

User Guide

Potassium
Ion Selective
Electrode



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This publication supersedes all previous publications on this subject.

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Introduction

This user guide contains information on the preparation, operation and maintenance for the potassium ion selective electrode (ISE). General analytical procedures, electrode characteristics and electrode theory are also included in this user guide. Potassium electrodes measure free potassium ions in aqueous solutions quickly, simply, accurately and economically.

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.

Potassium ionplus[®] Sure-Flow[®] Plastic Membrane Combination ISE, Cat. No. 9719BNWP

The potassium 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 stable readings. The potassium combination electrode is available with a waterproof BNC connector, Cat. No. 9719BNWP. Electrodes with a waterproof BNC connector can be used on any ISE or mV meter with a BNC connection.

Potassium Plastic Membrane Half-Cell ISE, Cat. No. 9319BN

The potassium half-cell electrode must be used with the double junction reference electrode, Cat. No. 900200. The potassium half-cell electrode is available with a BNC connector, Cat. No. 9319BN.

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.

Potassium 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 potassium electrode.

The 9319BN potassium half-cell electrode requires 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 potassium analysis.
5. Distilled or deionized water.
6. Potassium electrode filling solution.

Use Optimum Results™ E filling solution, Cat. No. 900065, for the 9719BNWP potassium combination electrode.

Use inner chamber filling solution, Cat. No. 900002, and dilute ISA for the double junction reference electrode that is used with the 9319BN potassium half-cell electrode. Prepare the dilute ISA for the outer chamber filling solution by adding 2 mL of ISA, Cat. No. 931911, to a 100 mL volumetric flask and diluting to the mark with distilled water.

7. 0.1 M KCl potassium calibration standard, Cat. No. 921906.

1000 ppm potassium solution – Add 25.6 mL of the 0.1 M potassium standard to a 100 mL volumetric flask, dilute to the mark with distilled water and mix the solution.

8. Potassium ionic strength adjuster (ISA), Cat. No. 931911. ISA provides a constant background ionic strength for samples and standards.

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 standard (391 ppm as K^+) –**
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 standard (39.1 ppm as K^+) –**
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 standard (3.91 ppm as K^+) –**
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 potassium standard from a 3910 ppm potassium standard:

$$C_1 = 3910 \text{ ppm potassium}$$

$$V_1 = \text{unknown}$$

$$C_2 = 100 \text{ ppm potassium}$$

$$V_2 = 100 \text{ mL}$$

$$3910 \text{ ppm} * V_1 = 100 \text{ ppm} * 100 \text{ mL}$$

$$V_1 = (100 \text{ ppm} * 100 \text{ mL}) / 3910 \text{ ppm} = 2.56 \text{ mL}$$

Electrode Setup

9719BNWP Potassium Combination Electrode Preparation

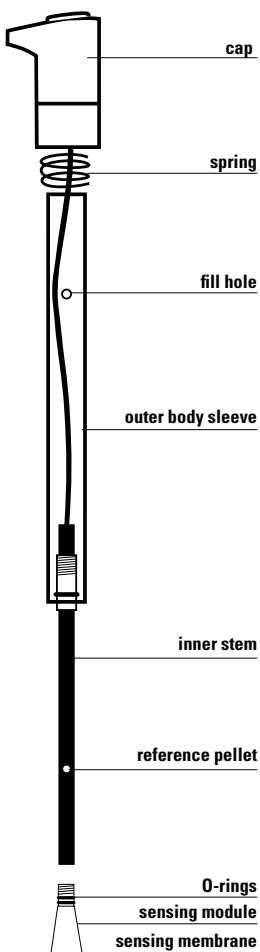
Note: Do not touch the sensing membrane or reference pellet during the electrode assembly.

1. Remove the sensing module from the vial and save the vial for storage. Make sure that both O-rings are in place on the module. Remove the electrode handle from the box.
2. Unscrew the electrode cap. Slide the cap and spring down the electrode cable.
3. Hold the outer body sleeve and gently push the inner stem through the outer body. Slide the outer body sleeve down the electrode cable until it is beyond the inner stem.
4. Grasp the middle of the inner stem without touching the reference pellet. If a red storage tip is connected to the inner stem, unscrew it and save it for storage.
5. Screw the sensing module into the stem until it stops and the module is flush against the stem. Tighten the module an additional one-quarter turn. The module should be firmly attached to the stem. Do not overtighten the module.
6. Hold the electrode cable and slide the outer body, spring and cap over the inner stem.
7. Grasp the outer body sleeve, without touching the sensing membrane, and gently screw the cap onto the inner stem while pulling on the cable. Stop when an opposite force is felt. Do not overtighten or continue to turn the cap. The cap will not completely stop. If the inner body turns at all, the cap is too tight. Remove the cap and reassemble.
8. Press on the top of the cap with your thumb to make sure that the electrode has a smooth flushing motion and the outer body sleeve returns to its original position.
9. Install the flip spout cap onto the Optimum Results E filling solution bottle and lift the flip spout to a vertical position. Insert the spout into the electrode fill hole and add a small amount of filling solution to the reference chamber.
10. Hold the electrode body 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. Release the electrode cap.

11. If the sleeve does not return to its original position, add filling solution and repeat step 10 until the sleeve returns to its original position.
12. Add filling solution to the electrode up to the fill hole.
13. Rinse the electrode with distilled water and soak it in a 100 ppm or 10^{-2} M potassium standard for 1 to 2 hours prior to use.

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
9719BNWP Potassium Combination Electrode



9319BN Potassium Half-Cell Electrode Preparation

Remove the sensing module from the vial and save the vial for electrode storage. Make sure that the rubber electrode washer on the sensing module is in place. See **Figure 2**. Screw the sensing module into the electrode body until the module is finger-tight. To ensure electrical continuity, shake the electrode down like a clinical thermometer. Rinse the potassium electrode with distilled water and then soak it in a 100 ppm or 10^{-2} M potassium standard for 1 to 2 hours prior to use.

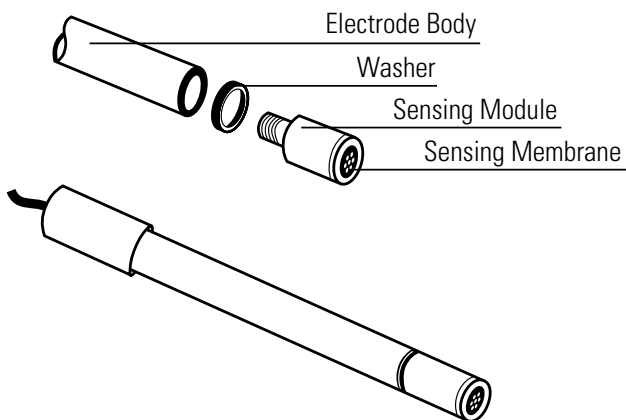
Note: Do not immerse the electrode past the rubber electrode washer.

900200 Double Junction Reference Electrode Preparation

Prepare the reference electrode according to the reference electrode user guide. Fill the reference electrode with inner chamber filling solution, Cat. No. 900002, and dilute ISA as the outer chamber filling solution. Prepare the dilute ISA for the outer chamber filling solution by adding 2 mL of ISA, Cat. No. 931911, to a 100 mL volumetric flask and diluting to the mark with distilled water.

Note: Do not use the outer chamber filling solution that ships with the 900200 double junction reference electrode because it contains interferences for potassium measurements.

Figure 2
9319BN Potassium Half-Cell 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. Add 100 mL of distilled water and 2 mL of ISA into a 150 mL beaker. Stir the solution thoroughly.
4. Rinse the electrode with distilled water and place the electrode into the solution prepared in step 3.
5. Select either a 0.1 M or 1000 ppm potassium standard. 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. There should be a 54 to 60 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

Potassium 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)	ppm as K ⁺	ppm as KCl
1.0	39100	74600
10 ⁻¹	3910	7460
10 ⁻²	391	746
10 ⁻³	39.1	74.6
10 ⁻⁴	3.91	7.46

Sample Requirements

All samples must be aqueous and must not contain organic solvents. Contact Technical Support for information on using the electrode for specific applications.

The solution temperature must be less than 40 °C.

Samples and standards should be at the same temperature. A 1 °C difference in temperature for a 10⁻³ M potassium solution will give rise to about a 2.5% error.

Interferences should be absent from all samples. See the **Interferences** section for a list of possible interferences.

In all analytical procedures, ISA must be added to all samples and standards before measurements are taken.

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 module.
- Store the potassium electrode in a 10^{-2} M or 100 ppm potassium standard between measurements.
- The 9319BN potassium half-cell electrode should be immersed in standards and samples to approximately half the length of the potassium module. Do not immerse the potassium electrode past the electrode washer. Immerse the reference electrode to the same depth as the potassium electrode.
- Allow all standards and samples to reach the same temperature for precise measurements.
- 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%, 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

Potassium Combination Electrode Storage, Cat. No. 9719BNWP

For storage between measurements and up to three days, store the electrode in a 10^{-2} M or 100 ppm potassium standard. 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 reference chamber with distilled water, disassemble the electrode and store the sensing module in the glass vial.

1. Grasp the outer body sleeve and unscrew the electrode cap. Slide the cap and spring assembly down the electrode cable.
2. Push the inner stem of the electrode handle out through the outer electrode sleeve, exposing the sensing module.
3. Rinse the inner stem and module well with distilled water. Gently blot dry to prevent damaging the sensing module.
4. Carefully unscrew the sensing module from the inner stem, taking care not to touch the sensing membrane.
5. Place the potassium sensing module in the glass vial until it is needed again. Gently blot dry the inside of the inner stem and O-ring area, reassemble the electrode handle without the module and store it dry.

Potassium Half-Cell Electrode Storage, Cat. No. 9319BN

The potassium half-cell electrode should be rinsed thoroughly with distilled water and stored in a 10^{-2} M or 100 ppm potassium standard. When storing the electrode for more than three days, rinse the potassium half-cell electrode thoroughly with distilled water, shake the electrode dry, disassemble the electrode and store the sensing module in the glass vial.

Double Junction Reference Electrode Storage, Cat. No. 900200

The double junction reference electrode may be stored in the dilute ISA filling solution 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.

Electrode Maintenance

Cleaning the Potassium Sensing Module

If the electrode is exposed to high levels of interfering ions, it may drift and become sluggish in response. When this happens, restore normal performance by soaking the electrode for an hour in distilled water, emptying the old filling solution, filling the electrode with fresh filling solution and then soaking the electrode for a few hours a 10^{-2} M or 100 ppm potassium standard. If soaking the electrode does not restore normal electrode performance, replace the potassium sensing module.

Potassium Combination Electrode and Double Junction Reference Electrode Flushing

If the area between the electrode outer body 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 all of the filling solution out of the electrode.
2. Fill the electrode with distilled water and then push down on the cap until all the water is drained from the chamber. Repeat this procedure until all of the sample or precipitate is removed from the electrode.
3. Fill the electrode with fresh filling solution up to the fill hole. Push down on the cap to allow a few drops of filling solution to drain out of the electrode and then replenish the lost filling solution.
4. Rinse the electrode with distilled water and soak it in a 10^{-2} M or 100 ppm potassium standard for 1 to 2 hours.

Replacing the Potassium Sensing Module

The sensing membrane of plastic membrane electrodes will wear over time, indicated by low slope values, drift, poor reproducibility and loss of response in low level samples. The electrode response can be restored by replacing the sensing module. Each sensing module will last about six months with normal laboratory use, but the actual lifespan of the sensing module will depend on the type of samples that are measured.

For the 9719BNWP potassium combination electrode, use the 97 series potassium module, Cat. No. 971901.

Drain the electrode and flush the reference chamber with distilled water. Hold the outer body sleeve and unscrew the electrode cap. Slide the cap and spring assembly down the electrode cable. Push the inner stem of the electrode handle out through the outer electrode sleeve, exposing the sensing module. Rinse the inner stem and module well with distilled water. Gently blot dry to prevent damaging the sensing module. Carefully unscrew the sensing module from the inner stem and dispose of the old sensing module. Obtain a new 97 series potassium module, Cat. No. 971901, and refer to the **9719BNWP Potassium Combination Electrode Preparation** section for detailed instructions on assembling the electrode.

For the 9319BN potassium half-cell electrode, use the 93 series potassium module, Cat. No. 931901.

Rinse the electrode with distilled water. Carefully unscrew the sensing module from the electrode and dispose of the old sensing module. Obtain a new 93 series potassium module, Cat. No. 931901, and refer to the **9319BN Potassium Half-Cell Electrode Preparation** section for detailed instructions on assembling the electrode.

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

Low Level Calibration is similar to the direct calibration technique. This method is recommended when the expected sample concentration is less than 0.4 ppm or 10^{-5} M potassium. 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.

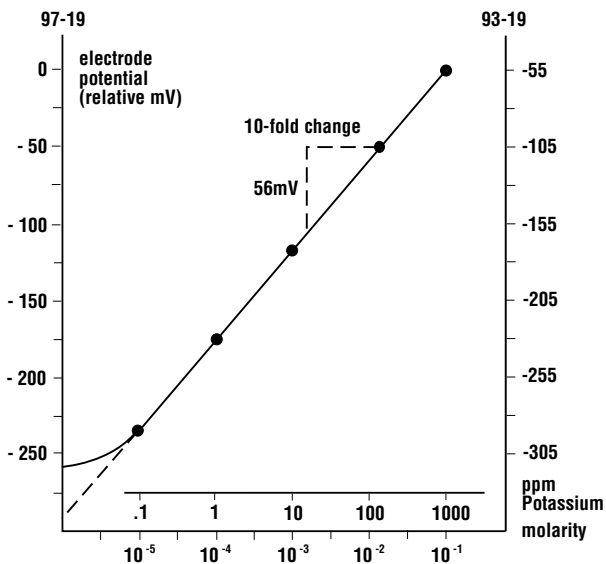
Known Addition is useful for measuring dilute samples, checking the results of direct calibration (when no complexing agents are present), or measuring the total concentration of an ion in the presence of an excess complexing agent. The electrode is immersed in the sample solution and an aliquot of a 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.

Direct Calibration Technique

Typical 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 3
Typical Direct Calibration Curve



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 0.4 ppm or 10^{-5} M potassium. 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. 931911, 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.

Direct Calibration Setup

1. Prepare the electrode as described in the **Electrode Preparation** section. If using the 9719BNWP combination potassium electrode, fill the electrode with Cat. No. 900065. If using the 9319BN half-cell potassium electrode with the 900200 reference electrode, fill the reference electrode with inner chamber filling solution, Cat. No. 900002, and dilute ISA as the outer chamber filling solution.
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.

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.

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.

Small Volume Direct Calibration Technique

Take advantage of special design features available with the 9719BNWP ionplus combination potassium 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 potassium standards and ISA is reduced. This method is also convenient when making field measurements, since the 9719BNWP combination potassium electrode does not require a separate reference electrode. All samples should have a concentration greater than 1 ppm or 2.5×10^{-5} M potassium. 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 9719BNWP ionplus combination potassium 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.

Small Volume Direct Calibration Setup

1. Prepare the 9719BNWP combination potassium electrode as described in the **Electrode Preparation** section and fill the electrode with Optimum Results E filling solution, Cat. No. 900065.
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.

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.

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.

Low Level Calibration Technique

These procedures are for solutions that have a potassium concentration of less than 0.4 ppm or 10^{-5} M potassium. For solutions low in potassium 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 potassium measurements.
- Adequate time must be allowed for electrode stabilization. Longer response time will be needed at low level measurements.
- Stir all standards and samples at a uniform rate.

Low Level Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to the meter. Set the meter to the mV mode.
3. Prepare the low level ISA by pipetting 20 mL of the ISA, Cat. No. 931911, 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 100 ppm or 10^{-3} M potassium standard.

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 100 ppm or 10^{-3} M potassium 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	0.1	1.0×10^{-6}
2	1 mL	0.1 mL	0.2	2.0×10^{-6}
3	1 mL	0.2 mL	0.4	3.9×10^{-6}
4	1 mL	0.2 mL	0.6	5.9×10^{-6}
5	1 mL	0.4 mL	1.0	9.8×10^{-6}
6	2 mL	2.0 mL	2.9	2.9×10^{-5}
7	2 mL	2.0 mL	4.7	4.7×10^{-5}

Known Addition Technique

Known addition is a convenient technique for measuring samples in the linear range of the electrode (greater than 0.4 ppm or 10^{-5} M potassium) 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.

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 potassium 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

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.

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:

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

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.

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

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
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

ΔE	Q Concentration Ratio			
	57.2	58.2	59.2	60.1
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
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

ΔE	Q Concentration Ratio			
	57.2	58.2	59.2	60.1
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

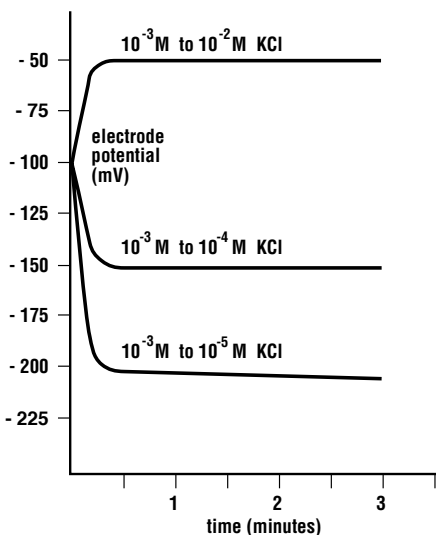
Electrode Characteristics

Electrode Response

The electrode potential plotted against concentration on semi-logarithmic paper results in a straight line with a slope of about 54 to 60 mV per decade change in concentration.

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 4
Typical Electrode Response to Potassium 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 electrode measurements reproducible to $\pm 2\%$ can be obtained.

Limits of Detection

In pure potassium solutions, the upper limit of detection is 1 M. When possible, dilute the sample into the linear range of the electrode. If samples are not diluted, the possibility of a liquid reference junction potential and the salt extraction effect, need to be considered. At high salt concentrations, salts may be extracted into the electrode membrane, causing deviation from theoretical response. To measure samples between 10^{-1} and 1 M, calibrate the electrode at 4 or 5 intermediate points or dilute the sample.

The lower limit of detection is determined by the slight water solubility of the ion exchanger, which causes deviation from theoretical response. **Figure 3** shows the theoretical response at low levels of potassium compared to the actual response. If potassium measurements are made below 0.4 ppm or 10^{-5} M potassium, a low level measurement procedure is recommended.

Electrode Life

Each sensing module will last approximately six months with normal laboratory use, but the actual lifespan of the sensing module will depend on the type of samples that the electrode is used in. Refer to the **Electrode Maintenance** section for instructions on changing the sensing module. In time, the electrode slope will decrease and readings will start to drift, indicating that the module should be changed. Before replacement, refer to the **Troubleshooting** section to make sure that the difficulties are caused by the sensing module.

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 2.5 %. 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 6**. If the temperature changes, the meter and electrode should be recalibrated.

The electrode can be used at temperatures from 0 to 40 °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.

Table 6
Theoretical Slope vs. Temperature Values

Temperature (°C)	Slope (mV)
0	54.20
10	56.18
20	58.16
25	59.16
30	60.15
40	62.13

If sample temperatures vary, use of the 9719BNWP combination potassium electrode is recommended. The Optimum Results E filling solution that is included with the electrode will minimize junction potentials and provide optimum temperature and time response. Optimum Results E filling solution produces an isopotential point of 1.54 M potassium. 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 potassium 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

Cations, if present at high enough levels, are electrode interferences and will cause measurement errors. **Table 7** indicates levels of common cations that will cause 10% errors at different concentrations of potassium.

If the electrode is exposed to high levels of interfering ions, it may drift and become sluggish in response. When this happens, restore normal performance by soaking the electrode for an hour in distilled water, emptying the old filling solution, filling the electrode with fresh filling solution and then soaking the electrode for a few hours a 10^{-2} M or 100 ppm potassium standard. If soaking the electrode does not restore normal electrode performance, refer to the **Electrode Maintenance** section for instructions on how to replace the sensing module.

When the level of interferences in samples is constant, it is sometimes possible to measure potassium accurately when interference levels are higher than those in **Table 7**. For example, potassium can be measured in sea water by using synthetic ocean water for calibration. Contact our Technical Support Chemists for more information.

Table 7
Potassium Electrode Interferences

Interferences Moles/Liter	10^{-4} M Potassium	10^{-3} M Potassium	10^{-2} M Potassium
Cs ⁺	3×10^{-5}	3×10^{-4}	3×10^{-3}
NH ₄ ⁺	6×10^{-4}	6×10^{-3}	6×10^{-2}
Tl ⁺	6×10^{-4}	6×10^{-3}	6×10^{-2}
H ⁺	1×10^{-3}	1×10^{-2}	0.1
Ag ⁺	0.1	1.0	10
Tris ⁺ *	0.1	1.0	10
Li ⁺	0.2	2.0	20
Na ⁺	0.2	2.0	20

* Tris is the cation of tris(hydroxymethyl) aminomethane.

Interferences ppm	1 ppm Potassium	10 ppm Potassium	100 ppm Potassium
Cs⁺	1.0	10	100
NH₄⁺	2.7	27	270
Tl⁺	31.4	314	3140
H⁺	3.6 pH	2.6 pH	1.6 pH
Ag⁺	2765	27650	276500
Tris⁺ *	3105	31050	310500
Li⁺	356	3560	35600
Na⁺	1179	11790	117900

* Tris is the cation of tris(hydroxymethyl) aminomethane.

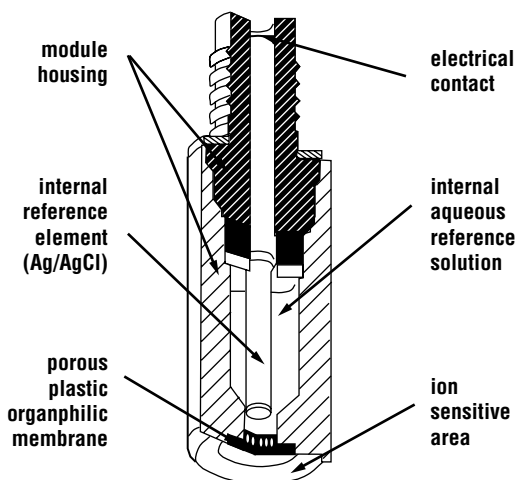
pH Effects

Although the electrode can be used over a wide pH range, hydrogen ion interferes with measurements of low levels of potassium ion. Refer to **Table 7** to determine the minimum pH at which low level potassium measurements can be made without more than a 10% error due to hydrogen ion interference.

Theory of Operation

The potassium electrode consists of a replaceable, pretested sensing module connected to an epoxy body. The sensing module contains a liquid internal filling solution in contact with a gelled organophilic membrane that contains a potassium selective ion exchanger.

Figure 5
Example of an Ion Sensing Module



When the module is in contact with a solution containing potassium ions, an electrode potential develops across the module. This potential, which depends on the level of free potassium ion 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 potassium ion in solution is described by the Nernst equation.

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

E = measured electrode potential

E_o = reference potential (a constant)

A = potassium ion activity level in solution

S = electrode slope (about 57 mV per decade)

$S = (2.3 RT) / nF$

R and F are constants, T = temperature in degrees K and

n = ionic charge

The level of potassium ions, A , is the activity or “effective concentration” of free potassium ions in solution. The potassium ion activity is related to free potassium ion concentration, C_f , by the activity coefficient, γ .

$$A = \gamma * C_f$$

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.

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

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 potassium standards and samples so that the background ionic strength is high and constant relative to variable concentrations of potassium. For potassium, the recommended ISA is NaCl. Other solutions can be used as long as they do not contain ions that would interfere with the electrode response to potassium.

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. If the electrode fails this procedure again and the half-cell potassium electrode is being used, determine whether the potassium 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 that the correct electrode filling solution was used.
- 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 9319BN potassium half-cell electrode require a separate reference electrode, Cat. No. 900200.
- Electrode is clogged or dirty –
Refer to the **Electrode Maintenance** section for electrode cleaning and flushing instructions.
- Sensing module is not installed properly, dirty or defective –
Refer to the **Electrode Preparation** section and verify that the electrode was assembled correctly. Refer to the **Electrode Maintenance** section for instructions on installing a new sensing module.
- Standards are contaminated or made incorrectly –
Prepare fresh standards. Refer to the **Serial Dilution, Measurement Hints** and **Analytical Techniques** sections.
- ISA not used or incorrect ISA used –
ISA must be added to all standards and samples. Refer to the **Required Equipment** section for information on the ISA.
- Samples and standards at different temperatures –
Allow solutions to reach the same temperature.
- Air bubble on sensing module –
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
9719BNWP	Potassium ionplus Sure-Flow combination electrode, waterproof BNC connector
900065	Optimum Results E electrode filling solution, 5 x 60 mL bottles
9319BN	Potassium half-cell electrode, BNC 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
921906	0.1 M potassium standard, 475 mL bottle
931911	ISA for potassium measurements, 475 mL bottle
971901	97 series sensing module for 9719BNWP potassium combination electrode
9700BNWP	Replacement body for 9719BNWP potassium combination electrode (requires separate 97 series sensing module)
931901	93 series sensing module for 9319BN potassium half-cell electrode
9300BNWP	Replacement body for 9319BN potassium half-cell electrode (requires separate 93 series sensing module)

Specifications

Concentration Range

10^{-6} M to 1 M (0.04 ppm to 39,000 ppm)

pH Range

2.5 to 11

Low level measurements may be influenced by hydrogen or hydroxide ion interferences

Temperature Range

0 to 40 °C

Electrode Resistance

Less than 50 megohms

Reproducibility

± 2%

Minimum Sample Size (9719BNWP)

5 mL in a 50 mL beaker

Size— 9719BNWP

Body Diameter: 13 mm

Body Length: 110 mm

Cap Diameter: 16 mm

Cable Length: 1 meter

Size— 9319BN

Body Diameter: 12 mm

Body Length: 110 mm

Cap Diameter: 16 mm

Cable Length: 1 meter

** Specifications are subject to change without notice*

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