

Instruction Manual

HI 4012
HI 4112
Lead Ion
Selective Electrode

Half-cell
Combination

HI 4012 Lead Half-cell **HI 4112 Lead Combination Electrode**

I. Introduction:

The Hanna HI 4012 and HI 4112 are ion selective electrodes designed for the measurement of Lead ions in aqueous solutions. The HI 4012 is a solid state half-cell sensor that requires a separate reference. The HI 4112 is a combination ion selective electrode.

II. Specifications

Type: Solid State electrode with a lead sulfide pellet.

Ion(s) measured: Lead (Pb^{+2})

Measurement range: 0.1 M to 1×10^{-6} M
20700 to 0.21 ppm

Interfering ions: Silver, Copper, Cadmium
Iron ($2+$ $3+$) and Mercury must be absent. Any ion that forms a more insoluble sulfide than lead sulfide will interfere with the electrode response. Long term exposure in this ion will poison the lead surface. Oxidation of the lead surface will also poison the electrode.

Operating Temperature: 0-80°C

Operating pH: 4 to 7 pH
(recommended)

Dimensions: 12 mm (OD) X 120 mm
nominal insertion
(0.47" X 4.72")

Connection: BNC

III. Theory of Operation:

The HI 4012 or HI 4112 lead electrodes are potentiometric devices used for the rapid determination of free lead ions in plating baths and as a detector for the titration of sulfate or thorium with lead perchlorate. Lead sensors are “electrodes of the third kind” because they detect cations which also form low-solubility salts with sulfide anions and forms low-solubility salts with silver.

The electrode functions as a sensor or ionic conductor. The HI 4012 requires a separate reference electrode to complete its electrolytic circuit. The HI 4112 incorporates a reference electrode. The mixed lead sulfide/ silver sulfide membrane produces a potential change due to changes in the sample’s lead ion activity. When the ionic strength of the sample is fixed by the addition of ISA, the voltage is proportional to the concentration of Lead ions in solution and the electrode follows the Nernst equation.

$$E = E_0 + 2.3 RT/nF \log A_{ion}$$

E = observed potential

E_0 = Reference and fixed internal voltages

R = gas constant (8.314 volt coulomb/K Mole)

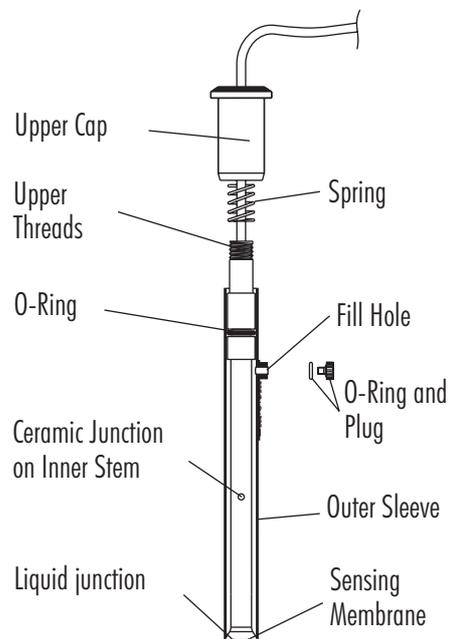
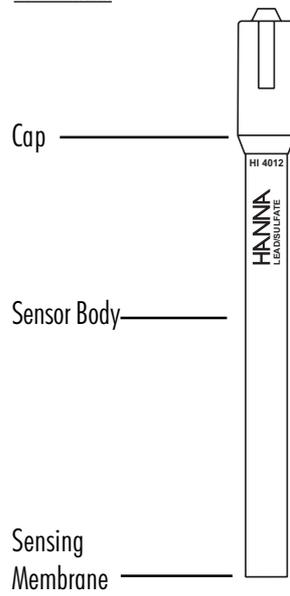
n = Charge on ion (2+)

A_i = ion activity in sample

T = absolute temperature in K

F = Faraday constant (9.648×10^4 coulombs/mole)

IV. Design elements of the HI 4012 and HI 4112 electrodes



V. Equipment required:

- Hanna HI 5315 Double Junction Reference Electrode with HI 7072 Fill Solution for HI 4012.
- 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 TFE coated stirring bars (HI 731320). 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 Lead Measurements

0.1 M lead standard, (500 mL) HI 4012-01
ISA, (5 X 100 mL) HI 4012-00

For Sulfate Titrations

(used to standardize lead perchlorate solutions)

0.1 M sulfate standard, (500 mL) HI 4012-21
See Section XII ; Titrations

User supplied solutions:

A user supplied Methanol/Formalin solution is required to decrease pellet solubility and oxidative effects. To prepare, add 200 μ L 37 wt. % formalin in H₂O to 500 mL of reagent grade methanol. Stir and store in tightly closed glass bottle. This solution is used at a dose of 50 parts of the Methanol/Formalin solution to 50 parts standard or sample.

For Direct lead measurements- Using volumetric pipettes and glassware, make dilutions of HI 4012-01 to bracket the concentration of the samples. Note: 0.1M lead standard is equivalent to 20,720 ppm. Standards with concentrations $< 10^{-3}M$ (207ppm) should be prepared daily. Store in tightly closed plastic bottle. To 50 parts standard or sample add 50 parts Methanol/Formalin solution plus 2 mL of ISA.

VII. General Guidelines

- Use of a hood and protective clothings is advised when handling lead solutions.
- Concentrated samples ($>0.10\text{ M}$) should be diluted before measurement. Multiply the final result by the corresponding dilution factor.
- Calibration standards and sample solutions should have the same ionic strength. ISA and Methanol/Formalin should be added to both samples and standards in the same ratio. 2 parts ISA to 50 parts standard (or sample)/50 parts Methanol/Formalin is the normal dosing. Note: no correction for dilution factor is required for this because standards and samples are treated in the same way.
- For high ionic strength samples, use standard addition or titration methods.
- Calibration standards and sample solutions should be at same temperature.
- The magnetic stirrer may generate heat. Thermally insulate beaker containing standard or sample from magnetic stirrer by placing cork or other insulative sheet between beaker and stirrer plate.
- Calibration standards and sample solutions should be stirred at the same rate using identical sized TFE coated stir bars.
- Rinse electrode pair with distilled or deionized water between samples and gently dab dry with soft disposable absorbent toweling. Do not rub electrodes.
- Presoaking lead sensor in a dilute standard will optimize response. Use concentrations approximately 10^{-3} M or less with Methanol/Formalin and ISA added.
- A scratched, pitted, or oxidized pellet surface can cause drift, a loss of low level response, or poor repeatability. Optimum response can be restored by removing the damaged surface with the microabrasive strip HI 4000-70. Use gloves to protect skin.
- Avoid large changes in temperature (thermal shock) as it may damage the sensor.

- Gas bubbles may form from solution out-gassing due to temperature change. Gently tap body of sensor to dislodge them from sensing membrane.

HI 4012

- Remove protective cover from sensor tip.

HI 4112

- Remove the protective plastic wrap that covers the ceramic junction before assembling sensor for the first time.
- HI 7072 reference fill solution should be added daily to electrolyte reservoir before electrode use.
- 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 fill 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. Fill solution must cover the ceramic found on the inner stem.
- If an erratic measurement occurs, check to see if foreign matter is seen trapped near the internal cone. Drain, wipe off outer cone while depressing cap, release cap and refill with fresh fill solution.

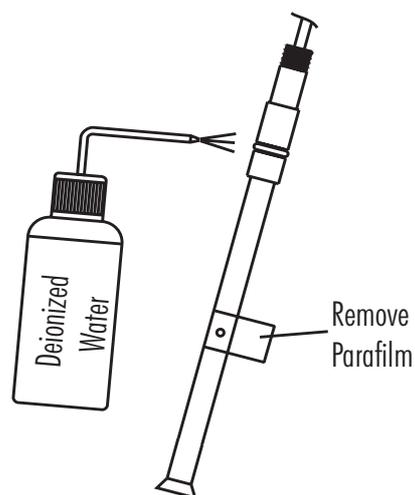
VIII. Electrode Preparation

HI 4012

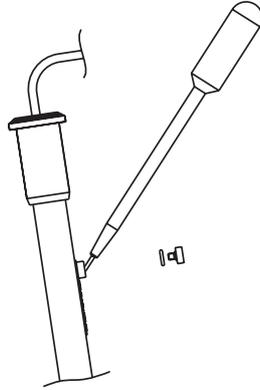
1. Remove protective cover from sensor tip.
2. Prepare reference electrode by filling outer electrolyte reservoir with HI 7072.
3. Place sensor and reference electrodes into electrode holder and connect cable connectors to meter.

HI 4112

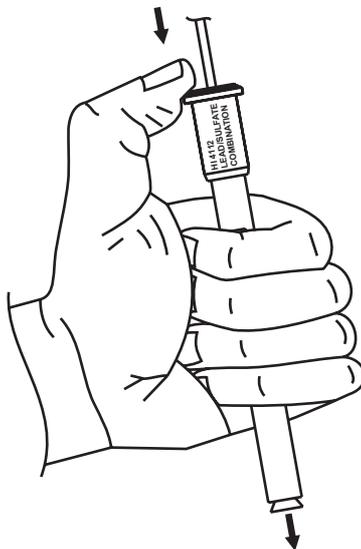
1. Unwrap plastic film seal found over ceramic junction on inner stem and discard. This is only used for shipping and long term storage.
2. Rinse inner stem with deionized water making certain to wet the o-ring found on the inner stem.



3. Reassemble electrode by gently pushing the inner assembly into the outer body, sliding spring down cable, and screwing cap into place.
4. Remove fill hole cover and o-ring on fill hole spout.
5. Using the dropper pipette provided, add a few drops HI 7072 fill solution to the electrode, wetting the o-ring and rinsing out the fill solution chamber.



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



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

IX. Quick Check of Electrode Slope

Use of a hood and protective clothing is strongly advised.

- Connect sensors to pH/mV/ISE meter
- Place meter in mV mode.
- Place 50 mL of deionized water into a beaker with stir bar and 2 mL of HI 4012-00 ISA. Add 50 mL of the methanol/Formalin mixture. Add stir bar and place on magnetic stirrer.
- Place electrodes into prepared sample.
- Add 1 mL of the stock standard HI 4012-01 (or .01 M or .001 M standard by dilution) to the beaker. Record the mV value when reading has stabilized.
- Add an additional 10 mL of standard HI 4012-01 (or same dilute standard) to the solution. Record the mV when reading has stabilized. This value should be more positive than the previous noted.
- Determine the difference between the two mV values. An acceptable value for this slope is $+27 \pm 4$ mV.

X. Corrective action

- Verify protective cap has been removed (HI 4012).
- Verify plastic film has been removed from inner stem (HI 4112).
- Verify electrodes are connected properly to meter and meter is powered.
- Verify standard has been properly stored. Remake standards if appropriate.
- If the sensor slope just misses the suggested slope window, soaking the sensor in a dilute standard with the methanol/formalin added may solve the problem. ($<10^{-3}$ M standard).
- A scratched, pitted or oxidized sensing surface can be polished with HI 4000-70 polishing strip. Cut off approximately 1 inch of the micro-abrasive strip. Wear protective gloves. Wet the frosted side with deionized water and place against damaged membrane of the electrode. Place your gloved thumb against the shiny backing and slowly rotate back and forth while

applying gentle pressure. Continue polishing until you are satisfied with the surface. If dark deposits appear on polishing strip move the paper slightly and continue polishing.

- 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 sensor should be replaced.

XI. Direct Calibration and Measurement

This method is a simple procedure for measuring many samples. Use of protective clothing is advised when handling lead samples and standards. 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. The meter is calibrated with two or more freshly made standards that are in the linear measurement range of the unknowns. Two mL of ISA (HI 4001-12) is added to each 50 mL volume of standard or sample. Fifty milliliters of the methanol/formalin mixture is also added to each sample or standard. More calibration standards are required in non-linear regions. Unknowns are read directly.

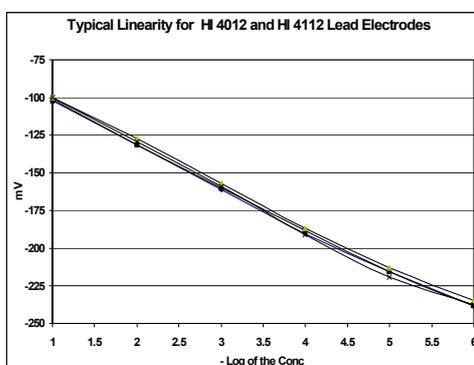
Samples with concentration greater than 0.1 M should be diluted to be within the working range of the electrodes. The final result must be multiplied by the corresponding dilution factor to determine the actual concentration.

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

These values are plotted on the 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

- 1) Follow sections VIII and IX to prepare sensors for measurement.
- 2) Follow section VI to prepare standards / solution. Standards should bracket and fall within the range of interest.
Two mL HI 4012-00 ISA is added to 50 mL of both samples and standards. Fifty milliliters of the methanol/formalin mixture is also added to each sample or standard. Add stir bar and mix before taking measurements.
- 3) Follow section VII; General Guidelines to optimize test set-up.
- 4) During calibration it is best to start with lower concentration samples first. Wait for a stable measurement before recording values. Slightly longer equilibrations are required at lower concentrations .
- 5) To prevent carry over and contamination of samples, rinse sensors with deionized and dab dry with absorbant laboratory tissue between samples.



XII. Other Measurement Techniques

Known Addition (for Pb^{2+})

An unknown concentration can be determined by adding a known amount (volume and concentration) of measured ion to a known volume of the sample. A mV value is taken before and after the addition of standard, and using the equation provided, the unknown concentration is found.

This technique is called Known Addition. The method can use an ideal sensor slope, but actual determined slopes at the temperature of measurement should be used if known. The volume and concentration of the added standard must cause a mV change of at least 8 mV. This method is preprogrammed in the Hanna HI 4222 pH/ISE/mV meter, which simplifies the method greatly. The method works well for samples with high ionic strengths.

Example: Lead ion determination in samples with concentrations less than $1 \times 10^{-3} \text{ M}$ using known addition.

1. A 25 mL sample of unknown concentration (V_{sample}) is placed in a clean plastic beaker with a lead sensor with 1 mL of HI 4012-00 ISA ($V_{\text{ISA}=1 \text{ mL}}$) and 25 mL of the methanol/formalin solution. The stable mV value (mV_1) is recorded after the sample is mixed.
2. 5mL (V_{std}) of 10^{-1} M standard (C_{std}) is added to the beaker and the mV value increases as does the concentration. ΔE is calculated as $mV_2 - mV_1$. The unknown lead concentration in the original sample (C_{sample}) can then be determined by the following equation. Note: The methanol/formalin volume is included into the volume calculations.

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

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

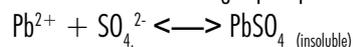
$$(V_{\text{sample}} + V_{\text{ISA}} + V_{\text{MeOH-Form}}) = V_S$$

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

Titration of Sulfate

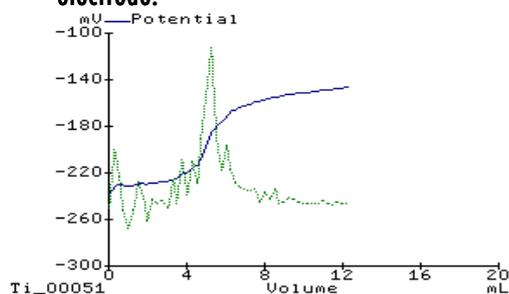
A Lead electrode may be used as an indicator to follow the progress and detect the endpoint of a precipitation titration of sulfate (with concentration $> 50 \text{ ppm}$) with lead perchlorate standard. During the titration the sensor follows the lead concentration while small additions of lead perchlorate titrant are added. The lead reacts with

the sulfate ions forming a precipitate.



At the stoichiometric end point, a change in mV occurs. Measurements may be automated by use of the Hanna Titrator HI 901 or titrated manually.

Plot generated on Hanna HI 901 Titrator during automated sulfate titration using HI 4112 electrode.



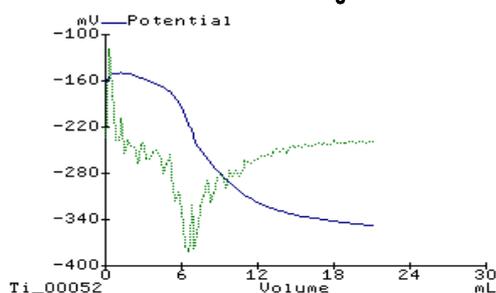
Notes:

- Use of the methanol/formalin antioxidant is advised to increase sensitivity.
- Addition of ISA is suggested (2mL/50mL sample).
- pH adjustment of the sample to 4-6 range is advised. If required, use perchloric acid or sodium hydroxide.
- The lead titrant should be 10X more concentrated than the expected sulfate and should be standardized against a standard sulfate solution.

Titration of Lead

A Lead electrode may be used as an indicator to follow the progress and detect the endpoint of a chelometric titration of lead with disodium EDTA. During the titration the sensor follows the decreasing lead concentration as small additions of disodium EDTA titrant are added. The EDTA reacts with the lead forming a complex. The EDTA also can react with a host of other metals so optimizing pH of the Pb-EDTA complex and masking possible interferents should be considered. Consult a comprehensive Analytical Chemistry Treatise for techniques concerning your particular interferent. At the end point, a larger change in mV occurs. The Hanna Titrator, HI 901 may be used to automate this procedure.

Plot generated on Hanna HI 901 Titrator during automated lead titration using HI 4112 electrode.



Notes:

- Use of the methanol/formalin antioxidant is advised to increase sensitivity.
- pH adjustment of the sample to 4-7 pH is advised to favor the Pb-EDTA formation constant.

XIII. pH

HI 4112 and HI 4012 electrodes may be used in solutions with pH values between 4 and 6. Samples that fall beyond this range should be adjusted with perchloric acid or sodium hydroxide.

XIV. Storage and Care of the HI 4012 and HI 4112 sensors

The HI 4012 and HI 4112 sensor can be stored in very dilute standards ($< 10^{-3}M$) for short periods of time. The HI4012 should be stored dry with its protective cap on for longer periods. For longer term storage of the model HI 4112 combination electrode ;Drain and wash of salts with distilled or deionized water. Unscrew the upper cap and move outer sleeve up cable. Wrap the ceramic junction on the inner stem with Parafilm® or other sealing wrap. Place the protective cap provided over the dried membrane and store in original storage box provided with electrode.

XV. Conversion Tables For Pb²⁺ Multiply

Moles/L (M) to ppm (mg/L)	2.072×10^5
ppm (mg/L) to M (moles/L)	4.826×10^{-6}

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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