

METHOD 9212

POTENTIOMETRIC DETERMINATION OF CHLORIDE IN AQUEOUS SAMPLES WITH ION-SELECTIVE ELECTRODE

1.0 SCOPE AND APPLICATION

1.1 This method can be used for measuring total solubilized chloride in drinking waters, natural surface waters, groundwaters, domestic and industrial wastewaters, and in soil extracts (ASTM methods D4646-87, D5233-92 or D3987-85).

NOTE: This method is for the analysis of simple chloride ion rather than total chloride, as analysis using the ion-selective electrode is not preceded by a distillation step.

1.2 The method detection limit is 2.0 mg/L. Chloride concentrations from 0.4 to 1,000 mg/L may be measured. However, when using a linear calibration, results less than 2.0 mg/L may be biased up to approximately 60 percent high.

1.3 ISEs must be used carefully and results must be interpreted cautiously, since an ISE may be affected by numerous analytical interferences which may either increase or decrease the apparent analyte concentration, or which may damage the ISE. Effects of most interferences can be minimized or eliminated by adding appropriate chemical reagents to the sample. Obtaining the most accurate results, therefore, requires some knowledge of the sample composition.

NOTE: ISE manufacturers usually include a list of interferences in the instruction manual accompanying an ISE, along with recommended methods for minimizing or eliminating effects of these interferences.

1.4 The chloride ISE should not be used in solutions containing high concentrations of bromide or iodide, cyanide, or sulfide since these ions form silver salts less soluble than silver chloride. The chloride ISE will also give erroneous readings and will be damaged when used in solutions containing free ammonia, since such solutions dissolve silver chloride.

2.0 SUMMARY OF METHOD

2.1 Total solubilized chloride is determined potentiometrically using a chloride ion-selective electrode (ISE) in conjunction with a double-junction reference electrode, or a chloride combination ISE, and a pH meter with an expanded millivolt scale or an ISE meter capable of being calibrated directly in terms of chloride concentration.

2.2 Standards and samples are mixed 50:1 with an ionic strength adjustment solution (ISA). Calibration is performed by analyzing a series of standards and plotting mV vs. chloride concentration on semilog paper or by calibrating the ion meter directly in terms of chloride concentration.

3.0 INTERFERENCES

3.1 Polyvalent cations (e.g., Fe^{+3} and Al^{+3}) interfere by forming complexes with chloride which are not measured by the chloride ISE. (See Table 1.) Aluminum and iron(III) ions (at concentrations of 300 mg/L and higher) form complexes with chloride ions having approximately

equal stability. (A sample with high solubilized Fe^{+3} and Al^{+3} concentrations will be distinctly colored yellow-brown.) Dilute sulfuric acid has no effect on the chloride concentration because silver sulfate is soluble, and because hydrogen chloride is a strong acid (completely ionized) in water. Chloride concentration in the presence of high concentrations of polyvalent cations can be measured by treating the sample with an equal volume of EDTA or by the method of standard additions.

3.2 Bromide, sulfide, cyanide, and ammonia interfere with the determination by reacting directly with and damaging the ISE. Sulfide, cyanide, and ammonia can be removed by acidifying the sample to a pH of 4 with dilute sulfuric acid. Bromide and iodide can be removed by treating the acidified sample with potassium bromate, which converts the ions to bromine and iodate.

CAUTION: Use hood to avoid exposure to toxic gases released during acidification.

3.3 Temperature changes affect electrode potentials. Using an ISE calibrated at 22°C , a 40.0 mg/L chloride solution was measured as 40.0 mg/L at 22°C and 24.8 mg/L at 32° (see Ref. 3). Therefore, standards and samples must be equilibrated at the same temperature ($\pm 1^\circ\text{C}$).

3.4 The user should be aware of the potential of interferences from colloidal substances and that, if necessary, the samples may be filtered.

4.0 APPARATUS AND MATERIALS

4.1 pH/mV meter capable of reading to 0.1 mV or an ISE meter.

4.2 Combination chloride ISE (Orion 9617 or equivalent), or separate chloride ISE (Orion 9417 or equivalent) and double-junction reference electrode (Orion 9002 or equivalent).

4.3 Thermally isolated magnetic stirrer, polytetrafluoroethylene (PTFE)-coated stir bar, and stopwatch.

4.4 Volumetric flask, 100 mL.

5.0 REAGENTS

5.1 Reagent grade chemicals shall be used in all tests. Unless otherwise indicated, it is intended that all reagents shall conform to the specifications of the Committee on Analytical Reagents of the American Chemical Society, where such specifications are available. Other grades may be used, provided it is first ascertained that the reagent is of sufficiently high purity to permit its use without lessening the accuracy of the determination.

5.2 Reagent water. All references to water in this method refer to reagent water, as defined in Chapter One.

5.3 ISA solution (5M NaNO_3): Dissolve 42.5 g of sodium nitrate in sufficient reagent water to make 100 mL of solution. Store in a clean glass or plastic container.

5.4 Ethylenediaminetetraacetate (EDTA), disodium salt ($2\% \text{C}_{10}\text{H}_{12}\text{N}_2\text{O}_8\text{Na}_2$). Use as directed in Section 3.1.

5.5 Dilute sulfuric acid ($0.01 \text{M H}_2\text{SO}_4$): use as directed in Section 3.2.

5.6 Potassium bromate (1%, KBrO_3): use as directed in Section 3.2.

5.7 Chloride calibration stock solution (1,000 mg/L Cl^-): Dissolve 0.1649 g of sodium chloride (dried two hours at 110°C and stored in a desiccator) in reagent water and dilute to 100 mL in a volumetric flask. Store in a clean bottle.

5.8 Chloride calibration standards: Prepare a series of calibration standards by diluting the 1,000 mg/L chloride standard. A suitable series is given in the table below.

mL of 1,000 mg/L Cl^- Solution	Concentration when Diluted to 50.0 mL (mg/L Cl^-)
0.050	1.00
0.150	3.00
0.50	10.0
1.50	30.0
5.0	100.0

6.0 SAMPLE COLLECTION, PRESERVATION, AND HANDLING

6.1 All samples must have been collected using a sampling plan that addresses the considerations discussed in Chapter Nine of this manual.

6.2 Samples should be stored at 4°C . There are no other special sample handling or preservation requirements.

7.0 PROCEDURE

7.1 Calibration

7.1.1 If using a chloride combination ISE, ensure that the ISE is filled with the solution recommended by the manufacturer. Change the solution if the ISE has not been used for a week. If using a chloride ISE and a separate double-junction reference electrode, ensure that reference electrode inner and outer chambers are filled with solutions recommended by the manufacturer. In either case, equilibrate the electrode(s) for at least one hour in a 30.0 mg/L chloride standard before use.

7.1.2 Calibrate the chloride ISE using standards that narrowly bracket the expected sample concentration. If the sample concentration is unknown, calibrate with 10.0 mg/L and 100 mg/L chloride standards. Add 50.0 mL of standard and 1.00 mL of ISA to a 100 mL beaker. Add a PTFE-coated magnetic stir bar, place the beaker on a magnetic stir plate, and stir at slow speed (no visible vortex). Immerse the electrode tips to just above the rotating stir bar. If using an ISE meter, calibrate the meter in terms of chloride concentration following the manufacturer's instructions. If using a pH/mV meter, record the meter reading (mV) as soon as the reading is stable, but in no case should the time exceed five minutes after immersing the electrode tips. Prepare a calibration curve by plotting measured potential (mV) as a function of the logarithm of chloride concentration. The slope must be 54-60 mV per decade of chloride concentration. If the slope is not acceptable, the ISE may not be working properly. For corrective action, consult the ISE operating manual.

7.2 Allow samples and standards to equilibrate to room temperature.

7.3 Prior to and between analyses, rinse the electrodes thoroughly with reagent water and gently shake off excess water. Low-level measurements are faster if the electrode tips are first immersed for five minutes in reagent water.

7.4 Add 50.0 mL of sample and 1.00 mL of ISA to a 100 mL beaker. Add a PTFE-coated magnetic stir bar. Place the beaker on a magnetic stir plate and stir at a slow speed (no visible vortex). Immerse the electrode tip(s) to just above the rotating stir bar. Record the meter reading (mV or concentration) as soon as the reading is stable, but in no case should the time exceed five minutes after immersing the electrode tips. If reading mV, determine chloride concentration from the calibration curve.

7.5 When analyses have been completed, rinse the electrodes thoroughly and store them in a 30.0 mg/L chloride standard solution. If the electrodes will not be used more than one day, drain the internal filling solutions, rinse with reagent water, and store dry.

8.0 QUALITY CONTROL

8.1 Refer to Chapter One for specific quality control procedures.

8.2 Initial Calibration Verification standard (ICV): After performing the calibration step (7.1), verify calibration by analyzing an ICV. The ICV contains a known chloride concentration at the mid-range of the calibration standards and is from an independent source. ICV recovery must be 90-110 percent. If not, the error source must be found and corrected. An acceptable ICV must be analyzed prior to sample analysis. The ICV also serves as a laboratory control sample.

8.3 Continuing Calibration Verification standard (CCV): After every 10 samples, and after the final sample, a CCV must be analyzed. The CCV contains a known chloride concentration at mid-calibration range. CCV recovery must be 90-110 percent. If not, the error source must be found and corrected. If ISE calibration has changed, all samples analyzed since the last acceptable CCV must be re-analyzed.

8.4 Reagent blank: After the ICV and after every CCV, a reagent blank must be analyzed. A reagent blank is reagent water mixed 50:1 with ISA. The indicated reagent blank concentration must be less than 1 mg/L chloride. If not, the contamination source must be found and corrected. All samples analyzed since the last acceptable reagent blank must be re-analyzed.

8.5 Matrix spike: Follow the matrix spike protocols presented in Chapter One. The spike concentration must be 10 times the detection limit and the volume added must be negligible (less than or equal to one-thousandth the sample aliquot volume). Spike recovery must be 75-125 percent. If not, samples must be analyzed by the method of standard additions.

9.0 METHOD PERFORMANCE

9.1 In a single-laboratory evaluation, a series of standards with known chloride concentrations was analyzed with a chloride ISE. Measurements were conducted over three consecutive days using an Orion 9609 chloride combination ISE connected to an Orion 940 ISE meter. A two-point calibration (4.00 and 40.0 mg/L chloride) was performed prior to analysis. The results are listed in Table 2.

9.2 In the same study, six groundwater samples were spiked with chloride at four different concentrations and were measured with the chloride ISE. (The groundwater samples initially contained 1.3-23 mg/L chloride.) Each spiked sample was analyzed at each concentration and the mean recoveries and RSDs are given in Table 3.

9.3 A 50 g portion of soil, which initially contained 17.3 mg/kg chloride, was spiked with 25.0 mg/kg chloride to obtain an anion concentration in a single extract volume within the linear range of the ISE. The extract was then analyzed for chloride using this ISE method, and 109% of the soil spike was recovered.

10.0 REFERENCES

1. Franson, Mary Ann H., Ed. Standard Methods for the Examination of Water and Wastewater, 18th Edition. American Public Health Association, Washington, DC, 1992.
2. Model 96-17 Chloride Combination Electrode Instruction Manual. Orion Research, Inc., Boston, MA, 1988.
3. Miller, E.L., Waltman, D.W., and Hillman, D.C. Single-Laboratory Evaluation of Fluoride, Chloride, Bromide, Cyanide, and Nitrate Ion-Selective Electrodes for Use in SW-846 Methods. Lockheed Engineering and Sciences Company for Environmental Monitoring Systems Laboratory, U.S. EPA. September 1990. EPA/600/X-90/221.
4. Cotton, F. Albert, and Geoffrey Wilkinson; *Advanced Inorganic Chemistry, 2nd Edition*; Interscience Publishers, New York, NY; 1966.
5. Weast Robert C., Ed.; *CRC Handbook of Chemistry and Physics, 58th Edition*; CRC Press, Inc., Cleveland, Ohio; 1977.
6. Kolthoff, I.M., E.B. Sandell, E.J. Meehan, and Stanley Bruckenstein; *Quantitative Chemical Analysis, 4th Edition*; The MacMillan Company, New York, NY; 1969.

TABLE 1
CHLORIDE ISE INTERFERENCES

Analyte Concentration (mg/L)	Interference	Measured Concentration (mg/L)	RSD (%)
20.0	None	19.9	2.2
200.0	None	200.0	1.3
20.0	300 mg/L Fe ⁺³	19.6	3.0
200.0	300 mg/L Fe ⁺³	183.0	4.5
20.0	300 mg/L Al ⁺³	19.3	3.3
200.0	300 mg/L Al ⁺³	175.0	6.2
200.0	0.01 M H ₂ SO ₄	201.0	1.5
200.0	200 mg/L CN ⁻ + 0.01 M H ₂ SO ₄	198.0	1.0
20.0	200 mg/L S ⁻² + 0.01 M H ₂ SO ₄	19.9	0.5

TABLE 2
RESULTS FROM A SINGLE-LABORATORY ACCURACY EVALUATION
OF A CHLORIDE ISE

Chloride Concentration (mg/L)	Chloride Detected (mg/L)	Chloride Recovery (%)	Rel. Std. Deviation (%)
0.400	0.64	160	21
1.00	1.32	132	9
2.00	2.07	104	4
4.00	4.0	100	3
10.0	10.0	100	4
20.0	19.4	97	7
40.0	40.0	100	3
100	100	100	4
200	201	101	1
400	390	99	4
1,000	970	97	3

TABLE 3
MEAN SPIKE RECOVERIES OF CHLORIDE IN SIX GROUNDWATER SAMPLES

Analyte Spike Concentration (mg/L)	Spike Recovery (%)	Rel. Std. Deviation (%)
2.00	107	8.2
3.00	95	3.6
5.00	93	3.6
10.0	102	4.3

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