

Silver Sulphide

Silver Sulphide Ion Electrode Manual

PCE-80-SS1001

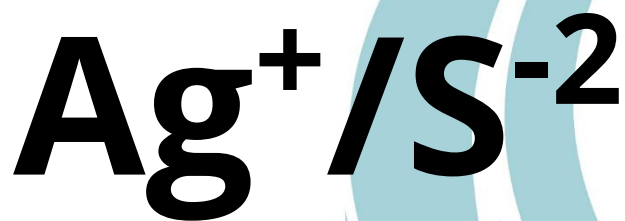




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SILVER SULPHIDE ELECTRODE MANUALGENERAL INSTRUCTIONS**Introduction**

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

Required Equipment

1. A pH/mV meter or an ion meter, either line-operated or portable.
2. Semi-logarithmic 4-cycle graph paper for preparing calibration curves when using the meter in the mV mode. Gran's plot paper (10% volume corrected) is recommended for low level chloride measurement.
3. A magnetic stirrer.
4. The MANTECH Silver/Sulfide Ion Electrode.
5. Polishing Paper, to polish dirty or etched electrode membranes.

Required Solutions

1. Deionized or distilled water for solution and standard preparation. Water used in the preparation of sulfide standards and of SAOB should also be de-aerated.

For Silver:

2. Ionic Strength Adjuster (ISA), 5M NaNO₃. To prepare this solution from your own laboratory stock, half fill a 1000 mL volumetric flask with distilled water and add 425 grams of reagent-grade sodium nitrate, NaNO₃. Swirl the flask to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend the flask several times to mix the contents.
3. Silver Standard Solution, 0.1M AgNO₃. To prepare this solution from your own laboratory stock, dry reagent-grade, pulverized silver nitrate in a laboratory oven for one hour at 150°C. Quantitatively transfer 16.99

- grams of the dried silver nitrate to a 1 liter flask containing about 500 mL of distilled water. Swirl the flask to dissolve the solid. Fill the flask to the mark with distilled water, cap and upend several times to mix the solution. Store the solution in a brown bottle, tightly capped, in a dark place.
4. Silver Standard, 1000 ppm as Ag^+ . To prepare this solution from your own laboratory stock, dry reagent- grade, pulverized silver nitrate in a laboratory oven for one hour at 150°C . Quantitatively transfer 1.57 grams of the dried silver nitrate to a 1 liter volumetric flask containing about 500 mL of distilled water. Swirl the flask to dissolve the solid. Fill the flask to the mark with distilled water, cap, and upend several times to mix the solution. Store the solution in a brown bottle, tightly capped, in a dark place.
 5. Chloride Titrant (low level), $2.82 \times 10^{-3}\text{M}$ AgNO_3 . Dry reagent-grade, pulverized silver nitrate as described above in Silver Standards. Quantitatively transfer 0.479 grams of dried silver nitrate to a 1 liter volumetric flask about half-full of distilled water. Swirl the flask to dissolve the solid. Fill to the mark with distilled water, cap, and upend several times to mix the solution. Store in a brown bottle in a dark place.

For Sulfide:

2. Sulfide Anti-Oxidant Buffer (SAOB) kit. This buffer must be used fresh and will range in color from clear to yellow-brown. It has become oxidized when it turns dark brown and should then be discarded. Store fresh SAOB in a tightly stoppered bottle. To prepare SAOB from your own stock, fill a 1 liter volumetric flask with about 500 mL of distilled, deaerated water, 200 mL of 10M NaOH, 35 grams of ascorbic acid, and 67 grams of disodium EDTA. Swirl the mixture until the solids dissolve and fill to the mark with distilled, deaerated water.
3. Lead Perchlorate Solution, 0.1M. This solution is used for titration of sulfide standards.
4. Sulfide Standard. To prepare a stock solution of saturated sodium sulfide, add about 100 grams of reagent grade $\text{Na}_2\text{S}\cdot 9\text{H}_2\text{O}$ to 100 mL of distilled, deaerated water. Shake well and let stand overnight, storing in a tightly stoppered bottle in a hood.

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

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

The calculation is as follows:

Where:

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

C = concentration as ppm sulfide

V_t = volume of titrant at endpoint

V_s = volume of standard used (10 mL)

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

GENERAL PREPARATION

Electrode Preparation

Remove the rubber caps covering the electrode tips and the rubber insert covering the filling hole of the reference electrode. Fill the combination electrode or the reference electrode with the filling solution shipped with the electrode to a level just below the fill hole. No preparation is required for a sealed reference electrode. Connect the electrodes to the proper terminals as recommended by the meter manufacturer.

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

Using silver standards:

1. To a 150-mL beaker, add 100 mL of distilled water and 2 mL of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tips into the solution.
2. Using a pipet, add 1 mL of 0.1M or 1000 ppm silver standard to the beaker. When the reading has stabilized, record the millivolt reading.

3. Using a pipet, add 10 mL of the same silver standard used above to the beaker. When the reading has stabilized, record the millivolt reading.
4. Determine the difference between the two readings. A difference of 57 ± 2 mV indicates correct electrode operation, assuming the solution temperature is between 20° and 25°C. See the **TROUBLESHOOTING** section if the potential change is not within this range.

Using sulfide stock solutions:

1. To a 150-mL beaker, add 50 mL of distilled water and 50 mL of SAOB solution. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tips into the solution.
2. Using a pipet, add 1 mL of weekly standard sulfide solution to the beaker. When the reading has stabilized, record the millivolt reading.
3. Using a pipet, add 10 mL of weekly standard sulfide used above to the beaker. When the reading has stabilized, record the millivolt reading.
4. Determine the difference between the two readings. A difference of 26 ± 2 mV indicates correct electrode operation, assuming the solution temperature is between 20° and 25°C. See the **TROUBLESHOOTING** section if the potential change is not within this range.

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

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

Using silver standards:

1. Prepare standard silver solutions whose concentrations vary by tenfold. Use either the 0.1M AgNO₃ 1000 ppm stock solutions. Use the serial dilution method for this preparation.
2. To a 150-mL beaker, add 100 mL of the lower value standard and 2 mL of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution. Assure that the meter is in the concentration mode.

3. Adjust the meter to the concentration of the standard and fix the value in the memory according to the meter manufacturer's instructions.
4. Rinse the electrodes with distilled water and blot dry.
5. To another 150-mL beaker, add 100 mL of the higher value standard and 2 mL of ISA. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution.
6. Adjust the meter to the concentration of the standard and fix the value in the memory.
7. Read the electrode slope according to the meter manufacturer's instructions. Correct electrode operation is indicated by a slope of 90-100%. See the **TROUBLESHOOTING** section if the potential is not within this range.

Using sulfide stock solutions:

1. Prepare standard sulfide solutions whose concentrations vary by tenfold. Use the serial dilution method and the weekly sulfide standard to prepare these solutions.
2. To a 150-mL beaker, add 50 mL of the lower value standard, 25 mL of SAOB, and 25 mL of distilled water. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution. Assure that the meter is in the concentration mode.
3. Adjust the meter to the concentration of the standard and fix the value in the memory according to the meter manufacturer's instructions.
4. Rinse the electrodes with distilled water and blot dry.
5. To a 150-mL beaker, add 50 mL of the higher value standard, 25 mL of SAOB, and 25 mL of distilled water. Place the beaker on a magnetic stirrer and begin stirring at a constant rate. Lower the electrode tips into the solution.
6. Adjust the meter to the concentration of the standard and fix the value in the memory.
7. Read the electrode slope according the meter manufacturer's instructions. Correct electrode operation is indicated by a slope of 90-

100%. See the **TROUBLESHOOTING** section if the slope is not within this range.

MEASUREMENT

Measuring Hints

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

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

All silver samples and silver standards should be stored away from light. Always dilute sulfide samples with SAOB (1:1) when they are collected.

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

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

Electrode Response

For low level silver measurements, use labware of plastic.

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

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

Sample Requirements

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

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



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

Samples containing silver must be below pH 8 to avoid reaction with OH^{-1} . Silver samples should be acidified with 1M HNO_3 , if necessary.

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

Units of Measurement

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

TABLE 1: Concentration Unit Conversion Factors

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

MEASUREMENT PROCEDURE

Direct Measurement

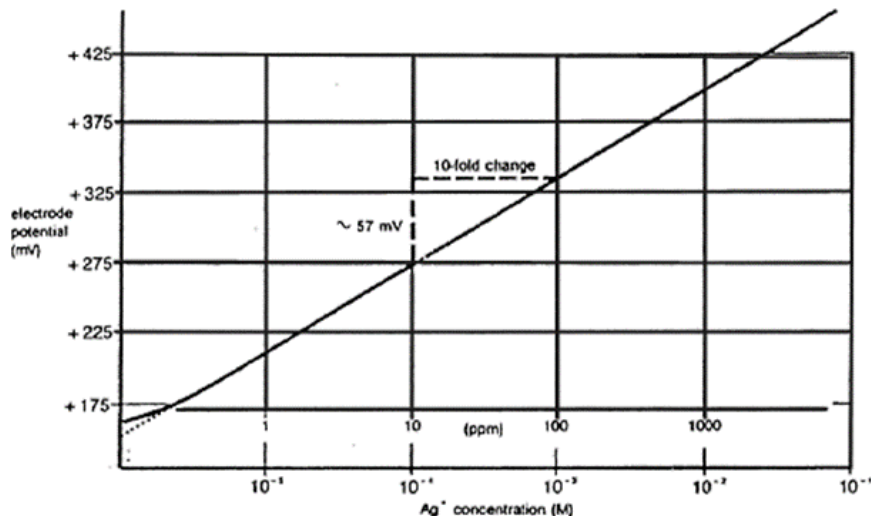
Direct measurement is a simple procedure for measuring a large number of samples. A single meter reading is all that is required for each sample. The ionic strength of samples and standards should be made the same by adjustment with SAOB for all sulfide solutions and with ISA for all silver solutions.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



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

1. By serial dilution of the 0.1M or 1000 ppm standards, prepare 10^{-2} , 10^{-3} , and 104M or 100 and 10 ppm silver standards. Add 2 mL of ISA per 100 mL of standard. Prepare standards with a composition similar to the samples if the samples have an ionic strength above 0.1M.
2. Place the most dilute solution (1.0×10^{-4} M or 10 ppm) on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tips into the solution. When the reading has stabilized, record the mV reading.
3. Place the midrange solution (1.0×10^{-3} M or 100 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrodes with distilled water, blot dry and immerse the electrode tips in the solution. When the reading has stabilized, record the mV reading.
4. Place the most concentrated solution (1.0×10^{-2} M or 1000 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrodes with distilled water, blot dry and immerse the electrode tips in the solution. When the reading has stabilized, record the mV reading.
5. Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against concentration (log axis).

Extrapolate the curve down to about 2.0×10^{-6} M or 0.2 ppm. A typical calibration curve can be found in Figure 1.

FIGURE: 1

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

6. To a clean, dry 150-mL beaker, add 100 mL of sample and 2 mL of ISA. Place the beaker on the magnetic stirrer and begin stirring. Place the electrode tips in the solution. When the reading has stabilized, record the mV reading. Determine the concentration directly from the calibration curve.
7. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tips in the mid-range standard. After the reading has stabilized, compare it to the original reading recorded in Step 3 above. A reading differing by more than 0.5 mV or a change of ambient temperature will necessitate the repetition of Steps 2-5 above. A new calibration curve should be prepared daily.

1. By serial dilution of the 0.1M or 1000 ppm silver standard, prepare two silver standards whose concentration is near the expected sample concentration. Measure out 100 mL of each standard into individual 150-mL beakers and add 2 mL of ISA to each.
2. Place the more dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode.
3. Lower the electrode tips into the solution.
4. Adjust the meter to the concentration of the silver standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
5. Rinse the electrodes with distilled water and blot dry.
6. Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate.
7. Lower the electrode tips into the solution.
8. Adjust the meter to the concentration of the silver standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
9. For low level measurements, place the rinsed, dried electrodes into the solution containing 100 mL of distilled water and 2 mL of ISA. After stabilization, fix the blank value in the meter according to the meter manufacturer's instructions.
10. Place 100 mL of the sample and 2 mL of ISA in a 150-mL beaker, place it on the magnetic stirrer, and begin stirring.
11. Immerse the electrode tips in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.
12. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tips in the first silver standard. After the reading has stabilized, compare it to the original reading in Step 4 above. A reading differing by more than 0.5

mV or a change in the ambient temperature will necessitate the repetition of Steps 2-8(9) above. The meter should be re-calibrated daily

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

1. By serial dilution of the weekly standard, prepare three standard sulfide solutions. Measure out 50 mL of each standard into individual 150-mL beakers and add 25 mL of SAOB and 25 mL of distilled water to each.
2. Place the most dilute solution on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tips into the solution. When the reading has stabilized, record the mV reading.
3. Place the midrange sulfide standard on the magnetic stirrer and begin stirring. After rinsing the electrodes with distilled water, blot dry and immerse the electrode tips in the solution. When the reading has stabilized, record the mV reading.
4. Place the most concentrated sulfide standard on the magnetic stirrer and begin stirring. After rinsing the electrodes with distilled water, blot dry and immerse the electrode tips in the solution. When the reading has stabilized, record the mV reading.
5. Using the semi-logarithmic graph paper, plot the mV reading (linear axis) against concentration (log axis).
6. To a clean, dry 150-mL beaker, add 50 mL of the sulfide sample, 25 mL of SAOB, and 25 mL of distilled water. Place the beaker on the magnetic stirrer and begin stirring. Place the electrode tips in the solution. When the reading has stabilized, record the mV reading. Determine the concentration directly from the calibration curve.
7. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tips in the mid-range standard. After the reading has stabilized, compare it to the original reading recorded in Step 3 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the repetition of Steps 2-5 above. A new calibration curve should be prepared daily.



Direct Measurement of Sulfide (using an ion meter)

1. By serial dilution of the weekly standard, prepare two sulfide standards whose concentration is near the expected sample concentration. Measure out 50 mL of each standard into individual 150-mL beakers and add 25 mL of SAOB and 25 mL of distilled water to each.
2. Place the more dilute solution on the magnetic stirrer and begin stirring at a constant rate. Assure that the meter is in the concentration mode.
3. Lower the electrode tips into the solution.
4. Adjust the meter to the concentration of the sulfide standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
5. Rinse the electrodes with distilled water and blot dry.
6. Place the more concentrated solution on the magnetic stirrer and begin stirring at a constant rate.
7. Lower the electrode tips into the solution.
8. Adjust the meter to the concentration of the sulfide standard and fix the value in the memory according to the meter manufacturer's instructions after stabilization of the reading.
9. For low level measurements, place the rinsed, dried electrodes into the solution containing 50 mL of SAOB and 50 mL of distilled water. After stabilization, fix the blank value in the meter according to the meter manufacturer's instructions.
10. Place 50 mL of the sample, 25 mL of SAOB, and 25 mL of distilled water in a 150-mL beaker, place it on the magnetic stirrer, and begin stirring.
11. Immerse the electrode tips in the solution and wait for the reading to stabilize. Read the concentration directly from the meter display.
12. The calibration should be checked every two hours. Assuming no change in ambient temperature, place the electrode tips in the first sulfide standard. After the reading has stabilized, compare it to the original reading in Step 4 above. A reading differing by more than 0.5 mV or a change in the ambient temperature will necessitate the

repetition of Steps 2-8(9) above. The meter should be re-calibrated daily.

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

This procedure is recommended for solutions with ionic strengths less than 1.0×10^{-2} M. If the solution is high in ionic strength, but low in silver, use the same procedure, but prepare a calibration solution with a composition similar to the samples.

1. Using 1 mL of standard ISA, dilute to 100 mL with distilled water. This low level ISA (1.0M NaNO_3) is added at the rate of 1 mL low level ISA to each 100 mL of sample. The background ionic strength will be 1.0×10^{-2} M.
2. Dilute 1 mL of 0.1M standard to one liter to prepare a 1.0×10^{-4} M solution for measurements in moles per liter. Prepare a 10 ppm standard solution by diluting 1 mL of the 1000 ppm standard to 100 mL of solution for measurements in ppm. Standards should be prepared fresh daily.
3. Add 1 mL of low level ISA to a 100 mL volumetric flask and fill to the mark with distilled water. Pour this solution into a 150-mL beaker and place the beaker on the magnetic stirrer. Begin stirring at a constant rate.
4. Place the electrode tips in the solution. Assure that the meter is in the mV mode.
5. Add increments of the 1.0×10^{-4} M or 10 ppm silver standard as given in Table 2 below.
6. After the reading has stabilized, record the mV reading.

TABLE 2: Stepwise Calibration for Low Level Silver Measurements

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

Pipet A = 1-mL graduated pipet

Pipet B = 2-mL pipet

Solutions: additions of 10 ppm or 1.0×10^{-4} M standard to 100 mL of ISA as prepared in Step 3 above.

7. On semi-logarithmic graph paper, plot the millivolt reading (linear axis) against the concentration (log axis).
8. Rinse the electrodes in distilled water and blot dry.
9. Measure out 100 mL of the sample into a 150-mL beaker, add 1 mL of low level ISA, and place the beaker on the magnetic stirrer. Begin stirring. Lower the electrode tips into the solution. After the reading has stabilized, record the mV reading and determine the concentration from the low level calibration curve.
10. Prepare a new low level calibration curve daily. Check the calibration curve every two hours by repeating Steps 2-7.

Titration

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

Titration of Sulfide

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

1. Using MANTECH Lead Perchlorate Solution, 0.1M, prepare a lead titrant that is about 10-20 times as concentrated as the expected sample concentration by dilution.
2. Dilute 25 mL of the sample with 25 mL of SAOB in a 150-mL beaker. Place the beaker on the magnetic stirrer and begin stirring. Lower the tips of the electrodes into the solution.
3. Using a 10 mL burette, add titrant in 0.5-1.0 mL increments. Record the mV reading against the volume of titrant added. As the mV potential change increases, add smaller increments, down to 0.1-0.2 mL increments. Continue to add titrant and record the mV potential against the volume until little change is noted in the mV reading even when adding 0.5-1.0 mL increments.
4. Using linear graph paper, plot the mV readings (y-axis) against the volume (x-axis). The end point is determined at the steepest slope on the titration curve.
5. The sample concentration, C_s , is calculated before the dilution with SAOB, as follows:

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

Where:

V_s = sample volume before dilution (25mL)

V_t = titrant volume at endpoint

C_t = titrant concentration (M)

Titration of Silver

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



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

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

1. Using Sodium Chloride Solution, 0.1M NaCl, for silver titrations, or the 0.1M silver standard for halide titrations, prepare a titrant about 10-20 times the expected sample concentration by dilution.
2. Measure out 50 mL of the sample into a 150-mL beaker, place the beaker on the magnetic stirrer, and begin stirring. Place the tips of the electrodes in the solution.
3. Using a 10 mL burette, add titrant in 0.5-1.0 mL increments. Record the mV reading against the volume of titrant added. As the mV potential change increases, add smaller increments, down to 0.1-0.2 mL increments. Continue to add titrant and record the mV potential against the volume until little change is noted in the mV reading even when adding 0.5-1.0 mL increments.
4. Using linear graph paper, plot the mV readings (y-axis) against the volume (x-axis). The endpoint is determined at the steepest slope on the titration curve.
5. The sample concentration, C_s , is calculated as follows:

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

Where:

V_s = sample volume (50 mL)

V_t = titrant volume at endpoint

C_t = titrant concentration (M)

Low Level Chloride Titration

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



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

1. Using 20 mL of standard ISA, dilute to 100 mL with distilled water. This low level ISA (1.0M NaNO_3) is added at the rate of 1 mL low level ISA to each 100 mL of sample. The background ionic strength will be $1.0 \times 10^{-2} \text{M}$.
2. Measure out 100 mL of distilled water into a 150-mL beaker, add 1 mL of low level ISA, place the beaker on the magnetic stirrer, and begin stirring.
3. Prepare a 10-mL burette with the low level chloride titrant ($2.82 \times 10^{-3} \text{M AgNO}_3$) mentioned in the GENERAL INSTRUCTIONS, Required Solutions.
4. Lower the tips of the electrodes into the solution.
5. Add 1 mL of titrant and record the mV reading after stabilization. Repeat this operation four more times.
6. Using Gran's Plot paper, plot the values as follows:
 - a) The horizontal axis is the volume axis. Each major division is equal to 1 mL of titrant used.
 - b) The vertical axis is the mV axis. Each major division is equal to 5 mV. The axis should be scaled so that the mV value obtained after 5 mL of titrant added is near the top of the graph.
7. After drawing a straight line through the points, the line should intersect the horizontal axis at 0 mL.
8. Measure out 100 mL of the sample into a 150-mL beaker, add 1 mL of low level ISA, place the beaker on the magnetic stirrer, and begin stirring.
9. Prepare a 10 mL burette with the low level chloride titrant mentioned in Step 3 above.
10. Allow the titrant to run slowly into the sample until the mV reading is near the value recorded for the first 1 mL increment added in Step 5 above. Record the mV reading and the total volume added.

11. Add 1-mL increments of titrant and record the mV reading vs the total volume until the mV reading approaches the highest mV reading recorded in Step 5 above.
12. Plot the mV reading vs total volume for all points on the Gran's Plot paper. Draw a straight line through as many points as possible, extending the line to the horizontal axis. The volume intercept value is equal to the chloride concentration in ppm.

Indicator Titration

A special method for measuring low level cyanide concentration. The silver/sulfide electrode is capable of cyanide measurements down to 0.03 ppm. (Midgley, D.; Torrance, K., 1991, Potentiometric Water Analysis, 2nd Edition, P. 406-413, John Wiley & Sons, Chichester.)

ELECTRODE CHARACTERISTICS

Reproducibility

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

Interferences

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

All silver samples must be free of mercury. Sulfide samples will not have mercury present due to the extreme insolubility of HgS and Hg₂S. Biological samples and protein in food interferes with silver measurements, but the protein interference can be removed by acidifying to pH 2-3 with 1M HNO₃.

Complexation

Total concentration (C_t) whether sulfide or silver ions, consists of free ions (C_f) and complexed or bound ions (C_c) in solution:

$$C_t = C_f + C_c$$

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

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

Sulfide ions form complexes with hydrogen ions (HS^- and H_2S). Sulfide ions also form soluble complexes with elemental sulfur (S_2^{-2} , S_3^{-2} , S_4^{-2} , etc.) and tin, arsenic, and antimony ions.

Temperature Influences

Samples and standards should be within $\pm 1^\circ\text{C}$ of each other, since electrode potentials are influenced by changes in temperature. Because of the solubility equilibria on which the electrode depends, the absolute potential of the reference electrode changes slowly with temperature. The slope of the electrode, as indicated by the factor "S" in the Nernst equation, also varies with temperature. Table 3 gives values for the "S" factor in the Nernst equation for each ion.

TABLE 3: Temperature vs. Values for the Electrode Slope

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

If changes in temperature occur, the electrodes should be re-calibrated.

The temperature range for the MANTECH Silver/Sulfide Ion Electrode is $0^\circ\text{--}80^\circ\text{C}$, provided that temperature equilibrium has occurred. If the temperature varies substantially from room temperature, equilibrium times up to one hour are recommended.

Electrode Response

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

potential is plotted against the sulfide concentration, but the slope is about 26 mV per decade.

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

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

To polish the membrane:

1. If using polishing paper, cut off a 1-2" piece and place it face up on the lab bench.
2. Put a few drops of distilled or deionized water in the center of the paper.
3. Holding the paper (cotton) steady with one hand, bring the membrane of the electrode down perpendicular to the paper and, with a slight swirling motion, gently polish the tip of the electrode against the surface of the polishing paper (cotton) for a few seconds.
4. Rinse the electrode surface with distilled or deionized water and soak the electrode tip in standard solution for about five minutes before use.
5. If using jeweller's rouge, place a cotton ball on the table top and flatten it using the bottom of a beaker.
6. Put 1-2 drops of distilled or deionized water in the center of the cotton pad.
7. Add a small amount of jeweller's rouge to the damp cotton.
8. Continue with Steps 3 and 4 above.

Limits of Detection

The upper limit of detection in pure silver nitrate solutions is 1M. In the presence of other ions, the upper limit of detection is above $1.0 \times 10^{-1} \text{M}$ silver, but two factors influence this upper limit. Both the possibility of a liquid junction potential developing at the reference electrode and the salt extraction effect influence this upper limit. Some salts may extract into the electrode membrane at high salt concentrations, causing deviation from the theoretical response. Either dilute

samples between 1M and 1.0×10^{-1} M or calibrate the electrode at 4 or 5 intermediate points.

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

pH Effects

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

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

Electrode Life

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

Electrode Storage

The MANTECH Silver/Sulfide Electrodes may be stored for short periods of time in 1.0×10^{-2} M silver (or sulfide) solution. For longer storage (longer than two weeks), rinse and dry the sensing pellet and cover the membrane tip with any protective cap shipped with the electrode. The reference portion of the combination electrode (or the outer chamber of the

reference electrode) should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole.

ELECTRODE THEORY

Electrode Operation

The MANTECH Silver/Sulfide Ion Electrode is composed of a silver sulfide crystal membrane bonded into an epoxy or glass body. When an electrode potential develops across the membrane, the membrane is in contact with a solution

containing sulfide or silver ions and is capable of measuring free sulfide or silver ions. This electrode potential is measured against a constant reference potential, using a pH/mV meter or an ion meter. The level of sulfide or silver ions, corresponding to the measured potential, is described by the Nernst equation:

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

Where:

E = measured electrode potential

E_o = reference potential (a constant)

S = electrode slope (-26 mV for sulfide; +57 mV for silver)

X = level of sulfide or silver in solution

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

$$X = Y C_f$$

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

$$I = \frac{1}{2} \sum C_x Z_x^2$$

Where:

C_x = concentration of ion X

Z_x = charge of ion X

Σ = sum of all of the types of ions in the solution.

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

To adjust the background ionic strength to a high and constant value, ionic strength adjuster (ISA) is added to samples and standards. The recommended solution for sulfide is SAOB, used to prevent oxidation and free sulfide ion from hydrogen ion, in addition to adjusting the ionic strength. The recommended ISA for silver is NaNO₃. Solutions other than these may be used as ionic strength adjusters as long as ions that they contain do not interfere with the electrode's response to sulfide ions or to

silver ions. Samples with high ionic strength (greater than 0.1M) do not need ISA added and standards for these solutions should be prepared with a composition similar to the samples.

The reference electrode must also be considered. When two solutions of different composition are brought into contact with one another, liquid junction potentials arise. Millivolt potentials occur from the inter-diffusion of ions in the two solutions. Electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions, since ions diffuse at different rates. When making measurements, it is important to remember that this potential be the same when the reference is in the standardizing solution as well as in the sample solution or the change in liquid junction potential will appear as an error in the measured electrode potential. The composition of the liquid junction filling solution in the reference electrode is most important. The speed with which the positive and negative ions in the filling solutions diffuse into the sample should be as nearly equal as possible, that is, the filling solution should be equitransferent. No junction potential can result if the rate of which positive and negative charge carried into the sample solution is equal.

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

TROUBLESHOOTING GUIDE

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

Meter

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

Glassware

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

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

1. Be sure to use distilled or deionized water when following the procedures given in Electrode Slope Check.
2. If the electrode fails to respond as expected, see the sections Measuring Hints and Electrode Response. Repeat the slope check.
3. If the electrodes still fail to respond as expected, substitute another silver/sulfide ion electrode that is known to be in good working order for the questionable electrode. If the problem persists and you are using an electrode pair, try the same routine with a working reference electrode.
4. If the problem persists, the reagent may be of poor quality, interferences in the sample may be present or the technique may be faulty. (See Standards & Reagents, Sample, and Technique sections below.)
5. If another electrode is not available for test purposes, or if the electrode in use is suspect, review the instruction manual and be sure to:
 - Clean and rinse the electrodes thoroughly.
 - Prepare the electrodes properly.
 - Use the proper filling solution.
 - Adjust the pH and the ionic strength of the solution by the use of the proper ISA.
 - Measure correctly and accurately.
 - Review TROUBLESHOOTING HINTS.

Standards & Reagents

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



Sample

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

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

Technique

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

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

TROUBLESHOOTING HINTS

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



	defective electrode electrode exposed to interferences	replace electrode soak electrode in silver or sulfide standard
Drift (reading slowly changing in one direction)	samples and standards at different temperatures incorrect reference filling solution	allow solutions to come to room temperature before measurement check section entitled Complexation use recommended filling solution
Low Slope or No Slope	standards contaminated or incorrectly made ISA not used standard used as ISA electrode exposed to complexing agents air bubble on membrane	prepare fresh standards use recommended ISA use ISA check section entitled Complexation remove bubble by re-dipping probe
“Incorrect Answer” (but calibration curve is good)	incorrect scaling of semi-log paper incorrect sign incorrect standards wrong units used	plot millivolts on the linear axis. On the log axis, be sure concentration be sure to note sign of millivolt number correctly prepare fresh standards apply correct conversion factor: $1.0 \times 10^{-3} \text{M} = 32.$



	complexing agents in sample	1 ppm S-2 = 2.0×10^{-3} N (S-2); 1.0×10^{-3} M = 108 ppm Ag+1 check section entitled Complexation
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SPECIFICATIONS

- Concentration Range: 1M to 1.0×10^{-7} M sulfide (32,000 to 0.003ppm)
 1M to 1.0×10^{-7} M silver (108,000 to 0.01ppm)
- pH Range: 2 to 12
- Temperature Range: 0°-80°C
- Resistance: <1 Mohm
- Reproducibility: +/-2%
- Samples: aqueous solutions only; no organic solvents
- Size: 110 mm length
 12 mm diameter
 1 m cable length
- Storage: Store in silver or sulfide solution

ORDERING INFORMATION

P/N	DESCRIPTION
PCE-80-SS1001	Silver/Sulfide Ion Electrode
PC-AGSISA	Sulfide Anti-Oxidant Buffer (SAOB) kit
PC-R001015	Reference Electrode Filling Solution, 1M KNO ₃

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Version	Date	Author	Changes
2	25-July-2019	Heather Jasumani	<ul style="list-style-type: none"> • Document ID assigned • Formatting



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