



*"When Accuracy Matters"*



Perchlorate Ion Selective Electrode



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## **GENERAL INSTRUCTIONS**

### **Introduction**

The Van London Co. Perchlorate Ion Selective Electrode is used to quickly, simply, accurately, and economically measure perchlorate in aqueous solutions.

### **Required Equipment**

1. An ion meter
2. Perchlorate Ion Sensing Electrode
3. Plastic syringe, pipets, volumetric flasks, 150 ml beakers

### **Required Solutions**

1. Deionized or distilled water for solution preparation.
2. Van London Co. Ionic Strength Adjuster (ISA), Cat# PERIS01.
3. Perchlorate Standard, 1000 ppm  $\text{ClO}_4^-$ , Cat.# PERAS02.  
**NOTE:** Perchloric acid is explosive in contact with reducible substances and is a strong oxidizing agent. Use extreme caution when handling.
4. Perchlorate Electrode Reference Fill Solution, Cat# R001044.

## **GENERAL PREPARATION**

### **Electrode Preparation**

Remove the rubber cap covering the electrode tip and the rubber insert covering the filling hole of the reference electrode. Fill the combination electrode with the filling solution shipped with the electrode to a level just below the fill hole. No preparation is required with a sealed reference electrode. Gently shake the electrode downward in the same manner as a clinical thermometer to remove any air bubbles which may be trapped behind the perchlorate membrane. Connect the electrode to the proper terminals of the meter as recommended by the meter manufacturer. Store the black shipping cap for later use.

### **Electrode Slope Check (for Ion meters which display mV)**

1. To a clean, dry, 150 ml beaker, add 100 ml of distilled water and 2 ml of ISA. After assuring that the meter is in the millivolt mode, lower the electrode tip into the solution. Stir moderately. Remove air bubbles on the clear plastic membrane by re-dipping probe.
2. Using a pipet, add 1 ml of 1000 ppm perchlorate standard into the solution. Stir moderately. After 1 minute, record the mV reading.
3. Using a pipet, add 10 ml of the 1000 ppm perchlorate standard to the beaker. Stir moderately. After 1 minute, record the mV reading.
4. Determine the difference between the two readings. The electrode is operating correctly if a slope difference of  $56 \pm 3$  mV is found, assuming the solution temperature is  $25^\circ\text{C}$ . Slope is defined as the change in mV observed when the concentration changes by a factor of 10.

### **Measurement using an Ion Meter (in the Concentration Mode)**

1. By serial dilution of the 1000 ppm perchlorate standard, prepare two ammonia standards whose concentration is near the expected sample concentration. (e.g. 10 ppm and 100 ppm) For example, to make a 100 ppm standard, pipet 10 ml of the 1000 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. Next to make a 10 ppm standard, pipet 10 ml of the newly-made 100 ppm standard into a 100 ml volumetric flask and dilute to volume with deionized water. A 1 ppm standard is made by further dilution of the 10 ppm standard. Measure out 100 ml of each standard into individual 150 ml beakers.

2. Assure that the meter is in the concentration mode and set for a 2-point calibration.
3. Lower the electrode tip into the least concentrated solution. Begin stirring at a constant rate. Add 2 ml of ISA to the solution and continue stirring.
4. After 1 minute, adjust the meter to the concentration of the more dilute perchlorate standard and fix the value in the memory according to the meter manufacturer's instructions.
5. Rinse the electrode tip with distilled water and blot dry.
6. Lower the electrode tip into the more concentrated solution. Begin stirring at a constant rate. Add 2 ml of ISA to the solution and continue stirring.
7. After 1 minute, adjust the meter to the concentration of the more concentrated perchlorate standard and fix the value in the memory according to the meter manufacturer's instructions.
8. Add 100 ml of the sample and 2 ml of ISA in a 150 ml beaker. Lower the electrode tip into the solution. Begin stirring at a constant rate. Ensure that the meter is in sample mode.
9. After 1 minute, read the concentration directly from the meter display.
10. The electrode should be re-calibrated every 2-3 hours. Simply repeat Steps 2-7 above.

### **Measuring Hints**

As perchlorate electrodes are used or stored for long periods, they will experience some deterioration in performance and slope errors will increase. By using the meter's calibration controls this error can be corrected. If an electrode is able to be calibrated and is stable and responsive, it is still a functional electrode and may be used in service even though it no longer meets "new" electrode specifications.

All samples and standards should be at the same temperature for precise measurement. A difference of 1°C in temperature will result in approximately a 2% error.

Always rinse the electrode with distilled water and blot dry between measurements. Use a clean, dry tissue to prevent cross-contamination.

Constant, but not violent, stirring is necessary for accurate measurement.

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

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

A slow responding electrode may be caused by interferences to the electrode. To restore proper performance, soak the electrode in distilled water for about 5 minutes to clean the membrane, rinse, and soak in standard solution for about 5 minutes.

All samples must be aqueous and not contain organics which can dissolve in the membrane or extract out the liquid ion exchanger.

Interferences should be absent. If they are present, use the procedures found in the **Interferences** section to remove them.

The pH range for the perchlorate ion electrode is 2.5-11. Neutralize samples outside this range with acid or base to bring them in range.

### **ELECTRODE CHARACTERISTICS**

### **Reproducibility**

Electrode measurements reproducible to  $\pm 2\%$  can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuation, drift, and noise limit reproducibility.

### **Interferences**

Certain anions are electrode interferences and will cause electrode malfunction, drift or measurement errors if present in high enough levels. The level of interfering common anions that will cause a 10% error at three levels of perchlorate is given in Table 1.

**TABLE 1: Concentration of Possible Interferences Causing a 10% Error at Various Levels of Perchlorate; Background Ionic Strength of 0.12M (NH<sub>4</sub>)<sub>2</sub>SO<sub>4</sub>.**

Interferences (ppm)	100 ppm	10 ppm	1 ppm
NO <sub>3</sub> <sup>-1</sup>	3.1x10 <sup>3</sup>	3.1x10 <sup>2</sup>	3.1x10 <sup>1</sup>
NO <sub>2</sub> <sup>-1</sup>	2.3x10 <sup>3</sup>	2.3x10 <sup>2</sup>	2.3x10 <sup>1</sup>
Br <sup>-1</sup>	3.2x10 <sup>3</sup>	3.2x10 <sup>2</sup>	3.2x10 <sup>1</sup>
CN <sup>-1</sup>	1.0x10 <sup>3</sup>	1.0x10 <sup>2</sup>	1.2x10 <sup>1</sup>
ClO <sub>3</sub> <sup>-1</sup>	1.7x10 <sup>3</sup>	1.7x10 <sup>2</sup>	1.7x10 <sup>1</sup>
I <sup>-1</sup>	2.5x10 <sup>2</sup>	2.5x10 <sup>1</sup>	2.5

Interferences such as bromide, iodide and cyanide can be removed by precipitation with 0.5 grams of silver sulfate added to 100 ml of sample. Nitrite interference can be removed by adding 0.3 grams of sulfamic acid to 100 ml of sample.

The above interference removal procedures require similar treatment of standards as well as samples.

If the electrode is exposed to high levels of interfering ions which cannot be removed, the electrode reading may drift and the response may become sluggish. Restore performance by soaking in distilled water for 30 minutes followed by soaking in perchlorate standard for 30 minutes.

### **Temperature Influences**

The electrode response will shift and change slope with change in temperature. Standards and samples should be at the same temperature. A 2% error results with a 1°C temperature change for a 10 ppm solution.

The electrode can be used at temperatures from 0° - 40°C. Room temperature measurements are recommended, since measurements at temperatures quite different from room temperature may require equilibrium times up to one hour.

### **Electrode Response**

Plotting the mV potential against the perchlorate concentration results in a straight line with a slope of 56±3 mV between 10 ppm and 100 ppm at 25°C. For perchlorate concentrations above 10 ppm F, the electrode exhibits good time response (95% of total mV reading in 30 seconds or less). Response times are longer below this value.

### **Limits of Detection**

Perchlorate concentration down to 0.7 ppm perchlorate can be measured in neutral solutions. Since sample contamination can be a factor in low level Perchlorate measurements, care must be taken in making determinations below 1.0 ppm. The upper limit of detection in pure sodium Perchlorate solutions is Saturated.

### **pH Effects**

The operating range of the Perchlorate electrode is from pH 2.5 to pH 11.

### **Electrode Life**

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

Since Perchlorate electrodes have a limited shelf life, it is important to have a backup electrode which is in working condition when required.

### **Electrode Storage**

The Perchlorate electrode may be stored for short periods of time in 10 ppm Perchlorate solution. For longer storage (longer than two weeks), rinse and dry the sensing tip and cover the membrane tip with any protective cap shipped with the electrode. The reference portion of the combination electrode (or the outer chamber of the reference electrode) should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole.

## **TROUBLESHOOTING HINTS**

<b><u>Symptom</u></b>	<b><u>Possible Causes</u></b>	<b><u>Next Step</u></b>
Out of Range Reading	defective meter	check meter with shorting strap (see meter instruction manual)
	defective electrode	check electrode operation
	electrodes not plugged in properly	unplug electrodes and reseat
	reference electrode not filled	be sure reference electrode is filled
	air bubble on membrane	remove bubble by re-dipping electrode
Noisy or Unstable Readings (readings continuously or rapidly changing)	electrodes not in solution	put electrodes in solution
	defective meter	check meter with shorting strap
	air bubble on membrane	remove bubble by re-dipping electrode
	defective electrode	replace electrode
	ISA not used	use recommended ISA
	meter or stirrer not grounded	ground meter or stirrer
	electrode exposed to interferences	soak electrode in Perchlorate standard
	outer filling solution level too low	fill electrode to level just below the fill hole

Drift (reading slowly changing one direction)	samples and standards at different temperatures	allow solutions to come to room temperature before measurement
	electrode exposed to interferences	soak electrode in Perchlorate standard
	incorrect reference filling solution	use recommended filling solution
Low Slope or No Slope	standards contaminated or incorrectly made	prepare fresh standards
	ISA not used	use recommended ISA
	standard used as ISA	use ISA
	electrode exposed to interferences	soak electrode in Perchlorate standard
	defective electrode	check electrode operation
	air bubble on membrane	remove bubble by re-dipping probe
Incorrect Answer	incorrect standards	prepare fresh standards
	wrong units used	apply correct conversion factor: $10^{-3}\text{M} = 99.5 \text{ ppm as ClO}_4$
	sample carryover	rinse electrodes thoroughly between samples

### **SPECIFICATIONS**

Concentration Range:	saturated solutions to 0.7 ppm
pH Range:	2.5 to 11
Slope:	$56 \pm 3$ mV between 10 ppm and 100 ppm at 25°C
Temperature Range:	0° to 40°C
Interferences:	No significant interferences
Reproducibility:	$\pm 2\%$
Size:	110 mm length 12 mm diameter 1 m cable length
Storage:	store in dilute perchlorate standard
Samples:	aqueous solutions only no organic solvents

### **ELECTRODE THEORY**

#### **Electrode Operation**

The Perchlorate electrode consists of an electrode body containing a liquid internal filling solution in contact with a gelled organophilic membrane containing a perchlorate ion exchanger. When the membrane is in contact with a solution containing free perchlorate ions, an electrode potential develops across the membrane.

This electrode potential is measured against a constant reference potential, using a standard pH/mV meter or an ion meter. The level of perchlorate ions, corresponding to the measured potential, is described by the Nernst equation:

$$E = E' - S \log X$$

where:  $E$  = measured electrode potential  
 $E'$  = reference potential (a constant)  
 $S$  = electrode slope ( $\approx 56$  mV/decade)  
 $X$  = level of perchlorate ions in solution

The activity,  $X$ , represents the effective concentration of the ions in solution. The total perchlorate ion concentration,  $C_t$ , is the sum of free perchlorate ion,  $C_f$ , and complexed or bound perchlorate ion,  $C_b$ . The electrode is able to respond to only the free ions, whose concentration is :

$$C_f = C_t - C_b$$

Since perchlorate ions form very few stable complexes, the free ion concentration may be equated to the total ion concentration.

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

$$X = \gamma C_f$$

Activity coefficients vary, depending on total ions strength,  $I$ , defined as:

$$I = 1/2 \sum C_x Z_x^2$$

where:  $C_x$  = concentration of ion X  
 $Z_x$  = charge of ion X  
 $\sum$  = sum of all of the types of ions in the solution

In the case of high and constant ionic strength relative to the sensed ion concentration, the activity coefficient,  $\gamma$ , is constant and the activity,  $X$ , is directly proportional to the concentration.