# TABLE OF CONTENTS

**General Instructions** .......................................................................................................................................................... 3
  - Introduction ............................................................................................................................................................................ 3
  - Required Equipment ............................................................................................................................................................. 3
  - Required Solutions .............................................................................................................................................................. 3

**General Preparation** .......................................................................................................................................................... 4
  - Electrode Preparation ........................................................................................................................................................... 4
  - Electrode Slope Check (with pH/mV meter) ........................................................................................................................ 4
  - Electrode Slope Check (with ion meter) ............................................................................................................................. 4

**Measurement** ..................................................................................................................................................................... 4
  - Measuring Hints ................................................................................................................................................................. 4
  - Sample Requirements ......................................................................................................................................................... 6
  - Units of Measurement .......................................................................................................................................................... 6
  - Measurement Procedure ....................................................................................................................................................... 6
  - Direct measurement ............................................................................................................................................................ 6
  - Direct Measurement of Potassium (with pH/mV meter) .................................................................................................... 6
  - Direct Measurement of Potassium (with ion meter) ......................................................................................................... 8
  - Low Level Potassium Determination (with pH/mV meter) ............................................................................................... 8
  - Low Level Potassium Determination (with ion meter) .................................................................................................... 10

**Electrode Characteristics** ................................................................................................................................................ 10
  - Reproducibility ..................................................................................................................................................................... 10
  - Interferences ......................................................................................................................................................................... 10
  - Temperature Influences ...................................................................................................................................................... 11
  - Electrode Response ............................................................................................................................................................. 11
  - Detection Limit .................................................................................................................................................................... 12
  - pH Effects ............................................................................................................................................................................ 12
  - Electrode Life .................................................................................................................................................................... 13
  - Electrode Storage ............................................................................................................................................................... 13

**Electrode Theory** ............................................................................................................................................................... 13
  - Electrode Operation ............................................................................................................................................................ 13

**Troubleshooting Guide** ..................................................................................................................................................... 14

**Troubleshooting Hints** ...................................................................................................................................................... 17

**Electrode Specifications** .................................................................................................................................................... 19

**Ordering Information** ....................................................................................................................................................... 19
GENERAL INSTRUCTIONS

The Cole-Parmer Potassium Ion Electrodes are used to quickly, simply, accurately, and economically measure potassium ions in aqueous solutions.

Introduction

The Cole-Parmer Potassium Ion Electrodes are used to quickly, simply, accurately, and economically measure free potassium ion in aqueous solutions.

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.
3. A magnetic stirrer.
5. Cole-Parmer Filling Solution, Cat. No. 27503-78 for the 27502-39 and 27504-26 electrodes.

Required Solutions

1. Deionized or distilled water for solution and standard preparation.
2. Cole-Parmer Potassium Standard, 0.1M KCl, Cat. No. 27503-29. To prepare this standard, add 7.46 grams of reagent-grade potassium chloride to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.
3. Cole-Parmer Potassium Standard, 1000 ppm K⁺, Cat. No. 27503-30. To prepare this standard, add 1.91 grams of reagent-grade potassium chloride to a 1 liter volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution.
4. Cole-Parmer Ionic Strength Adjuster, 5M NaCl, Cat. No. 27503-53 to keep a constant background ionic strength present in the solution. To prepare the 5M NaCl ISA from your own laboratory stock, add 292 grams of reagent-grade
sodium chloride (NaCl) to a 1000 ml volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid and fill to the mark with distilled water. Cap the flask and invert several times to mix the solution. Add 2 ml of ISA to every 100 ml of sample or standard solution for a background ionic strength of 0.10M.

GENERAL PREPARATION

Electrode Preparation

Remove any rubber cap covering the electrode tip and the rubber inserts covering the filling hole of the reference electrode. Fill the combination electrode with the filling solution shipped with the electrode to a level just below the fill hole. No preparation is required for a sealed reference electrode. Gently shake the electrode downward in the same manner as a clinical thermometer to remove any air bubbles which might be trapped behind the potassium membrane. Prior to first usage, or after long term storage, immerse the potassium electrode in potassium standard for thirty minutes. The electrode is now ready for use.

Connect the electrode to the proper terminal(s) as recommended by the meter manufacturer.

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

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

Using a pipet, add 1 ml of 0.1M or 1000 ppm potassium standard to the beaker. When the reading is stable, record the millivolt reading.

Using a pipet, add 10 ml of the same potassium standard used above to the beaker. When the reading has stabilized, record the millivolt reading.

Determine the difference between the two readings. A difference of 56 ± 2mV 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 electrode each day)

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

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

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

Rinse the electrode with distilled water and blot dry.

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

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

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 slope is not within this range.

**MEASUREMENT**

**Measuring Hints**

The sensing membrane is normally subject to water uptake and might appear milky. This has no effect on performance.

All samples and standards should be at the same temperature for precise measurement, preferably ambient temperature.

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

Always rinse the electrode tip with distilled water and blot dry with a fresh tissue between readings to prevent solution carryover.

Check the electrode for air bubbles adhering to the membrane surface after immersion in solution. Agitate the electrode gently to remove the air bubbles.

A slow or sluggish electrode response may indicate surface contamination of the potassium electrode membrane. Soak the electrode tip in distilled water for about 5 minutes to clean the membrane. Rinse the membrane and soak in diluted standard solution for about 5 minutes to restore performance.

When measuring samples with high ionic strength, prepare standards with compositions similar to that of the sample.

Dilute concentrated samples (over 0.1M) before measurement.

Recalibrate every few hours for routine measurement.
Sample Requirements

Make sure that the samples and standards are at the same temperature. About a 2% error will be introduced for a 1°C difference in temperature. Temperature should normally be less than 40°C with intermittent measurements allowed to 50°C.

All samples and standards must be aqueous. They must not contain organic solvents.

Interferences found in Table 3 should be absent.

Units of Measurement

Potassium concentrations are measured in units of parts per million as potassium, parts per million as KCl, moles per liter, or any other convenient concentration unit. Table 1 indicates some of the concentration units.

<table>
<thead>
<tr>
<th>ppm K⁺¹</th>
<th>ppm KCl</th>
<th>moles/liter K⁺¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.91</td>
<td>7.46</td>
<td>1 x 10⁻⁴</td>
</tr>
<tr>
<td>39.10</td>
<td>74.60</td>
<td>1 x 10⁻³</td>
</tr>
<tr>
<td>391.00</td>
<td>746.00</td>
<td>1 x 10⁻²</td>
</tr>
</tbody>
</table>

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 ISA for all potassium samples. The temperature of both sample solution and of standard solutions should be the same.

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

1. Prepare 10⁻², 10⁻³, and 10⁻⁴ M or 100, 10, and 1 ppm standards by serial dilution of the 0.1M or 1000 ppm standard. Measure out 100 ml of each standard into individual 150 ml beakers. Add 2 ml of ISA per 100 ml of standard.

2. Place the most dilute solution (10⁻⁴ M or 1 ppm) on the magnetic stirrer and begin stirring at a constant rate. After assuring that the meter is in the mV mode, lower the electrode tip into the solution. When the reading has stabilized, record the mV reading.

3. Place the midrange solution (10⁻³ M or 10 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrode with distilled water and blotting dry, immerse the electrode tip in the solution. When the reading has stabilized, record the mV reading.
4. Place the most concentrated solution (10^{-2} M or 100 ppm) on the magnetic stirrer and begin stirring. After rinsing the electrode with distilled water and blotting dry, immerse the electrode tip 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 the concentration (log axis). Extrapolate the curve down to about 1 \times 10^{-5} M or 0.2 ppm. A typical calibration curve can be found in Figure 1.

![Figure 1: Typical Potassium Electrode Calibration Curve](image)

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 tip in the solution. When the reading has stabilized, record the millivolt reading. Determine the concentration directly from the calibration curve.

7. The electrode should be re-calibrated every 1-2 hours. Simply repeat Steps 2-5 above.
Direct Measurement of Potassium (using an ion meter)

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

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

3. Lower the electrode tip into the solution.

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

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

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

7. Lower the electrode tip into the solution.

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

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

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

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

12. The electrodes should be re-calibrated every 1-2 hours. Simply repeat Steps 2-8 (2-9) above.

Low Level Potassium Determination (using a standard pH/mV meter)

This procedure is recommended for solutions with ionic strengths less than $1.0 \times 10^{-2}$ M. If the solution is high in ionic strength, but low in potassium, use the same procedure, but prepare a calibration solution with a composition similar to the sample.
1. Using 20 ml of stock ISA, dilute to 100 ml with distilled water.

2. Dilute 1 ml of the 0.1M standard to 100 ml to prepare a $1.0 \times 10^{-3}$ M standard solution for measurements in moles per liter. Dilute 10 ml of the 1000 ppm standard to 100 ml to prepare a 100 ppm standard solution for measurements in ppm.

3. To a 150 ml beaker, add 100 ml of distilled water and 1 ml of low level ISA. Place the beaker on the magnetic stirrer and begin stirring at a constant rate.

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

5. Add increments of the $1.0 \times 10^{-3}$ M or 100 ppm standard as given in Table 2 below.

6. After the reading has stabilized, record the mV reading after each addition.

**TABLE 2: Stepwise Calibration for Low Level Potassium Measurements**

<table>
<thead>
<tr>
<th>Step</th>
<th>Pipet</th>
<th>Added Volume (ml)</th>
<th>Concentration</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A</td>
<td>0.1</td>
<td>$1.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>2</td>
<td>A</td>
<td>0.1</td>
<td>$2.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>3</td>
<td>A</td>
<td>0.2</td>
<td>$4.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>4</td>
<td>A</td>
<td>0.2</td>
<td>$6.0 \times 10^{-6}$</td>
</tr>
<tr>
<td>5</td>
<td>A</td>
<td>0.4</td>
<td>$9.9 \times 10^{-6}$</td>
</tr>
<tr>
<td>6</td>
<td>B</td>
<td>2</td>
<td>$2.9 \times 10^{-5}$</td>
</tr>
<tr>
<td>7</td>
<td>B</td>
<td>2</td>
<td>$4.8 \times 10^{-5}$</td>
</tr>
</tbody>
</table>

Pipet A = 1 ml graduated pipet  
Pipet B = 2 ml pipet  
Solutions: additions of $1.0 \times 10^{-3}$ M or 100 ppm standard to 100 ml of distilled water

7. On semi-logarithmic graph paper, plot the mV reading (linear axis) against the concentration (log axis) as in Figure 1.

8. Rinse the electrode 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 tip into the solution.

10. After the reading has stabilized, record the mV reading and determine the concentration from the low level calibration curve.
11. Prepare a new low level calibration curve daily. Check the calibration curve every 1-2 hours by repeating Steps 3-7 above.

**Low Level Potassium Determination (using an ion meter)**

Follow the procedure given for normal potassium determinations using an ion meter and the blank correction procedure.

**ELECTRODE CHARACTERISTICS**

**Reproducibility**

Direct electrode measurements reproducible to ±2% can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuations, drift, and noise limit reproducibility.

Reproducibility is independent of concentration within the electrode’s operating range.

**Interferences**

Table 3 lists some common cations that, if present in high enough levels, will cause electrode interferences and measurement errors or electrode drift when using the potassium ion electrodes.

Electrode drift and slow response could indicate the presence of high interference from the ions listed. Soak the electrode in distilled water for an hour, then for two hours in potassium standard solution to restore proper response.

**TABLE 3: Concentration of Possible Interferences Causing a 10% Error at Various Levels of KCl; Background Ionic Strength is 0.12M NaCl.**

<table>
<thead>
<tr>
<th>Interferences (moles/liter)</th>
<th>$10^{-2}$M K$^{+1}$</th>
<th>$10^{-3}$M K$^{+1}$</th>
<th>$10^{-4}$M K$^{+1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs$^{+1}$</td>
<td>$3.0 \times 10^{-3}$</td>
<td>$3.0 \times 10^{-4}$</td>
<td>$3.0 \times 10^{-5}$</td>
</tr>
<tr>
<td>NH$_4^{+1}$</td>
<td>$6.0 \times 10^{-2}$</td>
<td>$6.0 \times 10^{-3}$</td>
<td>$6.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>Tl$^{+1}$</td>
<td>$6.0 \times 10^{-2}$</td>
<td>$6.0 \times 10^{-3}$</td>
<td>$6.0 \times 10^{-4}$</td>
</tr>
<tr>
<td>H$^{+1}$</td>
<td>$1.0 \times 10^{-1}$</td>
<td>$1.0 \times 10^{-2}$</td>
<td>$1.0 \times 10^{-3}$</td>
</tr>
<tr>
<td>Ag$^{+1}$</td>
<td>$1.0 \times 10^{1}$</td>
<td>$1.0$</td>
<td>$1.0 \times 10^{1}$</td>
</tr>
<tr>
<td>+Tris$^{+1}$</td>
<td>$1.0 \times 10^{1}$</td>
<td>$1.0$</td>
<td>$1.0 \times 10^{1}$</td>
</tr>
<tr>
<td>Li$^{+1}$</td>
<td>$2.0 \times 10^{1}$</td>
<td>$2.0$</td>
<td>$2.0 \times 10^{1}$</td>
</tr>
<tr>
<td>Na$^{+1}$</td>
<td>$2.0 \times 10^{1}$</td>
<td>$2.0$</td>
<td>$2.0 \times 10^{1}$</td>
</tr>
</tbody>
</table>

+Tris$^{+1}$ is the cation of tris(hydroxymethyl)aminomethane
Table of Content

Interferences

(1 ppm K\(^+\))

<table>
<thead>
<tr>
<th>Ion</th>
<th>100 ppm K(^+)</th>
<th>10 ppm K(^+)</th>
<th>1 ppm K(^+)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cs(^+)</td>
<td>1.0 x 10(^2)</td>
<td>1.0 x 10(^1)</td>
<td>1.0</td>
</tr>
<tr>
<td>K(^+)</td>
<td>2.7 x 10(^2)</td>
<td>2.7 x 10(^1)</td>
<td>2.7</td>
</tr>
<tr>
<td>Tl(^+)</td>
<td>3.1 x 10(^3)</td>
<td>3.1 x 10(^2)</td>
<td>3.1 x 10(^1)</td>
</tr>
<tr>
<td>H(^+)</td>
<td>1.6 pH</td>
<td>2.6 pH</td>
<td>3.6 pH</td>
</tr>
<tr>
<td>Ag(^+)</td>
<td>2.7 x 10(^5)</td>
<td>2.7 x 10(^4)</td>
<td>2.7 x 10(^3)</td>
</tr>
<tr>
<td>Li(^+)</td>
<td>3.5 x 10(^4)</td>
<td>3.5 x 10(^3)</td>
<td>3.5 x 10(^2)</td>
</tr>
<tr>
<td>Na(^+)</td>
<td>1.1 x 10(^5)</td>
<td>1.1 x 10(^4)</td>
<td>1.1 x 10(^3)</td>
</tr>
</tbody>
</table>

Temperature Influences

Samples and standards should be at the same temperature, since electrode potentials are influenced by changes in temperature. A 1°C difference in temperature results in a 2% error at the 1.0 x 10\(^{-3}\) M level.

Provided that temperature equilibria has occurred, the potassium electrodes can be used at temperatures from 0° - 50°C continuously and 40° - 50°C intermittently. Room temperature measurements are recommended, since measurements at temperatures markedly different from room temperature may require equilibrium times up to one hour.

Table 4 indicates the variation of theoretical slope with temperature.

**TABLE 4:** Temperature vs Value for the Electrode Slope

<table>
<thead>
<tr>
<th>Temp (°C)</th>
<th>“S”(slope)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>54.20</td>
</tr>
<tr>
<td>10</td>
<td>56.18</td>
</tr>
<tr>
<td>20</td>
<td>58.16</td>
</tr>
<tr>
<td>25</td>
<td>59.16</td>
</tr>
<tr>
<td>30</td>
<td>60.15</td>
</tr>
<tr>
<td>40</td>
<td>62.13</td>
</tr>
<tr>
<td>50</td>
<td>64.11</td>
</tr>
</tbody>
</table>

Electrode Response

Plotting the electrode mV potential against the potassium concentration on semi-logarithmic paper results in a straight line with a slope of about 56mV per decade. Refer to Figure 1.
The time needed to reach 99% of the stable electrode potential reading, the electrode response time, varies from one minute or less for potassium concentration above 1.0 x 10^{-5} M to several minutes near the detection limit. Refer to Figure 2.

**Detection Limit**

The upper limit of detection is 1M in pure potassium chloride solutions. The upper limit of detection is above 1.0 x 10^{-1} M when other ions are present, but the possibility of a liquid junction potential developing at the reference electrode and the “salt extraction effect” are two limiting factors. Some salts may be extracted into the electrode membrane at high salt concentrations causing deviation from theoretical response. Calibrate the electrode at four or five intermediate points, or dilute the sample, to measure samples between 1.0 x 10^{-1} M and 1M.

The slight water solubility of the ion exchanger in the sensing module, which causes deviation from theoretical response, determines the lower limit of detection. The theoretical response at low levels of potassium chloride compared to actual response is shown in Figure 1. A low level measurement is recommended if potassium measurements are made below 1.0 x 10^{-5} M (0.39 ppm as potassium).

**pH Effects**

Hydrogen ion interferes with measurements of low levels of potassium ion although the electrode can be used over a wide pH range. Table 3 should be used 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.
Electrode Life

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

Electrode Storage

The Cole-Parmer Potassium Ion Electrodes may be stored in 1.0 x 10^{-2} M potassium standard for short periods of time. For storage over 3 weeks, rinse and dry the potassium membrane electrode and cover the tip with any protective cap shipped with the electrode. The reference portion of the combination electrode should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole.

ELECTRODE THEORY

Electrode Operation

The potassium electrode consists of an electrode body containing an ion exchanger in a sensing module. This sensing module contains a liquid internal filling solution in contact with a gelled organophilic membrane containing a potassium selective ion exchanger.

An electrode potential develops across the membrane when the membrane is in contact with a potassium solution. Measurement of this potential against a constant reference potential with a digital pH/mV meter or with a specific ion meter depends on the level of free potassium ion in solution. The level of potassium ions, corresponding to the measured potential, is described by the Nernst equation:

\[ E = E_0 + S \log X \]

where:
- \( E \) = measured electrode potential
- \( E_0 \) = reference potential (a constant)
- \( S \) = electrode slope (~ 56 mV/decade)
- \( X \) = level of potassium ions in solution

The activity, \( X \), represents the effective concentration of the ions in solution. Total potassium concentration, \( C_t \), includes free potassium ions, \( C_f \), plus bound or complexed potassium ions, \( C_b \). Since the potassium electrodes only respond to free ion, the free ion concentration is:

\[ C_f = C_t - C_b \]

The activity is related to the free ion concentration, \( C_f \), by the activity coefficient, \( \gamma \), by:

\[ X = \gamma C_f \]
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 \( X \)
- \( \sum \) = sum of all of the types of ions in the solution.

In the case of high and constant ionic strength relative to the sensed ion concentration, the activity coefficient, \( \gamma \), 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 ISA for potassium is sodium chloride, NaCl. Solutions other than this may be used as long as ions that they contain do not interfere with the electrode’s response to potassium ions.

The reference electrode must also be considered. When two solutions of different composition are brought into contact with one another, liquid junction potentials arise. Millivolt potentials occur from the interdiffusion of ions into 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 solution diffuse into the sample should be as nearly equal as possible, that is, the filling solution should be equitransferant. No junction potential can result if the rate at which positive and negative charge carried into the sample 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 equitransferant salt. One must either calibrate the electrode(s) in the same pH range as the samples or use a known increment method for ion measurement.

**TROUBLESHOOTING GUIDE**

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

**Meter**

The meter may be checked by following the checkout procedure in the instrument instruction manual.
Glassware

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

Electrode

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

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

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

3. If the electrode still fail to respond as expected, substitute another potassium 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 Reagents, Sample, and Technique sections below.

5. If another electrode is not available for test purposes, or if the electrode in use is suspect, review the instruction manual and be sure to:
   - Clean and rinse the electrode thoroughly.
   - Prepare the electrode properly.
   - Use the proper filling solution.
   - Adjust the pH and the ionic strength of the solution by the use of the proper ISA.
   - Measure correctly and accurately.
   - Review TROUBLESHOOTING HINTS.

Reagents

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

Look for possible interferences, complexing agents, or substances which could affect the response or physically damage the sensing electrode (or the reference electrode) if the electrode 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 that Good Laboratory Practice has been followed.

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

If trouble still persists, call Cole-Parmer at 1-800-323-4340 and ask for the Technical Services Department.
# TROUBLESHOOTING HINTS

<table>
<thead>
<tr>
<th>Symptom</th>
<th>Possible Causes</th>
<th>Next Step</th>
</tr>
</thead>
<tbody>
<tr>
<td>Out of Range Reading</td>
<td>defective meter</td>
<td>check meter with shorting strap (see meter instruction manual)</td>
</tr>
<tr>
<td></td>
<td>defective electrode</td>
<td>check electrode operation</td>
</tr>
<tr>
<td></td>
<td>electrode not plugged in properly</td>
<td>unplug electrode and reseat</td>
</tr>
<tr>
<td></td>
<td>reference electrode not filled</td>
<td>be sure reference electrode is filled</td>
</tr>
<tr>
<td></td>
<td>air bubble on membrane</td>
<td>remove air bubble by re-dipping electrode</td>
</tr>
<tr>
<td></td>
<td>electrode not in solution</td>
<td>put electrode in solution</td>
</tr>
<tr>
<td>Noisy or Unstable Readings</td>
<td>defective meter</td>
<td>check meter with shorting strap (see meter instruction manual)</td>
</tr>
<tr>
<td>(readings continuously or rapidly changing)</td>
<td>air bubble on membrane</td>
<td>remove air bubble by re-dipping electrode</td>
</tr>
<tr>
<td></td>
<td>ISA not used</td>
<td>use recommended ISA</td>
</tr>
<tr>
<td></td>
<td>meter or stirrer not grounded</td>
<td>ground meter or stirrer</td>
</tr>
<tr>
<td></td>
<td>defective electrode</td>
<td>replace electrode</td>
</tr>
<tr>
<td></td>
<td>electrode exposed to interferences</td>
<td>soak electrode in potassium standard</td>
</tr>
<tr>
<td>Drift (reading slowly changing in one direction)</td>
<td>samples and standards at different temperatures</td>
<td>allow solutions to come to room temperature before measurement</td>
</tr>
<tr>
<td></td>
<td>electrode exposed to interferences</td>
<td>soak electrode in potassium standard</td>
</tr>
<tr>
<td></td>
<td>incorrect reference filling solution</td>
<td>use recommended filling solution</td>
</tr>
<tr>
<td>Symptom</td>
<td>Possible Causes</td>
<td>Next Step</td>
</tr>
<tr>
<td>-------------------------------</td>
<td>------------------------------------------------------</td>
<td>-----------------------------------------------------</td>
</tr>
<tr>
<td>Low Slope or No Slope</td>
<td>standards contaminated or incorrectly made</td>
<td>prepare fresh standards</td>
</tr>
<tr>
<td></td>
<td>ISA not used</td>
<td>use recommended ISA</td>
</tr>
<tr>
<td></td>
<td>standard used as ISA</td>
<td>use ISA</td>
</tr>
<tr>
<td></td>
<td>electrode exposed to interferences</td>
<td>soak electrode in potassium standard</td>
</tr>
<tr>
<td></td>
<td>air bubble on membrane</td>
<td>remove air bubble by re-dipping electrode</td>
</tr>
<tr>
<td>“Incorrect Answer”</td>
<td>incorrect scaling of semi-log paper</td>
<td>plot millivolts on the linear axis. On the log axis, be sure concentration numbers within each decade are increasing with increasing concentration</td>
</tr>
<tr>
<td>(but calibration is good)</td>
<td>incorrect sign</td>
<td>be sure to note sign of millivolt number correctly</td>
</tr>
<tr>
<td></td>
<td>incorrect standards</td>
<td>prepare fresh standards</td>
</tr>
<tr>
<td></td>
<td>wrong units used</td>
<td>apply correct conversion factor: $10^3 \text{M} = 39 \text{ppm}$ $\text{K}^+ = 75 \text{ppm}$ as KCl</td>
</tr>
<tr>
<td></td>
<td>sample carryover</td>
<td>rinse electrode thoroughly between samples</td>
</tr>
</tbody>
</table>
ELECTRODE SPECIFICATIONS

Concentration Range 1M to 1 x 10^6 M
(39,000 ppm to 0.04 ppm)

pH Range 2 to 12

Temperature Range 0° to 40°C (continuous)
40° to 50°C (intermittent)

Resistance 100 Mohms

Reproducibility ± 2%

Samples aqueous solutions only;
no organic solvents

Size 110 mm length
12 mm diameter
1 m cable length

Storage electrode should be stored in dilute potassium standard

ORDERING INFORMATION

<table>
<thead>
<tr>
<th>P/N</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>27502-39</td>
<td>Potassium Electrode, combination, glass</td>
</tr>
<tr>
<td>27504-26</td>
<td>Potassium Electrode, combination, epoxy</td>
</tr>
<tr>
<td>27503-29</td>
<td>Potassium Standard, 0.1 M KCl</td>
</tr>
<tr>
<td>27503-30</td>
<td>Potassium Standard, 1000 ppm K^+</td>
</tr>
<tr>
<td>27503-53</td>
<td>Potassium ISA (Ionic Strength Adjustor), 5 M NaCl</td>
</tr>
<tr>
<td>27503-78</td>
<td>27502-39 and 27504-26 Combination Electrode Filling Solution, 0.1 M NaCl</td>
</tr>
<tr>
<td>27502-89</td>
<td>ISE Solution Kit. Contains (1) bottle of 1000 ppm Potassium Standard, (1) bottle of ISA, (1) bottle of Reference Filling Solution, and (1) Syringe</td>
</tr>
</tbody>
</table>