

ionode

GOOD CHEMISTRY



IJ SERIES

INTERMEDIATE JUNCTION

Instruction Manual

- IJ 44 A/C** - pH electrode - spear tip
- IJ 40 A/C** - pH electrode- spear tip
- IJ 64** - ORP/Redox electrode
- IJ 46** - pH electrode - flat membrane
- IJ 14** - Reference electrode
- IJ Ag** - Silver Billet electrode
- IJ Au** - Gold ORP electrode

Including High Temperature (HT)
and Temperature Compensated (TC) Models

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V5.1

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1. Introduction

The IJ series of electrodes are designed to be versatile, robust, reliable, accurate and long lasting. The IJ “intermediate junction” reference system addresses an uncertainty in potentiometric measurement i.e. the condition of the contact zone between the reference electrolyte and the sample, which affects accuracy. This is achieved by an easily removable reference sleeve which allows frequent, easy and effective cleaning of the junction surrounding the contact zone. Interchangeable reference sleeves are provided: unprotected for direct insertion into semi-solid samples (meat, cheese, wet soils etc.), and protected for non-viscous samples. IJ electrodes are fully waterproof; allowing full immersion including the cable to 10m.

2. Parts List

- 1) pH /Ref/ORP/Metal Electrode Body
- 2) Protected Sleeve
- 3) Protected Sleeve Wetting Cap
- 4) Slimline Sleeve
- 5) Slimline Sleeve Wetting Cap
- 6) Potassium Chloride Gel Reference Electrolyte*
- 7) Syringe
- 8) Manual

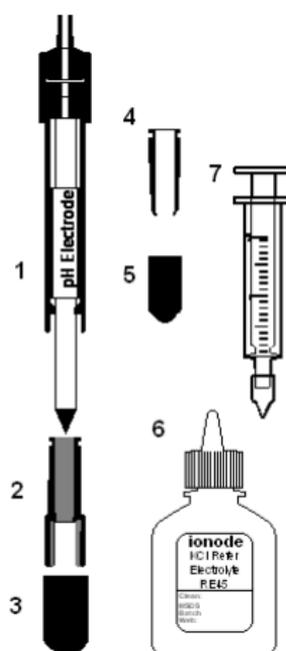


Figure 1

Check that the box contains these items

* IJAg is supplied with 1M potassium nitrate

3. Preparation

PLEASE NOTE: IJ series electrodes are shipped without sleeve electrolyte and must be filled prior to use.

- 1) Hold the electrode by the sleeve and gently ease the rubber wetting cap off the sleeve.
- 2) Hold the electrode body just above the sleeve and remove the sleeve by gently rotating and pulling along the axis of the electrode (see Figure 2). **DO NOT BEND!**



Figure 2

- 3) Invert the electrode. Fill the annular space (see Figure 3) with electrolyte (see 4.5.3 [Sleeve Electrolytes](#)).



Figure 3

- 4) Slide the sleeve back on the electrode and push home until the black O-ring is properly seated. **DO NOT EXERT A SIDEWAYS FORCE WHICH MAY FRACTURE THE STEM!** Excess electrolyte will be expelled

out the end of the electrode through the ground junction. Check this has occurred. Insufficient electrolyte will produce an air space in the sleeve. This will cause a noisy or off scale reading. Wash excess electrolyte off the electrode.

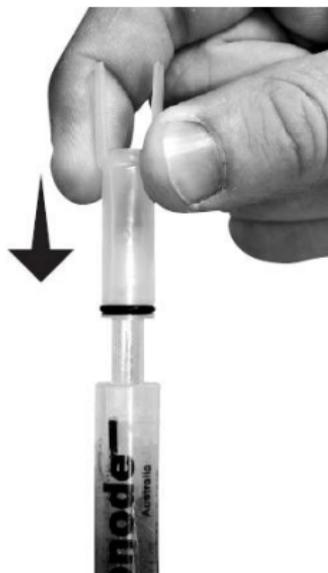


Figure 4

- 5) With the IJ44 pH electrode, flick the electrode downward to remove any bubble from within the green membrane.



Figure 5

- 6) Store in 2-3M KCl before use.

4. pH

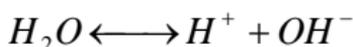
4.1. Theory

pH is a scale of active hydrogen ion concentration in aqueous solution. In pure water, the concentration of hydrogen ions is 10^{-7} M. The pH scale converts this to a convenient positive number:

$$pH = -\log([a_{H^+}])$$

pH indicates acidity ($pH < 7$), alkalinity ($pH > 7$) or neutrality ($pH = 7$).

Pure water undergoes autoprotolysis to yield equal numbers of hydrogen and hydroxide ions:



The equilibrium constant at 25 °C is:

$$K_w = [H^+] \times [OH^-] = 10^{-14}$$

pOH is the negative logarithm of the active hydroxide concentration. The equilibrium expression can be rewritten as:

$$pK_w = pH + pOH = 14$$

This equation applies for all aqueous systems. Very strong acids and bases can have pH's < 0 and > 14 respectively.

Although pH is defined for aqueous solutions, measurements can be made in non-aqueous solutions provided the solvent is sufficiently conductive, or a conductive solvent is added to a non-conductive sample.

4.2. Electrode Characteristics

4.2.1. Construction

A pH electrode consists of two electrochemical half-cells usually co-axially combined into a single housing called a "combination electrode" to form an electrical circuit. The sensing half-cell comprises a pH sensitive glass membrane attached to a sealed insulating tube containing a solution of fixed pH in contact with a silver-silver chloride element. A voltage proportional to pH is measured between the sensing half-cell and a reference half-cell which ideally maintains a stable potential independent of the sample.

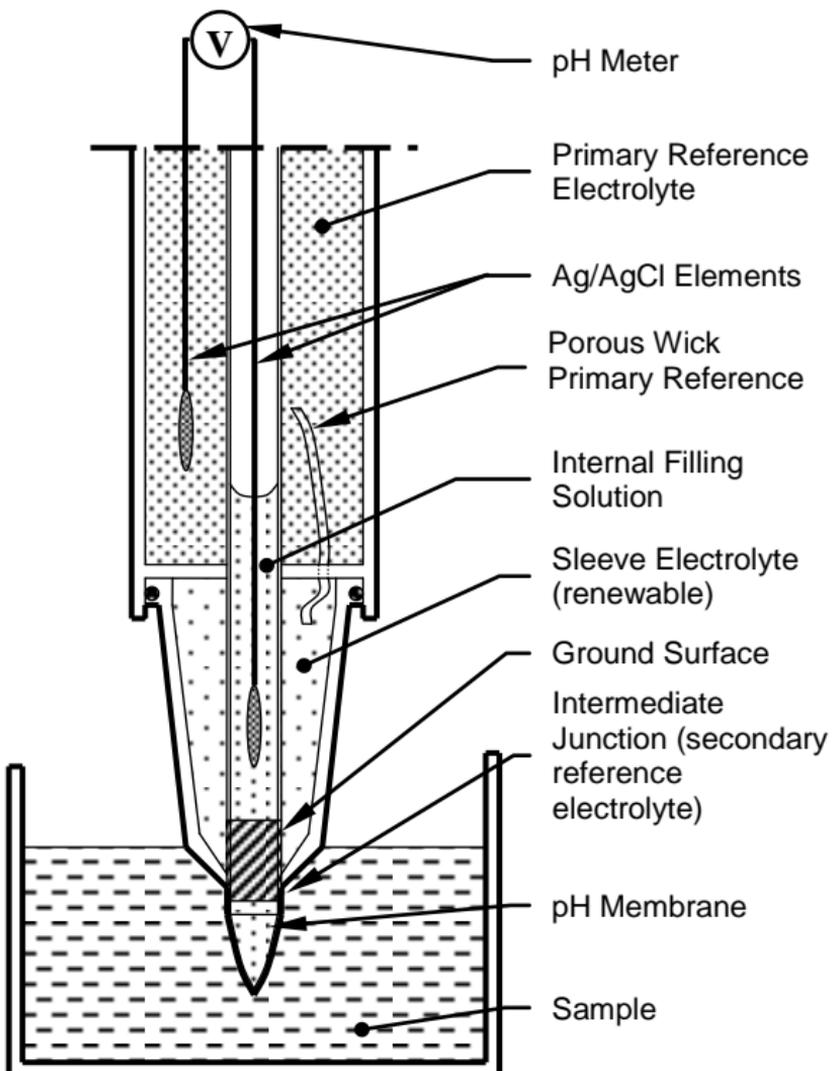


Figure 6

Part of the circuit is electronic (heavy lines) (see Figure 6). The remainder is ionic. Unlike other pH electrode measuring systems which rely on electron transfer such as antimony and quinhydrone, the pH glass electrode is insensitive to ORP.

pH glass is modified lithium silica which is a lithium ion conductor at room temperature. Hydrated glass ion exchange layers exist on both sides of the membrane (see Figure 7 - Figure 9). These allow reversible exchange between hydrogen and lithium ions.

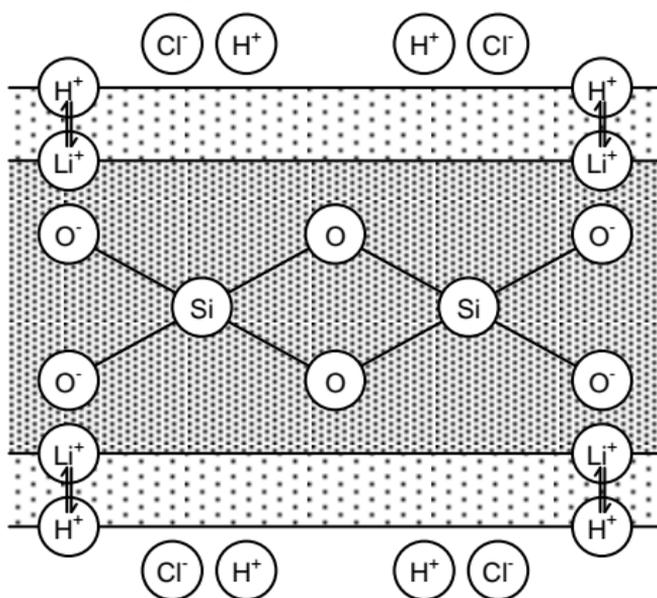


Figure 7

Equal concentrations of H⁺ on either side of the membrane causes no potential to develop across the membrane (see Figure 7).

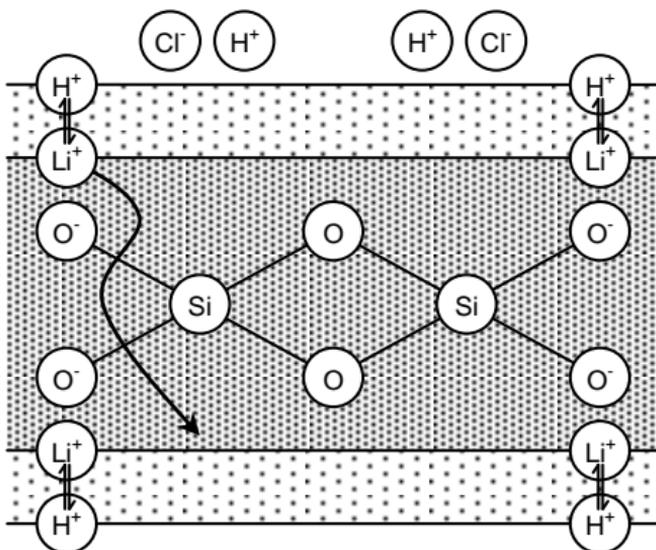


Figure 8

Unequal concentrations of H^+ on either side of the membrane cause the system to equalise the number of positive ions on either side of the membrane. This causes migration of a lithium ion through the membrane (see Figure 8).

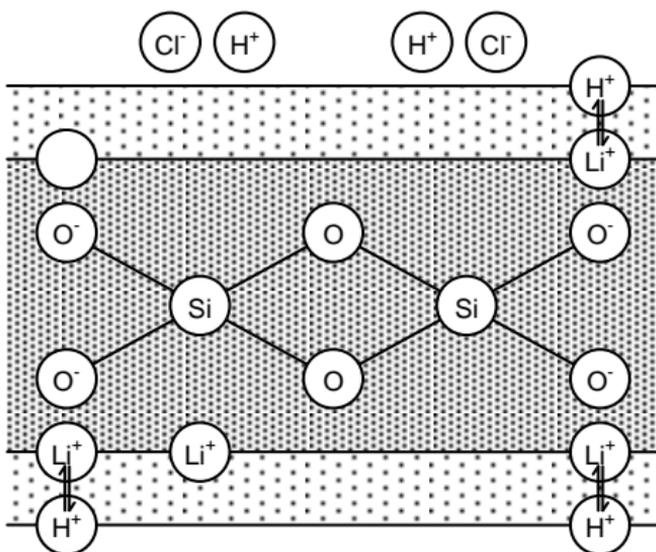


Figure 9

As the negatively charged oxygen counter ions are fixed in the glass structure, a potential develops across the membrane (see Figure 9). This builds until the charge developed opposes further migration according to the Nernst equation.

The reference half-cell completes the circuit. The primary IJ reference is a silver/silver chloride element in a gelled saturated potassium chloride electrolyte. This makes solution contact with the secondary sleeve electrolyte through a low porosity wick. Usually, the sleeve electrolyte is concentrated potassium chloride. However, as the IJ reference has a double junction, it allows the use of other suitable sleeve electrolytes. Potassium chloride is the most commonly used reference electrolyte because of the similar size and mobility of the potassium and chloride ions. This minimizes charge separation when the sleeve electrolyte diffuses into the sample

Solution contact between the sleeve electrolyte and the sample is through the porous junction between the ground stem and the sleeve. This constriction allows uninhibited movement of ions between the sample and reference half cell to assure a repeatable reference junction potential. At the same time it does not grossly contaminate the sample with reference ions.

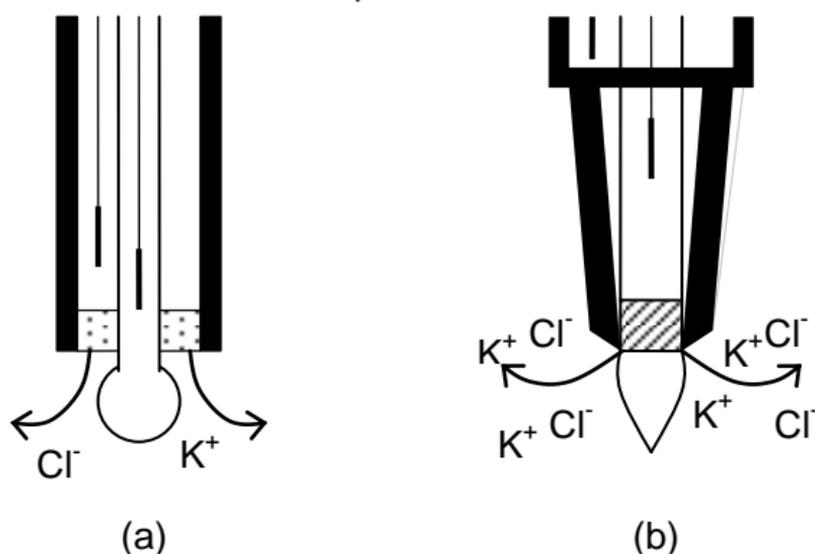


Figure 10

In common electrode designs, a porous restriction (typically a porous ceramic or fibre wick) is used to slow the flow (see Figure 10a).

If the restriction becomes clogged and movement of ions becomes inhibited, the electrode will appear to be stable in buffer solutions, but it may produce errors in non-ideal and low buffering capacity samples. The IJ reference system overcomes this by allowing free movement of ions past the restriction, allowing the junction to be cleaned and the sleeve electrolyte to be easily replaced. The result is a reference electrode system of assured reliability (see Figure 10b).

References:

- 1) [John A. Illingworth "A common source of error in pH measurement", Biochem. J., \(1981\) 195, p. 259-262.](#)

4.2.2. Output

The voltage output is related to the hydrogen ion activity by the Nernst equation:

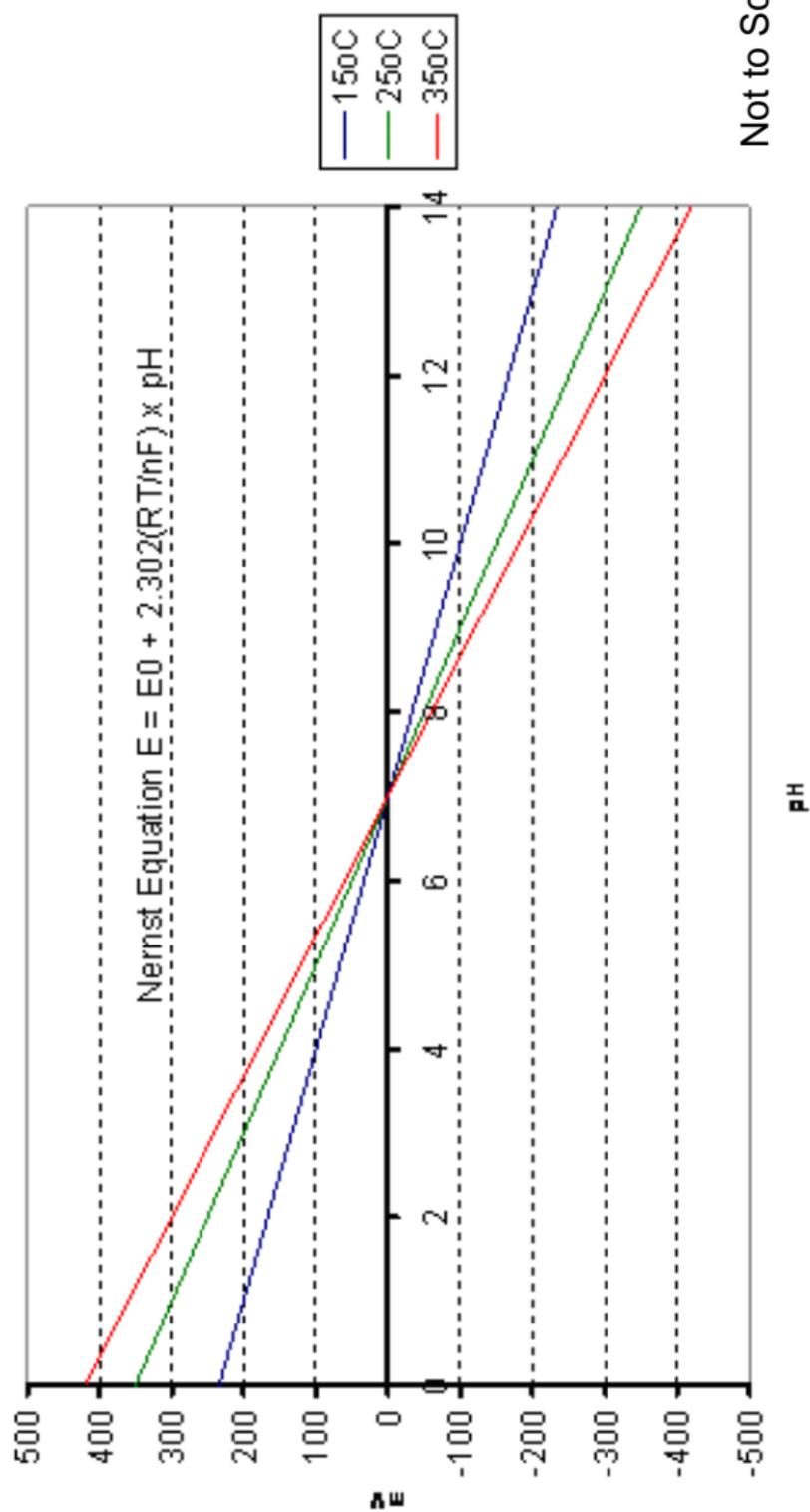
$$E = E_0 - \frac{RT}{nF} \ln([H^+])$$

This can be rewritten in linear form by substituting in the definition of pH and grouping all the constants to give:

$$E = E_0' + SLOPE(T) \times pH$$

E_0' is referred to as the isopotential point. Theoretically, it is the pH which has no temperature dependence.

The IJ44 has been designed so that it is compatible with all modern pH meter



Not to Scale

Figure 11

Offset

Each pH electrode has a small offset which varies from electrode to electrode. It is due to an “asymmetry potential” across the membrane. It is usually within ± 0.2 pH for a new electrode, and requires correction by calibration in a buffer at or near pH 7. The offset increases as the electrode ages and is also an indication of the condition of the electrode, especially cleanliness. A clean IJ44 should read within ± 30 mV (± 0.5 pH) in a pH 7 buffer.

Slope

The SLOPE is a function of temperature (T) and contains the conversion of the natural logarithm to the base ten logarithm. It is defined as the number of mV per unit of pH. It is manually or automatically (ATC) compensated in pH meters.

Table 1: Theoretical (Nernstian) Slope

T (°C)	SLOPE(T) (mV)	T (°C)	SLOPE(T) (mV)
0	54.197	30	60.149
5	55.189	35	61.141
10	56.181	38	61.737
15	57.173	40	62.133
20	58.165	45	63.126
25	59.157	50	64.118

A new electrode should have a slope between 95-102% of theoretical. Sub-Nernstian slope is corrected by calibration with a second buffer. As the pH membrane ages, the slope decreases. This affects the accuracy. For best performance, the slope should be $>95\%$. Some meters calculate and display % slope after

calibration. It can also be accurately measured using the mV mode of a pH meter.

- 1) Measure the temperature of two buffers and select the pH values for the buffers at this temperature (see [Table 2: pH Values of Standard Buffers at Various Temperatures](#))
- 2) Measure the mV readings for the two buffers. Allow several minutes for the electrode to attain thermal equilibrium with the buffers.
- 3) Divide the measured difference by the theoretical difference (see [Table 1](#)) and multiply by 100.

Example:

Buffer 1 (pH 6.865 @ 25°C): +11 (mV)

Buffer 2 (pH 4.008 @ 25°C): +174 (mV)

SLOPE(T=25°C): 59.157 (mV/pH)

$$\% \text{ Slope} = \frac{(174 - 11)}{(6.865 - 4.008) \times 59.157} \times 100 = 96.4\%$$

Note that ATC provided by pH meters only corrects the temperature term in the Nernst equation. It does not correct the temperature coefficients of buffers unless they are specified and the meter software calculates accordingly. With the exceptions of fully dissociated strong acids and bases, all samples have temperature coefficients as well. These vary depending on the nature of the sample and cannot be corrected by the pH meter. For best reporting, the temperature at which the measurement has been made should be stated.

Inbuilt temperature compensation is offered as an option for models IJ44 and IJ64. Temperature sensor types include Pt1000 RTDs, and 10K and 30K NTC thermistors. For

further details, please contact Ionode specifying make and model of pH/mV meter or titrator.

Sodium Error

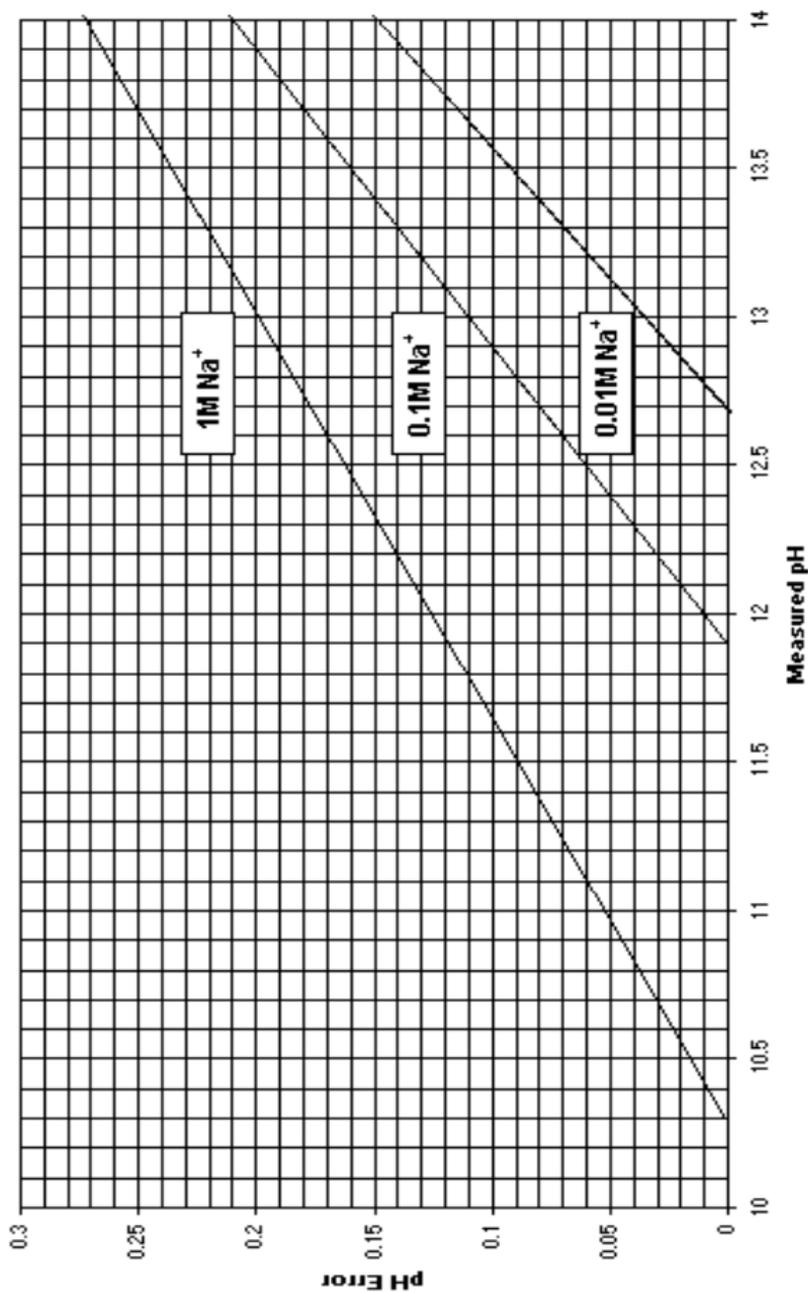
The selectivity of H^+ over Na^+ is extremely high, but small errors become apparent at high pH (i.e. low H^+ concentration) and high Na^+ concentration.

The pH glass used in the IJ44C has a very low sodium error. Corrections to the measurement can be made if the sodium concentration of the sample is known. There are typical sodium errors for a new IJ44 pH electrode (see [Graph 1](#)). The sodium error increases with aging.

A measured pH can be corrected by locating it on the x-axis and drawing a line straight up until it intersects the sodium concentration line of the sample (extrapolate between lines for sodium concentrations not drawn). Draw a line from the intersection directly over to the y-axis to determine the error in the measurement. The actual pH of the sample is determined by adding the error to the measured pH. For example, if a sample with 1M Na^+ concentration measures pH 12.6, then the actual pH is 12.77.

The sodium error is larger in the “A” glass pH electrodes. As a consequence, “A” glass pH electrodes are best suited to pH measurements below pH12. The “A” glass would be preferred for measurements in strong acids, titrations and for measurement in lower conductivity samples.

Glass C Sodium Error



Graph 1

Response Time

This varies according to the pH glass composition, membrane wall thickness, pH meter filtering, buffering capacity of the sample, measurement temperature (longest at <10C), lack of thermal equilibrium between the electrode and buffers/samples, cleanliness of the junction, and the age, chemical exposure history and cleanliness of the membrane. Most increases in response time for new electrodes are due to the latter (see [4.4.1 Cleaning](#)).

The IJ44C is a balance between chemical resistance (see [Sodium Error](#)), electrical resistance and robustness. This results in a long life membrane of moderate response time. The response time can be reduced by using a different composition of pH glass (IJ44A). This has good resistance to strong acids but reduced resistance to alkali, and should be used sparingly above pH 12.

Impedance

pH membranes typically have resistances of 100 – 1000MΩ. This requires the pH meter to have an input impedance of at least $10^{12}\Omega$ in order to avoid signal loss and polarisation of the electrode. The latter occurs when a significant current flows through the electrode. This alters the Ag/AgCl/sat KCl half cell potentials and permanently damages the membrane. Polarisation can be caused by damp or shorted connectors, poor connector insulation, a low impedance meter or meter circuit malfunction.

4.3. Measurement

- 1) Turn on the pH meter and connect the pH electrode. Connect a temperature sensor (ATC) if appropriate.
- 2) Remove the electrode from its wetting cap or storage solution and rinse with distilled water.
- 3) The electrode must be initially calibrated for offset and then for slope.
- 4) For offset calibration, immerse the electrode in a first buffer (pH 7.0 or 6.88) and stir until the reading is constant. Stop the stirring and take the reading when stable. For meters without automatic buffer recognition, adjust the offset control to the first buffer.
- 5) Rinse the electrode and repeat the process for a second buffer. The second buffer should bracket the expected pH of the sample and ideally be at least 3 pH units apart from the first. Do not use this buffer for the primary calibration (see **Step 4 above**). For meters without automatic buffer recognition, adjust the slope control to the second buffer value.
- 6) Rinse again and check in the first buffer. For a new electrode, the reading should be within ± 0.02 pH of the buffer value. Otherwise, repeat the calibration. Check the slope (see [Slope](#)). If necessary, clean the electrode with Jif and re-check.
- 7) Rinse the pH electrode with deionised water or portions of the sample to be measured.
- 8) Immerse the pH electrode in the sample. Stop stirring and take the reading when stable.
- 9) Periodically check the offset and slope (see [Offset](#) and [Slope](#))

4.3.1. Helpful Hints

- 1) Use the same technique to measure samples as was used for calibration. Be consistent with stirring rates, times and conditions.
- 2) Ideally, the buffers and samples should be at the same temperature.
- 3) Calibrate the pH electrode regularly, e.g. typically once an hour for accuracy to within ± 0.01 pH, or once a day for accuracy to within ± 0.1 pH.
- 4) Use fresh buffers for calibration. Avoid contamination of the stock buffer solution. Do not use buffers beyond the expiry date. Note alkaline buffers (pH 9.18 and 10.01) absorb carbon dioxide from the air and become inaccurate. The magnitude depends on the exposure time.
- 5) Keep all connections dry.
- 6) Use a dedicated high impedance pH meter.
- 7) Immerse the electrode so that the reference junction is below the surface (see [Figure 6](#)).
- 8) Do not use in solutions of fluoride ion at low pH. This will etch the glass membrane.
- 9) Sulphide vapours can permeate the electrode wick and contaminate the reference element. Minimize contact in such environments and change the sleeve electrolyte frequently.
- 10) The IJ44 is suitable for use in TRIS buffers because the sleeve electrolyte does not contain silver ions. In some conventional single junction electrodes, silver ions in the potassium chloride electrolyte react with TRIS and cause spurious potentials at the contact zone.

4.4. Maintenance

- 1) When not in use, keep the electrode immersed in 2-3M KCl (saturated KCl is approx 4M). This assists in maintaining a stable junction potential and is preferable to deionised water or buffers.
- 2) pH membranes are **NOT** damaged if allowed to dry. Ionode pH glasses re-hydrate very quickly, typically in less than an hour. Any impurities which have dried on the membrane should be removed before re-hydration (see 4.4.1 [Cleaning](#)).
- 3) How often does the sleeve electrolyte need replacing? This depends on the sample being measured and is best determined by experience. Error can be determined by comparing readings before and after renewal of the electrolyte on the same sample. Normally, errors of less than a few hundredths of a pH can be expected after a full day's use and electrolyte need only require weekly replacement.
- 4) For long term storage, remove and clean the sleeve. Replace the sleeve without electrolyte and attach the wetting cap, filled with 20% KCl solution. After long term storage algae or mould growth may occur inside the wetting cap. This can be removed by soaking in dilute chlorine (bleach) solution.

4.4.1. Cleaning

As pH and ORP are surface based measurements, the cleanliness of the sensor and junction is critical for accurate measurement. For new electrodes, drift, poor slope and long response times are often due to an unclean sensor and/or junction.

Clean the electrode periodically depending on the application.

Remove the sleeve (see [3. Preparation](#)). Clean the membrane, ground glass stem and sleeve with solvents, detergents, or acid. **DO NOT USE ABRASIVE MATERIALS!**

- a) Alkaline samples and scale: soak the membrane in approximately 1M HCl for an hour. Wash well with tap water and soak before use.
- b) Grease and oil: wipe the membrane and ground stem with cotton or tissue soaked in acetone followed by methylated spirits. Wash with deionised water and soak before use.
- c) Solids and organics: wipe the membrane and junction with cotton or tissue soaked in a mild non-alkaline detergent (e.g. Palmolive™). Wash with deionised water and soak before use.
- d) Strongly absorbed impurities and chemically bonded substances such as silicones can be removed with non-abrasive Jif™ detergent. This removes a fine layer of contaminated pH glass without damaging the membrane. Jif™ can also be used for routine cleaning (e.g. every three months). Use Jif™ undiluted on a soft cloth and scrub the membrane well. Wash well and soak.
- e) Protein contamination: soak the membrane in 1% pepsin in 0.1M HCl for 15 minutes followed by rinsing with deionised water, and soak in 20% KCl before use.

4.5. Calibration Standards

4.5.1. NBS pH Buffers

pH 4.01: 0.05M Potassium Hydrogen Phthalate

Dissolve 10.12g of potassium hydrogen phthalate in distilled water and make up to 1L.

pH 6.87: 0.025M Potassium Dihydrogen Phosphate / 0.025M Disodium Hydrogen Phosphate

Dry each salt at 120°C for 2 hours and then cool in a desiccator. Dissolve 3.533g disodium hydrogen phosphate and 3.388g potassium dihydrogen phosphate in distilled water and make up to 1L.

pH 7.413: 0.008695M Potassium Dihydrogen Phosphate / 0.03043M Disodium Hydrogen Phosphate

Prepare salts as above and dissolve 1.179g potassium dihydrogen phosphate and 4.302g disodium hydrogen phosphate in distilled water and make up to 1L.

pH 9.18: 0.01M Sodium Tetraborate Decahydrate

Dissolve 3.80g of sodium tetraborate decahydrate (borax) in distilled water and make up to 1L. This solution is susceptible to pH change from carbon dioxide and should be prepared fresh regularly.

pH 10.01: 0.025M Sodium Bicarbonate / 0.025M Sodium Carbonate

Use anhydrous reagent grade salts to prepare this buffer. Dissolve 2.092g of sodium bicarbonate and 2.640g of sodium carbonate in distilled water and make up to 1L.

4.5.2. Secondary pH Buffers

pH 7.65: Tris Buffer

Dry Tris (2-amino-2-(hydroxymethyl)propane-1,3-diol) and Tris hydrochloride at 80°C and 40°C, respectively. Dissolve 1.999g of Tris and 7.800g of Tris hydrochloride in water and make up to 1L. Alternatively, prepare the solution by dissolving 8.008 g of Tris in 50mL of 1M HCl and make up to 1L with deionised water.

pH 7.00 @ 25°C: Phosphate Buffer

Prepare 500mL of 0.1M KH_2PO_4 from the dried salt. Accurately prepare 500mL of 0.1M NaOH. Mix 500mL of the KH_2PO_4 solution with 296.3mL of the NaOH solution in a 1L volumetric flask and fill to the mark with deionised water.

Table 2: pH Values of Standard Buffers at Various Temperatures

Temperature (T)	0.05M potassium hydrogen phthalate	0.025M KH_2PO_4 0.025M Na_2HPO_4	IUPAC pH 7.000	0.0087M KH_2PO_4 0.03M Na_2HPO_4	0.01M borax	0.025M NaHCO_3 0.025M Na_2CO_3	Tris buffer
0	4.003	6.984	7.118	7.534	9.464	10.32	8.40
5	3.999	6.951	7.087	7.500	9.395	10.25	
10	3.998	6.923	7.059	7.472	9.332	10.18	8.08
15	3.999	6.900	7.036	7.448	9.276	10.12	
20	4.002	6.881	7.016	7.429	9.225	10.06	7.79
25	4.008	6.865	7.000	7.413	9.180	10.01	7.65
30	4.015	6.853	6.987	7.400	9.139	9.97	7.51
35	4.024	6.844	6.977	7.389	9.93	9.9.	
40	4.035	6.838	6.970	7.380	9.068	9.89	

4.5.3. Sleeve Electrolytes

The IJ reference system allows a variety of sleeve electrolytes. For high viscosity samples which contaminate the membrane and junction quickly, aqueous saturated potassium chloride may be preferred, with frequent renewal. For low viscosity samples, Ionode's Potassium Chloride Gel Electrolyte requires less frequent replacement. Other specialized electrolytes can also be used.

Ionode Potassium Chloride Gel Electrolyte

Table 3: Composition of 3M Potassium Chloride Gel Electrolyte

CAS#	Components	% (w/v)
7447-40-7	Potassium Chloride	20-25
9004-62-0	Hydroxyethyl Cellulose	1-5
112-27-6	Triethylene Glycol	5-10
7732-18-5	Water	To 100%

Note: CAS refers to the Chemical Abstracts Service Registry Number.

MSDS for the gel is available [here](#)

Or visit our support page at our website at www.ionode.com.au

Saturated Potassium Chloride

Dissolve 34g of potassium chloride in 100mL of distilled water. Use the supernatant.

1M Potassium Nitrate

Add 10.1g of AR grade KNO_3 to a 100ml volumetric flask and make up to the mark with distilled water. This electrolyte can be used where chloride ions cause interference (i.e. Ag^+). Also use in the IJ14 when used with Iodide/Cyanide and Chloride ISE's.

3M Sodium Chloride

Add 17.5g of NaCl to 100 mL volumetric flask and fill to the mark with distilled water. This electrolyte can be used where potassium and ammonium ions cause interference.

1M Lithium Chloride

Add 4.24g LiCl to a 100ml volumetric flask and fill to the mark with distilled water. This electrolyte is used in non-aqueous measurements and titrations. In less polar solvents, making up the LiCl in ethanol or isopropanol may give better results.

4.6. Troubleshooting

A fault may develop in either the meter or electrode. If a number of electrodes and/or meters are available, interchange to isolate the fault.

Table 4: Problem Indication

Symptom	Possible Causes	Remedy
Drift	Junction Blocked	Remove sleeve. Clean glass stem and sleeve. See 4.4.1 Cleaning
	Membrane not Clean	Remove sleeve. Clean glass membrane. See 4.4.1 Cleaning
	Membrane Aged or Damaged (e.g. by Abrasion)	Allow longer measuring time or replace.
	Electrode Polarised	Replace electrode
Noisy	Bubble in Membrane	Flick electrode downward.
	Poor Connection to Meter	Check connection
	Junction not Immersed properly	Lower electrode into solution below level of junction (see Figure 6).
	Insufficient Electrolyte	See 3. Preparation

Symptom	Possible Causes	Remedy
Low Slope (<94%)	Contaminated Buffers	Replace buffers
	Membrane not Clean	See 4.6 Troubleshooting Drift
	Membrane Aged	Allow more time for stabilisation, or replace
	Electrode Polarised	Replace electrode
Slow Response	Membrane not Clean	See 4.6 Troubleshooting Drift
	Membrane Aged	Allow more time for stabilisation, or replace
Incorrect Sample Reading after successful calibration	Ground Loop. Often Occurs in Process Systems	Verify by removing the sample from its environment and measuring in a glass beaker. May require special circuitry.
	Junction Blocked or unclean	See 4.6 Troubleshooting Drift
Displays pH7 for all Buffers	Electrical Short	Check connector
	Internal Short	Replace electrode
Displays pH4-5 for all Buffers	Membrane or Stem Cracked	Replace electrode

Symptom	Possible Causes	Remedy
Large Offset (>0.5pH)	Insufficient Sleeve Electrolyte	See 3. Preparation
	Junction Blocked or unclean	See 4.6 Troubleshooting Drift
	Electrode Polarised	Replace electrode
Non-Linear Over three Buffers	Contaminated Buffers	Replace buffers Note: alkaline buffers absorb carbon dioxide and become inaccurate when exposed to air.

4.7. Specifications

Table 5: IJ44 pH electrode specifications

Parameter	Operating Range
pH Range	0-14 pH (C glass) 0-12 pH (A glass)
Accuracy	±0.02 pH
Zero Potential Point	pH 7.0 ±0.5
Temperature Range	0 – 60°C
Temperature sensor types (optional)	Pt1000, NTC 10K & 30K Accuracy better than ±0.5C
Maximum Pressure	345 kPa (T = 25°C)
Reference Type	Double Junction Primary Reference Ag/AgCl/saturated KCl gel
Body and sleeve	Polypropylene
O-ring	EPDM as standard. Viton on request
Overall Length	150mm
Barrel Diameter	12mm
Cap Diameter	16mm
Cable Length	1m standard, longer to order. Maximum 10m
Connector	To suit common meters

5. ORP

5.1. Theory

ORP stands for oxidation reduction potential. Ideal ORP obeys the Nernst equation:

$$E = E_0 - \frac{RT}{nF} \ln \left(\frac{[Ox]}{[Re]} \right)$$

Where [Ox] is the active concentration of an oxidized species such as ferric ion Fe^{3+} and [Re] is the active concentration of the reduced form of that species namely ferrous ion Fe^{2+} . The pair provides a redox couple.

The following is required for a stable ORP reading:

- 1) Significant concentrations of both species of the couple
- 2) Both species must be capable of readily transferring electrons to or from each other (reversible redox couple) and readily accepting or removing electrons from an inert metal surface.

Ferric/ferrous, iodine/iodide and quinone/hydroquinone are examples of reversible redox couples and are used for ORP standards (see [Table 7 - Table 9](#))

Generally, most practical ORP measurements are made on samples which do not meet the above criteria. This results in poor reproducibility, drift, stirring rate dependence and non-Nernstian behaviour. Nevertheless, ORP is useful for measuring changes in a system rather than absolute values (e.g. process control to an ORP set-point and titrations).

Like pH, ORP represents an intensity factor. It does not characterize the capacity of the system for oxidation or reduction, in the same

way pH does not characterize the buffering capacity.

5.1.1. Output

ORP values are determined by measuring the potential difference between an inert sensing half-cell and a reference half-cell as in pH. The sensing half-cell acts as a platform for electron transfer to or from the sample. The sensor does not undergo oxidation or reduction. It is typically platinum. Gold (Model IJAu) and Silver (Model IJAg) sensors can also be used. The former is substantially inert, whereas the latter responds to silver and halide ions, and can be used for silver titrations. The standard hydrogen electrode (SHE) is the reference from which all formal redox potentials are determined and has been assigned an arbitrary half cell potential of 0.0 mV. However, it is fragile and impractical for routine laboratory use. Therefore, Ag/AgCl and saturated calomel (SCE) reference electrodes are used. Earlier literature often used SCE. The use of SCE is now rare because it contains mercury. The voltages of the different reference electrodes can be interrelated (see [Table 6](#)). The IJ64 uses an Ag/AgCl/saturated KCl reference electrode.

Table 6: Potential Relationships (mV) of Several Reference Electrodes at 25°C

SHE	SCE Saturated KCl	Ag/AgCl/ 1M KCl	Ag/AgCl/ 4M KCl	Ag/AgCl Saturated KCl
0	+245	+236	+200	+199

For example, a reading of 100mV using an Ag/AgCl/Saturated KCl reference could be referred to a SHE reference by adding 199mV.

Although the resistance of an ORP electrode is very low compared to a pH electrode, it is preferable to use a high impedance meter in order to avoid polarising the Ag/AgCl/sat KCl half cell.

Reference:

- 2) "2580 Oxidation Reduction Potential" Standard Methods for the Examination of Water and Wastewater, 19th edition, published by American Public Health Ass., American Water Works Ass., and Water Pollution Control Fed., 1995, 2-73.

5.2. Measurement

Unlike a pH electrode, an ORP electrode does not require asymmetry potential and slope corrections. However, it can develop an offset depending on the cleanliness of the sensing tip and reference junction. It should be checked periodically in standards.

- 1) Set the pH/mV meter to mV mode.
- 2) Connect the electrode to the pH/mV meter. Rinse thoroughly with deionised water.
- 3) Place the electrode in an ORP standard. Measure the temperature and determine the potential (see [Table 7 - Table 9](#)). Note that ORP standards have significant temperature coefficients. Allow the reading to stabilize. It should be within +/-20 mV of the correct value (see 5.4 Calibration Standards). If not, clean the electrode as described in 4.4.1 [Cleaning](#) and replenish the sleeve electrolyte. Repeat the check.
- 4) Rinse with deionised water.
- 5) Place the electrode in the sample and stir. Most irreversible redox couples require vigorous stirring to attain a plateau response. Lack of adequate stirring usually results in a lower potential.
- 6) Allow the reading to stabilize and record.

5.2.1. Helpful Hints

- 1) ORP samples are generally unstable and should not be stored or preserved. Measure samples on site whenever possible.
- 2) Clean the sensing tip regularly (see 4.4.1 [Cleaning](#)). An unclean sensing tip is the most common cause of error in ORP measurement.
- 3) Allow adequate time for stabilization, especially between samples of considerably

different potentials and irreversible redox couples.

- 4) Use only a high impedance mV meter.
- 5) Use fresh standards.
- 6) Use polyethylene, Teflon™ or glass beakers and stir with a magnetic Teflon™ coated stirrer bar.

5.3. Maintenance

- 1) When not in use, store the electrode in 2-3M KCl. This assists in maintaining a stable reference potential and is preferred to distilled water or an ORP standard.
- 2) How often does the sleeve electrolyte need replacing? This depends on the sample being measured and the desired accuracy. It is best determined by experience. An error can be determined by comparing readings before and after renewal of the electrolyte on the same sample.
- 3) For long term storage, remove and clean the sleeve. Replace the sleeve without electrolyte and attach the wetting cap filled with 20% Potassium chloride solution.

5.3.1. Cleaning

Refer to 4.4.1 pH [Cleaning](#)

Metals (e.g. copper and zinc) that have plated onto the platinum tip can be removed with dilute (approx 0.1M) nitric acid.

5.4. Calibration Standards

Light's solution and ZoBell's solution are NBS standards which are stable for several months if stored in a dark plastic bottle in the refrigerator. The quinhydrone standards are highly unstable. They must be made fresh and discarded after use.

Light's Solution

39.21g ferrous ammonium sulphate,
 $\text{Fe}(\text{NH}_4)_2(\text{SO}_4)_2 \cdot 6\text{H}_2\text{O}$

48.22g ferric ammonium sulphate,
 $\text{Fe}(\text{NH}_4)(\text{SO}_4)_2 \cdot 12\text{H}_2\text{O}$

56.2mL sulphuric acid (sp. gr. 1.84)
made to 1L with distilled water

Table 7: Light's Solution (Ref: Ag/AgCl Saturated KCl)

Temperature (°C)	Potential (mV)
25	476

ZoBell's Solution

1.408g potassium ferrocyanide,
 $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$

1.098g potassium ferricyanide, $\text{K}_3\text{Fe}(\text{CN})_6$

7.456g potassium chloride, KCl
made to 1L with distilled water

Note: ZoBell's solution is more stable prepared in two parts, which are accurately combined 1:1 just prior to use.

Part 1: 1.408g potassium ferrocyanide plus 7.456g of potassium chloride made up to 500mL.

Part 2: 1.098g potassium ferricyanide made up to 500mL.

Table 8: ZoBell's Solution vs Ag/AgCl/Sat KCl Reference)

Temperature (°C)	Potential (mV)
5	273
10	262
15	251
20	240
25	229
30	218

pH 4 Quinhydrone Solution

Add sufficient quinhydrone to NBS pH 4.01 buffer to make a saturated solution.

pH 6.86 Quinhydrone Solution

Add sufficient quinhydrone to NBS pH 6.87 buffer to make a saturated solution.

pH 9.18 Quinhydrone Solution

Add sufficient quinhydrone to NBS pH 9.18 buffer to make a saturated solution.

Table 9: Quinhydrone Solution (Ref: Ag/AgCl/Saturated KCl)

Temperature (°C)	Potential (mV)		
	pH 4.01	pH 6.87	pH 9.18
20	+268	+105	-23
25	+264	+98	-32
30	+260	+91	-41

5.5. Troubleshooting

A fault may develop in either the meter or electrode. If a number of electrodes and/or meters are available, interchange to isolate the fault.

Table 10: Problem Indication

Symptom	Possible Causes	Remedy
Drift	Junction Blocked	Remove sleeve. Clean glass stem and sleeve. See 3. Preparation
	Sensor not Clean	See 4.4.1 Cleaning
	Reading is Stable in Standards, but not in Samples	See 5.1 ORP Theory
	Electrode Polarised	Replace electrode
Noisy	Poor Connection to Meter	Check connection
	Junction not Immersed	Lower electrode into solution below level of junction. See Figure 6
	Insufficient Electrolyte	See 3. Preparation

Symptom	Possible Causes	Remedy
Not within Tolerance ($\pm 20\text{mV}$)	Contaminated Standards	Replace standards
	Correlating to the Wrong Reference Electrode	Calculate what the standard would read using a saturated KCl Ag/AgCl reference. See 5.1 ORP Theory
	Platinum not Clean	See 4.4.1 pH Cleaning
	Electrode Polarised	Replace electrode
Displays 0mV for all Solutions	Electrical Short	Check connector
	Internal Short	Replace electrode
Displays off Scale	Noise	See 5.5 Troubleshooting Noisy

5.6. Specifications

Table 11: IJ64 and IJ64_xx specifications

Parameter	Operating Range
Range	-2000mV to +2000mV
Accuracy	±10mV
Temperature Range	0 – 60°C
Maximum Pressure	345 kPa (T = 25°C)
Sensor	Platinum wire
Temperature sensor types (only for IJ64_xx)	Pt1000, NTC 10K & 30K Accuracy better than ±0.5C
Reference Type	Double Junction Primary Reference Ag/AgCl, saturated KCl gel
Body and sleeve	Polypropylene
O-ring	EDPM as standard Viton on request
Overall Length	150mm
Barrel Diameter	12mm
Cap Diameter	16mm
Cable Length	1m standard, longer to order. Maximum 20m.
Connector	To suit common meters

6. Metal

6.1. Application - IJAu

The IJAu uses a gold rod as sensor and is designed for determining ORP measurements in cyanide solutions, and in other applications where Pt is easily poisoned.

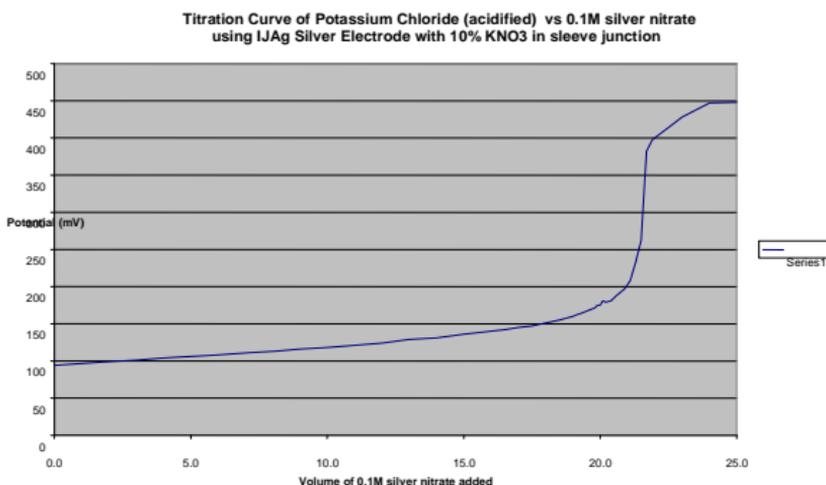
See 5.3 and 5.3.1 for Cleaning/Maintenance

6.2. Application - IJAg

The IJAg uses a silver rod as sensor and can be used for determining the activity of silver ions by direct or indirect potentiometry, and for determination of halides and cyanide by argentimetric titration. The most common application is for determination of chloride or salt in environmental and food samples by titration with silver nitrate.

A typical titration curve for potassium chloride vs 0.1M silver nitrate is shown below.

Maintenance – clean off excess silver chloride deposits from the electrode after use. Replenish electrolyte (with 1M KNO_3 regularly), and do not leave the electrode immersed in silver containing solutions when not in use.



6.3. Specifications

Table 12: IJAu and IJAg specifications

Parameter	Operating Range
Range	-2000mV to +2000mV
Accuracy	±10mV
Temperature Range	0 – 60°C
Maximum Pressure	345 kPa (T = 25°C)
Sensor rod material	Gold (IJAu), Silver (IJAg)
Reference Type	Double Junction Primary Reference Ag/AgCl, saturated KCl gel
Body and sleeve	Polypropylene
O-ring	EDPM as standard Viton on request
Overall Length	150mm
Barrel Diameter	12mm
Cap Diameter	16mm
Cable Length	1m standard, longer to order. Maximum 20m.
Connector	To suit common meters

7. Optional Accessories

RE45 - 3M KCl reference electrolyte gel, 45mL

KS200 – Electrode storage solution, 200ml

KC200 – Saturated KCL solution, 200ml

BU40 – 1L pH buffer 6.86 @ 25C

BU50 – 1L pH buffer 4.01 @ 25C

CC-0.1-DIN - Cable adapter DIN - BNC

CC-0.1-Semo – Cable adapter Lemo – BNC

CC-0.1-Raso – Cable adapter Type 7 - BNC

MK01 - Process IJ mounting kit. This consists of an electrode mounting tube which is glued into a standard PVC 1/2" BSP pipe fitting. For more details, please refer to our website.



Warranty

Any electrode found to be faulty due to manufacture will be replaced. All IJ electrodes have a serial number which identifies the date of manufacture. Electrode use should commence within two years of this date. Please return the completed proof of purchase card as soon as you receive the electrode.

Normally, IJ electrodes will have a lifetime of 2-4 years in ideal samples at room temperature. This will be reduced in chemically aggressive or abrasive samples and elevated temperatures. All IJ series electrodes are given a pro-rata one year warranty from the proof of purchase date. However, if in our opinion the electrode is not suitable for the application, we reserve the right to void the warranty.