait for a stable reading and then adjust the meter to display the value of the second standard, as described in the meter user guide.

5. Record the resulting slope value. The slope should be between -25 to -30 mV when the standards are between 20 to 25 °C.

6. Measure 25 mL of the sample and 25 mL of Sulfide anti-oxidant buffer and pour the solutions into a clean 150 mL beaker. Stir the solution thoroughly.

   Note: If the sample was preserved by adding Sulfide anti-oxidant buffer, do not add more Sulfide anti-oxidant buffer before measuring the sample.

7. Rinse the electrode with distilled water, blot it dry and place the electrode into the sample. The concentration of the sample will be displayed on the meter.

Note: Smaller volumes of solutions may be used as long as the ratio of standard or sample to Sulfide anti-oxidant buffer does not change. For example, 50 mL of standard or sample requires the addition of 50 mL of Sulfide anti-oxidant buffer.

Direct Calibration Using a Meter with a Millivolt Mode

1. Adjust the meter to measure mV.

2. Measure 25 mL of the less concentrated standard and 25 mL of Sulfide anti-oxidant buffer and pour the solutions into a 150 mL beaker. Stir the solution thoroughly.

3. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the less concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.

4. Measure 25 mL of the more concentrated standard and 25 mL of Sulfide anti-oxidant buffer and pour the solutions into a second 150 mL beaker. Stir the solution thoroughly.

5. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker with the more concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.

6. Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis.

7. Measure 25 mL of the sample and 25 mL of Sulfide anti-oxidant buffer and pour the solutions into a clean 150 mL beaker. Stir the solution thoroughly.

   *Note*: *If the sample was preserved by adding Sulfide anti-oxidant buffer, do not add more Sulfide anti-oxidant buffer before measuring the sample.*

8. Rinse the electrode with distilled water, blot it dry and place the electrode into the sample. When a stable reading is displayed, record the mV value.

9. Using the calibration curve prepared in step 6, determine the unknown concentration of the sample.

Sulfide Titration

Titration is the recommended measurement method for sulfide samples. For accurate results, titration must be used for solutions that have a sulfide concentration of less than 0.32 mg/L sulfide (1×10^{-5} mol/L sulfide).

Sulfide may be titrated with a lead perchlorate standard solution. For sulfide measurements, titrations produce an extremely sharp endpoint, even at low levels of sulfide. With careful technique, titrations accurate to $\pm$ 0.1% of the total sulfide ion concentration of the sample can be performed.
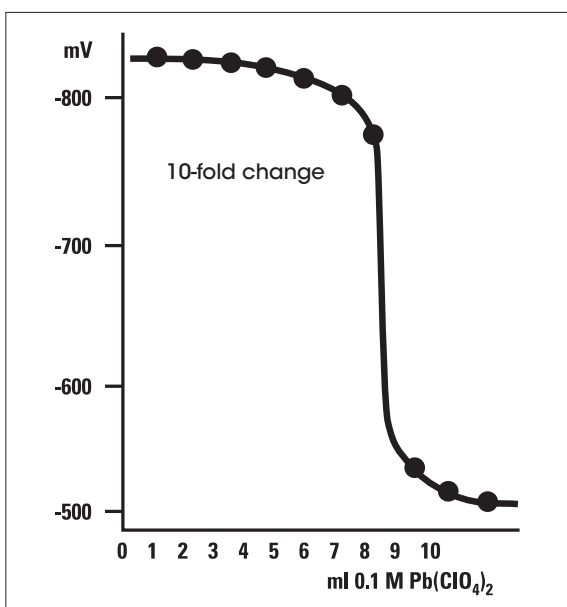
Figure 5 – *Typical Titration of 25 mL of 0.03 mol/L Sulfide Sample (Before Dilution) with 0.01 mol/L Pb(ClO$_4$)$_2$*

Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.

2. Connect the electrode to the meter.

3. Prepare a lead titrant solution that is 10 to 20 times more concentrated than the sample by diluting the 0.1 mol/L lead perchlorate standard solution.

Titration

1. Place 50 mL of sample (previously diluted 1:1 with Sulfide antioxidant buffer) into a 150 mL beaker. Place the electrode into the sample. Stir the solution thoroughly.

2. Modify a the titration template 'EQP' available in the Tx Excellence or G20 Compact titrator and perform an equivalence point (EQP) titration. The equivalence point is the point of the greatest slope (inflection point) in the titration curve. See **Figure 5**.
   The concentration of the sample solution is calculated using the following equation:

R (mol/L) = Q*C/m

where

Q = VEQ*c*TITER

VEQ = Volume at the EQP

c = nominal concentration of the silver titrant

TITER = Titer of the lead titrant

C = 1/z, z=1 (equivalent number of the lead titrant)

m = volume of the sample solution

Analyte Subtraction

Analyte subtraction is recommended for occasional sulfide measurements because it uses a silver standard solution rather than the easily oxidized sulfide standard solution. The sample must not contain species that react with silver (e.g. halide ions or Sulfide anti-oxidant buffer). All samples and standards should be at the same temperature. All concentration units are in moles per liter (mol/L).

Setup

Note: *Do not dilute samples with Sulfide anti-oxidant buffer when using this procedure.*

1. Prepare the electrode as described in the **Electrode Preparation** section.

2. Connect the electrode to the meter.

3. Prepare a silver standard solution about equal to half the expected sample sulfide concentration by diluting a 0.1 mol/L silver nitrate standard. Add 2 mL of ISA (P/N 51344760) to every 100 mL of standard.

4. Determine the electrode slope by performing the procedure in the **Checking Electrode Operation (Slope)** section.

5. Rinse the electrode with distilled water.

Analyte Subtraction Using a Meter with an ISE Mode

Note: *See the meter user guide for more specific information.*

1. Measure 100 mL of the silver standard into a beaker. Rinse the electrode with distilled water, blot it dry and place the electrode into the standard solution. Stir the solution thoroughly.

2. Wait for a stable reading and then adjust the meter to display the value of the standard, as described in the meter user guide.

3. Pipette 10 mL of the sulfide sample into the silver standard. Stir the solution thoroughly.

4. When a stable reading is displayed, record the sample concentration.

Analyte Subtraction Using a Meter with a mV Mode

1. Adjust the meter to measure mV.

2. Measure 100 mL of the silver standard into a beaker. Rinse the electrode with distilled water, blot it dry and place the electrode into the standard solution. Stir the solution thoroughly.

3. When a stable reading is displayed, record the mV value.

4. Pipette 10 mL of the sulfide sample into the silver standard. Stir the solution thoroughly.

5. When a stable reading is displayed, record the mV value.

6. Determine the potential change, ΔE, by subtracting the first mV reading from the second.

7. Use **Table 6** to find the Q value that corresponds to the change in potential, ΔE. To determine the original sample concentration, calculate the sample sulfide concentration in moles per liter (mol/L):

$$C_{sample} = 0.5 \ Q * C_{standard}$$

where

$C_{standard}$ = silver standard concentration (mol/L)
C_{sample} = sample concentration
Q = value from **Table 6**

Table 6 – Q Values for Analyte Subtraction

ΔE	Q Concentration Ratio by Slope			
	-28.6	**-29.1**	**-29.6**	**-30.1**
5.0	0.503	0.487	0.472	0.458
5.2	0.539	0.523	0.507	0.493
5.4	0.575	0.558	0.542	0.527
5.6	0.610	0.593	0.576	0.561
5.8	0.645	0.628	0.611	0.595
6.0	0.680	0.662	0.645	0.629
6.2	0.715	0.696	0.679	0.662
6.4	0.749	0.730	0.712	0.695
6.6	0.783	0.764	0.745	0.728
6.8	0.817	0.797	0.778	0.761
7.0	0.851	0.830	0.811	0.793
7.2	0.884	0.863	0.843	0.825
7.4	0.917	0.896	0.876	0.857
7.6	0.950	0.928	0.908	0.888
7.8	0.982	0.960	0.939	0.920
8.0	1.014	0.992	0.971	0.951
8.2	1.046	1.024	1.002	0.982
8.4	1.078	1.055	1.033	1.012
8.6	1.109	1.086	1.064	1.043
8.8	1.141	1.117	1.094	1.073
9.0	1.172	1.148	1.124	1.103
9.2	1.202	1.178	1.154	1.133
9.4	1.233	1.208	1.184	1.162
9.6	1.263	1.238	1.214	1.191
9.8	1.293	1.268	1.243	1.221
10.0	1.323	1.297	1.272	1.249
10.2	1.352	1.326	1.301	1.278
10.4	1.381	1.355	1.330	1.306
10.6	1.410	1.384	1.358	1.334
10.8	1.439	1.412	1.386	1.362
11.0	1.468	1.441	1.414	1.390
11.2	1.496	1.469	1.442	1.418
11.4	1.524	1.497	1.470	1.445
11.6	1.552	1.524	1.497	1.472
11.8	1.580	1.552	1.524	1.499
12.0	1.607	1.579	1.551	1.526
12.2	1.634	1.606	1.578	1.552
12.4	1.661	1.633	1.605	1.579
12.6	1.688	1.659	1.631	1.605
12.8	1.715	1.685	1.657	1.631
13.0	1.741	1.712	1.683	1.656
13.2	1.767	1.737	1.709	1.682
13.4	1.793	1.763	1.734	1.707
13.6	1.819	1.789	1.759	1.732
13.8	1.844	1.814	1.784	1.757
14.0	1.870	1.839	1.809	1.782
14.2	1.895	1.864	1.834	1.806
14.4	1.920	1.889	1.859	1.831
14.6	1.944	1.913	1.883	1.855
14.8	1.969	1.938	1.907	1.879
15.0	1.993	1.962	1.931	1.903
15.5	2.053	2.021	1.990	1.961
16.0	2.112	2.080	2.048	2.019
16.5	2.169	2.137	2.105	2.076
17.0	2.226	2.193	2.161	2.131

| ΔE	Q Concentration Ratio by Slope			
	-28.6	**-29.1**	**-29.6**	**-30.1**
17.5	2.281	2.248	2.215	2.185
18.0	2.335	2.302	2.269	2.239
18.5	2.388	2.355	2.322	2.291
19.0	2.440	2.406	2.373	2.342
19.5	2.491	2.457	2.424	2.393
20.0	2.541	2.507	2.473	2.442
20.5	2.590	2.556	2.522	2.491
21.0	2.638	2.604	2.570	2.538
21.5	2.685	2.651	2.617	2.585
22.0	2.731	2.697	2.663	2.631
22.5	2.777	2.742	2.708	2.676
23.0	2.821	2.786	2.752	2.720
23.5	2.864	2.829	2.795	2.763
24.0	2.907	2.872	2.837	2.805
24.5	2.949	2.914	2.879	2.847
25.0	2.990	2.954	2.920	2.888
25.5	3.030	2.995	2.960	2.928
26.0	3.069	3.034	2.999	2.967
26.5	3.107	3.072	3.038	3.006
27.0	3.145	3.110	3.076	3.044
27.5	3.182	3.147	3.113	3.081
28.0	3.218	3.183	3.149	3.117
28.5	3.254	3.219	3.185	3.153
29.0	3.289	3.254	3.220	3.188
29.5	3.323	3.288	3.254	3.222
30.0	3.356	3.322	3.288	3.256
31.0	3.421	3.387	3.353	3.321
32.0	3.483	3.449	3.416	3.384
33.0	3.543	3.509	3.476	3.445
34.0	3.601	3.567	3.534	3.503
35.0	3.656	3.623	3.590	3.560
36.0	3.709	3.676	3.644	3.614
37.0	3.760	3.728	3.696	3.666
38.0	3.809	3.777	3.745	3.716
39.0	3.856	3.824	3.793	3.764
40.0	3.901	3.870	3.839	3.811
41.0	3.944	3.914	3.884	3.855
42.0	3.986	3.956	3.926	3.898
43.0	4.026	3.996	3.967	3.940
44.0	4.064	4.035	4.007	3.979
45.0	4.101	4.073	4.045	4.018
46.0	4.137	4.109	4.081	4.055
47.0	4.171	4.143	4.116	4.090
48.0	4.203	4.177	4.150	4.124
49.0	4.235	4.209	4.182	4.157
50.0	4.265	4.239	4.213	4.188
51.0	4.294	4.269	4.243	4.219
52.0	4.322	4.297	4.272	4.249
53.0	4.349	4.324	4.300	4.277
54.0	4.374	4.351	4.327	4.304
55.0	4.399	4.376	4.352	4.330
56.0	4.423	4.400	4.377	4.355
57.0	4.446	4.423	4.401	4.380
58.0	4.467	4.446	4.424	4.403
59.0	4.488	4.467	4.446	4.425
60.0	4.509	4.488	4.467	4.447

5. Electrode Characteristics

Electrode Response

The electrode potential plotted against silver concentration on semi-logarithmic paper results in a straight line, until the concentration reaches 10^{-6} mol/L, with a slope of about 54 to 60 mV per decade change in concentration. See **Figure 2**.

The electrode potential plotted against sulfide concentration on semi-logarithmic paper results in a straight line, until the concentration reaches 10^{-5} mol/L, with a slope of about -25 to -30 mV per decade change in concentration. See **Figure 4**.

The electrode exhibits a time response (99% of the stable potential reading) of one minute or less for concentrations in the linear range of the electrode. The response time will vary with concentrations below the linear range of the electrode and may require several seconds in more concentrated solutions to several minutes near the limit of detection. See **Figure 6**.
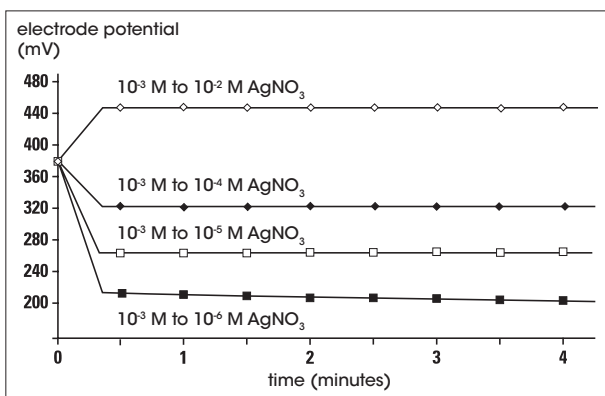
Figure 6 – *Typical Electrode Response*

Reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift and noise. Within the operating range of the electrode, reproducibility is independent of concentration. With hourly calibrations, direct silver measurements reproducible to ± 2% can be obtained and direct sulfide measurements reproducible to ± 4% can be obtained.

Temperature Effects

Since electrode potentials are affected by changes in temperature, samples and standard solutions should be within ± 1 °C (± 2 °F) of each other. At the 10^{-3} mol/L level, a 1 °C difference in temperature results in a 2% error with silver measurements or a 4% error with sulfide measurements. The absolute potential of the reference electrode changes slowly with temperature because of the solubility equilibria on which the electrode depends. The slope of the silver/sulfide electrode also varies with temperature, as indicated by the factor S in the Nernst equation. Theoretical values of the slope at different temperatures are given in **Table 7**. If temperature changes occur, the meter and electrode should be recalibrated.

The electrode can be used at temperatures from 0 to 100 °C, provided that temperature equilibrium has occurred. For use at temperatures substantially different from room temperature, calibration standards should be at the same temperature as samples. The electrode should be used only intermittently at temperatures above 80 °C.

For sulfide measurements, Ion Electrolyte A Reference filling solution will minimize junction potentials and provide optimum temperature and time response. Ion Electrolyte A Reference filling solution produces an isopotential point of 3×10^{-5} mol/L S^{2-}. For silver measurements, Ion Electrolyte C Reference filling solution provides optimum temperature and time response. Ion Electrolyte C Reference filling solution produces an isopotential point of 2×10^{-3} mol/L Ag^+.

The isopotential point is the concentration at which the potential of the electrode does not vary with temperature. Since the isopotential point produced by both filling solutions is known, the perfectION™ combination silver/sulfide electrode may be used on meters that allow automatic temperature compensation for ISE. By programming the isopotential point and placing an ATC probe into the sample, the meter will automatically adjust the slope of the calibration curve any time the temperature changes, resulting in more accurate measurement results.

Table 7 – *Theoretical Slope vs. Temperature Values*

Temperature (°C)	Silver Slope (mV)	Sulfide Slope (mV)
0	54.2	- 27.1
10	56.2	- 28.1
20	58.2	- 29.1
25	59.2	- 29.6
30	60.1	- 30.1
40	62.1	- 31.1
50	64.1	- 32.1

Interferences

Mercury must be absent from all silver samples. Since HgS and Hg_2S are extremely insoluble, mercury will not be present in any sulfide sample. Proteins in food and biological samples interfere with silver measurements. Remove the protein interference by acidifying the solution to pH 2-3 with 1 mol/L HNO_3. The sensing element of the electrode is oxidized by H_2O_2.

If the electrode is exposed to high levels of interfering ions, it may become unstable and sluggish in response. When this happens, restore normal performance by soaking the electrode for 30 minutes in a 0.2 mol/L silver nitrate solution.

pH Effects

In ammonia-free basic solutions, silver reacts with hydroxide ions to form a precipitate of Ag_2O. This can be avoided by keeping solutions slightly acidic; use 1 mol/L HNO_3 to adjust the pH of silver solutions below pH 8 if necessary.

Hydrogen ion complexes sulfide ion to form bisulfide ion (HS^-) and hydrogen sulfide (H_2S). The lower the pH, the larger the amount of sulfide ion complexed. In acid solutions, sulfide is chiefly in the form of H_2S. In the intermediate pH range (up to approximately pH 12) almost all the sulfide is in the form HS^-. Only in very basic solutions does the sulfide exist primarily as free ion (S^{2-}). The use of Sulfide anti-oxidant buffer in all samples and standards maintains a fixed level of S^{2-}.

Complexation

For both silver and sulfide ions, the total concentration (C_t) consists of free ions (C_f) and bound or complexed ions in solution (C_b):

$$C_t = C_f + C_b$$

The electrode responds only to free ions, so any complexing agent in the solution reduces the measured concentration of silver or sulfide. Known addition is a recommended procedure for measuring silver in the presence of complexing agents.

Silver ions form complexes with a large number of species, including common species such as EDTA and other chelating agents, ammonia, thiosulfate and cyanide.

Sulfide forms complexes with hydrogen ion (HS^- and H_2S). In addition, sulfide ion forms soluble complexes with elemental sulfur, tin, antimony, and arsenic ions.

Theory of Operation

The silver/sulfide electrode consists of a sensing element bonded into an epoxy body. When the sensing element is in contact with a solution containing either silver or sulfide ions, an electrode potential develops across the sensing element. This potential, which depends on the level of free silver or sulfide ions in solution, is measured against a constant reference potential with a digital pH/mV meter or ISE (concentration) meter. The measured potential corresponding to the level of silver/sulfide ion in solution is described by the Nernst equation.

$$E = E_o + S * log (A)$$

where

E = measured electrode potential

E_o = reference potential (a constant)

A = silver/sulfide ion activity level in solution

S = electrode slope (about 57 mV per decade for silver and about 27 mV per decade for sulfide)

The level of silver or sulfide ions, A, is the activity or "effective concentration" of free silver or sulfide ions in solution. The silver or sulfide ion activity is related to free silver or sulfide ion concentration, C_f, by the activity coefficient, y_i.

$$A = y_i * C_f$$

Ionic activity coefficients are variable and largely depend on total ionic strength. Ionic strength is defined as:

Ionic strength $= 1/2 \sum C_i Z_i^2$

where

C_i = concentration of ion i

Z_i = charge of ion i

$\sum$ symbolizes the sum of all the types of ions in solution
If background ionic strength is high and constant relative to the sensed ion concentration, the activity coefficient is constant and activity is directly proportional to the concentration. Ionic strength adjustor (ISA) is added to all silver standards and samples so that the background ionic strength is high and relatively constant. Sulfide anti-oxidant buffer is added to sulfide

standards and samples to prevent oxidation, free sulfide ions from hydrogen ions and adjust the background ionic strength. Other solutions can be used as long as they do not contain ions that would interfere with the electrode response to silver or sulfide. If samples have a high ionic strength (above 0.1 mol/L), standards should be prepared with a composition similar to the samples.

Reference electrode conditions must also be considered. Liquid junction potentials arise any time two solutions of different composition are brought into contact. The potential results from the interdiffusion of ions in the two solutions. Since ions diffuse at different rates, electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions. In making electrode measurements, it is important that this potential be the same in the standardizing solution as in the sample solution. Otherwise, the change in liquid-junction potential will appear as an error in the measured electrode potential.

perfectION™ reference filling solutions are specifically designed to meet all reference electrode conditions. The filling solution is equitransferent. Therefore, the speed with which the positive and negative ions in the filling solution diffuse into the sample is as nearly equal as possible. If the rate at which positive and negative charge is carried into the sample solution is equal, then minimum junction potential can result.

6. Troubleshooting

Follow a systematic procedure to isolate the problem. The measuring system can be divided into four components for ease in troubleshooting: meter, electrode, sample/application and technique.

Meter/Titrator

The meter/titrator is the easiest component to eliminate as a possible cause of error. Consult the meter/titrator user guide for directions.

Electrode

1. Rinse the electrode thoroughly with distilled water.

2. Verify the electrode performance by performing the procedure in the **Checking Electrode Operation (Slope)** section.

3. If the electrode fails this procedure, review the **Measuring Hints** section. Clean the electrode thoroughly as directed in the **Electrode Maintenance** section. Drain and refill the electrode with fresh filling solution.

4. Repeat the procedure in the **Checking Electrode Operation (Slope)** section.

5. If the electrode passes the procedure, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error.

6. Before replacing a faulty electrode, review this user guide and be sure to thoroughly clean the electrode; correctly prepare the electrode; use the proper filling solutions, ISA or Sulfide anti-oxidant buffer, and standards; correctly measure the samples and review the **Troubleshooting Checklist** section.

Sample/Application

The quality of results depends greatly upon the quality of the standards. Always prepare fresh standards when problems arise, it could save hours of frustrating troubleshooting. Errors may result from contamination of prepared standards, accuracy of dilution, quality of distilled water, or a mathematical error in calculating the concentrations.

The best method for preparation of standards is **Serial Dilution**. Refer to the silver and sulfide **Direct Calibrations** sections. The electrode and meter may operate with standards, but not with the sample. In this case, check the sample composition for interferences, incompatibilities or temperature effects. Refer to the **Sample Requirements, Temperature Effects** and **Interferences** sections.

Technique

If trouble persists, review operating procedures. Review calibration and measurement sections to be sure proper technique has been followed. Verify that the expected concentration of the ion of interest is within the limit of detection of the electrode.

Check the method of analysis for compatibility with your sample. **Direct measurement** may not always be the method of choice. If a large amount of complexing agents are present, **Known Addition** may be the best method. If the sample is viscous, analyte addition may solve the problem. If working with low-level samples, follow the recommended **Low-Level Measurement** procedure.

Troubleshooting Checklist

Symptom: Off-scale or over-range reading

Electrode is clogged or dirty – Refer to the **Electrode Maintenance** section for cleaning instructions.

Electrode junction is dry – Push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.

Reference filling solution not added – Fill the electrode up to the fill hole with reference filling solution. Refer to the **Electrode Preparation** section for details.

Air bubble on the sensing element – Remove bubbles by gently tapping the side of the electrode.

Electrode not in solution – Insert the electrode in solution.

Electrode not plugged into the meter properly – Unplug and reconnect the electrode.

Defective meter/titrator – Refer to the meter/titrator user guide.

Symptom: Low slope or no slope

Insufficient reference filling solution – Fill the electrode up to the fill hole with reference filling solution.

Electrode is clogged or dirty – Refer to the **Electrode Maintenance** section for cleaning instructions.

Electrode junction is dry – Push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.

Standards contaminated or made incorrectly– Prepare fresh standards.

ISA or Sulfide anti-oxidant buffer not used – For silver measurements, ISA must be added to all standards and samples. For sulfide measurements, Sulfide anti-oxidant buffer must be added to add standards and samples, unless the analyte subtraction procedure is used. Refer to the **Required Equipment** and **Analytical Techniques** sections for information on ISA and Sulfide anti-oxidant buffer solutions.

Electrode exposed to interferences – Refer to the **Electrode Maintenance** section for cleaning instructions.

Symptom: High Sulfide Slope

Sulfide is being oxidized – Always use deaerated water when preparing sulfide standards to prevent the oxidation of sulfide.

Symptom: Noisy or unstable readings (erratic, rapidly changing)

Insufficient reference filling solution – Fill the electrode up to the fill hole with reference filling solution.

Electrode is clogged or dirty – Refer to the **Electrode Maintenance** section for cleaning instructions.

Electrode junction is dry – Push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.

ISA or Sulfide anti-oxidant buffer not used – For silver measurements, ISA must be added to all standards and samples. For sulfide measurements, Sulfide anti-oxidant buffer must be added to add standards and samples, unless the analyte subtraction procedure is used. Refer to the **Required Equipment** and **Analytical Techniques** sections for information on ISA and Sulfide anti-oxidant buffer solutions.

Air bubble on the sensing element – Remove bubbles by gently tapping the side of the electrode.

Meter/titrator or stir plate not properly grounded – Check the meter/titrator and stir plate for proper grounding.

Defective meter/titrator – Refer to the meter/titrator user guide.

Symptom: Wrong answer but calibration curve is correct

Standards contaminated or made incorrectly – Prepare fresh standards.

Incorrect scaling of semi-logarithmic paper – Refer to the **Direct Calibration** section.

Incorrect millivolt sign used – Make sure to correctly record the sign of mV values.

Incorrect units used – Apply the correct conversion factor.
For silver measurements: 10^{-3} mol/L = 107.9 mg/L silver
For sulfide measurements: 10^{-3} mol/L = 32.06 mg/L sulfide

Complexing agents in sample – Use known addition, titration techniques or a decomplexing procedure.

ISA or Sulfide anti-oxidant buffer added to standards, but not samples – Add the same proportion of ISA or Sulfide anti-oxidant buffer to all standards and samples.

Symptom: Drift
(reading slowly changing in one direction)

Insufficient reference filling solution – Fill the electrode up to the fill hole with reference filling solution.

Electrode is clogged or dirty – Refer to the **Electrode Maintenance** section for cleaning instructions.

Electrode junction is dry – Push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.

Samples and standards at different temperatures – Allow solutions to come to room temperature before measurement.

Incorrect electrode filling solution used – Refer to the Electrode Preparation section to verify the correct electrode filling solution.

Sulfide is being oxidized – Always use deaerated water when preparing sulfide standards to prevent the oxidation of sulfide. Dilute sulfide samples 1:1 with Sulfide anti-oxidant buffer as they are collected, except when using the analyte subtraction measurement technique.

Total level of dissolved species above 1 mol/L – Dilute solutions.

Meter or stirrer improperly grounded – Check meter and stirrer for grounding issues.

Magnetic stirrer generating heat – Place insulating material between the magnetic stirrer and beaker.

7. Ordering Information

Parts	Order No.
Combined Silver/Sulfide electrode with BNC connector perfectION™ comb Ag^+/S^{2-}:	**51344700**
Combined Silver/Sulfide electrode with Lemo connector perfectION™ comb Ag^+/S^{2-} Lemo:	**51344800**
Ion Electrolyte B:	**51344751**
Ion Electrolyte C (precise Silver):	**51344752**
Ion Electrolyte A (precise Sulfide) :	**51344750**
Silver Standard Solution 1000 mg/L:	**51344770**
Sulfide Standard Solution 1000 mg/L:	**51344781**
ISA solid state ISE:	**51344760**
Removable cone:	**00022986**

8. Electrode Specifications

Membrane type

solid state

Concentration Range

Silver:	10^{-7} to 1 mol/L
	0.01 to 108'000 mg/L
Sulfide:	10^{-7} to 1 mol/L
	0.003 to 32'000 mg/L

pH Range

pH 2 to 12

Temperature Range

0 to 80 °C continuous use,
80 to 100 °C intermittent use

Electrode Resistance

Less than 1 MΩ

Reproducibility

Silver	± 2%
Sulfide	± 4%

Size

Body Diameter: 13 mm
Cap Diameter: 16 mm
Cable Length: 1.2 m

* Specifications are subject to change without notice

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For more information