User Guide

Silver/Sulfide Ion Selective Electrode

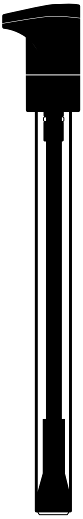

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Table of Contents

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. Silver/sulfide electrodes measure free silver 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.

Technical Support Chemists can be consulted for assistance and troubleshooting advice. Within the United States call 1.800.225.1480 and outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized dealer. For the most current contact information, visit www.thermo.com/contactwater.

For the latest application and technical resources for Thermo Scientific Orion products, visit www.thermo.com/waterapps.

Silver/Sulfide ionplus® Sure-Flow® Solid State Combination ISE, Cat. No. 9616BNWP

The silver/sulfide combination electrode has the sensing and reference half-cells built into one electrode, which decreases the amount of required solutions and reduces waste. The built-in Sure-Flow reference junction prevents electrode clogging and provides fast and stabile readings. The silver/sulfide combination electrode is available with a waterproof BNC connector, Cat. No. 9616BNWP. Electrodes with a waterproof BNC connector can be used on any ISE or mV meter with a BNC connection.

Silver/Sulfide Solid State Half-Cell ISE, Cat. No. 9416BN and 9416SC

The silver/sulfide half-cell electrode must be used with the double junction reference electrode, Cat. No. 900200. The silver/sulfide half-cell electrode is available with a BNC connector, Cat. No. 9416BN, and a screw cap connector, Cat. No. 9416SC. Electrodes with a screw cap connector require a separate cable.

Required Equipment

1. Thermo Scientific Orion ISE meter, such as the 4-Star pH/ISE meter or 5-Star pH/ISE/DO/conductivity meter; equivalent ISE meter; or mV meter with a 0.1 mV resolution.

   Silver/sulfide electrodes can be used on any ISE or mV meter with a BNC connection. The electrodes can also be used on meters with a variety of inputs when an adapter cable is used. Visit www.thermo.com/water for details.

2. Thermo Scientific Orion silver/sulfide electrode.

   The 9416BN and 9416SC silver/sulfide half-cell electrodes require a separate reference electrode, Cat. No. 900200.

3. Magnetic stirrer or Thermo Scientific Orion stirrer probe, Cat. No. 096019. The stirrer probe can be used with 3-Star, 4-Star and 5-Star benchtop meters.

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

5. Distilled or deionized water.

6. Silver/sulfide electrode filling solution.

   Use Optimum Results™ B filling solution, Cat. No. 900062, for the 9616BNWP silver/sulfide combination electrode. Optimum Results B filling solution is supplied with the electrode and can be used for most silver or sulfide measurements and titrations.

   Optimum Results A and Optimum Results C filling solutions may also be used with the 9616BNWP silver/sulfide combination electrode. They provide an optimum temperature and time response when sample temperatures vary. Optimum Results A filling solution, Cat. No. 900061, is recommended for precise sulfide measurements. Optimum Results C filling solution, Cat. No. 900067, is recommended for precise silver measurements.

   Use inner chamber filling solution, Cat. No. 900002, and outer chamber filling solution, Cat. No. 900003, for the double junction reference electrode that is used with the 9416BN and 9416SC silver/sulfide half-cell electrodes.

7. Silver ionic strength adjuster (ISA), Cat. No. 940011.
   ISA provides a constant background ionic strength for samples and standards.

8. Silver calibration standards.

   0.1 M 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 grams 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 ppm 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 grams 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.

9. Sulfide anti-oxidant buffer (SAOB II) reagent pack, Cat. No. 941609. All water must be deaerated to prevent oxidation.

10. Sulfide calibration standards and 0.1 M lead perchlorate solution, Cat. No. 948206, for titrations of sulfide standard solutions. All water must be deaerated to prevent oxidation.

    Saturated sodium sulfide stock solution – Dissolve 100 grams 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 pipeting 10 mL of the stock solution into a 1 L volumetric flask. Add 500 mL of SAOB II reagent 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 M lead perchlorate, using the silver/sulfide electrode as the endpoint indicator and calculating:

    $$\mathbf{C = 3206\ (V_t / V_s)}$$

    C = concentration, ppm 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, pipet 10 mL of the standard into a 100 mL volumetric flask, add 45 mL SAOB II and dilute to volume with distilled, deaerated water.

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 10^{-2} M silver standard (1079 ppm silver) –** Pipet 10 mL of the 0.1 M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

2. **To prepare a 10^{-3} M silver standard (107.9 ppm silver) –** Pipet 10 mL of the 10^{-2} M standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

3. **To prepare a 10^{-4} M silver standard (10.79 ppm silver) –** Pipet 10 mL of the 10^{-3} M 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 100 ppm silver standard from a 10790 ppm silver standard:

C_1 = 10790 ppm silver

V_1 = unknown

C_2 = 100 ppm silver

V_2 = 100 mL

$10790 \text{ ppm} * V_1 = 100 \text{ ppm} * 100 \text{ mL}$

$V_1 = (100 \text{ ppm} * 100 \text{ mL}) / 10790 \text{ ppm} = 0.93 \text{ mL}$

Electrode Setup

Electrode Preparation

9416BN and 9416SC Silver/Sulfide Half-Cell Electrode – Remove the protective shipping cap from the sensing element and save the cap for storage.

900200 Double Junction Reference Electrode – Prepare the reference electrode according to the reference electrode user guide. Fill the reference electrode with inner chamber filling solution, Cat. No. 900002, and outer chamber filling solution, Cat. No. 900003.

9616BNWP Silver/Sulfide Combination Electrode – Remove the protective shipping cap from the sensing element and save the cap for storage. Fill the electrode with Optimum Results B filling solution, Cat. No. 900062.

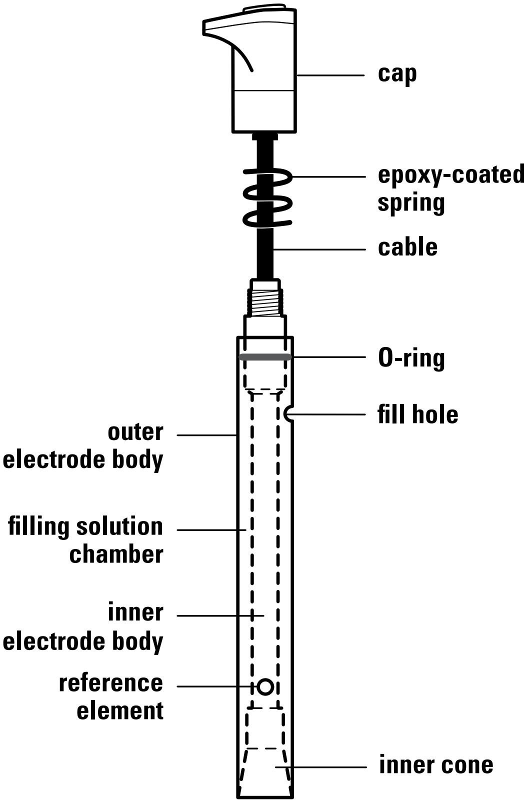
Optimum Results A and Optimum Results C filling solutions may also be used with the 9616BNWP silver/sulfide combination electrode. They provide an optimum temperature and time response when sample temperatures vary. Optimum Results A filling solution, Cat. No. 900061, is recommended for precise sulfide measurements. Optimum Results C filling solution, Cat. No. 900067, is recommended for precise silver measurements.

9616BNWP Silver/Sulfide Combination Electrode Filling Instructions

1. Lift the flip spout on the filling solution bottle to a vertical position.
2. Insert the spout into the filling 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 top O-ring and then 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, check if the O-ring is moist and repeat steps 2 through 4 until the sleeve is in 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 one inch above the level of sample in the beaker to ensure a proper flow rate. The fill hole should always be open when taking measurements.*

Figure 1
9616BNWP Silver/Sulfide Combination Electrode



Checking Electrode Operation (Slope)

These are general instructions that can be used with most meters to check the electrode operation. Refer to the meter user guide for more specific information.

This procedure measures electrode slope. Slope is defined as the change in millivolts observed with every tenfold change in concentration. Obtaining the slope value provides the best means for checking 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 a meter with a mV mode. Set the meter to the mV mode.

3. For silver analysis – Add 100 mL of distilled water and 2 mL of silver ISA, Cat. No. 940011, to a 150 mL beaker. Stir the solution thoroughly. Use a 0.1 M or 1000 ppm silver standard in the following steps.

   For sulfide analysis – Add 50 mL of distilled water and 50 mL of SAOB II reagent, Cat. No. 941609, to a 150 mL beaker. Stir the solution thoroughly. Use a 100 ppm sulfide standard in the following steps.

4. Rinse the electrode with distilled water and place the electrode into the solution prepared in step 3.

5. Pipet 1 mL of the standard into the beaker and stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.

6. Pipet 10 mL of the same standard into the same beaker and stir the solution 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.

Measurement Units

Silver or sulfide concentration can be measured in moles per liter (M), parts per million (ppm) or any convenient concentration unit.

Table 1
Concentration Unit Conversion Factors

Moles/Liter (M) Silver	ppm Silver
10^{-1}	10790
10^{-2}	1079
9.27×10^{-3}	1000
10^{-3}	107.9
10^{-4}	10.79
9.27×10^{-6}	1

Moles/Liter (M) Sulfide	ppm Sulfide
10^{-1}	3206
3.12×10^{-2}	1000
10^{-2}	320.6
10^{-3}	32.06
10^{-4}	3.206
3.12×10^{-5}	1

Sample Requirements

The epoxy body of the silver/sulfide electrode is resistant to damage by aqueous solutions. The electrode may be used intermittently in solutions that contain methanol, benzene or acetone. Contact Technical Support for information on using the electrode for specific applications.

Samples and standards should be at the same temperature. A 1 °C difference in temperature for a 10^{-3} M silver solution will give rise to about a 2% error and a 1 °C difference in temperature for a 10^{-3} M sulfide solution will give rise to about a 4% error.

The solution temperature must be less than 80 °C.

Silver samples must be acidified to below pH 8 with 1 M HNO_3 to avoid a reaction with hydroxide ions.

Sulfide samples must be buffered above pH 12 with SAOB II 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

- Stir all standards and samples at a uniform, moderate rate. Place a piece of insulating material, such as Styrofoam or cardboard, between the magnetic stir plate and beaker to prevent measurement errors from the transfer of heat to the sample.

- Always use freshly prepared 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 reach the same temperature for precise measurements.

- Concentrated samples (greater than 10^{-1} M silver or sulfide) should be diluted before measurement.

- 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 and gently tapping it.

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

- The fill hole cover must be open during measurements to ensure a uniform flow of filling solution.

- If the combination electrode is used and 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.

Electrode Storage

Silver/Sulfide Half-Cell Electrode Storage, Cat. No. 9416BN and 9416SC

The silver/sulfide half-cell electrode should be rinsed thoroughly with distilled water and stored dry in the air at all times. When storing the electrode for long periods of time, cover the sensing element with the protective shipping cap.

Double Junction Reference Electrode Storage, Cat. No. 900200

The double junction reference electrode may be stored in the outer chamber filling solution, Cat. No. 900003, between sample measurements and up to one week. The filling solution inside the electrode should not be allowed to evaporate, as crystallization will result.

For storage longer than one week, drain the reference electrode, flush the inside with distilled water and store the electrode dry.

Silver/Sulfide Combination Electrode Storage, Cat. No. 9616BNWP

For storage between measurements and up to one week, store the electrode in a 4 M potassium chloride solution. Do not add ISA to the storage 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.

Electrode Maintenance

Polishing the Silver/Sulfide Combination Electrode and Silver/Sulfide Half-Cell 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 a polishing strip, Cat. No. 948201. The polishing strip can also be used if the sensing surface has been etched or chemically poisoned.

1. Cut off about an inch 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 soak the electrode in a 1 ppm or 10^{-5} M silver standard for ten minutes.

Silver/Sulfide Combination Electrode and Double Junction Reference Electrode Flushing

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 electrode. 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 replenish the lost filling solution.

Disassembling and Reassembling 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 electrode.

2. Unscrew the cap counterclockwise and then slide the cap and spring up the cable.

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

4. Grasp the inner 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, as it will damage to the pellet. Rinse the outside of the electrode body and the entire sleeve with distilled water. Allow it to air dry.

5. 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.

6. 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.

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

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 SAOB II reagent is added to all solutions to ensure that samples and standards have similar ionic strength.

Low Level Calibration is a similar to the direct calibration technique. This method is recommended when the expected sample concentration is less than 0.5 ppm or 4.6×10^{-6} M silver. A minimum three point calibration is recommended to compensate for the electrode's non-linear response at these concentrations. A special calibration standard preparation procedure is the best means of preparing low level calibration standards.

Incremental Techniques provide a useful method for measuring samples, since a calibration is not required. 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 to 100 times) excess of complexing agents. As in direct calibration, any convenient concentration unit can be used.

> **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.
>
> **Analate 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, but are more time-consuming. For sulfide measurements, titrations produce an extremely sharp endpoint, even at low levels of sulfide. Titration is the recommended measurement method for sulfide samples.

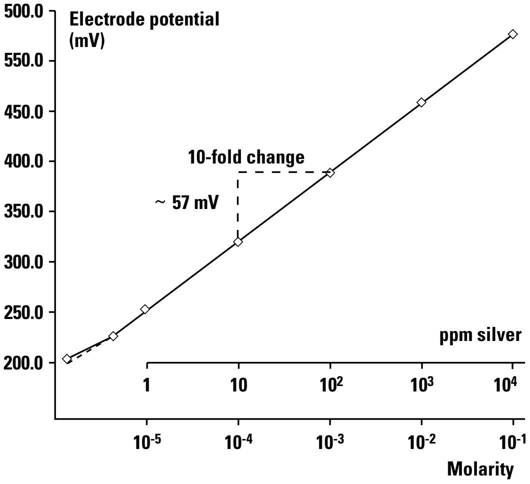
Indicator Titration Method is useful for measuring ionic species where an ion specific electrode does not exist. With this method the electrodes sense a reagent species that has been added to the sample before titration. The silver/sulfide electrode may be used in indicator titrations for many different metal ions. A procedure for measuring low levels of cyanide ion down to 0.03 ppm, using the silver electrode, is described in this user guide.

Silver Direct Calibration

Typical Silver Direct 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. These direct calibration procedures are given for concentrations in the region of linear electrode response. Low level measurement procedures are given in a following section for measurements in the non-linear electrode region.

Figure 2
Typical Silver Direct Calibration Curve



Silver Direct Calibration Overview

The following direct measurement procedures are recommended for moderate to high level measurements. Samples must be in the linear range of the electrode – greater than 0.5 ppm or 4.6×10^{-6} M silver. A two point calibration is sufficient, although more points can be used. When using an ISE meter, sample concentrations can be read directly from the meter. When using a mV meter, a calibration curve can be prepared on semi-logarithmic graph paper, or a linear regression (against logarithmic concentration values) can be performed using a spreadsheet or graphing program.

Calibration Hints

- Standard concentrations should bracket the expected sample concentrations.

- Always add 2 mL of ISA, Cat. No. 940011, per 100 mL of standard or sample.

- For high ionic strength samples that have an ionic strength of 0.1 M or greater, prepare standards with a background composition similar to that of the samples, or measure the samples using the known addition method.

- During calibration, measure the least concentrated standard first, and work up to the most concentrated standard.

- Store all silver samples and standards away from light.

Silver Direct Calibration Setup

1. Prepare the electrode as described in the **Electrode Preparation** section. If using the 9616BNWP combination silver/sulfide electrode, fill the electrode with Cat. No. 900062 or Cat. No. 900067. If using the 9416BN or 9416SC half-cell silver/sulfide electrode with the 900200 reference electrode, fill the reference electrode with inner chamber filling solution, Cat. No. 900002, and outer chamber filling solution, Cat. No. 900003.

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.

Silver Direct Calibration Procedure Using a Meter with an ISE Mode

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

1. Add 100 mL of the less concentrated standard and 2 mL of ISA to a 150 mL beaker and stir the solution thoroughly.

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

3. Add 100 mL of the more concentrated standard and 2 mL of ISA to a second 150 mL beaker and stir the solution thoroughly.

4. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the more concentrated standard. Wait for a stable reading and 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 and 60 mV when the standards are between 20 and 25 °C.

6. Add 100 mL of sample and 2 mL of ISA to a clean 150 mL beaker and stir the solution thoroughly.

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

Note: *Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.*

Silver Direct Calibration Procedure Using a Meter with a mV Mode

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

1. Set the meter to the mV mode.

2. Add 100 mL of the less concentrated standard and 2 mL of ISA to a 150 mL beaker and stir the solution thoroughly.

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

4. Add 100 mL of the more concentrated standard and 2 mL of ISA to a second 150 mL beaker and stir the solution thoroughly.

5. Rinse the electrode with distilled water, blot it dry and place it 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. Add 100 mL of sample and 2 mL of ISA to a clean 150 mL beaker and stir the solution thoroughly.

8. Rinse the electrode with distilled water, blot it dry and place it into the beaker. 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.

Note: *Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.*

Silver Small Volume Direct Calibration

Take advantage of special design features available with the 9616BNWP ionplus combination silver/sulfide electrode to meet your measuring needs. Due to the Sure-Flow reference, this electrode is able to measure sample volumes as small as 5 mL using a modified direct measurement procedure. Because less solution volume is required, the chemical usage of silver or sulfide standards and ISA is reduced. This method is also convenient when making field measurements, since the 9616BNWP combination silver/sulfide electrode does not require a separate reference electrode. All samples should have a concentration greater than 1 ppm or 10^{-5} M silver. A two point calibration is sufficient, although more points can be used. The following procedure recommends using 25 mL of sample. Smaller sample volumes can be used, as long as the final volume of solution is sufficient to cover the bottom of the electrode.

Calibration Hints

- Use the 9616BNWP ionplus combination silver/sulfide electrode.
- Standard concentrations should bracket the expected sample concentrations.
- Always keep the ratio of standard or sample to ISA at 50:1.
- For high ionic strength samples that have an ionic strength of 0.1 M or greater, prepare standards with a background composition similar to that of the samples, or measure the samples using the known addition method.
- During calibration, measure the least concentrated standard first, and work up to the most concentrated standard.
- Calibrate with the same volume of standard as the volume of sample that is available for analysis.

Silver Small Volume Direct Calibration Setup

1. Prepare the 9616BNWP combination silver/sulfide electrode as described in the **Electrode Preparation** section and fill the electrode with Optimum Results B filling solution, Cat. No. 900062, or Optimum Results C filling solution, Cat. No. 900067.

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.

Silver Small Volume Direct Calibration Procedure Using a Meter with an ISE Mode

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

1. Add 25 mL of the less concentrated standard and 0.5 mL of ISA to a 50 mL beaker and swirl the solution to mix.
2. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the less concentrated standard. Wait for a stable reading and adjust the meter to display the value of the standard, as described in the meter user guide.
3. Add 25 mL of the more concentrated standard and 0.5 mL of ISA to a second 50 mL beaker and swirl the solution to mix.
4. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the more concentrated standard. Wait for a stable reading and 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 and 60 mV when the standards are between 20 and 25 °C.
6. Add 25 mL of sample and 0.5 mL of ISA to a clean 50 mL beaker and swirl the solution to mix.
7. Rinse the electrode with distilled water, blot it dry and place it into the sample. The concentration of the sample will be displayed on the meter.

Note: *Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.*

Silver Small Volume Direct Calibration Procedure Using a Meter with a mV Mode

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

1. Set the meter to the mV mode.

2. Add 25 mL of the less concentrated standard and 0.5 mL of ISA to a 50 mL beaker and swirl the solution to mix.

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

4. Add 25 mL of the more concentrated standard and 0.5 mL of ISA to a second 50 mL beaker and swirl the solution to mix.

5. Rinse the electrode with distilled water, blot it dry and place it 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. Add 25 mL of sample and 0.5 mL of ISA to a clean 50 mL beaker and swirl the solution to mix.

8. Rinse the electrode with distilled water, blot it dry and place it into the beaker. 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.

Note: *Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.*

Silver Low Level Calibration

These procedures are for solutions that have a silver concentration of less than 0.5 ppm or 4.6×10^{-6} M silver. For solutions low in silver but high in total ionic strength (greater than 10^{-1} M), perform the same procedure by preparing a calibrating solution with a composition similar to the sample.

Accurate results require 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.

Silver 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 pipeting 20 mL of the ISA, Cat. No. 940011, into a 100 mL volumetric flask and diluting to the mark with distilled water. Use low level ISA for low level measurements only.
4. Select a standard solution. Use either a 10 ppm silver standard or a 10^{-4} M silver standard.

   To prepare the 10 ppm silver standard, pipet 10 mL of the 1000 ppm silver standard into a 1 liter volumetric flask. Dilute to the mark with distilled water and mix the solution thoroughly.

   To prepare the 10^{-4} M silver standard, pipet 1 mL of the 0.1 M silver standard into a 1 liter volumetric flask. Dilute to the mark with distilled water and mix the solution thoroughly.

Silver Low Level Calibration and Measurement

1. Add 100 mL of distilled water and 1 mL of low level ISA to a 150 mL beaker.

2. Rinse the electrode with distilled water, blot it dry and place it into the beaker. Stir the solution thoroughly.

3. Add increments of the 10 ppm or 10^{-4} M silver standard to the beaker using the steps outlined in **Table 2**. 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 2
Calibration Curve For Low Level Calibrations
Additions of standard to 100 mL distilled water and 1 mL low level ISA solution.

Step	Pipet Size	Volume Added	Concentration ppm	M
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}

Silver Known Addition

Known addition is a convenient technique for measuring samples in the linear range of the electrode (greater than 0.5 ppm 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 results require 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.
- With double or multiple known addition, the final addition should be 10 to 100 times the sample concentration.
- Add 2 mL of ISA to every 100 mL of sample before analysis.

Silver 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 3** 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 3
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

Silver 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. Pipet 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.

Silver 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, set the meter to read 0.0 mV. If the reading cannot be adjusted to 0.0 mV, record the actual mV value.

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

5. When a stable reading is displayed, record the mV value. If the meter could not be set to 0.0 mV in step 3, 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:

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

   $C_{standard}$ = 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.

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

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

Calculating Known Addition for Samples using Lotus, Excel, or Quattro Spreadsheets

If it is more convenient, a simple spreadsheet can be set up to calculate the known addition results, using any ratio of sample to addition. A typical worksheet is shown in **Table 4**. The numbers shown are examples, but the formulas and their locations should be copied exactly.

Table 4
Known Addition Calculations using Lotus, Excel, or Quattro Spreadsheets

A	B	C
1		Enter Value
2	Volume of sample and ISA (mL)	102
3	Volume of addition (mL)	10
4	Concentration of addition	10
5	Volume of sample	100
6	Initial mV reading	45.3
7	Final mV reading	63.7
8	Electrode slope	59.2
9		
10		Derived Values
11	Delta E	+C7 - C6
12	Solution volume ratio	+C3/C2
13	Antilog term	+10^ (C11/C8)
14	Sample volume ratio	+C2/C5
15	Q term	+C12*C14/(((1+C12)*C13)-1)
16	Calculated initial concentration in same units as addition	+C15*C4

Note: *For Excel, use = instead of + at start of formulas.*

Table 5
Q Values for a 10% volume change,
slopes (in column heading) are in units of mV/decade

ΔE	Q Concentration Ratio			
	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

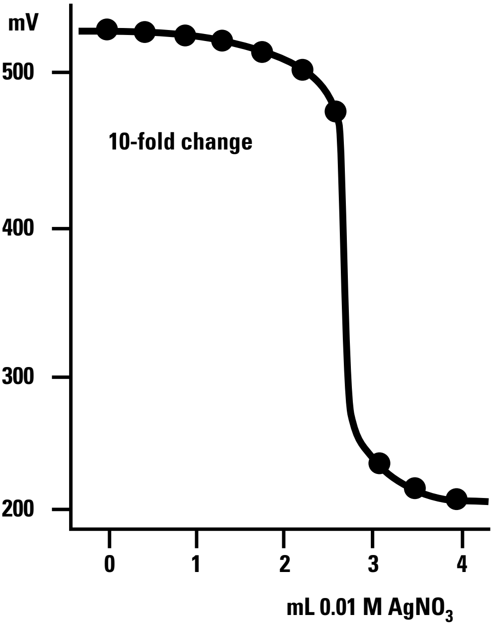
ΔE	Q Concentration Ratio			
	57.2	**58.2**	**59.2**	**60.1**
14.0	0.1076	0.1098	0.1120	0.1140
14.2	0.1058	0.1080	0.1102	0.1121
14.4	0.1041	0.1063	0.1084	0.1103
14.6	0.1024	0.1045	0.1067	0.1086
14.8	0.1008	0.1029	0.1050	0.1069
15.0	0.0992	0.1012	0.1033	0.1052
15.5	0.0953	0.0973	0.0994	0.1012
16.0	0.0917	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
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

ΔE	**Q Concentration Ratio**			
	57.2	**58.2**	**59.2**	**60.1**
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
49.5	0.0142	0.0147	0.0153	0.0158
50.0	0.0139	0.0144	0.0150	0.0155
50.5	0.0135	0.0141	0.0146	0.0151
51.0	0.0132	0.0138	0.0143	0.0148
51.5	0.0129	0.0135	0.0140	0.0145
52.0	0.0126	0.0132	0.0137	0.0142
52.5	0.0124	0.0129	0.0134	0.0139
53.0	0.0121	0.0126	0.0131	0.0136
53.5	0.0118	0.0123	0.0128	0.0133
54.0	0.0116	0.0120	0.0125	0.0130
54.5	0.0113	0.0118	0.0123	0.0127
55.0	0.0110	0.0115	0.0120	0.0125
55.5	0.0108	0.0113	0.0118	0.0122
56.0	0.0106	0.0110	0.0115	0.0119
56.5	0.0103	0.0108	0.0113	0.0117
57.0	0.0101	0.0106	0.0110	0.0114
57.5	0.0099	0.0103	0.0108	0.0112
58.0	0.0097	0.0101	0.0105	0.0110
58.5	0.0095	0.0099	0.0103	0.0107
59.0	0.0093	0.0097	0.0101	0.0105
59.5	0.0091	0.0095	0.0099	0.0103
60.0	0.0089	0.0093	0.0097	0.0101

Low Level Chloride Titration

The silver/sulfide electrode makes a highly sensitive endpoint detector for titration of silver samples with a halide standard and titration of halides with a silver standard. The low-level chloride titration is an example of a halide titration with a silver standard. Titrations are more time consuming than direct electrode measurement, but results are more accurate and reproducible. With careful technique, titrations accurate to ± 0.1% of the total chloride ion concentration of the sample can be performed.

Figure 3
Typical Titration of 25 mL of 1 x 10^{-3} M Chloride Sample (Before Dilution) with 0.01 M $AgNO_3$



Low Level Chloride Titration 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 M silver standard solution.

   Low level chloride titrant, 2.82×10^{-3} M $AgNO_3$ equivalent to 100 ppm 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 grams 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 Titration Procedure

1. Place 50 mL of sample into a 150 mL beaker. Place the electrode in the sample and stir the solution thoroughly.

2. Using a 10 mL burette, add increments of titrant and plot the electrode potential against mL of titrant added. The endpoint is the point of greatest slope (inflection point). See **Figure 3**.

3. Calculate the sample concentration before dilution:

   $$\mathbf{C_{sample} = C_t (V_t / V_{sample})}$$

   C_{sample} = sample concentration
   C_t = titrant concentration
   V_{sample} = sample volume
   V_t = titrant volume added at endpoint.

Low Level Cyanide Indicator Titration

The silver/sulfide electrode can be used for cyanide measurements down to 0.03 ppm 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 the 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.

Low Level Cyanide Indicator Titration Setup

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

2. Connect the electrode to the meter.

3. Prepare the following solutions:

   Ethylemediamine – Anhydrous (98% purity or better) for the removal of formaldehyde.

   Silver nitrate titrant (1 mL = 1 mg CN^-) – Crush about 5 grams of reagent-grade silver nitrate ($AgNO_3$) crystals and dry at 150 °C for 1 hour. Add 3.265 grams 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 grams 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 grams of reagent-grade di-sodium hydrogen phosphate ($Na_2HPO_4 \bullet 7H_2O$) and 80 mL of distilled water to a 100 mL volumetric flask. Stir the solution for 30 minutes. Add 2.2 grams of reagent-grade sodium hydroxide (NaOH), 0.1 gram of silver potassium cyanide [$KAg(CN)_2$] and 3.4 mL of ethylemediamine 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 ppm stock solution, 1 mL equals approximately 1 mg of CN^-) – Dissolve approximately 2 grams of reagent-grade sodium hydroxide (NaOH) and 2.51 grams of reagent-grade potassium cyanide (KCN) in 1 liter 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. Pipet 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. Fill a 25 mL burette with the silver nitrate titrant.

3. Add 0.5 to 1 mL increments of the silver nitrate titrant in the beginning of the titration and 0.1 to 0.25 mL increments in the region of the endpoint. Continue the titration 3 to 4 mL past the endpoint.

4. Record the solution potential after each addition of titrant and plot the mL of titrant added versus the mV readings on standard graph paper. The point of inflection is the endpoint.

5. Prepare a blank solution by dissolving 2 grams of reagent-grade NaOH in 1 liter of distilled water. Titrate 20 mL of the blank solution using the instructions in steps 1 through 4.

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

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

   A = mL of titrant added at the endpoint (cyanide solution)
   B = mL of titrant added at the endpoint (blank)
   C = mL of cyanide stock solution used for the titration

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

8. Prepare a 100 ppm cyanide standard daily by diluting the stock solution with the NaOH diluent. The 100 ppm solution is prepared by pipeting 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 (ppm) of cyanide stock solution.

   V = 10000 / D

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

Low Level Cyanide Indicator Titration Procedure Using a Meter with an ISE Mode

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

1. Use the standards prepared in step 9 of the **Standardization of KCN Stock Solution** section. Standards should be at the same temperature as the samples. Measure 100 mL of each standard and the 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 it into the beaker with the less concentrated standard. Wait for a stable reading and 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 it into the beaker with the next standard. Wait for a stable reading and adjust the meter to display the value of the second 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 -116 to -122 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.

Low Level Cyanide Indicator Titration Procedure Using a Meter with a mV Mode

1. Use the standards prepared in step 9 of the **Standardization of KCN Stock Solution** section. Standards should be at the same temperature as the samples. Measure 100 mL of each standard and the 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 it into the beaker with the less 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 it 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.

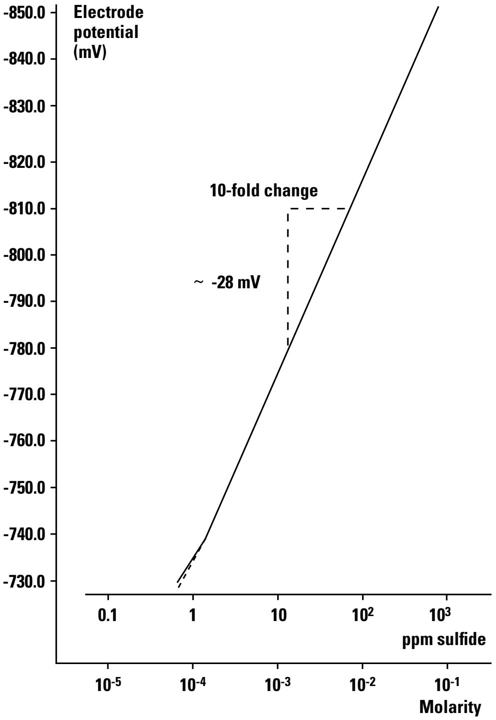
7. Using the calibration curve prepared in step 5, determine the concentration of the sample.

Sulfide Direct Calibration

Typical Sulfide Direct 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. These direct calibration procedures are given for concentrations in the region of linear electrode response. Low level measurement procedures are given in a following section for measurements in the non-linear electrode region.

Figure 4
Typical Sulfide Direct Calibration Curve



Sulfide Direct Calibration Overview

The following direct measurement procedures are recommended for moderate to high level measurements. Samples must be in the linear range of the electrode – greater than 0.32 ppm or 1 x 10^{-5} M sulfide. A two point calibration is sufficient, although more points can be used. When using an ISE meter, sample concentrations can be read directly from the meter. When using a mV meter, a calibration curve can be prepared on semi-logarithmic graph paper, or a linear regression (against logarithmic concentration values) can be performed using a spreadsheet or graphing program.

Calibration Hints

- Standard concentrations should bracket the expected sample concentrations.
- Always use deaerated water when preparing sulfide standards to prevent the oxidation of sulfide.
- Always add the SAOB II reagent, Cat. No. 941609, to the standard or sample in a 1:1 ratio.
- Add the SAOB II reagent to sulfide samples as they are collected, except when using the sulfide analate subtraction technique. If samples have been preserved with SAOB II, do not add more SAOB II before measuring the samples.
- For high ionic strength samples that have an ionic strength of 0.1 M or greater, prepare standards with a background composition similar to that of the samples, or measure the samples using the known addition method.
- During calibration, measure the least concentrated standard first, and work up to the most concentrated standard.

Sulfide Direct Calibration 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.

Sulfide Direct Calibration Procedure Using a Meter with an ISE Mode

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

1. Add 25 mL of the less concentrated standard and 25 mL of SAOB II to a 150 mL beaker and stir the solution thoroughly.

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

3. Add 25 mL of the more concentrated standard and 25 mL of SAOB II to a second 150 mL beaker and stir the solution thoroughly.

4. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the more concentrated standard. Wait for a stable reading and 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 and -30 mV when the standards are between 20 and 25 °C.

6. Add 25 mL of sample and 25 mL of SAOB II to a clean 150 mL beaker and stir the solution thoroughly.

   Note*: If the sample was preserved by adding SAOB II, do not add more SAOB II before measuring the sample.*

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

Note: *Other solution volumes may be used, as long as the ratio of solution to SAOB II remains 1:1.*

Sulfide Direct Calibration Procedure Using a Meter with a mV Mode

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

1. Set the meter to the mV mode.

2. Add 25 mL of the less concentrated standard and 25 mL of SAOB II to a 150 mL beaker and stir the solution thoroughly.

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

4. Add 25 mL of the more concentrated standard and 25 mL of SAOB II to a second 150 mL beaker and stir the solution thoroughly.

5. Rinse the electrode with distilled water, blot it dry and place it 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. Add 25 mL of sample and 25 mL of SAOB II to a clean 150 mL beaker and stir the solution thoroughly.

   Note*: If the sample was preserved by adding SAOB II, do not add more SAOB II before measuring the sample.*

8. Rinse the electrode with distilled water, blot it dry and place it into the beaker. 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.

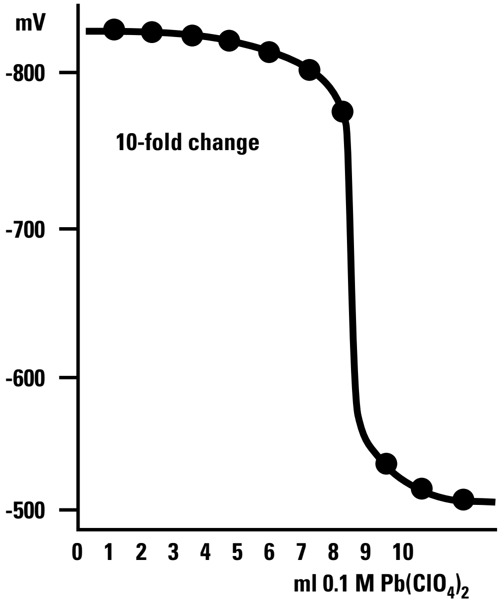
Note: *Other solution volumes may be used, as long as the ratio of solution to SAOB II remains 1:1.*

Sulfide Titration

Titration is the recommended measurement technique for sulfide samples. For accurate results, the titration must be used for solutions that have a sulfide concentration of less than 0.32 ppm or 1 x 10^{-5} M 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. Titrations are more time consuming than direct electrode measurement, but results are more accurate and reproducible. With careful technique, titrations accurate to ± 0.1% of the total sulfide ion concentration of the sample can be performed.

Figure 5
Typical Titration of 25 mL of 0.03 M Sulfide Sample (Before Dilution) with 0.1 M $Pb(ClO_4)_2$



Sulfide Titration Setup

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

2. Connect the electrode to the meter.

3. Prepare a lead perchlorate solution that is 10 to 20 times more concentrated than the sample by diluting the 0.1 M lead perchlorate standard solution, Cat. No. 948206.

Sulfide Titration Procedure

1. Add 25 mL of sample and 25 mL of SAOB II to a clean 150 mL beaker. Place the electrode in the sample and stir the solution thoroughly.

2. Using a 10 mL burette, add increments of titrant and plot the electrode potential against mL of titrant added. The endpoint is the point of greatest slope (inflection point). See **Figure 5**.

3. Calculate the sample concentration before dilution:

   $$\mathbf{C_{sample} = C_t \, (V_t \, / \, V_{sample})}$$

   C_{sample} = sample concentration
   C_t = titrant concentration
   V_{sample} = sample volume
   V_t = titrant volume added at endpoint.

Sulfide Analate Subtraction

Analate 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 SAOB II). All samples and standards should be at the same temperature. All concentration units are in moles per liter (M).

Sulfide Analate Subtraction Setup

Note: *Do not dilute samples with SAOB II 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 of the expected sample sulfide concentration by diluting the 0.1 M silver nitrate standard. Add 2 mL of ISA, Cat. No. 940011, 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.

Analate Subtraction Using a Meter with a Known Subtraction Mode

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

1. Set the meter to measure in the known subtraction mode.
2. Measure 100 mL of the silver standard and 2 mL of ISA and pour the solutions into a beaker. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the silver standard and ISA.
3. When a stable reading is displayed, set the meter as described in the meter user guide, if required.
4. Pipet 10 mL of the sulfide sample into the silver standard. Stir the solution thoroughly.
5. When a stable reading is displayed, record the sample concentration.

Analate Subtraction Using a Meter with a Millivolt Mode

1. Set the meter to the millivolt mode.

2. Measure 100 mL of the silver standard and 2 mL of ISA and pour the solutions into a beaker.

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

4. Pipet 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:

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

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

Table 6
Q Values for Analate Subtraction

ΔE	Q Concentration Ratio			
	-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			
	-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

Electrode Characteristics

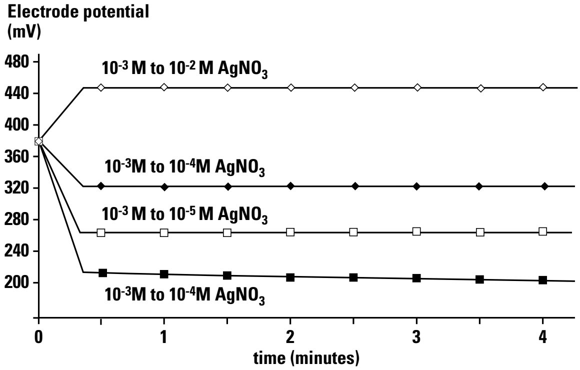
Electrode Response

The electrode potential plotted against silver concentration on semi-logarithmic paper results in a straight line 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 with a slope of about -25 to -30 mV per decade change in concentration. See **Figure 4**.

The time response of the electrode (the time required to reach 99% of the stable potential reading) varies from several seconds in concentrated solutions to several minutes near the limit of detection.

Figure 6
Typical Electrode Response to Step Changes Concentration



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} M level, a 1 °C difference in temperature results in errors greater than 2% with silver measurements and 4% 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 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 the temperature changes, the meter and electrode should be recalibrated.

The electrode can be used at temperatures from 0 to 80 °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 must be used only intermittently at solution temperatures above 80 °C.

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

If sample temperatures vary, use of the 9616BNWP combination silver/sulfide electrode is recommended. For silver measurements, Optimum Results C filling solution, Cat. No. 900067, provides optimum temperature and time response. Optimum Results C filling solution produces an isopotential point of 2 x 10^{-3} M silver. For sulfide measurements, Optimum Results A filling solution, Cat. No. 900061, will minimize junction potentials and provide optimum temperature and time response. Optimum Results A filling solution produces an isopotential point of 3 x 10^{-5} M sulfide.

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

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 between pH 2 and pH 3 with 1 M HNO_3. The sensing element of the electrode is oxidized by H_20_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 electrode performance by cleaning it. Refer to the **Electrode Maintenance** section.

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 M 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 SAOB II 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 either free silver ions or free 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 or sulfide ion in solution is described by the Nernst equation.

$$\mathbf{E = E_o + S * \log (A)}$$

E = measured electrode potential
E_o = reference potential (a constant)
A = silver or sulfide ion activity level in solution
S = electrode slope (about 57 mV per decade for silver and about -28 mV per decade for sulfide)
$S = (2.3\ R\,T) / nF$
R and F are constants, T = temperature in degrees K and
n = ionic charge

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.

$$\mathbf{A = y * C_f}$$

Ionic activity coefficients are variable and largely depend on total ionic strength. The ionic strength of a solution is determined by all of the ions present. It is calculated by multiplying the concentration of each individual ion by the square of its charge, adding all these values up and then dividing by two.

$$\textbf{Ionic strength} = \mathbf{1/2 \sum (C_i Z_i^2)}$$

C_i = concentration of ion i
Z_i = charge of ion i
$\sum$ symbolizes the sum of all the types of ions in solutions

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 concentration. Ionic strength adjustor (ISA) is added to all silver standards and samples so that the background ionic strength is high and constant relative to variable concentrations of silver. Sulfide anti-oxidant buffer (SAOB II) is added to all sulfide standards and samples to prevent oxidation, free sulfide ions from hydrogen ions and adjust the background ionic strength so that the background ionic strength is high and constant relative to variable concentrations of sulfide.

If samples have a high ionic strength (above 0.1 M), standards should be prepared with a composition similar to the samples.

Reference electrode conditions must also be considered. Liquid junction potentials arise any time when 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, the 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 is the same when the reference is in the standardizing solution as well as in the same solution; otherwise, the change in liquid junction potential will appear as an error in the measured specific ion electrode potential.

The most important variable that analysts have under their control is the composition of the liquid junction filling solution. The filling solution should be equitransferent. That is, the speed with which the positive and negative ions in the filling solution diffuse into the sample should be nearly as equal as possible. If the rate at which positive and negative charge is carried into the sample solution is equal, then no junction potential can result. Optimum Results filling solutions are specifically designed to meet all reference electrode conditions.

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

The meter is the easiest component to eliminate as a possible cause of error. Thermo Scientific Orion meters include an instrument checkout procedure and shorting cap for convenience in troubleshooting. Consult the meter 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. It the electrode fails this procedure again and the half-cell silver/sulfide electrode is being used, determine whether the silver/sulfide or reference electrode is at fault. To do this, substitute a known working electrode for the electrode in question and repeat the procedure in the **Checking Electrode Operation (Slope)** section.
6. 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.
7. 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 solution, ISA, 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 **Serial Dilution** section. 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**, **Interferences and pH Effects** 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 working with low level samples, follow the procedure in the **Low Level Calibration** section.

Assistance

After troubleshooting all components of your measurement system, contact Technical Support. Within the United States call 1.800.225.1480 and outside the United States call 978.232.6000 or fax 978.232.6031. In Europe, the Middle East and Africa, contact your local authorized dealer. For the most current contact information, visit www.thermo.com/contactwater.

For the latest application and technical resources for Thermo Scientific Orion products, visit www.thermo.com/waterapps.

Warranty

For the most current warranty information, visit www.thermo.com/water.

Troubleshooting Checklist

- No electrode filling solution added – Fill the electrode with filling solution up to the fill hole. Refer to the **Electrode Preparation** section for details.

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

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

- No reference electrode present – The 9416BN and 9416SC silver/sulfide half-cell electrodes require a separate reference electrode, Cat. No. 900200.

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

- Sensing element is dirty or etched – Refer to the **Electrode Maintenance** section for cleaning instructions.

- Standards are contaminated or made incorrectly – Prepare fresh standards. Refer to the **Measurement Hints** and **Analytical Techniques** sections.

- ISA not used or incorrect ISA used for silver measurements – ISA must be added to all silver standards and samples. Refer to the **Required Equipment** section for information on ISA.

- ISA added to silver standards, but not silver samples – Add the same proportion of ISA to all silver standards and samples.

- SAOB II not used or incorrect SAOB II used for sulfide measurements – SAOB II must be added to all sulfide standards and samples. Refer to the **Required Equipment** section for information on SAOB.

- SAOB II added to sulfide standards, but not sulfide samples – Add the same proportion of SAOB II to all sulfide standards and samples.

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

- Samples and standards at different temperatures – Allow solutions to reach the same temperature.

- Air bubble on sensing element – Remove air bubble by reimmersing the electrode in solution.

- Electrode not properly connected to meter – Unplug and reconnect the electrode to the meter.

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

- Static electricity present – Wipe plastic parts on the meter with a detergent solution.

- Defective meter – Check the meter performance. See the meter user guide.

Ordering Information

Cat. No.	Description
9616BNWP	Silver/sulfide ionplus Sure-Flow combination electrode, waterproof BNC connector
900062	Optimum Results B electrode filling solution, 5 x 60 mL bottles, for most silver or sulfide measurements and titrations
900061	Optimum Results A electrode filling solution, 5 x 60 mL bottles, for precise sulfide measurements and titrations
900067	Optimum Results C electrode filling solution, 5 x 60 mL bottles, for precise silver measurements and titrations
9416BN	Silver/sulfide half-cell electrode, BNC connector (requires separate reference electrode)
9416SC	Silver/sulfide half-cell electrode, screw cap connector (requires separate reference electrode)
900200	Double junction reference electrode, pin tip connector
900002	Inner chamber filling solution for the double junction reference electrode, 5 x 60 mL bottles
900003	Outer chamber filling solution for the double junction reference electrode, 5 x 60 mL bottles
940011	ISA for silver measurements, 475 mL bottle
941609	SAOB II reagent pack for sulfide measurements, 4 x 475 mL
948206	0.1 M lead perchlorate solution, 475 mL bottle
984201	Polishing strips

Specifications

Concentration Range (Silver)

10^{-7} M to 0.1 M (0.01 ppm to 108,000 ppm)

Concentration Range (Sulfide)

10^{-7} M to 0.1 M (0.003 ppm to 32,000 ppm)

pH Range

2 to 12

Temperature Range

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

Electrode Resistance

Less than 1 megohms

Reproducibility (Silver)

± 2%

Reproducibility (Sulfide)

± 4%

Minimum Sample Size (9616BNWP)

5 mL in a 50 mL beaker

Specifications (continued)

Size– 9616BNWP

Body Diameter: 13 mm

Body Length: 110 mm

Cap Diameter: 16 mm

Cable Length: 1 meter

Size– 9416BN and 9416SC

Body Diameter: 12 mm

Body Length: 110 mm

Cap Diameter: 16 mm

Cable Length: 1 meter (9416BN only)

* *Specifications are subject to change without notice*

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