Ozarks Environmental and Water Resources Institute (OEWRI)
Missouri State University (MSU)

Standard Operating Procedure for:

accumet Excel (XL25) Dual Channel pH/Ion Meter for Chloride Concentration Determination

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Identification of the test method
Operation of the accumet Excel XL25 Dual Channel pH/Ion Meter for chloride concentration determination.

Applicable matrix or matrices
This method is suitable for the determination of chloride concentrations in potable, surface, and waste waters. The accumet Excel XL25 Meter has an operating range of 1 x 10^{-5} to 100 ppm (mg Cl/L) chloride.

Detection limit
The practical detection limit is 0.1 ppm (mg Cl/L).

Scope of the test method
This standard operating procedure provides Missouri State University (MSU) laboratory personnel protocol for determining chloride concentration in water samples.

Summary of test method
A water sample is combined with an ionic strength adjuster to create a uniform background ionic strength, which provides more accurate and reproducible measurements with the ion selective electrode (ISE) used for these determinations. The chloride electrode is introduced to the sample and the electrode's sensing membrane develops an electrical potential which is proportional to the activity of the chloride anion in the sample. The sample activity is compared to the activity of the range of standards used to calibrate the instrument and chloride concentration is calculated.

Definitions
1. Analytical batch: The set of samples processed at the same time.
2. Calibration standard: A solution prepared from the primary dilution standard solution or stock standard solutions. The calibration standards are used to calibrate the instrument response with respect to analyte concentration.
3. Chain of Custody (COC): Used to describe the written record of the collection possession and handling of samples. Chain of Custody forms should be completed as described in the Chain of Custody SOP (OEWRI-SOP-001). Chain of custody (COC) forms are located on a board in Temple Hall 125.
4. Field Duplicate (FD): Two samples taken at the same time and place under identical circumstances and treated identically throughout field and laboratory procedures. Analysis of field duplicates indicates the precision associated with sample collection, preservation, and storage, as well as laboratory procedures.

5. Ionic Strength Adjuster (ISA): Buffer solution added to the samples and standards to create a uniform background ionic strength for increased accuracy and precision.
6. Laboratory Duplicate (LD): Two aliquots of the same environmental sample treated identically throughout a laboratory analytical procedure. Analysis of laboratory duplicates indicates precision associated with laboratory procedures but not with sample collection, preservation, or storage procedures.
7. Laboratory Reagent Blank (LRB): An aliquot of HPLC water that is used to calibrate the instrument at the beginning of the analysis and is analyzed within the batch analysis sequence to determine if analytes or interferences are present in the laboratory environment or the apparatus.
8. Method detection limit (MDL): The lowest level at which an analyte can be detected with 99 percent confidence that the analyte concentration is greater than zero. To calculate the MDL:
    a) Analyze seven aliquots of HPLC water including all sample processing steps prior to the determination.
    b) Calculate the standard deviation (*s*).
    c) The multiplier used to derive the MDL is from a table of a one-sided *t* distribution where the value of *t* for 7 – 1 = 6 degrees of freedom at the 99% level was selected. This value is 3.14.
    d) The product 3.14 times *s* is the desired MDL.
9. Relative Percent Difference (RPD): calculated as the difference between a sample and duplicate results, divided by the average of the sample and duplicate results, multiplied by 100%.
10. Standard Check: Standards analyzed as samples to monitor instrument shift or analyst error.

Interferences

Cyanide, thiosulfate, and ammonia are potential interferences to the chloride electrode and could significantly influence electrode response. Samples should be free of sulfide as it destroys the electrode surface. Wastewater samples should be screened for sulfide and ammonia content prior to being exposed to the electrode associated with this meter.

Health and safety

This analysis involves handling freshwater samples that may contain live microorganisms and therefore pose some threat of infection. Laboratory personnel who are routinely exposed to such water samples are encouraged to protect themselves from water borne illnesses by wearing clean disposable gloves and washing their hands frequently.

Personnel qualifications

Laboratory personnel shall have a working knowledge of this analytical procedure and will have received training from an MSU employee knowledgeable of the proper sample analysis procedures. Prior to the first batch of sample analyses, the analyst will complete a demonstration of capability exercise as described below in the Quality control section.

Equipment and supplies

1. Fisher accumet Excel XL 25 with Chloride ISE Electrode.
2. Fisher Scientific stir plate.
3. 100 ml Griffin Beakers (Fisher Cat. No. S63242).
4. Stir bars (Fisher Cat. No. 14-513-58SIX).
5. 1000 µL pipette and tips (Fisher Cat. No. 21-377-146).
6. 10 µL pipette and tips.

Reagents and standards

1. Chloride Electrode Storage Solution: 98.4% H_2O, 1% KHP, and 0.6% KCl (98.4 ml H_2O, 1 g KHP, and 0.6 g KCl).
2. DI water: For rinsing electrode between samples.
3. Fisher accumet Chloride ISE Electrode Filling Solution (Fisher Cat. No. 13-620-432): Reference solution for electrode.
4. HPLC (Fisher Cat. No. W5-4): For mixing standards.
5. Ricca Chemical Company Chloride Standard, 500 ppm (0.0141 N) (Fisher Cat. No. 195032).
6. Thermo Scientific Orion ISE Ionic Strength Adjuster (Fisher Cat. No. 13-641-852): Use 2 ml/100 ml sample to produce a uniform background ionic strength.

Sample collection, preservation, shipment and storage

1. Refer to the Water Sampling SOP for appropriate collection procedures (SOP: 1040R03 Water Sampling Collection Procedures).
2. Samples are stored on ice for transport to the laboratory and are refrigerated immediately upon transfer to the laboratory. Chloride samples do not require any preservation solution addition.
3. There is a 28-day holding time for chloride (EPA-600/4-79-020), however, samples should be analyzed as soon as possible.

Quality control

1. Method detection limit and precision: initial demonstration of capability (for any new laboratory analyst)
    a. Initial demonstration of performance must be satisfied before the analytical procedure may be used for samples.
    b. The analyst should read this SOP and demonstrate to a previously trained analyst that the procedures outlined here are being followed and data is successfully reported to the laboratory manager.
    c. Method Detection Limit (MDL): To establish the ability to detect the analyte, the analyst shall determine the MDL by carrying through 7 or more separately prepared reagent blank solutions through the analytical procedure. The average value, X, and the standard deviation of the values, s, shall be calculated. The MDL is equal to 3s (3 × standard deviation). The MDL and average value, X, must both be less than 0.10 mg Cl/L.
    d. Initial Precision and Recovery: To establish the ability to generate acceptably precise and accurate results, the operator shall perform 10 replicates of a mid-range standard. Using the results of the replicates, compute the average value, X, and the standard deviation, s, for the analyte. The value of X should be within ± 10% of the true value. The standard deviation should be less than or equal to 10% of the average value.
2. Laboratory Duplicate (LD) Reproducibility: A laboratory duplicate is analyzed for every 10 samples analyzed to quantify precision.
    a. Measure the sample and a separate aliquot of the same sample (LD).
    b. The relative percent difference (RPD) between the two values should be ≤ 10% of their average value.
    c. Use equation 1 to calculate RPD:

    Equation 1: $$RPD\ (\%) = \frac{(A - B)}{(A + B)/2} \times 100\%$$

    Where: A = first measurement, and
    B = duplicate measurement

    d. Analyze one set of duplicates for every 10 samples analyzed.
3. Laboratory Reagent Blank (LRB): analysis of laboratory blanks is required to demonstrate freedom from contamination. Analyze one LRB for every 10 samples analyzed.

a. The laboratory shall, on an ongoing basis, demonstrate through calibration verification and analysis of the ongoing precision sample that the analysis system is accurate.
b. Each standard used to calibrate the instrument is re-analyzed at the end of the batch of after every 20 samples and at the end of the batch to verify calibration and quantify instrument drift.

4. The laboratory should maintain records to define the quality of data that is generated.

Calibration and standardization

1. The accumet Excel XL25 Chloride Meter will be calibrated prior to every batch analysis.
2. Calibration employs a standard curve derived from plotting electrical potential or the activity produced from the standard solutions (including the reagent blank) versus known chloride anion concentration in the standards. The data is fit to a linear equation using the software associate with the meter and concentration is presented on the screen.
3. The chloride electrode will always be stored in the Chloride Electrode Storage Solution: 98.4% HPLC H_2O, 1% KHP, and 0.6% KCl (98.4 ml H_2O, 1 g KHP, and 0.6 g KCl) or will be cleaned, drained, and stored within the original box when not in use for extended periods of time.
4. Clean and perform routine maintenance as outlined in the accumet excel XL25 operator's manual.
5. <u>Calibration Solutions Preparation</u>
   a. Prepare the Blank (0.00ppm) by using a 40 mL aliquot of HPLC water combined with 0.8 mL ionic adjuster.
   b. Prepare Standard 1 (10 ppm) by removing a 0.8 mL aliquot of Ricca 500 ppm Standard Stock Solution from the standard bottle with a pipette and clean tip and combining it with 39.2 ml HPLC water and 0.8 mL ionic strength adjuster in a clean beaker.
   c. Prepare Standard 2 (50 ppm) by removing a 4.0 mL aliquot of Ricca 500 ppm Standard Stock Solution from the standard bottle with a pipette and clean tip and combining it with 36 mL HPLC water and 0.8 mL ionic strength adjuster in a clean beaker.
   d. Prepare Standard 3 (100 ppm) by removing an 8.0 mL aliquot of Ricca 500 ppm Standard Stock Solution from the standard bottle with a pipette and clean tip and combining it with 32.0 mL HPLC water and 0.8 mL ionic strength adjuster in a clean beaker.
6. <u>Calibration Procedures</u>
   a. Add a clean stir bar to each standard and the blank.

b. Rinse the electrode with HPLC water and blot with paper towel.
c. Place the Blank on the stir plate and turn dial to 6.
d. Immerse electrode into the blank solution but DO NOT allow the stir bar to touch the electrode.
e. Press **Standardize** on the Ion Measure screen to access the standardization screen.
f. Press **Clear** if necessary to remove a previous standardization.
g. Proceed when the screen reads “Not standardized”.
h. Press **Blank**. A beaker icon labeled blank will be displayed on the Ion Measure screen.
i. Remove the Blank from the stir plate, rinse the electrode, and blot with a paper towel. Place Standard 1 on the stir plate and immerse the electrode in the standard.
j. Press **Standardize** and then **Standard**. The screen will flash each standard icon once and then a numeric keypad will appear. Input the value of the standard and press **Enter**.
k. The screen will illustrate the value of the standard solution in the flashing beaker. Wait until **Stable** appears on the screen and press **Confirm** once to confirm the standardization.
l. Repeat procedures i-k with Standard 2 and Standard 3.

Sample Analysis

1. Thoroughly shake sample in sample bottle and measure 40 mL into a clean labeled beaker.
2. Remove 0.8 mL of the ionic strength adjuster solution from the solution bottle with a pipette and clean tip and transfer it to the sample. Add a clean stir bar to each sample.
3. Rinse the electrode with HPLC and blot with paper towel.
4. Place the sample on the stir plate and turn dial to 6.
5. Immerse the electrode in the stirring sample but DO NOT allow the stir bar to touch the electrode.
6. Press **Measure** to begin the analysis of the sample.
7. Wait until **Stable** appears on the screen, press **Log Data,** and record the concentration on the chloride bench sheet.
8. Remove the electrode from the sample and rinse with HPLC water.
9. Repeat procedures 1-9 until all samples are analyzed.
10. Use a separate 40 ml aliquot of one of the samples to produce a Laboratory Duplicates (LD) for every 10 samples analyzed. Record the sample number and “-LD” on the bench sheet when recording the concentration of the laboratory duplicate.

11. Use the original standards and blank to check the calibration and instrument drift by analyzing each solution after every 20 samples and at the end of the batch.
12. Repeat procedures 1-9 for each standard and blank treating them as “samples” so the original calibration is used throughout the analysis. Record “Standard 1”, “Standard 2”, “Standard 3”, and “Blank” concentrations on the bench sheet.

Data acquisition, calculations, and reporting

1. Data Exporting Procedures
    a. Press **View** in the mV setup screen.
    b. Press **Export View and Header** to save data in HTML format.
    c. Press **SD Card** and name the file using the alphanumeric keypad at the bottom of the screen. The file name should include “Chloride Data”, the date of analyses, the project names and date of sample collection associated with the COCs completed during the analysis.
    d. Press **OK** in the upper right corner of the Save As screen.
    e. Close all applications prior to SD card removal.
    f. Press gently down on the card to unlock it and when the card disengages and pops up, pull it from the expansion slot.
    g. Data can be viewed using Windows Explorer:
        i. Press **Setup** and then **View**.
        ii. Data is listed inversely of analysis sequence.
2. The software associated with the meter calculates all concentrations based on the initial batch calibration.
3. Reporting results: Results should be reported to the 0.1 ppm (mg Cl/L) precision.

Computer hardware and software

1. This document and attached bench sheet are prepared using Microsoft Word.
2. Quality control charts are prepared and updated using Microsoft Excel.

Method performance

The desired performance criteria for this measurement are:

a. Detection limit: 0.1 ppm (mg Cl/L)
b. Precision: ± 10% RPD
c. Accuracy: ± 10% RPD
d. Minimum Quantification Interval: 0.1 ppm (mg Cl/L)

The applicable range for the method is 0.1 to 100 ppm (mg Cl/L) and may be extended by dilution.

Pollution prevention

1. All waste from these procedures shall be collected and disposed of according to existing waste policies within the MSU Geography, Geology, and Planning Department.
2. Volumes of reagents made should mirror the number of samples being analyzed. These adjustments should be made to reduce waste.

Data assessment and acceptable criteria for quality control measures

1. The analyst should review all data for correctness.
2. Precision values are calculated for pairs of duplicate analyses. The desired precision is ± 10% RPD.
3. Accuracy values are calculated for standard checks analyzed within and at the end of the batch. The desired accuracy is ± 10% RPD.
4. The desired detection limit is 0.1 ppm.
5. Completed chloride bench sheets are reviewed by the OEWRI laboratory manager and QA coordinator.

Corrective actions for out-of-control or unacceptable data

1. The results for precision, accuracy, and blank data are compared to acceptable values for these analyses: ± 10% RPD and 0.1 ppm (mg Cl/L) respectively.
2. If a blank value exceeds 0.1 ppm (mgCl/L) during batch analysis, then the analyst should immediately re-analyze the blank. If the blank continues to exceed the MDL, contact the laboratory manager.
3. If data are unacceptable for any reason, the analyst should review their analytical techniques prior to conducting these analyses again.
4. The batch may be re-analyzed as QA/QC dictates.
5. The meter may require trouble-shooting techniques if the data are unacceptable beyond regular maintenance including cleaning the electrode, changing the reference solution, or replacing the electrode. All maintenance and repairs must be recorded in the instrument log book.

Waste management

The waste generated in this method are not hazardous. The quantities generated are small and waste can be discarded in the laboratory sink.

Tables, diagrams, flowcharts, and validation data

1. There are no tables, diagrams, or flowcharts for this method.
2. The following page contains the chloride bench sheet. The analyst should copy this form and complete one for each batch of samples analyzed.

References

accumet Excel User Manual. Fisher Scientific. 2007.

OEWRI. Standard Operating Procedure for: Water Sample Collection. Ozarks Environmental and Water Resources Institute, Missouri State University. 2007. 1040R03.

OEWRI. Standard Operating Procedure for: Chain of Custody. Ozarks Environmental and Water Resources Institute, Missouri State University.2022. OEWRI-SOP-001.

USEPA. Methods for Chemical Analysis of Water and Wastes. United States Environmental Protection Agency.1983. 600/4-79-020.

Missouri State University
Ozarks Environmental and Water Resources Institute
Chloride Bench Sheet

Analyst: _____

Data reviewed by:

Date analyzed: _____

Projects COCs associated with Analysis: _____

Sample Data

Sample Identification	Date Sample Collected	Chloride Concentration (mg/l)	RPD %

	mV	Chloride Concentration (mg/l)		RPD %
Blank (0ppm)				
Std. 1 (10ppm)				
Std. 2 (50ppm)				
Std. 3 (100ppm)				

Comments: _____

Chloride – Bench Procedures

- Make blank and allow probe to sit in the blank for at least 24 hours before starting the test
- Make/Label bench sheet
- Set samples out to warm up to room temp
- Remake blank and make standards for calibration

	H_2O	IA	Cl^-
Blank (0ppm)	40.0 mL	0.8 mL	N/A
Std1 (10ppm)	39.2 mL	0.8 mL	0.8 mL
Std2 (50ppm)	36.0 mL	0.8 mL	4.0 mL
Std3 (100ppm)	32.0 mL	0.8 mL	8.0 mL

- Read blank/standards
    - Standardize, clear, standardize, blank: wait-confirm
    - Standardize, standard, enter #: wait-confirm

	ppm	mV
Blank	0	155.6
Std1	9-11	102.1-93
Std2	45-55	60.3-64.2
Std3	90-110	45-48.1

- Samples

	Sample	IA
Samples	40.0 mL	0.8 mL

- Rinse between each probe reading
- If any samples read ‘under range’ write that down
- LD every ~12 samples
- Run standards again after samples
- When finished, drain ISE, cover the hole with parafilm, cover sensor and store dry.

Chloride – Supply List

All supplies can be bought from Fisher Scientific

Filling Solution- ISE

Recommended-
Fisherbrand Filling Solutions for accumet ISE Electrodes, Fluoride
Catalog No. 13-620-432

Ionic Strength Adjuster

Recommended-
Thermo Scientific Orion ISE Ionic Strength Adjustors (ISA) and Special Reagents
Catalog No. 13-641-852