perfectION™ Guidebook

perfectION™

Combination Iodide Electrode

Successful Ion Measurement

METTLER TOLEDO

Contents

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1. Introduction

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

perfectION™ Combination Iodide Electrode

The reference and sensing electrodes are built into one electrode, which decreases the amount of required solution and reduces waste. The built-in Click & Clear™ reference junction prevents clogging of the diaphragm and provides fast and stable readings.
The perfectION™ Combination Iodide Electrode is available with a BNC connector (P/N 51344718) and a Lemo connector (P/N 51344818) for METTLER TOLEDO titrators.

2. Required Equipment

1. METTLER TOLEDO ISE meter, such as the SevenMulti™ benchtop meter or the SevenGo pro™ portable meter, or a METTLER TOLEDO titrator, such as the Tx (T50, T70, T90) Excellence or G20 Compact titrators.

   METTLER TOLEDO combined ISEs can be used on any ISE meter with a BNC connection.

2. perfectION™ combined iodide ion selective electrode

3. Stirrer

4. Volumetric flasks, graduated cylinders, beakers and pipettes. Plastic labware is required for low-level iodide analysis.

5. Distilled or deionized water

6. Ion Electrolyte D Reference filling solution (P/N 51344753)

7. Iodide standard solution 1000 mg/L (P/N 51344776)

   Store the iodide standards in plastic bottles and prepare fresh standards weekly. Lower concentration iodide standards used for calibration should be prepared daily.

8. Ionic strength adjuster (ISA) for Solid State Ion Selective Electrodes (P/N 51344760). To adjust ionic strength of samples and standards.

3. Electrode and Measurement Setup

Electrode Preparation

Remove the protective shipping cap from the sensing element and save the cap for storage. Fill the electrode with Ion Electrolyte D Reference filling solution.

Electrode Filling Instructions:

1. Install the flip spout cap on the filling solution bottle and lift the flip spout on the bottle to a vertical position.
2. Insert the spout into the fill hole on the outer body of the electrode and add a small amount of filling solution to the reference chamber. Invert the electrode to moisten the O-ring and return the electrode to the upright position.
3. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.
4. Release the electrode cap. If the sleeve does not return to its original position, see if the O-ring is moist and repeat steps 2 through 4 until the sleeve returns to the original position.
5. Add filling solution to the electrode up to the filling hole.

Note: *Add filling solution each day before using the electrode. The filling solution level should be at least 2.5 cm above the level of sample in the beaker to ensure a proper flow rate. The fill hole should always be open when taking measurements.*

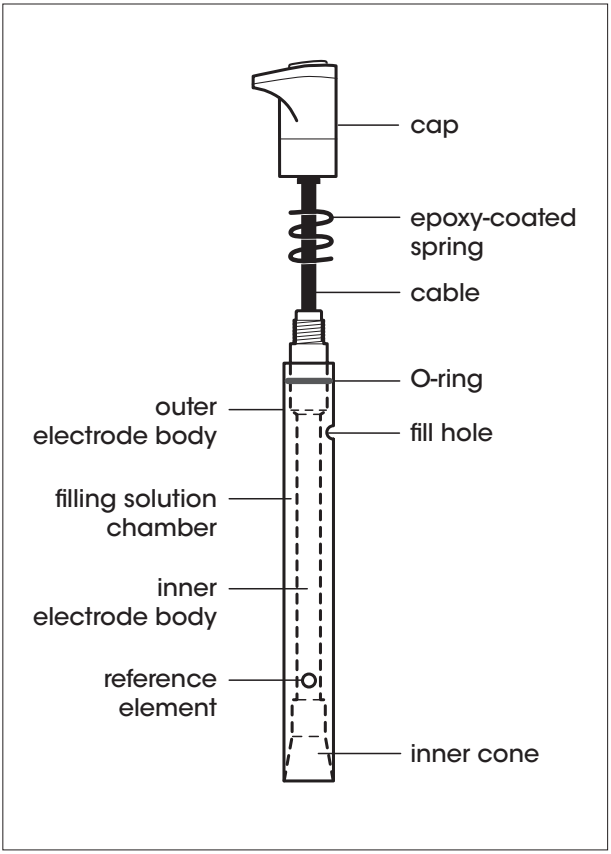


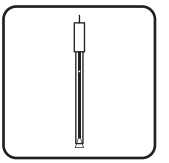
Figure 1 *– perfectION™ Iodide combination electrode*

Checking Electrode Operation (Slope)

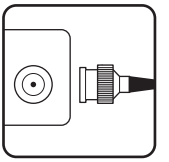
These are general instructions that can be used with most meters to check the electrode operation.

This procedure measures the electrode slope. Slope is defined as the change in millivolts observed with every tenfold change in concentration. The slope value provides the best means for checking the electrode operation.

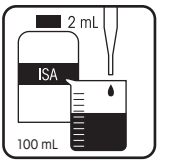
1. If the electrode has been stored dry, prepare the electrode as described in the **Electrode Preparation** section.



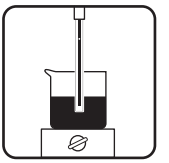
2. Connect the electrode to a meter with a mV mode. Set the meter to the mV mode.



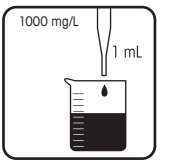
3. Add 100 mL of distilled water and 2 mL of ISA into a 150 mL beaker. Stir the solution thoroughly.



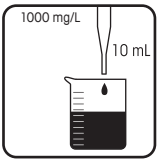
4. Rinse the electrode with distilled water and place the electrode into the solution prepared in step 3.



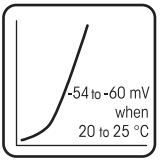
5. Select either a 0.1 mol/L or 1000 mg/L iodide standard. Pipette 1 mL of the standard into the beaker and stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.



6. Pipette 10 mL of the same standard into the same beaker and stir the solution thoroughly. When a stable reading is displayed, record the electrode potential in millivolts.



7. There should be a -54 to -60 mV difference between the two millivolt readings when the solution temperature is between 20 to 25 °C. If the millivolt potential is not within this range, refer to the **Troubleshooting** section.



Sample Requirements

The epoxy body of the iodide electrode is resistant to damage by aqueous solutions. The electrode may be used intermittently in solutions that contain methanol, benzene or acetone.

Samples and standards should be at the same temperature. A 1 °C difference in temperature for a 10^{-3} mol/L iodide solution will give rise to about a 2% error. The solution temperature must be less than 80 °C.

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

Measuring Hints

Iodide concentration can be measured in moles per liter (mol/L), milligrams per liter (mg/L) or any convenient concentration unit.

Table 1 *– Iodide Concentration Unit Conversion Factors*

mol/L	mg/L Iodide (I^-)
1.0	126900
10^{-1}	12690
10^{-2}	1269
7.88×10^{-3}	1000
10^{-3}	126.9
10^{-4}	12.69
7.88×10^{-6}	1

- Stir all standards and samples at a uniform, moderate rate. Place a piece of insulating material, such as Styrofoam or cardboard, between the magnetic stirrer and beaker to prevent measurement errors from the transfer of heat to the sample.
- Always use freshly prepared standards for calibration.
- Always rinse the electrode with distilled water between measurements and shake the electrode to remove the water and prevent sample carryover. Do not wipe or rub the electrode sensing element.

- Allow all standards and samples to come to the same temperature for precise measurements.
- Concentrated samples (greater than 10^{-1} mol/L iodide) should be diluted before measurement.
- Verify the electrode calibration every two hours by placing the electrode in a fresh aliquot of the least concentrated standard used for calibration. If the value has changed by more than 2%, recalibrate the electrode.
- After immersing the electrode in a solution, check the electrode sensing surface for air bubbles and remove air bubbles by reimmersing the electrode in the solution and gently tapping it.
- For high ionic strength samples, prepare standards with a background composition similar to the sample.
- The fill hole cover must be open during measurements to ensure a uniform flow of reference filling solution.
- If the electrode is used in dirty or viscous samples or the electrode response becomes sluggish, empty the electrode completely, hold the junction open and flush the junction with distilled water. Empty any water from the electrode and refill it with fresh filling solution. Press down on the electrode cap to let a few drops of the filling solution flow out of the electrode and then replenish any lost solution.
- Start the calibration or measurement with the lowest concentrated standard or sample.

Electrode Storage and Maintenance

Electrode Storage

For storage between measurements and up to one week, store the electrode in a 4 mol/L potassium chloride solution with iodide. The iodide concentration of the storage solution should be close to the least concentrated iodide calibration standard. **Do not add ISA to the storage solution.** The filling solution inside the electrode should not be allowed to evaporate, as crystallization will result.

For storage longer than one week, drain the electrode, flush the chamber with distilled water and store the electrode dry with the protective shipping cap covering the sensing element.

Polishing the Iodide Combination Electrode

The sensing surface of solid state electrodes can wear over time, which causes drift, poor reproducibility and loss of response in low-level samples. The electrode can be restored by polishing the sensing surface with a polishing strip. The polishing strip can also be used if the sensing surface has been etched or chemically poisoned.

1. Cut off about an inch of the polishing strip.
2. Hold the electrode with the sensing surface facing up.
3. Place a few drops of distilled water on the sensing surface.
4. With the frosted side of the polishing strip facing down, use light finger pressure to place the polishing strip on top of the sensing surface.
5. Rotate the electrode for about 30 seconds.
6. Rinse the electrode with distilled water and soak the electrode in a 1 mg/L or 10^{-5} mol/L iodide standard for ten minutes.

Flushing the Iodide Combination Electrode

If the area between the electrode sleeve and inner cone becomes clogged with sample or precipitate, flush the area with filling solution or distilled water.

1. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to drain the electrode. Push down on the cap until all the filling solution is drained from the chamber.
2. Fill the electrode with distilled water and then push down on the cap until all the water is drained from the chamber.
3. Fill the electrode with fresh filling solution up to the fill hole. Push down on the cap to allow a few drops of filling solution to drain out of the electrode and replenish the lost filling solution.

Disassembling and Reassembling the Iodide Combination Electrode

Note: *Disassembly is usually not required and should not be done unless a thorough cleaning is required.*

1. Tip the electrode so the filling solution moistens the O-ring on the electrode body. Hold the electrode body with one hand and use your thumb to push down on the electrode cap to drain the electrode.
2. Unscrew the cap counterclockwise and then slide the cap and spring up the cable.
3. Hold the outer sleeve with one hand and firmly push down on the threaded portion with your thumb and forefinger to separate the inner body from the sleeve.
4. Grasp the inner cone with a clean, lint-free tissue and withdraw the body from the sleeve using a gentle twisting motion. Do not touch the pellet above the cone, as it will damage the pellet. Rinse the outside of the electrode body and the entire sleeve with distilled water. Allow it to air dry.
5. Moisten the O-ring on the electrode body with a drop of filling solution. Insert the screw-thread end of the electrode body into the tapered, ground end of the sleeve.
6. Push the body into the sleeve using a gentle twisting motion until the bottom surface of the inner cone is flush with the tapered end of the sleeve.
7. Place the spring onto the electrode body and screw on the cap. Refill the electrode with filling solution.

Serial Delutions

Serial dilution is the best method for the preparation of standards. Serial dilution means that an initial standard is diluted, using volumetric glassware, to prepare a second standard solution. The second standard is similarly diluted to prepare a third standard, and so on, until the desired range of standards has been prepared.

1. **To prepare a 100 mg/L iodide standard** – Pipette 10 mL of the 1000 mg/L standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

2. **To prepare a 10 mg/L standard** – Pipette 10 mL of the 100 mg/L standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

3. **To prepare a 1 mg/L standard** – Pipette 10 mL of the 10 mg/L standard into a 100 mL volumetric flask. Dilute to the mark with deionized water and mix well.

To prepare standards with a different concentration use the following formula:

$$\mathbf{C_1 * V_1 = C_2 * V_2}$$

C_1 = concentration of original standard
V_1 = volume of original standard
C_2 = concentration of standard after dilution
V_2 = volume of standard after dilution

For example, to prepare 1000 mL of a 100 mg/L iodide standard from a 12690 mg/L iodide standard:

C_1 = 12690 mg/L iodide
V_1 = unknown
C_2 = 100 mg/L iodide
V_2 = 1000 mL
12690 mg/L * V_1 = 100 mg/L * 1000 mL
V_1 = (100 mg/L * 1000 mL) / 12690 mg/L = 7.9 mL

4. Analytical Techniques

A variety of analytical techniques are available to the analyst. The following is a description of these techniques.

Direct Calibration is a simple procedure for measuring a large number of samples. Only one meter reading is required for each sample. Calibration is performed using a series of standards. The concentration of the samples is determined by comparison to the standards. ISA is added to all solutions to ensure that samples and standards have similar ionic strength.

Incremental Techniques provide a useful method for measuring samples, since a calibration is not required. The different incremental techniques are described below. They can be used to measure the total concentration of a specific ion in the presence of a large (50 to 100 times) excess of complexing agents. As in direct calibration, any convenient concentration unit can be used.

- **Known Addition** is useful for measuring dilute samples, checking the results of direct calibration (when no complexing agents are present), or measuring the total concentration of an ion in the presence of an excess complexing agent. The electrode is immersed in the sample solution and an aliquot of a standard solution containing the measured species is added to the sample. From the change in potential before and after the addition, the original sample concentration is determined.

Direct Calibration Technique

Typical Direct Calibration Curve

In the direct calibration procedure, a calibration curve is constructed either in the meter memory or on semi-logarithmic paper. Electrode potentials of standard solutions are measured and plotted on the linear axis against their concentrations on the log axis. In the linear regions of the curves, only two standards are needed to determine a calibration curve. In non-linear regions, more points must be taken. These direct calibration procedures are given for concentrations in the region of linear electrode response. Low-level measurement procedures are given in a following section for measurements in the non-linear electrode region.

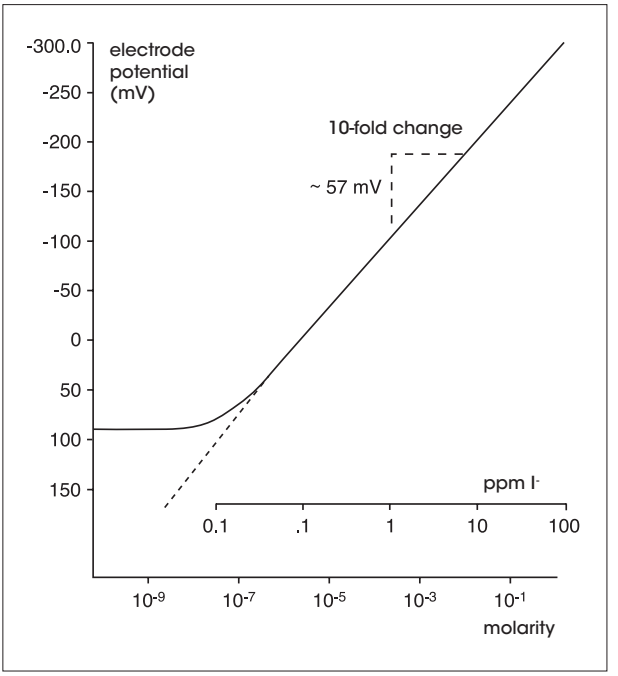


Figure 2 *– Typical Direct Calibration Curve*

Direct Calibration Overview

The following direct measurement procedures are recommended for low, moderate and high level measurements. Samples must be in the linear range of the electrode – greater than 5 x 10^{-8} mol/L iodide. A two point calibration is sufficient, although more points can be used. When using an ISE meter, sample concentrations can be read directly from the meter. When using a mV meter, a calibration curve can be prepared on semi-logarithmic graph paper, or a linear regression (against logarithmic concentration values) can be performed using a spreadsheet or graphing program.

Calibration Hints

- Standard concentrations should bracket the expected sample concentrations.
- Always add 2 mL of ISA per 100 mL of standard or sample.
- For high ionic strength samples that have an ionic strength of 0.1 mol/L or greater, prepare standards with a background composition similar to that of the samples, or measure the samples using the known addition method.
- During calibration, measure the least concentrated standard first, and work up to the most concentrated standard.

Direct Calibration Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to the meter.
3. Prepare at least two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. See the **Serial Dilution** section for instructions on how to prepare standards. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to the **Temperature Effects** section.

Direct Calibration Procedure Using a Meter with an ISE Mode

***Note*:** *See the meter user guide for more specific information.*

1. Add 100 mL of the less concentrated standard and 2 mL of ISA to a 150 mL beaker and stir the solution thoroughly.
2. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the less concentrated standard. Wait for a stable reading and adjust the meter to display the value of the standard, as described in the meter user guide.
3. Add 100 mL of the more concentrated standard and 2 mL of ISA to a second 150 mL beaker and stir the solution thoroughly.
4. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the more concentrated standard. Wait for a stable reading and adjust the meter to display the value of the second standard, as described in the meter user guide.
5. Record the resulting slope value. The slope should be between -54 and -60 mV when the standards are between 20 and 25 °C.
6. Add 100 mL of sample and 2 mL of ISA to a clean 150 mL beaker and stir the solution thoroughly.
7. Rinse the electrode with distilled water, blot it dry and place it into the sample. The concentration of the sample will be displayed on the meter.

Note: *Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.*

Direct Calibration Procedure Using a Meter with a mV Mode

Note: *See the meter user guide for more specific information.*

1. Set the meter to the mV mode.
2. Add 100 mL of the less concentrated standard and 2 mL of ISA to a 150 mL beaker and stir the solution thoroughly.
3. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the less concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
4. Add 100 mL of the more concentrated standard and 2 mL of ISA to a second 150 mL beaker and stir the solution thoroughly.
5. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the more concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis.
7. Add 100 mL of sample and 2 mL of ISA to a clean 150 mL beaker and stir the solution thoroughly.
8. Rinse the electrode with distilled water, blot it dry and place it into the beaker. When a stable reading is displayed, record the mV value.
9. Use the calibration curve prepared in step 6 on order to determine the unknown concentration of the sample.

Note: *Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.*

Small Volume Direct Calibration Technique

Take advantage of special design features available with the perfectION™ combination iodide electrode to meet your measuring needs. Due to the Click & Clear™ reference, this electrode is able to measure sample volumes as small as 5 mL using a modified direct measurement procedure. Because less solution volume is required, the chemical usage of iodide standards and ISA is reduced. All samples should have a concentration greater than 5 x 10^{-8} mol/L iodide. A two point calibration is sufficient, although more points can be used. The following procedure recommends using 25 mL of sample. Smaller sample volumes can be used, as long as the final volume of solution is sufficient to cover the bottom of the electrode.

Calibration Hints

- Standard concentrations should bracket the expected sample concentrations.
- Always keep the ratio of standard or sample to ISA at 50:1.
- For high ionic strength samples that have an ionic strength of 0.1 mol/L or greater, prepare standards with a background composition similar to that of the samples, or measure the samples using the known addition method.
- During calibration, measure the least concentrated standard first, and work up to the most concentrated standard.
- Calibrate with the same volume of standard as the volume of sample that is available for analysis.

Small Volume Direct Calibration Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to the meter.
3. Prepare at least two standards that bracket the expected sample range and differ in concentration by a factor of ten. Standards can be prepared in any concentration unit to suit the particular analysis requirement. See the **Serial Dilution** section for instructions on how to prepare standards. All standards should be at the same temperature as the samples. For details on temperature effects on electrode performance, refer to the **Temperature Effects** section.

Small Volume Direct Calibration Procedure Using a Meter with an ISE Mode

Note: *See the meter user guide for more specific information.*

1. Add 25 mL of the less concentrated standard and 0.5 mL of ISA to a 50 mL beaker and swirl the solution to mix.
2. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the less concentrated standard. Wait for a stable reading and adjust the meter to display the value of the standard, as described in the meter user guide.
3. Add 25 mL of the more concentrated standard and 0.5 mL of ISA to a second 50 mL beaker and swirl the solution to mix.
4. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the more concentrated standard. Wait for a stable reading and adjust the meter to display the value of the second standard, as described in the meter user guide.
5. Record the resulting slope value. The slope should be between 25 and 30 mV when the standards are between 20 and 25 °C.
6. Add 25 mL of sample and 0.5 mL of ISA to a clean 50 mL beaker and swirl the solution to mix.
7. Rinse the electrode with distilled water, blot it dry and place it into the sample. The concentration of the sample will be displayed on the meter.

Note: *Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.*

Small Volume Direct Calibration Procedure Using a Meter with a mV Mode

Note: *See the meter user guide for more specific information.*

1. Set the meter to the mV mode.
2. Add 25 mL of the less concentrated standard and 0.5 mL of ISA to a 50 mL beaker and swirl the solution to mix.
3. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the less concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
4. Add 25 mL of the more concentrated standard and 0.5 mL of ISA to a second 50 mL beaker and swirl the solution to mix.
5. Rinse the electrode with distilled water, blot it dry and place it into the beaker with the more concentrated standard. When a stable reading is displayed, record the mV value and corresponding standard concentration.
6. Using semi-logarithmic graph paper, prepare a calibration curve by plotting the millivolt values on the linear axis and the standard concentration values on the logarithmic axis.
7. Add 25 mL of sample and 0.5 mL of ISA to a clean 50 mL beaker and swirl the solution to mix.
8. Rinse the electrode with distilled water, blot it dry and place it into the beaker. When a stable reading is displayed, record the mV value.
9. Using the calibration curve prepared in step 6, determine the unknown concentration of the sample.

Note: *Other solution volumes may be used, as long as the ratio of solution to ISA remains 50:1.*

Known Addition Technique

Known addition is a convenient technique for measuring samples in the linear range of the electrode (greater than 0.2 mg/L iodide) because no calibration curve is required. It can be used to verify the results of a direct calibration or to measure the total concentration of an ion in the presence of a large excess of a complexing agent. The sample potential is measured before and after addition of a standard solution.

Accurate results require the following conditions be met:

- Concentration should approximately double as a result of the addition.
- Sample concentration should be known to within a factor of three.
- Either no complexing agent or a large excess of the complexing agent may be present.
- The ratio of the uncomplexed ion to complexed ion must not be changed by addition of the standard.
- All samples and standards should be at the same temperature.
- With double or multiple known addition, the final addition should be 10 to 100 times the sample concentration.
- Add 2 mL of ISA to every 100 mL of sample before analysis.

Known Addition Setup

1. Prepare the electrode as described in the **Electrode Preparation** section.
2. Connect the electrode to the meter.
3. Prepare a standard solution that will cause the iodide concentration of the sample to double when added to the sample solution. Refer to **Table 2** for guidelines.
4. Determine the electrode slope by performing the procedure in the **Checking Electrode Operation (Slope)** section.
5. Rinse the electrode with distilled water.

Table 2 *– Guideline For Known Addition*

Volume of Addition	Concentration of Standard
1 mL	100 times sample concentration
5 mL	20 times sample concentration
10 mL*	10 times sample concentration

** Most convenient volume to use*

Known Addition Using a Meter with a Known Addition Mode

Note: *See the meter user guide for more specific information.*

1. Set the meter to measure in the known addition mode.
2. Measure 100 mL of the sample and 2 mL of ISA and pour the solutions into a beaker. Rinse the electrode with distilled water and place it into the sample solution. Stir the solution thoroughly.
3. When a stable reading is displayed, set the meter as described in the meter user guide, if required.
4. Pipette the appropriate amount of the standard solution into the beaker. Stir the solution thoroughly.
5. When a stable reading is displayed, record the sample concentration.

Known Addition Using a Meter with a Millivolt Mode

1. Set the meter to the relative millivolt mode. If a relative millivolt mode is not available, use the millivolt mode.
2. Measure 100 mL of sample and 2 mL of ISA and pour the solutions into a 150 mL beaker. Stir the solution thoroughly.
3. Rinse the electrode with distilled water, blot it dry and place the electrode into the beaker. When a stable reading is displayed, set the meter to read 0.0 mV. If the reading cannot be adjusted to 0.0 mV, record the actual mV value.
4. Pipette the appropriate amount of standard solution into the beaker. Stir the solution thoroughly.
5. When a stable reading is displayed, record the mV value. If the meter could not be set to 0.0 mV in step 3, subtract the first reading from the second reading to calculate ΔE.
6. Use **Table 4** to find the Q value that corresponds to the change in potential, ΔE. To determine the original sample concentration, multiply Q by the concentration of the added standard:

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

$C_{standard}$ = standard concentration
C_{sample} = sample concentration
Q = value from **Table 4**

The table of Q values is calculated for a 10% volume change. The equation for the calculation of Q for different slopes and volume changes is given below.

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

Q = value from **Table 4**
$\Delta E = E_2 - E_1$
S = slope of the electrode
p = volume of standard / volume of sample and ISA
r = volume of sample and ISA / volume of sample

Calculating Known Addition for Samples using Excel Spreadsheets

If it is more convenient, a simple spreadsheet can be set up to calculate the known addition results, using any ratio of sample to addition. A typical worksheet is shown in **Table 3**. The numbers shown are examples, but the formulas and their locations should be copied exactly.

Table 3 *– Known Addition Calculations using Excel Spreadsheets*

A	B	C
1		Enter Value
2	Volume of sample and ISA (mL)	102
3	Volume of addition (mL)	10
4	Concentration of addition	10
5	Volume of sample	100
6	Initial mV reading	-45.3
7	Final mV reading	-63.7
8	Electrode slope	-59.2
9		
10		Derived Values
11	Delta E	=C7 - C6
12	Solution volume ratio	=C3/C2
13	Antilog term	=10^ (C11/C8)
14	Sample volume ratio	=C2/C5
15	Q term	=C12*C14/ (((1+C12)*C13)-1)
16	Calculated initial concentration in same units as addition	=C15*C4

Table 4 *– Q Values for a 10% volume change, slopes (in column heading) are in units of mV/decade*

ΔE	Q Concentration Ratio			
	-57.2	**-58.2**	**-59.2**	**-60.1**
5.0	0.2917	0.2957	0.2996	0.3031
5.2	0.2827	0.2867	0.2906	0.2940
5.4	0.2742	0.2781	0.2820	0.2854
5.6	0.2662	0.2700	0.2738	0.2772
5.8	0.2585	0.2623	0.2660	0.2693
6.0	0.2512	0.2550	0.2586	0.2619
6.2	0.2443	0.2480	0.2516	0.2548
6.4	0.2377	0.2413	0.2449	0.2480
6.6	0.2314	0.2349	0.2384	0.2416
6.8	0.2253	0.2288	0.2323	0.2354
7.0	0.2196	0.2230	0.2264	0.2295
7.2	0.2140	0.2174	0.2208	0.2238
7.4	0.2087	0.2121	0.2154	0.2184
7.6	0.2037	0.2070	0.2102	0.2131
7.8	0.1988	0.2020	0.2052	0.2081
8.0	0.1941	0.1973	0.2005	0.2033
8.2	0.1896	0.1927	0.1959	0.1987
8.4	0.1852	0.1884	0.1914	0.1942
8.6	0.1811	0.1841	0.1872	0.1899
8.8	0.1770	0.1801	0.1831	0.1858
9.0	0.1732	0.1762	0.1791	0.1818
9.2	0.1694	0.1724	0.1753	0.1779
9.4	0.1658	0.1687	0.1716	0.1742
9.6	0.1623	0.1652	0.1680	0.1706
9.8	0.1590	0.1618	0.1646	0.1671
10.0	0.1557	0.1585	0.1613	0.1638
10.2	0.1525	0.1553	0.1580	0.1605
10.4	0.1495	0.1522	0.1549	0.1573
10.6	0.1465	0.1492	0.1519	0.1543
10.8	0.1437	0.1463	0.1490	0.1513
11.0	0.1409	0.1435	0.1461	0.1485
11.2	0.1382	0.1408	0.1434	0.1457
11.4	0.1356	0.1382	0.1407	0.1430
11.6	0.1331	0.1356	0.1381	0.1404
11.8	0.1306	0.1331	0.1356	0.1378
12.0	0.1282	0.1307	0.1331	0.1353
12.2	0.1259	0.1283	0.1308	0.1329
12.4	0.1236	0.1260	0.1284	0.1306
12.6	0.1214	0.1238	0.1262	0.1283
12.8	0.1193	0.1217	0.1240	0.1261
13.0	0.1172	0.1195	0.1219	0.1239
13.2	0.1152	0.1175	0.1198	0.1218
13.4	0.1132	0.1155	0.1178	0.1198
13.6	0.1113	0.1136	0.1158	0.1178
13.8	0.1094	0.1117	0.1139	0.1159
14.0	0.1076	0.1098	0.1120	0.1140
14.2	0.1058	0.1080	0.1102	0.1121
14.4	0.1041	0.1063	0.1084	0.1103
14.6	0.1024	0.1045	0.1067	0.1086
14.8	0.1008	0.1029	0.1050	0.1069

ΔE	Q Concentration Ratio			
	-57.2	-58.2	-59.2	-60.1
15.0	0.0992	0.1012	0.1033	0.1052
15.5	0.0953	0.0973	0.0994	0.1012
16.0	0.0917	0.0936	0.0956	0.0974
16.5	0.0882	0.0902	0.0921	0.0938
17.0	0.0850	0.0869	0.0887	0.0904
17.5	0.0819	0.0837	0.0856	0.0872
18.0	0.0790	0.0808	0.0825	0.0841
18.5	0.0762	0.0779	0.0797	0.0813
19.0	0.0736	0.0753	0.0770	0.0785
19.5	0.0711	0.0727	0.0744	0.0759
20.0	0.0687	0.0703	0.0719	0.0734
20.5	0.0664	0.0680	0.0696	0.0710
21.0	0.0642	0.0658	0.0673	0.0687
21.5	0.0621	0.0637	0.0652	0.0666
22.0	0.0602	0.0617	0.0631	0.0645
22.5	0.0583	0.0597	0.0612	0.0625
23.0	0.0564	0.0579	0.0593	0.0606
23.5	0.0547	0.0561	0.0575	0.0588
24.0	0.0530	0.0544	0.0558	0.0570
24.5	0.0514	0.0528	0.0541	0.0553
25.0	0.0499	0.0512	0.0525	0.0537
25.5	0.0484	0.0497	0.0510	0.0522
26.0	0.0470	0.0483	0.0495	0.0507
26.5	0.0456	0.0469	0.0481	0.0492
27.0	0.0443	0.0455	0.0468	0.0479
27.5	0.0431	0.0443	0.0455	0.0465
28.0	0.0419	0.0430	0.0442	0.0452
28.5	0.0407	0.0418	0.0430	0.0440
29.0	0.0395	0.0407	0.0418	0.0428
29.5	0.0385	0.0396	0.0407	0.0417
30.0	0.0374	0.0385	0.0396	0.0406
30.5	0.0364	0.0375	0.0385	0.0395
31.0	0.0354	0.0365	0.0375	0.0384
31.5	0.0345	0.0355	0.0365	0.0374
32.0	0.0335	0.0345	0.0356	0.0365
32.5	0.0327	0.0336	0.0346	0.0355
33.0	0.0318	0.0328	0.0337	0.0346
33.5	0.0310	0.0319	0.0329	0.0337
34.0	0.0302	0.0311	0.0320	0.0329
34.5	0.0294	0.0303	0.0312	0.0321
35.0	0.0286	0.0295	0.0305	0.0313
35.5	0.0279	0.0288	0.0297	0.0305
36.0	0.0272	0.0281	0.0290	0.0298
36.5	0.0265	0.0274	0.0282	0.0290
37.0	0.0258	0.0267	0.0275	0.0283
37.5	0.0252	0.0260	0.0269	0.0276
38.0	0.0246	0.0254	0.0262	0.0270
38.5	0.0240	0.0248	0.0256	0.0263
39.0	0.0234	0.0242	0.0250	0.0257
39.5	0.0228	0.0236	0.0244	0.0251

ΔE	Q Concentration Ratio			
	-57.2	-58.2	-59.2	-60.1
40.0	0.0223	0.0230	0.0238	0.0245
40.5	0.0217	0.0225	0.0232	0.0239
41.0	0.0212	0.0219	0.0227	0.0234
41.5	0.0207	0.0214	0.0221	0.0228
42.0	0.0202	0.0209	0.0216	0.0223
42.5	0.0197	0.0204	0.0211	0.0218
43.0	0.0192	0.0199	0.0206	0.0213
43.5	0.0188	0.0195	0.0202	0.0208
44.0	0.0183	0.0190	0.0197	0.0203
44.5	0.0179	0.0186	0.0192	0.0198
45.0	0.0175	0.0181	0.0188	0.0194
45.5	0.0171	0.0177	0.0184	0.0190
46.0	0.0167	0.0173	0.0179	0.0185
46.5	0.0163	0.0169	0.0175	0.0181
47.0	0.0159	0.0165	0.0171	0.0177
47.5	0.0156	0.0162	0.0168	0.0173
48.0	0.0152	0.0158	0.0164	0.0169
48.5	0.0148	0.0154	0.0160	0.0166
49.0	0.0145	0.0151	0.0157	0.0162
49.5	0.0142	0.0147	0.0153	0.0158
50.0	0.0139	0.0144	0.0150	0.0155
50.5	0.0135	0.0141	0.0146	0.0151
51.0	0.0132	0.0138	0.0143	0.0148
51.5	0.0129	0.0135	0.0140	0.0145
52.0	0.0126	0.0132	0.0137	0.0142
52.5	0.0124	0.0129	0.0134	0.0139
53.0	0.0121	0.0126	0.0131	0.0136
53.5	0.0118	0.0123	0.0128	0.0133
54.0	0.0116	0.0120	0.0125	0.0130
54.5	0.0113	0.0118	0.0123	0.0127
55.0	0.0110	0.0115	0.0120	0.0125
55.5	0.0108	0.0113	0.0118	0.0122
56.0	0.0106	0.0110	0.0115	0.0119
56.5	0.0103	0.0108	0.0113	0.0117
57.0	0.0101	0.0106	0.0110	0.0114
57.5	0.0099	0.0103	0.0108	0.0112
58.0	0.0097	0.0101	0.0105	0.0110
58.5	0.0095	0.0099	0.0103	0.0107
59.0	0.0093	0.0097	0.0101	0.0105
59.5	0.0091	0.0095	0.0099	0.0103
60.0	0.0089	0.0093	0.0097	0.0101

5. Electrode Characteristics

Electrode Response

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

The time response of the electrode (the time required to reach 99% of the stable potential reading) varies from several seconds in concentrated solutions to several minutes near the limit of detection.

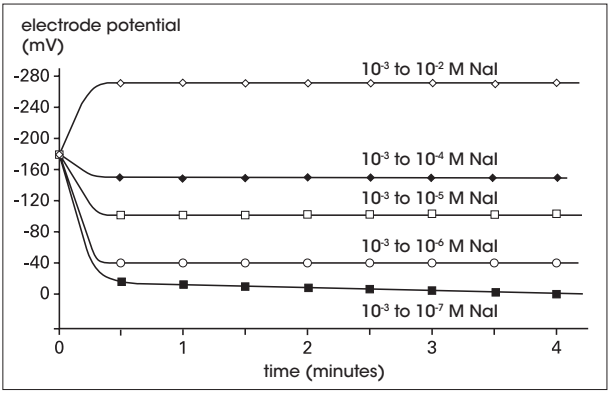


Figure 3 *– Typical Electrode Response*

Reproducibility

Reproducibility is limited by factors such as temperature fluctuations, drift and noise. Within the operating range of the electrode, reproducibility is independent of concentration. With hourly calibrations, direct electrode measurements reproducible to ± 2 % can be obtained.

Temperature Effects

Since electrode potentials are affected by changes in temperature, samples and standard solutions should be within ± 1 °C (± 2 °F) of each other. At the 10^{-3} mol/L level, a 1 °C difference in temperature results in errors greater than 2%. The absolute potential of the reference electrode changes slowly with temperature because of the solubility equilibria on which the electrode depends. The slope of the electrode also varies with temperature, as indicated by the factor S in the Nernst equation.
Theoretical values of the slope at different temperatures are given in **Table 5**. If the temperature changes, the meter and electrode should be recalibrated.

The electrode can be used at temperatures from 0 to 80 °C, provided that temperature equilibrium has occurred. For use at temperatures substantially different from room temperature, calibration standards should be at the same temperature as samples. The electrode must be used only intermittently at solution temperatures above 80 °C.

Table 5 *– Theoretical Slope vs. Temperature Values*

Temperature (°C)	Slope (mV)
0	27.1
10	28.1
20	29.1
25	29.6
30	30.1
40	31.1
50	32.1

The Ion Electrolyte D reference filling solution that is included with the electrode will minimize junction potentials and provide optimum temperature and time response.

Interferences

The electrode will malfunction if the ions listed in **Table 6**, which form insoluble salts, are present at sufficiently high concentrations to form a layer of the salt on the sensing element surface. In addition, the electrode must not be placed in strong reducing solutions, such as photographic developer, which form a layer of metal on the electrode sensing element. If the surface of the sensing element becomes contaminated, restore the electrode performance by polishing the sensing surface.

Mercury should be absent from all samples.

Table 6 gives the maximum allowable concentration of common interfering ions expressed as the ratio of the interfering ion concentration to the sample iodide concentration. If the ratio is exceeded, the electrode will malfunction. If the ratio is less than the value listed in the table, neither the accuracy of the measurement nor the sensing element surface will be affected.

Table 6 *– Iodide Electrode Interferences*

Interferences	Maximum Ratio (mol/L)	Maximum Ratio (mg/L)
(a) Cl^-	10^6	2.8×10^5
(a) Br^-	5×10^3	3.1×10^3
(b) S^{2-}	10^{-6}	2.5×10^{-8}
(b) CN^-	0.4	8.2×10^{-3}
(c) $S_2O_3^{2-}$	10^5	8.8×10^{-3}

(a) Mixed halides in solution can be measured by a Gran's plot titration.

(b) Sulfide and cyanide may be removed by adding a nickel (+2) solution.

(c) Represents a complexing species. Maximum level can be exceeded without electrode damage. Value shown is for 1% error.

Example

What is the maximum level of chloride tolerable in a sample whose iodide concentration is 10^{-3} mol/L? From **Table 6**, the maximum ratio is:

$[Cl^-] / [I^-] = 10^6$

$[Cl^-] = 10^6 * [I^-] = 10^6 * 10^{-3} =$

10^3 mol/L maximum chloride concentration

Limits of Detection

The lower limit of detection is determined by the very slight water solubility of the sensing element. At low levels the electrode responds to iodide in the sample as well as to ions dissolved from the sensing element. The discrepancy between the theoretical linear response in comparison with the actual response (full line) curves is due to the response to dissolved ions from the sensing element.

Allow longer stabilization time prior to recording the measurement to assure the best results.

Complexation

Iodide ions form complexes with some metal ions. Since the electrode responds only to free iodide ions, the presence of any complexing agents lowers the measured concentration. **Table 7** lists the levels of complexing metals causing a 20% error. Total concentration in the presence of a large excess (by a factor of at least 50 to 100) of complexing agent can be measured by the known addition method.

Table 7 *– Complexing Metals*

Complexing Agent	Maximum Level (mol/L)	Maximum Level (mg/L)
Bi^{3+}	2×10^{-5} mol/L	4 mg/L
Cd^{2+}	5×10^{-4} mol/L	50 mg/L
Pb^{2+}	5×10^{-3} mol/L	1000 mg/L

Theory of Operation

The iodide electrode consists of a sensing element bonded into an epoxy body. When the sensing element is in contact with a solution containing iodide ions, an electrode potential develops across the sensing element. This potential, which depends on the level of free iodide ion in solution, is measured against a constant reference potential with a digital pH/mV meter or ISE (concentration) meter. The measured potential corresponding to the level of iodide ion in solution is described by the Nernst equation.

$$\mathbf{E = E_0 + S * \log (A)}$$

E = measured electrode potential
E_0 = reference potential (a constant)
A = iodide ion activity level in solution
S = electrode slope (about -57 mV per decade)
S = (2.3 R T) / nF
R and F are constants, T = temperature in kelvin and
n = ionic charge

The level of iodide ions, A, is the activity or "effective concentration" of free iodide ions in solution. The iodide ion activity is related to free iodide ion concentration, Cf, by the activity coefficient, y.

$$\mathbf{A = y * C_f}$$

Ionic activity coefficients are variable and largely depend on total ionic strength. The ionic strength of a solution is determined by all of the ions present. It is calculated by multiplying the concentration of each individual ion by the square of its charge, adding all these values up and then dividing by two.

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

C_i = concentration of ion i
Z_i = charge of ion i
$\sum$ symbolizes the sum of all the types of ions in solution

If background ionic strength is high and constant relative to the sensed ion concentration, the activity coefficient is constant and activity is directly proportional to the concentration. Ionic strength adjustor (ISA) is added to all iodide standards and samples so that the background ionic strength is high and constant relative to variable concentrations of iodide. For iodide, the recommended ISA is 5 mol/L $NaNO_3$. Other solutions can be used as long as they do not contain ions that would interfere with the electrode response to iodide.

If samples have a high ionic strength (above 0.1 mol/L), standards should be prepared with a composition similar to the samples.

Reference electrode conditions must also be considered. Liquid junction potentials arise any time when two solutions of different composition are brought into contact. The potential results from the interdiffusion of ions in the two solutions. Since ions diffuse at different rates, the electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions. In making electrode measurements, it is important that this potential is the same when the reference is in the standardizing solution as well as in the sample solution; otherwise, the change in liquid junction potential will appear as an error in the measured specific ion electrode potential.

The most important variable that analysts have under their control is the composition of the liquid junction filling solution. The filling solution should be equitransferent. That is, the speed with which the positive and negative ions in the filling solution diffuse into the sample should be nearly as equal as possible. If the rate at which positive and negative charge is carried into the sample solution is equal, then no junction potential can result.
perfectION™ reference filling solutions are specifically designed to meet all reference electrode conditions.

6. Troubleshooting

Follow a systematic procedure to isolate the problem. The measuring system can be divided into four components for ease in troubleshooting: meter, electrode, sample/application and technique.

Meter/Titrator

The meter/titrator is the easiest component to eliminate as a possible cause of error. Consult the meter/titrator user guide for directions.

Electrode

1. Rinse the electrode thoroughly with distilled water.
2. Verify the electrode performance by performing the procedure in the **Checking Electrode Operation (Slope)** section.
3. If the electrode fails this procedure, review the **Measuring Hints** section. Clean the electrode thoroughly as directed in the **Electrode Maintenance** section. Drain and refill the electrode with fresh filling solution.
4. Repeat the procedure in the **Checking Electrode Operation (Slope**) section.
5. If the electrode passes the procedure, but measurement problems persist, the sample may contain interferences or complexing agents, or the technique may be in error.
6. Before replacing a faulty electrode, review this user guide and be sure to thoroughly clean the electrode; correctly prepare the electrode; use the proper filling solution, ISA, and standards; correctly measure the samples and review the **Troubleshooting Checklist** section.

Sample/Application

The quality of results depends greatly upon the quality of the standards. Always prepare fresh standards when problems arise, it could save hours of frustrating troubleshooting! Errors may result from contamination of prepared standards, accuracy of dilution, quality of distilled water, or a mathematical error in calculating the concentrations.

The best method for preparation of standards is serial dilution. Refer to the **Serial Dilution** section. The electrode and meter may operate with standards, but not with the sample. In this case, check the sample composition for interferences, incompatibilities or temperature effects. Refer to the **Sample Requirements, Temperature Effects, Interferences** and **pH Effects** sections.

Technique

If trouble persists, review operating procedures. Review calibration and measurement sections to be sure proper technique has been followed. Verify that the expected concentration of the ion of interest is within the limit of detection of the electrode.

Check the method of analysis for compatibility with your sample. **Direct measurement** may not always be the method of choice. If a large amount of complexing agents are present, **Known Addition** may be the best method. If working with low-level samples, follow the procedure in the **Low-level Calibration** section.

Troubleshooting Checklist

- No reference filling solution added – Fill the electrode with filling solution up to the fill hole. Refer to the **Electrode Preparation** section for details.
- Incorrect reference filling solution used – Refer to the **Electrode Preparation** section to verify the correct electrode filling solution.
- Electrode junction is dry – Push down on the electrode cap to allow a few drops of filling solution to drain out of the electrode.
- Electrode is clogged or dirty – Refer to the Electrode **Maintenance section** for cleaning instructions.
- Sensing element is dirty or etched – Refer to the **Electrode Maintenance** for cleaning instructions.
- Standards are contaminated or made incorrectly – Prepare fresh standards. Refer to the **Measurement Hints** and **Analytical Techniques** sections.
- ISA not used or incorrect ISA used – ISA must be added to all standards and samples. Refer to the **Required Equipment** section for information on the ISA.
- Samples and standards at different temperatures – Allow solutions to reach the same temperature.
- Air bubble on sensing element – Remove air bubble by reimmersing the electrode in solution.
- Electrode not properly connected to meter/titrator – Unplug and reconnect the electrode to the meter/titrator.
- Meter/Titrator or stir plate not properly grounded – Check the meter/titrator and stir plate for proper grounding.
- Static electricity present – Wipe plastic parts on the meter/titrator with a detergent solution.
- Defective meter/titrator – Check the meter/titrator performance. See the meter/titrator user guide.

7. Ordering Information

Parts	Order No.
Combined Iodide electrode with BNC connector perfectION™ comb I^-:	**51344718**
Combined Iodide electrode with Lemo connector perfectION™ comb I^- Lemo:	**51344818**
Ion Electrolyte D:	**51344753**
Iodide Standard Solution 1000 mg/L:	**51344776**
ISA solid state ISE:	**51344760**
Removable cone:	**00022986**

8. Electrode Specifications

Membrane type

solid state

Concentration Range

5 x 10^{-8} mol/L to 1 mol/L
0.005 mg/L to 127'000 mg/L

pH Range

pH 0 to 12

Temperature Range

0 to 80 °C continuous use

Electrode Resistance

Less than 0.1 MΩ

Reproducibility

± 2%

Minimum Sample Size

5 mL in a 50 mL beaker

Size

Body Diameter: 13 mm
Cap Diameter: 16 mm
Cable Length: 1.2 m

* Specifications are subject to change without notice

www.mt.com
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