Method # (D99-003): Free Chlorine Species ($HOCl^-$ and OCl^-) by Test Strip

Industrial Test Systems, Inc.
1875 Langston St.
Rock Hill, SC 29730
(803) 329-9712

Revision 3.0
November 21, 2003

Acknowledgments:

Inventors:	Ivars Jaunakais, Vasili Ramuna , Kami Yamuna
Researchers:	Corlyss Lewis, Christie Lofton, Brenda Taylor, Howard Ray
Author:	Howard Ray

Table of Contents

Introduction

This test strip method is designed as a screening test for free chlorine in a drinking water matrix. The analytes measured by this method are known as "free chlorine' and include hypochlorous acid (HOCl), hypochlorite ion (OCl-), and un-disassociated chlorine (Cl_2). Chloramines at levels typically found in drinking water do not have an impact on the method. The patented method (#5491094) typically requires less than one minute per test

To perform the method the operator dips one test strip in a 50 ml sample for 20 seconds. The strip is removed, and after a 20 second wait, is compared to a calibrated color chart.

Technical questions concerning the method, materials for the method, and additional copies of the method are available from:

Industrial Test Systems, Inc.
1875 Langston St.
Rock Hill, SC 29730
(803) 329-9712

Method # (D99-003)
Free Chlorine Species ($HOCl^-$ and OCl^-) by Test Strip

1.0 Scope and Application

1.1 This procedure detects free available chlorine in drinking water.

1.2 This method is based on the reaction of 3,3', 5,5' tetramethylbenzidine with hypochlorous acid, hypochlorite ion, and un-disassociated chlorine (CAS# [77782-50-5]).

1.3 The method is acceptable for use in potable water.

1.4 This method is not for use with preserved samples. Samples should be analyzed immediately.

1.5 The detection limit is 0.10mg/L (or ppm) as determined in drinking water. The method applies to the range of regulatory importance of 0.20ppm to 2.0ppm free available chlorine.

1.6 Each laboratory that uses this method must demonstrate the ability to generate acceptable results using the procedure in Section 9.0. Each analyst must be able to accurately differentiate the color variation represented on the color chart supplied with the test strips.

2.0 Summary of Method

2.1 A test strip is configured with a pad attached to a plastic holder. The pad is attached across an aperture (window) cut into the strip at the end opposite the handle. The end with the aperture is placed in a 50 ml sample, with gentle motion, for 20 seconds. The test strip is removed. After a waiting period of 20 seconds, the color of the strip is compared to colors on a calibrated chart.

2.2 This is a colorimetric method. Color is generated by the reaction of 3,3', 5,5' tetramethylbenzidine (TMB) with the free available chlorine species. The amount of color on the strip is directly proportional to the amount of free available chlorine in the sample.

3.0 Definitions

3.1 The definitions and purposes below are specific to this method, but have been conformed to common usage as much as possible.

3.2 aperture - An oval opening or window in one end of the test strip. The reactive pad is attached to this opening

3.3 MSDS - Material Safety Data Sheet

3.4 ppm - Concentration of analyte in milligrams per Liter (mg/L.)

3.5 reactive pad - Material attached to the test strip at aperture end that contains reagents needed to complete the test.

3.6 Reagent blank – Distilled or deionized water used as a zero standard.

3.7 stroke - Movement of the test strip in the sample such that the strip travels approximately one to two inches in one direction.

3.8 test strip – An ITS test device comprising a reactive pad attached to a plastic holder.

3.9 TMB - 3,3', 5,5' tetramethylbenzidine indicator.

4.0 Interferences

4.1 Small amounts of free available chlorine from previous determinations may cause inaccurate results. Use a clean container or rinse the sample container several times with the sample to be tested prior to running the method.

4.2 Other oxidizers such as permanganate, bromine, or iodine may cause positive interference with the method.

4.3 Chloramines up to 15ppm show no interference.

5.0 Safety

5.1 The test strip releases minute quantities of chemicals during use and is therefore classified as an article under OSHA 29CFR 1910.1200 (d). It is considered non-hazardous and no MSDS is required.

5.2 Do not ingest the test strip. Wash hands thoroughly upon completion of the method.

5.3 The toxicity of carcinogenicity of each analyte or reagent has not been precisely determined; however, each chemical should be treated as a potential health hazard. Exposure to these chemicals should be reduced to the lowest possible level.

5.4 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe work environment and a current awareness file of OSHA regulations regarding the safe handling of the chemicals specified in this method. A reference file of material safety data sheets (MSDSs) should be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in Reference Sections 16.1 and 16.2.

6.0 Equipment and Supplies

6.1 Free chlorine test strip and calibrated color chart (Industrial Test Systems, Inc.)

6.2 50-ml or 100-ml beaker

6.3 Thermometer

6.4 Laboratory timer or watch with second hand

6.5 Equipment for the laboratory reference method will be required for initial demonstration of performance (See Section 9.0). This equipment will vary depending upon the method in use.

7.0 Reagents and Standards

7.1 All reagents required for the method are included in the reaction pad of the test strip.

7.2 Reagents for the laboratory reference method will be required for initial demonstration of performance (See Section 9.0). These reagents will vary depending upon the method in use.

8.0 Sample Collection Preservation and Storage

8.1 Use glassware free of contamination with ammonia or ammonia compounds that can combine with free available chlorine to produce chloramines. Rinse the container several times with the sample to be tested prior to running the method.

8.2 If using tap water draw the water from the cold-water tap only. Allow the water to run 30 seconds prior to collection.

8.3 Do not use preserved samples.

8.4 For compliance monitoring, start chlorine determinations immediately after sampling, avoiding excessive light and agitation. Do not store samples to be analyzed for chlorine.

9.0 Quality Control

9.1 Each laboratory that uses this method is required to operate a formal quality assurance program. The minimum requirements of this program consist of an initial demonstration of laboratory capability, and ongoing analyses of standards and blanks as a test of continued performance. Laboratory performance is compared to established performance criteria to determine if the results of analyses meet the performance characteristics of the method.

9.1.1 The analyst shall make an initial demonstration of the ability to generate acceptable accuracy and precision with this method. This ability is established as described in Section 9.2

Note: *The calibration (color chart) is specific for this method. Changes to the method will negate the method calibration.*

9.1.2 Initial demonstration of performance will require an analysis of reagent blanks and a comparison of the test strip method to another reference method as found in 141.74(a)(2).

9.2 The initial demonstration of laboratory capability will consist of the following:

9.2.1 Analysis of blanks - Known blanks will be run in triplicate by the test strip method.

9.2.2 Calibration verification/precision - Free chlorine standards in a reagent water matrix will be prepared at 0.2ppm, 0.8ppm, and 2.0ppm and verified by the reference method. The samples will then be measured by the test strip method in triplicate. Acceptable results are within one color block of the accepted value, with a standard deviation within 1 color block. (Data shows a standard deviation of $\leq$ 0.073 mg/L is possible.)

9.3 A daily quality control check is to be performed. The concentration of the standard used should reflect the concentration range of the samples normally analyzed by the user.

9.4 At least one duplicate analysis should be included on a daily basis.

10.0 Calibration and Standardization

10.1 Calibration is fixed and provided in the form of a color chart. No calibration or standardization is required prior to running the method.

11.0 Procedure

11.1 Choose a 50ml or 100ml container and rinse well with the sample to be tested. Collect 50mls of the sample.

11.2 Measure the temperature of the sample to within $\pm$ 2^{o}C ($\pm$ 4^{o}F). Refer to the temperature compensation chart (Table 1) for the optimum dip time.

11.3 Remove one test strip from its packaging. Reseal immediately if it is multi-use packaging. Do not handle the strip by the end with the test pad.

11.4 Dip the test strip in the sample. Move the test strip with a gentle back and forth motion for the appropriate dip time determined in step 11.2. The motion is optimal when one forward and one backward stroke of 1 to 2 inches is completed each second (2 strokes per second). A brown color may form in the sample. This is normal.

11.5 Remove the strip and shake it once, briskly, to remove excess sample that may be clinging to the test strip.

11.6 Hold the strip with the aperture facing up and wait 20 seconds.

11.7 Fold the strip in half on an axis perpendicular to the strip so that the end of the handle provides a consistent viewing background for the aperture (Figure1). View the color through the aperture and compare it to the color chart provided to determine parts per million of free chlorine. Complete matching within one (1) minute.

Note: *It is critical that the procedure be followed as written. Maximum accuracy and precision is obtained with accurate sample volumes and attention to stroke speed.*

11.8 For best results:

11.8.1 Match the colors in a well-lighted area under incandescent, fluorescent, or natural light. Do not match colors in strong, direct light.

11.8.2 Do not touch the reactive pad. Materials on the hands may contaminate the pad and affect results.

11.8.3 Remove the strip from its packaging just prior to use and immediately re-seal the container. If the strip is exposed for more than five minutes prior to use obtain another strip.

11.8.4 Store the strips at room temperature and keep away from excessive humidity.

11.8.5 The sample pH should be between 6.5 and 8.

12.0 Data Analysis and Calculations

12.1 Results are read directly from the color chart and are reported as ppm free chlorine.

12.2 If results fall between color blocks on the color chart it is expected that the user will estimate the concentration between the blocks.

13.0 Method Performance

13.1 This method was validated as required for Tier 2 screening methods in the USEPA document "*Guidelines and Format of Methods to be Proposed at 40 CFR part 136 or part 141"*.

13.2 With multiple operators the method precision at 0.2ppm demonstrates a standard deviation ranging from 0 to 0.04ppm.

13.3 The stated method detection limit is 0.1ppm, although some operators report detection down to 0.025ppm.

14.0 Pollution Prevention

14.1 This method is non-hazardous. Used test strips and packaging may be discarded in the regular trash.

14.2 Tested sample may be discarded down a drain.

15.0 Waste Management

15.1 The test strips are considered non-hazardous and may be disposed of in regular trash. The tested sample may be discarded down a drain.

16.0 References

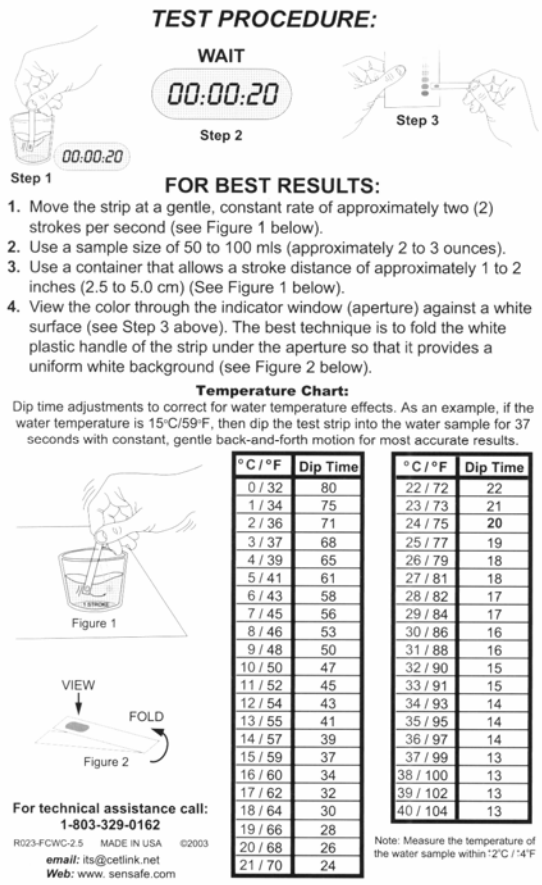
16.1 "OSHA Safety and Health Standards, General Industry," (29CFR Part 1910) with amendments as of Feb 3, 1997. Occupational Safety and Health Administration (CCH, Inc., Chicago, USA, 1997).

16.2 Mercer, Paul, Laboratory Safety Pocket Handbook. (Genium Publishing Corp., Schenectady, NY, USA, 1996).

16.3 Vasili V. Ramana; Kami R. Yamuna; Ivars Jauankais, "Test Strip for Free Chlorine Analysis," Patent # 5,491,094, February 13, 1996.

17.0 Tables, Diagrams, Flowcharts, and Validation Data

17.1 Table 1, Temperature Compensation Chart (particular layout may vary).



TEST PROCEDURE:

WAIT

00:00:20

Step 1 Step 2 Step 3

FOR BEST RESULTS:

1. Move the strip at a gentle, constant rate of approximately two (2) strokes per second (see Figure 1 below).
2. Use a sample size of 50 to 100 mls (approximately 2 to 3 ounces).
3. Use a container that allows a stroke distance of approximately 1 to 2 inches (2.5 to 5.0 cm) (See Figure 1 below).
4. View the color through the indicator window (aperture) against a white surface (see Step 3 above). The best technique is to fold the white plastic handle of the strip under the aperture so that it provides a uniform white background (see Figure 2 below).

Temperature Chart:

Dip time adjustments to correct for water temperature effects. As an example, if the water temperature is 15°C/59°F, then dip the test strip into the water sample for 37 seconds with constant, gentle back-and-forth motion for most accurate results.

Figure 1

VIEW FOLD

Figure 2

°C / °F	Dip Time
0 / 32	80
1 / 34	75
2 / 36	71
3 / 37	68
4 / 39	65
5 / 41	61
6 / 43	58
7 / 45	56
8 / 46	53
9 / 48	50
10 / 50	47
11 / 52	45
12 / 54	43
13 / 55	41
14 / 57	39
15 / 59	37
16 / 60	34
17 / 62	32
18 / 64	30
19 / 66	28
20 / 68	26
21 / 70	24

°C / °F	Dip Time
22 / 72	22
23 / 73	21
24 / 75	**20**
25 / 77	19
26 / 79	18
27 / 81	18
28 / 82	17
29 / 84	17
30 / 86	16
31 / 88	16
32 / 90	15
33 / 91	15
34 / 93	14
35 / 95	14
36 / 97	14
37 / 99	13
38 / 100	13
39 / 102	13
40 / 104	13

Note: Measure the temperature of the water sample within ±2°C / ±4°F

For technical assistance call:
1-803-329-0162

R023-FCWC-2.5 MADE IN USA ©2003

email: its@cetlink.net
Web: www. sensafe.com

17.2 Figure 1, Calibrated Color Chart (particular layout may vary).