Measurement of free and total chlorine in drinking water by Palintest ChloroSense

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This method was prepared by Stephen W Birch of Palintest Ltd.

The method was developed by S. W. Birch, J. Sutherland and T. Lendrem of Palintest Ltd.

Disclaimer

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Introduction

The electrochemical sensor method was developed by Palintest Ltd to provide a simple, rapid, reagent free analysis of drinking water for free and total chlorine, removing almost all sources of technique dependence.

This method is applicable to the determination of free and total chlorine including hypochlorous acid, hypochlorite ion, and undissociated chlorine. Water samples are analyzed by amperometry using pre-calibrated disposable sensors. There is no requirement for the addition of reagents to the sample.

Copies of the method can be obtained from, or questions concerning this method or its application should be addressed to:

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Method

Measurement of free and total chlorine in drinking water by Palintest ChloroSense

1.0 Scope and Application

This method is for the determination of free available and total chlorine including hypochlorous acid, hypochlorite ion and undissociated chlorine in drinking water.

1.1 The method detection limit (MDL) was determined to be 0.04 free and 0.05 total mg/L Cl/L, respectively. This was calculated from analysis of seven aliquots of chlorine free water fortified to 0.1mg Cl/L. The minimum level (ML) has been determined to be 0.1 and 0.2 mg Cl/L, respectively. The application range is 0.02 - 10 mg Cl/L free chlorine and 0.05 – 75 mg/L Cl/L total chlorine.

1.2 The laboratory is not allowed to omit any quality control analyses. Each operator that uses this method must demonstrate the ability to generate acceptable results using the IDC in Section 9.2.

2.0 Summary of Method

2.1 Chlorine may be present as free residual chlorine and as combined chlorine. The two forms may co-exist and can be determined together as total available chlorine. Free chlorine is present in the sample as hypochlorous acid, hypochlorite ion and undissociated chlorine. Combined chlorine may be present as monochloramine, dichloramine and nitrogen trichloride. Free available chlorine reacts with 3,3',5,5' tetramethylbenzidine (TMB) and the oxidized TMB is electrochemically reduced at the surface of the free chlorine electrode. Free available chlorine and combined chlorine react with potassium iodide (KI) to liberate iodine. The iodine can be reduced electrochemically at the surface of the total chlorine electrode. The current that flows in each case is proportional to the amount of free available chlorine or total available chlorine. The current is converted to mg Cl/L by reference to calibration parameters stored in the instrument software. The appropriate calibration parameters are transferred from a calibration chip that is provided with each batch of sensors. Quality is assured through calibration and verification with externally referenced standard solutions.

2.2 The test container is filled with a sample of water, approximately 100mL. No sample pre-treatment is required. A disposable sensor is inserted in to the instrument and the lid is closed to begin the test. After completion of the test, the values for free and total chlorine are read from the instrument display. The manufacturer's instructions should be followed regarding the use and care of the instrument.

3.0 Definitions

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

3.1 Calibration Check Standard (CC): An aqueous calibration standard containing the method analyte that is analyzed periodically to verify the accuracy of the existing calibration.

3.2 Initial demonstration of capability (IDC): Replicate reference samples are analyzed to demonstrate the ability to obtain acceptable precision and accuracy. An IDC is performed the first time this method is used by each operator.

3.3 Laboratory reagent blank (LRB): An aliquot of reagent water or other blank matrix that is treated as a sample including exposure to all glassware, equipment, solvents, and reagents that are used with other samples. The LRB is used to determine if method analytes or other interferences are present in the laboratory environment, the reagents or the apparatus.

3.4 Linear calibration range (LCR): The concentration range over which the instrument response is linear.

3.5 Material safety data sheet (MSDS): Written information provided for the chemical reagents concerning a chemical's toxicity health hazards, physical properties, fire, and reactivity data including storage, spill and handling precautions.

3.6 Minimum Reporting Level (MRL): The lowest level at which the entire analytical system gives a reproducible signal that meets the method quality objectives. It is never lower than the concentration of the lowest calibration check (CC) standard.

3.7 Quality control sample (QCS): A solution of method analyte of known concentration. The QCS is obtained from a source external to the laboratory or is prepared from standards obtained from a different source than the calibration standards. The purpose is to check laboratory performance using test materials that have been prepared independently from the normal calibration process.

3.8 Reagent water Water demonstrated to be free from the method analyte and interfering substances.

4.0 Interferences

4.1 Other disinfectant residuals such as bromine, chlorine dioxide, iodine, ozone and peroxide may react with TMB and KI or directly with the electrode surface and cause a positive interference.

4.2 No interferences have been encountered with the chemical species found naturally in drinking water or added as treatment chemicals. The method is without interference for the determination of 0.02 to 10 mg/L free chlorine in

the presence of: 0.5 mg/L aluminium, 5 mg/L zinc, 10 mg/l sodium tripoly-phosphate, 800 mg/L chloride, 4 mg/L fluoride, 4 mg/L phosphate, 500 mg/L sulfate, 300 mg/L $CaCO_3$ alkalinity, 350 mg/L calcium hardness, 300 mg/L magnesium hardness, 1000mg/L total dissolved solids

5.0 Safety

5.1 Use good laboratory practice throughout the test procedure. Follow the test instructions carefully.

5.2 When working with chlorine standards, it is appropriate to use a fume hood.

5.3 This method does not address all safety issues associated with its use. The laboratory is responsible for maintaining a safe working environment and a current awareness file of OSHA regulations regarding the safe handling of the chemical specified in this method. A reference file of material safety data sheets (MSDS) should be available to all personnel involved in these analyses. Additional information on laboratory safety can be found in References 16.1 to 16.3.

NOTE: Do not allow a water sample to remain in the instrument following analysis.

6.0 Equipment and Supplies

Note: *Brand names, suppliers and part numbers are for illustrative purposes only. No endorsement is implied.*

6.1 Sampling equipment:

6.1.1 Sample collection bottles-amber glass.

6.1.2 Palintest ChloroSense™ potentiostat dedicated to the analysis of free and total chlorine in drinking water.

6.1.3 Laboratory glassware and plasticware required includes sample containers, volumetric flasks, pipettes, sample storage vials, conical beakers (250-mL).

7.0 Reagents and Standards

7.1 DISPOSABLE SENSORS - Palintest Chlorosense sensors (catalogue number CS 110 or CS 150) are for the determination of free chlorine and total chlorine in drinking water. Disposable sensors have a shelf life of 24 months.

7.2 REAGENT WATER – Purified water (typically either deionized or distilled) is usually acceptable. Reagent water can be purchased from a scientific supply company, if it is not available on site. If a chlorine demand is present, suggested procedures for preparing chlorine demand-free water are included in ASTM D 1253-03 (16.4) and Standard Method 4500-Cl C (16.5).

7.3 CALIBRATION STANDARD SOLUTIONS – A concentrated stock standard solution can be purchased from a commercial source (e.g., Environmental Resource Associates, Catalog # 696; Hach, Product # 1426820, or equivalent). A purchased stock standard must be NIST traceable or certified in an equivalent manner. The stock standard must be stored according to the manufacturer's recommendations and only used within the manufacturer's designated lifespan (pre-expiration date). The stock solution is diluted using reagent water to obtain calibration standard solutions in the range of 0.2 mg/L to 4.0 mg/L. Calibration standards should be prepared fresh for each use. An example calculation is provided below:

$$\frac{(\text{mL Standard})}{(\text{mL Standard} + \text{mL Reagent water})} \times \text{standard Concentration (mg/L)} = \text{Final Concentration}$$

$$\frac{1\text{mL}}{(1\text{mL} + 100\text{mL})} \times 55.0\text{mg/L} = 0.54\text{mg/L}$$

7.4 CONTINUING CALIBRATION CHECK STANDARD - Calibration standards prepared above may also be used as calibration check standards. Calibration check standards must be freshly prepared.

7.5 QUALITY CONTROL SAMPLE – Purchase a chlorine standard solution that is NIST traceable or certified in an equivalent manner from a different source than the source of the calibration standards. Calibration standards and the independent reference samples that are purchased from the same supplier must be from different lots. The independent reference sample must be stored according to the manufacturer's recommendations and only used within the manufacturer's designated lifespan (pre-expiration date).

8.0 Sample Collection, Preservation and Storage

8.1 Collect samples in chlorine-demand free amber glass containers, filling the container headspace free. Avoid exposure to sunlight or agitation during sampling. Analyze immediately after sample collection, as chlorine in aqueous solution is not stable. A sample may be collected directly in the instrument sample container.

9.0 Quality Control

9.1 Quality Control (QC) requirements include the Initial Demonstration of Capability and ongoing QC requirements that must be met when preparing and analyzing field samples. This section describes each QC parameter, its required frequency, and the performance criteria that must be met in order to meet EPA quality objectives. These QC requirements are considered the minimum acceptable QC criteria. Laboratories are encouraged to institute additional QC practices to meet their specific needs.

9.2 INITIAL DEMONSTRATION OF CAPABILITY (IDC) – The IDC must be successfully performed prior to analyzing any field samples. Prior to conducting the IDC, the analyst must meet the calibration requirements outlined in Section 10. Requirements for the initial demonstration of laboratory capability are described in the following sections.

9.2.1 DEMONSTRATION OF LOW SYSTEM BACKGROUND – Analyze a LRB after processing through all sample collection steps outlined in Section 8.1. The method blank concentration must be ≤ ⅓ the MRL.

9.2.2 INITIAL DEMONSTRATION OF ACCURACY – Prepare and analyze five independent reference samples at the same concentration. The concentration of the samples should be at or below the mid range of the calibration curve. Calculate the average chlorine concentration for the five analyses. The average concentration for the five replicates must be within ± 15% of the expected value.

9.2.3 INITIAL DEMONSTRATION OF PRECISION – Using the same set of replicate data generated for Section 9.2.2 calculate the standard deviation and relative standard deviation (*RSD*) of the replicate values. The *RSD* is calculated using the equation

$$RSD = \frac{S}{\overline{X}} \times 100\%$$

where

S is the standard deviation for the replicate values,

and $\overline{X}$ is the average value for the replicates.

The RSD of the results of the replicate analyses must be ≤15%.

9.3 ONGOING QC REQUIREMENTS – This section describes the ongoing QC criteria that must be followed when processing and analyzing field samples.

9.3.1 DEMONSTRATION OF LOW SYSTEM BACKGROUND – Analyze a LRB with each analytical batch. The LRB should be processed through all sample collection steps outlined in Section 8.1. The method blank concentration must be ≤ ⅓ the MRL.

9.3.2 CONTINUING CALIBRATION CHECK – Analyze a CCC with each analytical batch. Prepare an aqueous calibration check standard at a concentration near the expected concentration of the water samples. Over time, vary the calibration check standard concentration. The grab sample measured concentration of the calibration check standard must be within ± 15% of the expected value. If this criterion is not met, then the analyst must identify and resolve the problem.

9.4 Laboratories/water systems are encouraged to institute additional QC practices to meet their specific needs. The remainder of this section describes various optional QC procedures that may be incorporated into a QC program.

9.4.1 QUALITY CONTROL SAMPLE (QCS) – Analysis of a sample from an external source (different from the calibration standards) provides an independent check of the calibration of the method. It is recommended semiannually or any time a new calibration curve is validated.

9.4.2 PROFICIENCY TESTING (PT) or PERFORMANCE EVALUATION (PE) SAMPLE – Successful participation in a PT or PE Study is a good QC tool for demonstrating proficiency with the grab sample method. A certified solution of chlorine whose concentration is unknown to the analyst can be purchased by the laboratory/water system. An aliquot of the certified solution is added to a known volume of reagent water and analyzed as a grab sample. The

analytical results are reported to the PT/PE Study Provider where they are compared to data from all analyses of the sample. Acceptance criteria are established by the provider for each study.

10.0 Calibration and Standardization

10.1 Verify the initial calibration curve. This must be done for each meter according to the procedure described below. This must also be performed when a new calibration code or lot of disposable sensors is put into service.

10.1.1 Prepare a set of at least three aqueous calibration check standards. The lowest concentration calibration standard must be at or below 0.2 mg/L. The standards must span the concentration range that is expected to be observed in the grab samples.

10.1.2 Analyze the calibration standards according to the grab sample procedure. (Note: If the highest concentration standard is above the maximum concentration specified for the meter, dilute and analyze it according to manufacturer's instructions. Use the data from this analysis to check the accuracy of the dilution process, not the calibration curve.)

10.1.3 To verify the factory set calibration curve, compare the measured concentration of each standard to the expected value. Each calibration point must calculate to be within ± 15% of its expected value. If the internal curve does not meet these criteria, the internal curve must be updated by following the manufacturers' instructions for generating or inputting a curve. Otherwise, send the meter to the manufacturer for repair/updating.

11.0 PROCEDURE

11.1 Press and hold the power button until the title screen is displayed.

11.2 When the instrument passes all internal functional checks on start up, the screen displays the current batch code and prompts the user to insert a sensor. If start up fails, an error message is displayed.

11.3 Ensure the calibration code shown on screen matches with the number on the foil of the batch of sensors in use. If it does not, enter the correct code (11.3.1)

11.3.1 Slide the front catch to the right and open the instrument case fully. . Press the blue lever to open the jaw and insert the contacts of the **calibration chip** fully into the slot revealed. Release the blue lever.
Close the instrument lid and view the display. Check the new code number displayed on screen matches the number on the sensor packaging. A test can now be performed.

11.4 Slide the front catch to the right, and open the instrument case fully.

11.5 Remove the sample container. Rinse and then fill to the stepped line with the water sample.

11.6 Replace the filled sample container in the instrument.

11.7 Tear open the foil near the mark (<). Holding the sensor through the foil pack, exposing the connecting tracks.

11.8 Press the blue lever to open the jaw of the sensor connector. Insert the exposed end of the sensor, connecting tracks uppermost, into the slot, and release the lever. The jaws will close to hold the sensor in place. Slide the foil pouch off to expose the sensor.

11.9 Gently close the instrument lid to immerse the sensor in the sample. The test starts automatically. The display indicates progress of the test. Do not disturb the instrument during the test.

11.10 In less than one minute the Free Chlorine result will be displayed. To obtain the Total Chlorine result, press the down arrow once. All results are automatically stored to the instrument log.

11.11 After completion of the test, open the instrument and press the blue lever to remove the used sensor. Empty and rinse the sample container.

Do not leave water in the instrument on completion of the test.

Note: *The instrument is programmed to recognize a number of user errors, such as unable to read, used sensor, missing sensor, faulty sensor or lid opened during test. The instrument will abort the test and display an error message. Always use a fresh portion of sample if a sensor has been immersed in the water sample.* ***Never leave water in the sample container in the instrument following analyses.***

12.0 Data Analysis and Calculations

12.1 If a sample dilution has been used using reagent water, multiply the answer by the appropriate dilution factor:

$$\text{Dilution Factor} = \frac{\text{Total Volume}}{\text{Sample Volume}}$$

where:

Sample Volume	*= Aliquot of sample taken for dilution (mL)*
Total Volume	*= Volume to which sample volume is diluted (mL)*
Corrected Concentration	*= Observed concentration x dilution factor*

12.2 Reporting

12.2.1 Report results in milligrams chlorine per liter (mg Cl/L).

12.2.2 Report results to two significant figures from 0.1 to 10 mg Cl/L for free and total Chlorine and two significant from 1.0 to 20 mg Cl/L for total chlorine. Above 20 mg Cl/L report whole numbers.

13.0 Method Performance

13.1 Using the Chlorosense, two different state certified laboratories reported that the standard deviation and mean of replicate observations (n =14) of a calibration standard containing 0.5 mg Cl/L was 0.021 mg Cl/L and 0.51 mg Cl/L respectively.

13.2 With multiple batches of sensors, the relative standard deviation of sets of observations (n = 10) of a calibration standard containing 0.5 mg Cl/L varied from 3.7 to 4.8%.

13.3 A single state certified laboratory reported the analysis of seven aliquots of a drinking water sample from a surface water source, initially containing 1.55 mg free Cl/L and 1.80 mg total Cl/L, that was fortified to a free chlorine concentration of 3.55 mg Cl/L and total chlorine concentration of 3.80 mg Cl/L. The mean percent recovery of the added 2.0 mg Cl/L free and total chlorine was 100 % free and 99 % total chlorine and the corresponding standard deviation of the percent recoveries was 0.08 free and 0.11 total chlorine.

14.0 Pollution Prevention

14.1 The quantity of chemical purchased should be based on expected usage during its shelf-life and disposal cost of unused material.

14.2 Standards should be prepared in volumes consistent with laboratory use to minimize the volume of expired standards to be disposed.

15.0 Waste Management

15.1 It is the laboratory's responsibility to comply with all federal, state, and local regulations governing waste management, particularly the hazardous waste identification rules and land disposal restrictions, and to protect the air, water, and land by minimizing and controlling all releases from fume hoods and bench operations. Compliance with all sewage discharge permits and regulations is also required.

15.2 Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner. The MSDS sheet gives details of product composition and may be consulted for guidance on waste disposal.

15.3 For further information on waste management, consult "The Water Management Manual for Laboratory Personnel", and "Less is Better: Laboratory Chemical Management for Waste Reduction", both available from the American Chemical Society's Department of Government Relations and Science Policy, 1155 16th Street N.W., Washington DC, 20036.

16.0 References

16.1 "Carcinogens-Working With Carcinogens", Department of Health, Education, and Welfare, Public Health Service, Center for Disease Control, National

Institute for Occupational Safety and Health, Publication No. 77-206, August 1977.

16.2 "OSHA Safety and Health Standards, General Industry", (29 CFR 1910), Occupational Safety and Health Administration, OSHA 2206 (Revised, January 1976).

16.3 "Safety in Academic Chemistry Laboratories", American Chemical Society, Committee on Chemical Safety, 3rd Edition, 1979.

16.4 Standard Test Method For Residual Chlorine in Water, ASTM D1253-08

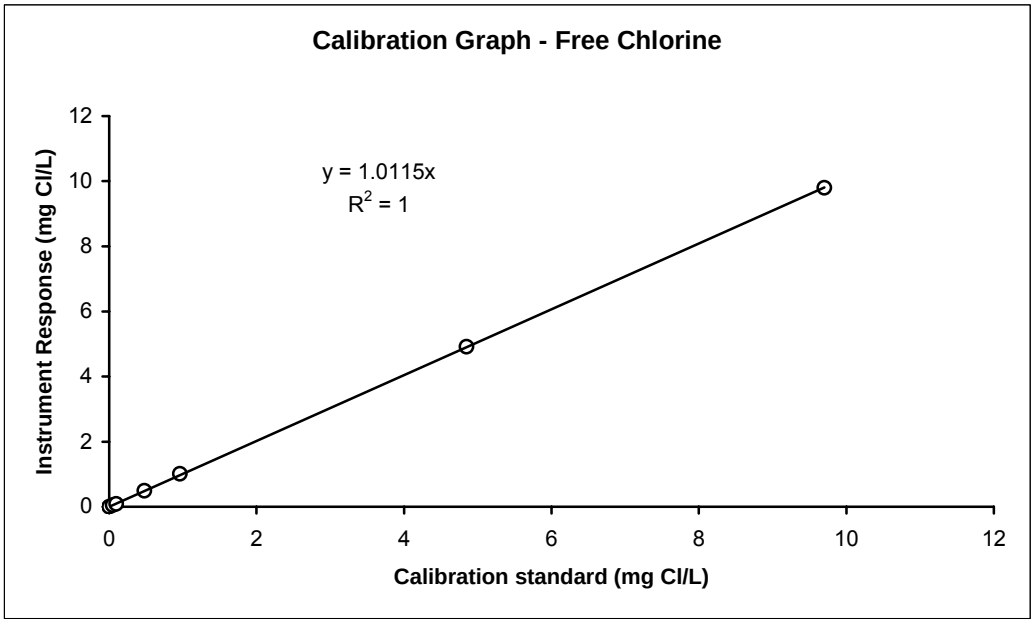
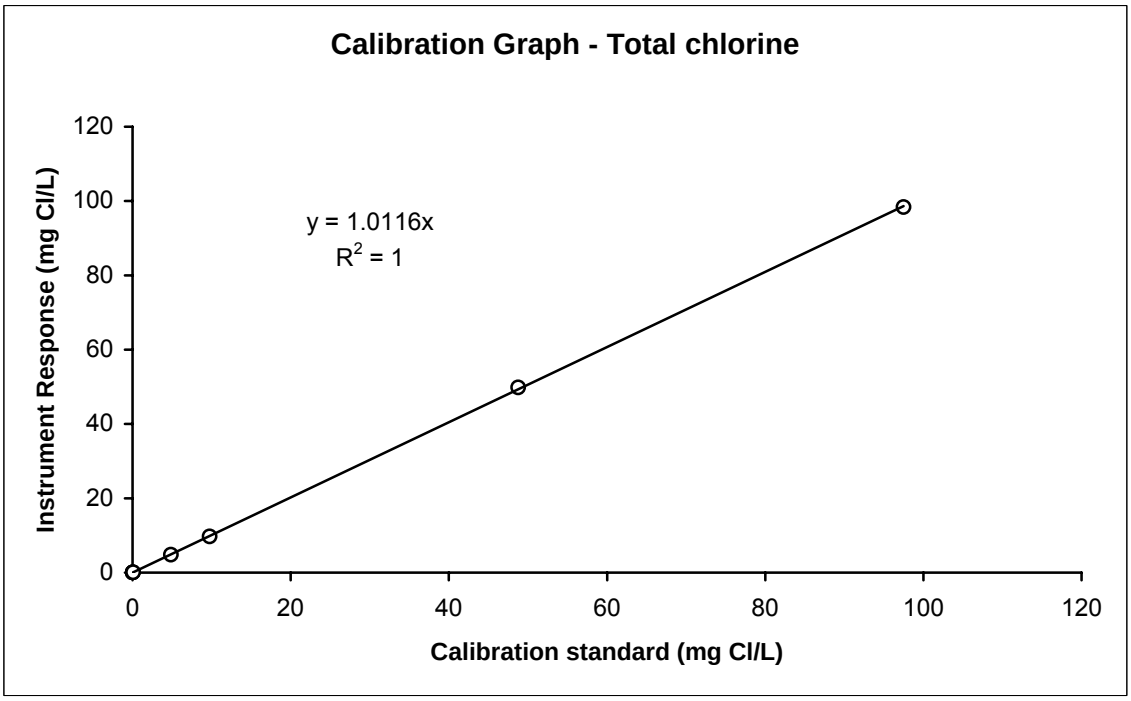
16.5 Standard Method 4500-Cl C, Standard Methods for the Examination of water and Wastewater

17.0 Tables and Graphs

17.1 Acceptance Criteria for Performance Tests

Acceptance Criterion	Section	Limit (%)
Initial accuracy and precision		
Accuracy (X)	9.2.2	±15
Precision (s)	9.2.3	≤15
Continuing calibration Check		
Accuracy (X)	9.3.2	±15
Calibration verification		
Accuracy (X)	10.1	±15

17.2 Graph 1 Example calibration graph



17.3 Graph 2 Example calibration graph