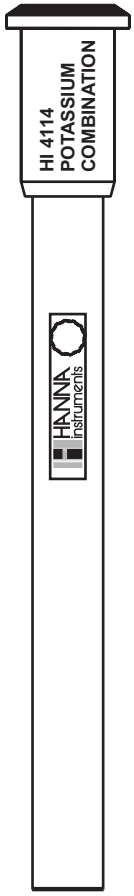
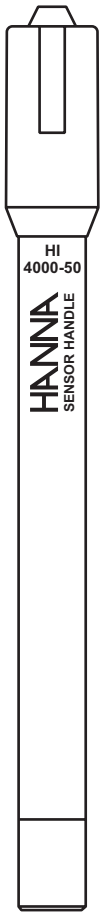




Instruction Manual

HI 4014
HI 4114

Potassium Ion
Selective Electrode

Half-cell
Combination

HANNA® instruments
With Great Products, Come Great Results™

HI 4014 Potassium half-cell
HI 4114 Potassium combination electrode

I. Introduction

The Hanna HI 4014 and HI4114 are ion selective electrodes designed for the measurement of potassium ions in aqueous solutions. They utilize a replaceable sensing module that contains an organic polymer membrane that is sensitive to potassium. HI 4014 is a half-cell electrode that requires a separate reference.
HI 4114 is a combination ion selective electrode.

II. Specifications

Type:	PVC membrane with organic ion exchanger
Ion measured:	Potassium (K^+)
Measurement range:	1M to 1X 10^{-6}M 39100 to 0.039ppm
Interference:	
Organic solvents and cationic detergents must be absent.	
Ratio of interfering ion to K^+ must be below	
	10 for NH_4^+
	300 for Li^+
	2000 for Na^+
	2000 for Ca^{2+}
Operating Temperature:	0-40°C
Operating pH:	1.5 to 12.0 pH
Dimensions:	12 mm (OD)(0.47") X 120 mm (4.72") (insertion)
Connection:	BNC

III. Theory of Operation:

The HI 4014 and HI 4114 potassium electrodes are potentiometric devices used for the rapid determination of free potassium ions in water, soft drinks, wine, and soils. The electrode functions as a sensor or ionic conductor. HI 4014 requires a separate reference electrode to complete its electrolytic circuit. HI 4114 is a combination electrode with a reference electrode incorporated in its design. The PVC membrane used on the sensor is impregnated with the organic ion exchanger valinomycin. This carrier ionophore encloses the ion like a cage. The outside of the ionophore molecule is uncharged and it can freely diffuse through the lipid layers of the membrane producing a charge imbalance between the test solution and internal cell of the sensor. This produces a voltage that changes in response to the sample's ion activity. When the ionic strength of the sample is fixed, the voltage is proportional to the concentration of potassium ions in solution. The sensor follows the Nernst Equation:

$E = E_a + 2.3\ RT/nF \log A_{ion}$

E = observed potential

E_a = Reference and fixed internal voltages

R = gas constant (8.314 J/K Mol)

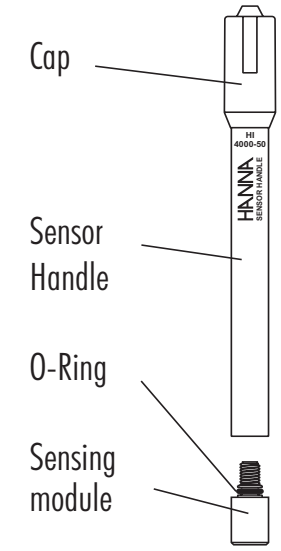
n = Charge on ion (equivalents/mol) (1+)

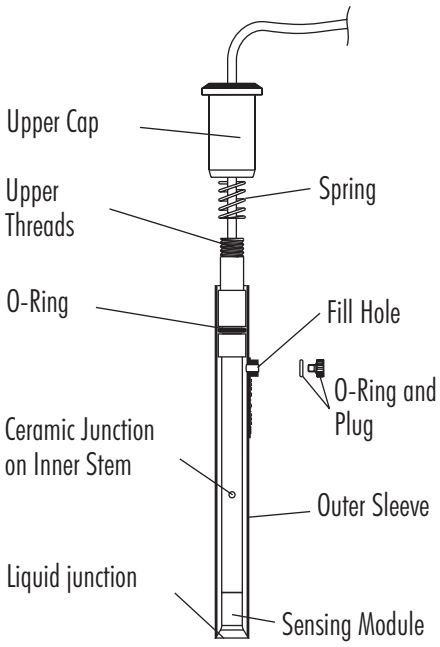
A_{ion} = ion activity in sample

T = absolute temperature in K

F = Faraday constant (9.648×10^4 C/equivalent)

IV. Design elements of the HI 4014 and HI 4114 electrodes





V. Equipment Required:

- HI 4014 requires the Hanna HI 5315 Double Junction reference electrode with HI 7076 as external electrolyte.
- Hanna HI 4222 pH/ISE/mV meter or other suitable ion or pH/mV meter. (Note: log/linear graph paper is useful if an ISE (ion) meter is not available).
- Hanna HI 180 magnetic stirrer or equivalent with magnetic stirring bars (Note: Isolate beakers from stirrer motor heat by placing insulating material such as foam or cork between them).
- Hanna HI 76404 electrode holder or equivalent.
- Plastic beakers (HI 740036P) or other suitable measurement vessel.

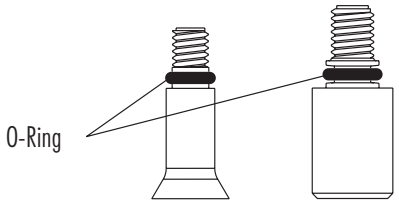
VI. Solutions Required for Potassium Measurements

0.1 M potassium standard, 500 mL	**HI 4014-01**
Ionic Strength Adjuster, 500 mL	**HI 4014-00**

Using volumetric pipettes and glassware make dilutions to bracket the concentration of the samples. Standards with concentrations $< 10^{-3}$ M should be prepared daily.
Store standards in plastic bottles. Add 2 mL of Hanna ISA HI 4014-00 to 100 mL sample or standard.

VII. General Guidelines

- Ensure the o-ring is installed on modules before screwing into the sensor handle or inner stem.



- Due to shipping or storage the internal solution inside the sensing modules may have developed an air pocket near the membrane. Gently shaking the sensor down (like the old style mercury thermometers) will place the internal solution next to the membrane.
- Presoaking the potassium sensor in a 10^{-2} M standard for at least half-hour before calibration will help to optimize the sensor response.
- Calibration standards and sample solutions should have the same ionic strength. ISA should be added to both samples and standards in the same ratios.
- Calibration standards and sample solutions should be at the same temperature.
- Thermally insulate solution vessel from magnetic stirrer.
- Calibration standards and sample solutions should be stirred at the same rate using identically sized TFE coated stir bars.
- Rinse electrode pair with distilled or deionized water between samples and dab dry with lab wipe or other soft disposable absorbent toweling. Do not rub membranes.
- Check for gas bubbles that may form near the sensing surface (due to temperature changes). Tap off gently.
- Avoid large changes in temperature (thermal shock) as it may damage the sensor.

Additional HI 4114 Guidelines

- Remove the protective plastic wrap that covers the ceramic junction before assembling sensor for the first time.
- Add reference fill solution HI 7076 to bottom of fill hole or empty and refill solution daily before using.
- During measurement always operate electrode with the fill hole open.
- During normal use, fill solution will slowly drain out of the tapered cone junction at the lower portion of the electrode. Excessive loss ($>$4 cm drop within 24 hours) is not normal. If this occurs verify cap is tightened and the interface between the internal cone and outer body is free of debris.
- Add filling solution daily to maintain a good head pressure. For optimum response, this level should be maintained and not be allowed to drop more than 2 -3 cm (1-inch) below fill hole.
- Do not use an electrode if crystallized salts are visible inside the electrode. Drain electrode, disassemble and rinse internal body with deionized water. Reassemble and refill with fresh fill solution.
- If an erratic measurement occurs, check to see if foreign matter is seen trapped near the internal cone. Drain by depressing the electrode cap then refill with fresh fill solution.

VIII. Electrode Preparation

HI 4014

The Hanna HI 4014 is a 2 piece design comprised of a sensor handle (HI 4050) and a sensing module (HI 4014-51).

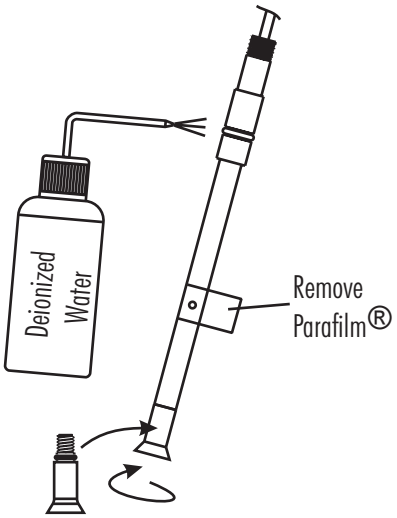
1) Remove sensing module from shipping vial. Do not touch the sensing membrane with the "H" hole pattern on it.
2) Screw the module into the sensor handle finger tight. Do not over tighten.

3) Holding the assembled electrode at the cable end, shake the sensor to ensure internal fill solution that may have separated during shipping is in contact with inner membrane surface.
4) Prepare reference electrode by filling outer electrolyte reservoir with fill solution HI 7076.
5) Place sensor (and reference) electrodes into electrode holder and connect cable connectors to meter.
6) Soak the potassium membrane in a potassium containing standard for a hour before calibration.

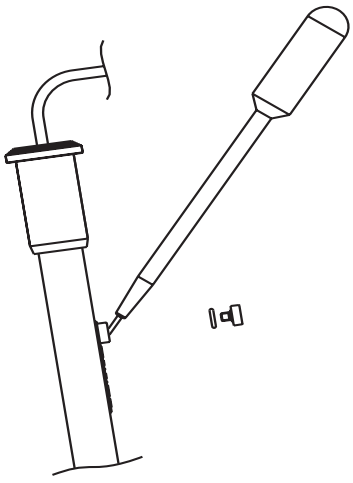
HI 4114

The Hanna HI 4114 is shipped dissembled.

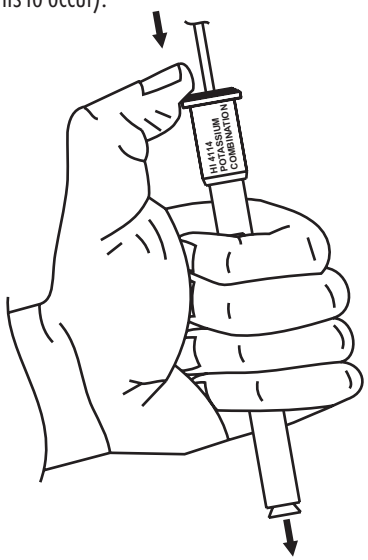
1. Unwrap Parafilm® seal found over ceramic junction on inner stem and discard. This is only used for shipping and long term storage.
2. Open the glass vial (HI 4114-51) and remove the potassium sensing cone. Do not touch the sensing membrane with the "H" hole pattern on it.
3. Ensure o-ring is installed on module before screwing the cone into the inner stem finger tight. Do not over tighten.



4. Rinse inner stem with deionized water making certain to wet o-ring found on the inner stem.
5. Reassemble electrode by gently pushing the inner assembly into the outer body, sliding spring down cable, and screwing cap into place.
6. Remove fill hole cover and o-ring on fill hole spout. Using the dropper pipette provided, add a few drops HI 7076 fill solution to the electrode, wetting the o-ring and rinsing out the fill solution chamber.



7. Holding the body of the electrode gently press the upper cap with your thumb. This permits the fill solution to drain out of the body.
8. Release the cap and verify electrode returns to its original position. (You may need to gently assist for this to occur).



9. Tighten the electrode cap onto the body and fill electrode body until fill solution volume is just below fill hole.
10. Position electrode in a Hanna HI 76404 electrode holder (or equivalent) and connect BNC connector to meter.

IX. Quick Check of Electrode Slope

- Connect electrode(s) to pH/mV/ISE meter.
- Place meter in mV mode.
- Place 100 mL of deionized water into a beaker with stir bar.
- Place reference and measuring half-cell or combination electrode into prepared sample.
- Add 1 mL of a standard to beaker. Record the mV value when stable.
- Add an additional 10 mL of standard to the solution. Record the mV when reading has stabilized. This value should be more than the previous value noted (more positive).
- Determine the difference between the two mV values. An acceptable value for this slope is 56 ± 4 mV at typical room temperatures (20-25°C).

X. Corrective Action

- Verify module has been screwed into sensor handle or inner stem.
- Verify seal has been removed from ceramic junction (HI 4114) or HI 5315 reference electrode.
- Verify electrodes are connected properly to meter and meter is powered.
- Verify dilute standards are freshly made and stored. Remake solutions if appropriate. Store in plastic bottles.
- If the reading is unstable, shake sensor down (see Section VII).
- If the sensor slope just misses the suggested slope window, soaking the sensor in a standard may solve the problem.
- If the membrane is damaged, the response becomes extremely sluggish, or the slope of the electrode has decreased significantly, and procedures above have not helped, the modules should be replaced.

Module replacement for HI 4014

1. Dry off module and sensor handle.
2. Unscrew sensing module and replace with a new one. (HI 4014-51).
3. Soak new assembled module in potassium solution to condition it before calibration.

Module replacement for HI 4114

1. Drain the fill solution by depressing cap. Rinse electrode with distilled or deionized water. Drain.
2. Unscrew upper cap and slide down cable toward connector.
3. Move spring and outer body down cable also.
4. Dry off inner stem and module with a soft tissue.

5. Hold inner stem and unscrew module and replace with a new one. (HI 4114-51).
6. Reassemble electrode (see section VII), and refill with electrolyte. Soak new membrane in potassium solution to condition before calibration.

XI. Direct Calibration and Measurement

This method is a simple procedure for measuring many samples. A direct reading ISE meter (HI 4222 or equivalent) determines concentration of the unknown by a direct reading after calibrating the meter with the standards. HI 4014-00 ISE is added to both samples and standards to adjust the ionic strength of the solutions at a dose of 2 mL per 100 mL standard or sample. The meter is calibrated with freshly made standards that are in the measurement range of the unknowns. Unknowns are then read directly. In the non-linear region, more calibration standards are required and more frequent calibrations are advised.

A pH/mV meter in mV mode and semi log graph paper may also be used. Two or more freshly prepared standards that are in the measurement range of the unknowns (with ISA added), are measured in mV mode on the meter.

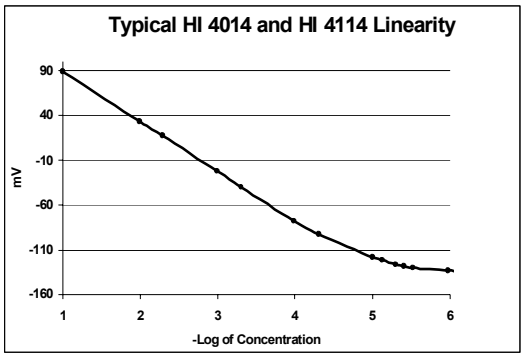
These values are plotted on semi-log paper and the points are connected to form a straight-line curve. When samples are measured, their mV values are converted to concentration by following the mV to the concentration axis on the semi-log plot.

Procedure:

Follow sections VIII and IX to prepare electrodes for measurement.

1) Follow section VI to prepare standards/ solution. Standards should bracket and fall within the range of interest. Standards and solutions should be at the same temperature.
   2 mL of HI 4014-00 is added to 100 mL of both samples and standards. Add stir bar and mix before taking measurements.

2) Follow section VII; General Guidelines to optimize test set-up.
3) During calibration it is best to start with lower concentration samples first. Wait for a stable reading before reading/ recording values. Permit longer equilibration at these levels (3 or 4 minutes).
4) To prevent carry over and contamination of samples, rinse sensors with deionized water and dab dry between samples. Do not rub membrane.



XII. Other Measurement Techniques

Known addition

An unknown concentration can be determined by adding a known amount (volume and concentration) of K^+ standard to the sample. mV values are noted before and after the addition of standard (ΔE). An ideal sensor slope can be used in the equation but actual determined slopes at the temperature of measurement should be used if known (S). This method is preprogrammed in the Hanna HI 4222 pH/ISE/mV meter, which greatly simplifies the method .

Example:

Potassium ion determination with known addition.

1. A 50 mL sample of unknown (V_{SAMPLE}) is placed in an clean plastic beaker with a thoroughly cleaned electrode (s). Add 1 mL of ISA to sample. Mix. The mV_1 is recorded.
2. 5 mL (V_{STD}) of 10^{-1}M (C_{STD}) standard is added to the beaker and the mV value increases. (Note: for other concentration samples, add a known volume and concentration of standard to produce approximately 30 mV change).
3. The unknown potassium concentration in the original sample (C_{SAMPLE}) can then be determined by using the equation that follows.

The procedure can be repeated with a second standard addition to verify slope and operation of the method.

$$C_{\text{sample}} = \frac{C_{\text{standard}} V_{\text{standard}}}{(V_T)10^{\Delta E/S} - (V_{S'})} \left(\frac{V_{S'}}{V_{\text{sample}}} \right)$$

$$(V_{\text{sample}} + V_{\text{standard}} + V_{\text{ISA}}) = V_T$$

$$(V_{\text{sample}} + V_{\text{ISA}}) = V_{S'}$$

XIII. pH

HI 4014/ HI 4114 potassium electrodes operate over a wide pH range. The pH range 1.5 - 12 is acceptable for measurements. Samples and standards can be adjusted to be within the working pH range.

XIV. Storage and Care of the HI 4014 sensor and HI 4114 electrode

HI 4014 sensor can be stored in dilute standards near the sample concentration for short periods of time and should be disassembled and stored dry in the shipping vial when not in use for long periods of time. Do not expose module to elevated temperatures. Refrigeration of module will extend life time.

HI 4114 combination electrode can be left in dilute standards near the sample concentration for short periods of time. If the electrode will be used frequently and needs to be ready for use, take measures to prevent evaporation of fill solution. Top off fill solution, replace o-ring, fill hole cover on the fill hole opening, and place in dilute potassium solution. Store electrode upright. Before using, flush junction once and top off fill solution.

For long-term storage, disassemble electrode and wash all salts from assembly with deionized water. Wrap ceramic junction on inner stem in Parafilm® or other sealing film. Unscrew module from the inner stem and blot dry. Store module in shipping vial. Store electrode assembly disassembled. Do not expose module to elevated temperatures. Refrigeration of module will extend its life.

XV. Conversion Tables

	Multiply by
Moles/L (M) K^+ to ppm K^+ (mg/L)	39100
ppm K^+ (mg/L) to M K^+(Moles/L)	2.56×10^{-5}

MAN4114 07/06 REV3

WARRANTY

Hanna Instruments Ion Selective Electrodes are warranted to be free of defects in material and workmanship for 6 months from date of purchase when used for their intended purpose and maintained according to instructions. If they fail to work when first used contact your dealer immediately. Damage due to accidents, misuse, misapplication, tampering or lack of prescribed maintenance is not covered.

Hanna Instruments reserves the right to modify the design, construction or appearance of its products without advance notice.

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