

Chloride

Chloride Ion Selective Electrode Manual

PCE-80-CL1001

Cl⁻





TABLE OF CONTENTS

GENERAL INSTRUCTIONS.....4

 Introduction 4

 Required Equipment 4

 Required Solutions..... 4

GENERAL PREPARATION.....5

 Electrode Preparation 5

MEASUREMENT5

 Measuring Hints 5

 Sample Requirements..... 5

 Units of Measurement 6

ELECTRODE CHARACTERISTICS.....6

 Reproducibility 6

 Interferences..... 6

 Removal of Various Interferences with CISA 7

 Complexation 7

 Temperature Influences..... 8

 Electrode Response..... 9

 Limits of Detection..... 10

 pH Effects 10

 Electrode Life 10

 Electrode Storage..... 11

ELECTRODE THEORY11

 Electrode Operation..... 11

TROUBLESHOOTING HINTS.....13

 Specifications13

 Ordering information 13



CHLORIDE ION SELECTIVE ELECTRODE INSTRUCTION MANUAL

GENERAL INSTRUCTIONS

Introduction

The MANTECH Chloride Ion Selective Electrode is used to accurately measure chloride ions in aqueous solutions.

Required Solutions

1. Deionized or distilled water for solution and standard preparation.
2. Ionic Strength Adjuster, 5M NaNO₃. To prepare this solution from your laboratory stock, half fill a 1000ml volumetric flask with distilled water and add 425 grams of reagent grade sodium nitrate, NaNO₃. Swirl the flask gently to dissolve the solid. Fill the flask to the mark with distilled water, replace cap, and upend several times to mix the solution. ISA is added at the rate of 2ml of ISA to each 100ml of standard or sample to adjust the ionic strength to about 0.1M.
3. Electrode Filling Solution, 1M KNO₃, catalogue number PC-R001015, for the chloride combination glass electrode.
4. Chloride Standard Solution, 0.1M NaCl. To prepare this solution from your own laboratory stock, add 5.84 grams of reagent-grade sodium chloride, NaCl, to a one litre volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid. Fill to the mark with distilled water, cap, and upend the flask several times to mix the solution.
5. Chloride Standard Solution, 1000ppm Cl⁻¹. To prepare this solution from your own laboratory stock, add 1.65 grams of reagent-grade sodium chloride, NaCl, to a one litre volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid. Fill to the mark with distilled water, cap, and upend the flask several times to mix the solution.
6. Chloride Standard Solution, 100ppm Cl⁻¹. To prepare this solution from your own laboratory stock, add 0.165 grams of reagent-grade sodium chloride, NaCl, to a one litre volumetric flask about half full of distilled water. Swirl the flask to dissolve the solid. Fill to the mark with distilled water, cap, and upend the flask several times to mix the solution.

GENERAL PREPERATION

Electrode Preparation

Remove the rubber caps covering the electrode tips 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.

MEASUREMENT

Measuring Hints

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

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

Always rinse the electrodes with distilled water between measurements to prevent cross-contamination.

For samples with high ionic strength, prepare standards whose composition is similar to the sample.

Always check that the membrane is free from air bubbles after immersion into standard or sample.

Sample Requirements

All samples must be aqueous and not contain organics, which can dissolve the cement bonding the sensing crystal to the electrode body. Infrequent measurements in solutions containing methanol, ethanol, benzene, or acetonitrile are permitted. Highly polar solvents slowly attack the electrode. Please check with MANTECH Associates before using the electrode in other organic solvents. The temperature of the standard solution and of the sample solution should be the same and below 50°C.

Interferences should be absent. If they are present, use the procedures found in the Interferences and Electrode Response sections to remove them.

The pH range of the chloride ion electrode is 2-12. Neutralize samples outside this range with acid or base to bring them in range.

Units of Measurement

Chloride concentrations are measured in units of parts per million, equivalents per litre, moles per litre, or any other convenient concentration unit. Table 1 indicates some of the concentration unit conversion factors.

ppm Cl ⁻¹	moles/litre Cl ⁻¹
1.0x10 ⁻²	354.50
1.0x10 ⁻³	35.45
1.0x10 ⁻⁴	3.55

Table 1

ELECTRODE CHARACTERISTICS

Reproducibility

Electrode measurements reproducible to ±2% can be obtained if the electrode is calibrated every hour. Factors such as temperature fluctuations, drift, and noise limit reproducibility. Reproducibility is independent of concentration within the electrode's operating range.

Interferences

A surface layer of silver metal may be formed by strongly reducing solutions. A layer of silver salt may be deposited on the membrane if high levels of ions forming very insoluble salts are present in the sample. Performance may be restored by polishing. See the section Electrode Response for proper polishing techniques. Though measurements can be made in solutions containing oxidizing agents such as MnO₄⁻¹, mercury ions must not be present in the samples.

The maximum allowable ratio of interfering ion to chloride ion is given in table 2. This ratio is expressed as the ratio of the interfering ion molarity to the chloride molarity. Readings will be in error if this ratio is exceeded. Neither accuracy of the measurement nor surface of the electrode membrane will be affected if the ratio is less than that listed in the table.

Interferences	Interfering Ion (M) Chloride
OH ⁻¹ (1)	80
NH ₃ (2)	1.2x10 ⁻¹
S ₂ O ₃ ⁻² (2)	1.0x10 ⁻²
Br ⁻¹ (3)	3.0x10 ⁻³
S ⁻² (4)	1.0x10 ⁻⁶
I ⁻¹ (3)	5.0x10 ⁻⁷
CN ⁻¹ (4)	2.0x10 ⁻⁷

Table 2

- 1) Acidify with 1M HNO₃ to pH 4 to remove hydroxide interference.
- 2) These substances represent complexing species whose maximum level can be exceeded without electrode damage. Value shown represents a 1% error.
- 3) Add CISA to solutions containing mixed halides to remove interferences. See the procedure below.
- 4) Add CISA or a solution of Ni⁺² to remove sulfide or cyanide interferences.

Removal of Various Interferences with CISA

CISA is an oxidizing agent, which will oxidize up to a 100-fold excess of CN⁻¹ over Cl⁻¹, 100ppm NH₃, 100ppm Br⁻¹ or I⁻¹, or 500ppm S⁻². Chloride measurement interferences may be removed by using CISA. The reagents used to prepare CISA are strong oxidizing agents and should be handled in a fume hood.

To prepare CISA, add approximately 800ml of distilled water to a one litre volumetric flask. Add 15.1 grams of NaBrO₃ to the flask and swirl to dissolve the solid. Slowly add 75ml of concentrated nitric acid (70% w/w or 15.9M), mix, and dilute to the mark with distilled water.

To use CISA, mix equal amounts of CISA and sample. Solutions should be allowed to stand for ten minutes before measuring. Since chloride will be oxidized upon prolonged standing, all standards or samples mixed with

CISA should be discarded after measuring. A fresh mixture of CISA and standard should be prepared for each calibration.

Complexation

Total concentration (C_t) whether sulfide or silver ions, consists of free ions (C_f) and complexed or bound ions (C_c) in solution:

$$C_t = C_f + C_c$$

Since the electrode only responds to free ions, any complexing agent in the solution reduces the measured concentration of ions. Chloride ions complex with some metal ions. Table 3 lists the levels of complexing metals causing a 10% error at $1.0 \times 10^{-4} \text{M}$ chloride.

Ion	Concentration
Bi^{+3}	4.0x (80ppm)
Cd^{+2}	2.0x (200ppm)
Mn^{+2}	2.0x (1100ppm)
Pb^{+2}	2.0x (400ppm)
Sn^{+2}	6.0x (700ppm)
Tl^{+3}	4.0x (8ppm)

Table 3

Temperature Influences

Samples and standards should be within $\pm 1^\circ\text{C}$ of each other, since electrode potentials are influenced by changes in temperature. Because the solubility equilibria on which the electrode depends, the absolute potential of the reference electrode changes slowly with temperature. The slope of the electrode, as indicated by the factor "S" in the Nernst equation, also varies with temperature. Table 4 gives values for the "S" factor in the Nernst equation for each ion.

Temp ($\pm\text{C}$)	"S"
0	54.2
10	56.2
20	58.2
25	59.2
30	60.1
40	62.1
50	64.1

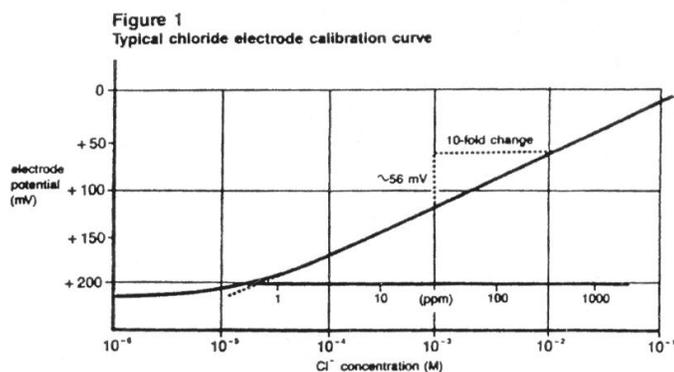
Table 4

If changes in temperature occur, the electrode should be re-calibrated.

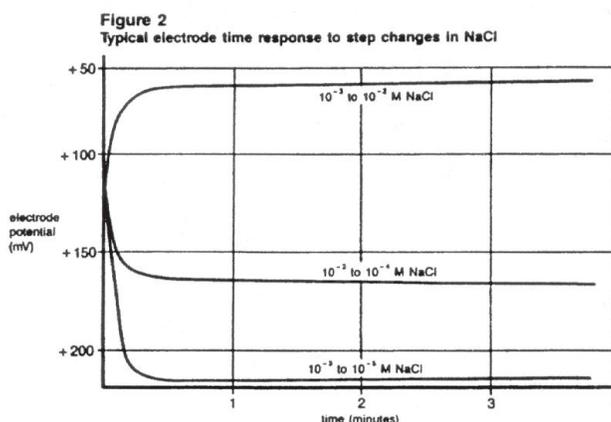
The temperature range for the MANTECH Chloride Ion Electrode is $0^\circ - 80^\circ\text{C}$, provided that temperature equilibrium has occurred. If the temperature varies substantially from room temperature, equilibrium times up to one hour are recommended.

Electrode Response

Plotting the electrode mV potential against the silver concentration on semi-logarithmic paper results in a straight line with a slope of about 56mV per decade as illustrated in Figure 1.



The time needed to reach 99% of the stable electrode potential reading, the electrode response time, varies from several seconds in highly concentrated solutions to several minutes near the detection limit. This is illustrated in Figure 2.



A drifting potential reading or a decrease in electrode slope may mean that the electrode membrane needs polishing. Use the following steps to polish the membrane:

1. If using polishing paper, cut off a ½" piece and place it face up on the lab bench.
2. Put a few drops of distilled or deionized water in the center of the paper.
3. Holding the paper (cotton) steady with one hand, bring the membrane of the electrode down perpendicular to the paper and, with a slight swirling motion, gently



polish the tip of the electrode against the surface of the polishing paper (cotton) for a few seconds.

4. Rinse the electrode surface with distilled or deionized water and soak the electrode tip in standard solution for about five minutes before use.
5. If using jeweler's rouge, place a cotton ball on the lab bench and flatten it using the bottom of a beaker.
6. Put 1-2 drops of distilled or deionized water in the center of the cotton pad.
7. Add a small amount of jeweler's rouge to the damp cotton.
8. Continue with steps 3 and 4 above.

Limits of Detection

The upper limit of detection in pure sodium chloride solutions is 1M. In the presence of other ions, the upper limit of detection is above 1.0×10^{-1} M chloride, but two factors influence this upper limit. Both the possibility of a liquid junction potential developing at the reference electrode and the salt extraction effect influence this upper limit. Some salts may extract into the electrode membrane at high salt concentrations, causing deviation from the theoretical response. Either dilute samples between 1M and 1.0×10^{-1} M or calibrate the electrode at 4 or 5 intermediate points.

The lower limit of detection is influenced by the slight water solubility of the electrode pellet. Refer to Figure 1 for a comparison of the theoretical response to the actual response at low levels of chloride.

pH Effects

Hydroxide ion interferes with measurements of low levels of chloride although the electrode can be used to determine the minimum pH at which low level chloride measurements can be made without more than a 10% error due to hydroxide ion interference.

Electrode Life

The chloride electrode will last 6 months in normal laboratory use. In time, the response time will increase and the calibration slope will decrease to the point where calibration is difficult and electrode replacement is required.

Electrode Storage

The chloride electrode may be stored for short periods of time in $1.0 \times 10^{-2} \text{M}$ chloride solution. For longer storage (longer than 2 weeks), rinse and dry the sensing pellet and cover the membrane tip with the protective cap shipped with the electrode. The reference portion of the combination electrode should be drained of filling solution, if refillable, and the rubber insert placed over the filling hole.

ELECTRODE THEORY

Electrode Operation

The MANTECH Chloride Ion Selective Electrodes are composed of a glass or an epoxy body and a silver chloride/silver sulfide membrane. When the electrode is in contact with a solution containing chloride ions, an electrode potential develops across the membrane. This electrode potential is measured against a constant reference potential. The level of chloride ions, corresponding to the measured potential, is described by the Nernst equation:

$$E = E_0 - S \log X$$

Where E = measured electrode potential

E_0 = reference potential (a constant)

S = electrode slope (-56mV/decade)

X = Level of chloride ions in solution

The activity, X, represents the effective concentration of the ions in the solution. The activity is related to the free ion concentration, C_f , by the activity coefficient, γ , by:

$$X = C_f \gamma$$

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

$$I = \frac{1}{2} \sum C_x Z_x^2$$

Where

C_x = concentration of ion X

Z_x = charge of ion X

I = sum of all types of ions in the solution

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

To adjust the background ionic strength to a high and constant value, ionic strength adjuster (ISA) is added to samples and standards. The recommended ISA for chloride is NaNO_3 . Solutions other than this may be used as ionic strength adjusters as long as ions that they contain do not interfere with the electrode's response to chloride ions. Samples with high ionic strength (greater than 0.1M) do not need ISA added and standards for these solutions should be prepared with a composition similar to the samples.

The reference electrode must also be considered. When two solutions of different composition are brought into contact with one another, liquid junction potentials arise. Millivolt potentials occur from the inter-diffusion of ions in the two solutions. Electrode charge will be carried unequally across the solution boundary resulting in a potential difference between the two solutions, since ions diffuse at different rates. When making measurements, it is important to remember that this potential be the same when the reference is in the standardizing solution as well as in the sample solution or the change in liquid junction potential will appear as an error in the measured electrode potential.

The composition of the liquid junction filling solution in the reference electrode is most important. The speed with which the positive and negative ions in the filling solution diffuse into the sample should be equitransferent. No junction potential can result if the rate at which positive and negative charge carried into the sample is equal.

Strongly acidic (pH=0-2) and strongly basic (pH=12-14) solutions are particularly troublesome to measure. The high mobility of hydrogen and hydroxide ions in samples make it impossible to mask their effect on the junction potential with any concentration of an equitransferent salt. One must either calibrate the electrode in the same pH range as the sample or use a known increment method for ion measurement.

Troubleshooting Hints

Symptom	Possible Cause	Next Step
Out of Range Reading	Defective Electrode	Check electrode operation
	Electrode not plugged in properly	Unplug and reconnect electrode
	Reference not filled	Refill reference
Noisy or unstable readings	Air bubble on membrane	Remove bubble by re-dipping electrode
	Defective electrode	Replace electrode
	Electrode exposed to interferences	Soak electrode in chloride standard
	ISA not used	Use ISA
Drift	Samples and standards at different	Allows solutions to come to room
	Electrode exposed to interferences	Soak electrode in calcium standard
	Incorrect reference filling solution	Use recommended
Low slope or no slope	Standards contaminated or incorrectly	Make fresh standards
	ISA not used	Use ISA
	Electrode exposed to complexing agents	Check section on complexation
	Air bubble on membrane	Remove bubble by re-dipping electrode
Incorrect Answers	Incorrect standards	Prepare fresh standards
	Complexing agents in sample	Check section on complexation

Specifications

Concentration Range: 1M to 5.0x10⁻⁵M (35,500 to 1.8ppm) pH range: 2 to 12

Temperature Range: 0±- 80±C Resistance: <1Mohm Reproducibility: ±2%

Size: 110mm length, 12mm diameter Storage: Store in chloride solution

Ordering Information

Part Number	Description
PCE-80-CL1001	Chloride Ion Electrode, combination, glass body
PCE-948201	Polishing paper for electrodes
PCE-948201	Polishing paper for electrodes
PCE-R001015	Electrode filling solution, 1M KN03/0



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