



## Parameter and Sample Type

Total Residual Chlorine in Wastewater by ISE

## Introduction

Total chlorine residual in wastewater is measured directly by the Orion 9770BNWP Chlorine ion-selective electrode regardless of color or turbidity. The Orion method is EPA-approved test procedure for total chlorine reporting in wastewater<sup>1</sup>. Concentrations from 0.05 to 20 mg/L may be analyzed. Samples above 20 mg/L should be diluted before measurement.

## Reference

1. Federal Register, March 12, 2007; 72 (47:11218).
2. Standard Methods for the Examination of Water and Wastewater, 20th edition, 1998; Part 4500-Cl I. Iodometric Electrode Technique for Chlorine Residual.

## Recommended Equipment

Orion Star Plus portable or benchtop meter (Orion 1219000 or 1119000, or 1215000, or 1115000); Residual Chlorine Solid State Combination Electrode (Orion 9770BNWP). Optional: printer (Orion 1010006); RS232 computer interface cable (1010053); Star Navigator Software (Orion 1010007); timer; 50µL syringe; automatic or glass pipettes; 100 -mL volumetric flasks; 50 -mL beakers.

## Required Solutions

Residual Chlorine Standard (Potassium iodate) 100 ppm Cl<sub>2</sub> (Orion 977007); Acid reagent for chlorine ISE (Orion 977011); Iodide reagent for chlorine ISE (Orion 977010); chlorine-free, chlorine demand free deionized water (DI). Optional: Chlorine water (user prepared); pH electrode cleaning solution B (Orion 900022).

## Solutions Preparation

- 1) Prepare daily 0.05, 0.2, 1.0, 5.0 mg/L calibration standards and a reagent blank: pipette into four volumetric flasks 0.05, 0.2, 1.00, and 5.00 mL of the Residual Chlorine Standard (Orion 977007); Add to each flask and fifth flask to be used as a reagent blank, 1 mL of each the Acid and Iodide Reagents. Stopper and mix thoroughly, let stand for 2 minutes to allow for complete reaction, then dilute with DI water up to the mark.
- 2) Chlorine water (approximately 100 mg/L as chlorine): dilute 0.4 mL of the Orion 900022 or 1 mL of a 5% hypochlorite solution (such as household bleach) to 500 mL with DI water.

## Meter Setup

Connect the electrode to the meter. Set measurement mode to ISE. In Setup mode, set read type to continuous, log delete to no (to allow overwrite the oldest data points), log auto to on, and set the following ISE settings: resolution to 3, units to mg/L, range to high, and auto blank to off. If all steps were followed

correctly, the meter display will show three digits in the top line and "ISE: mg/L" to the right of the top line.

## Electrode Setup

See the electrode manual for preparation of the electrode.

## Electrode Performance Check

Check slope at least daily according to the procedure described in the electrode manual; use the Orion 977007 Residual Chlorine Standard or chlorine water.

Drift may be checked by comparing a 1 minute to a 2 minute reading. Results should agree with desired criteria. See troubleshooting section of manual if slope or drift problems.

## Electrode Storage, Soaking, and Rinsing

For storage longer than one week, rinse the electrode with DI water and store the electrode dry with the protective shipping cap covering the sensing element. For short-term storage, store the electrode dry. Before the calibration, soak the electrode in a fresh aliquot of the reagent blank for 15 minutes.

## Sample Preservation

None required. Samples must be analyzed within 15 minutes after sampling.

## Sample Preparation

Pipette 1 mL acid reagent and 1 mL iodide reagent into volumetric flask. Add sample up to the mark. Stopper and mix thoroughly, let stand for 2 minutes to allow for complete reaction. Transfer about 35-40 mL of the prepared sample into the beaker.

## Calibration

After soaking electrode for 15 min. in an aliquot of a reagent blank, perform four point calibration using 0.05, 0.2, 1.0, and 5.0 mg/L standards. Do not stir during calibration. After the calibration, the electrode slope will be displayed and should be between 25 – 30 mV/decade. Analyze a mid-range standard to verify the calibration. If reading is not acceptable, see troubleshooting section of the electrode user guide.

## Analysis

Place electrode in the prepared sample, set timer, and wait 2 minutes. If the reading is not stable after 2 min, wait until a stable reading is achieved and the "ISE:mg/L" icon has stopped flashing. Press "MEASURE" key to print and log the result. Do not stir during measurement.

Note: for improved accuracy, condition electrode in a portion of the reagent blank for 5 min. prior to testing any low concentration (<0.2 mg/L) sample, standard, or reagent blank when switching from high to low level concentrations.

## Quality Control (QC)

Recommended QC procedures include: calibration and calibration verification, reagent blank analysis, sample duplicates, QC sample and/or matrix spikes.



**Results:** Total residual chlorine tests in two wastewater samples (chlorine contact and dechlorination tanks) and a commercially available performance evaluation (PE) sample with comparison of the Orion Chlorine ISE and Orion colorimetric analysis of samples by DPD:

Sample	Criteria	Chlorine Electrode Orion 9770BNWP		Orion DPD
		ISE #1	ISE #2	Avg
0.05 mg/L	78 - 116% R (1)	114.4%	105.8%	
0.1 mg/L	78 - 116% R	115.9%	110.6%	
0.2 mg/L	78 - 116% R	105.3%	105.3%	
1.0 mg/L	78 - 116% R	105.8%	102.5%	
5.0 mg/L	78 - 116% R	101.4%	93.1%	
Blank	<0.05 mg/L	0.017	0.017	
WW dechlor		0.00	0.00	0.01
Duplicate		0.00	0.00	0.00
0.1 mg/L matrix spike to WW dechlor.	76 - 118% R	0.00 (2)	0.00	
WW chlorinated	mg/L	1.50	1.48	1.60
Duplicate	mg/L	1.42	1.42	
Duplicate	21.0%	5.5%	4.1%	
1.2 mg/L spike to WW	76 - 118% R	85.8%	84.5%	
1.2 mg/L duplicate spike to WW	76 - 118% R	84.5%	81.3%	
PE	1.44-1.95 mg/L	1.62	1.56	1.85
PE duplicate	1.44-1.95 mg/L	1.67	1.55	1.80
PE duplicate	21.0%	3.2%	-0.5%	
1.5 mg/L spike to PE	76 - 118% R	97.7%	81.4%	

Notes: (1) - from EPA ATP QC acceptance criteria

(2) - Percent recovery for the matrix spike in the dechlorinated sample is zero due to presence of an overdose of sulfite - the reducing reagent used for the dechlorination. The sulfite exerts a chlorine demand that consumes the spike.

Results in blue meet performance criteria

