ThermoFisher SCIENTIFIC

DRINKING WATER METHOD:

Drinking Water Chloride for Thermo Scientific Gallery Discrete Analyzer

Name of the method:	Drinking Water Chloride
Reference:	Standard Methods (SM) 4500-Cl- B. Chloride /Argentometric [1]. Method is EPA approved under 40 CFR Appendix A to subpart C of Part 141 [2] and compliant to National Secondary Drinking Water Regulations, NSDWR, based on SDWA, Safe Drinking Water Act.
Intended use:	This paper presents Drinking Water Chloride method for Thermo Scientific™ Gallery™ discrete analyzer. The method meets the criteria of the reference method and is intended for compliance measurements under NSDWR.
Revision number:	01
Revision date (mm/dd/yyyy):	07/12/2023

1. Scope and Application

1.1 This automated photometric method covers the determination of chloride (CAS: 16887-00-6) in drinking, ground, and surface water with the Thermo Scientific Gallery discrete analyzers (Gallery, Gallery Aqua Master, Gallery Plus, Gallery Plus Aqua Master, later referred as Gallery). Each sample type needs to be validated before starting the analysis.

1.2 The method is applicable for NSDWR reporting. Each laboratory is responsible for validating their analytical methods for compliance measurements and for getting approval for the method from corresponding authority.

1.3 The method is based on photometric measurement of iron (III) thiocyanate complex which is formed as a result of chloride releasing thiocyanate ions from mercury (II) thiocyanate.

1.4 The primary range for this method is from 1 to 100 mg/L. An extension of the range to 500 mg/L is achieved when 1+4 automated dilution is configured. The automated dilution feature must be confirmed with acceptable analysis of quality control samples by the user.

2. Summary of Method

2.1 Chloride reacts with mercury (II) thiocyanate to form a soluble non-ionic compound. The released thiocyanate ions react in acid solution with iron (III) nitrate to form a red/brown iron (III) thiocyanate complex. The intensity of the stable color produced is measured photometrically at a wavelength of 480 nm and is proportional to the original chloride concentration.

3. Definitions

3.1 Units and symbols from the international metric system (SI) are used. Definitions, acronyms, and abbreviations are explained as they occur for the first time.

3.2 Alternative volume versions of this method that use the same reagents and molar ratios are acceptable provided they meet the quality control and performance requirements stated in the method.

3.3 Limited performance-based method modifications may be acceptable provided they are fully documented and meet or exceed requirements expressed in Section 9.0, Quality Control.

4. Interferences

4.1 It is recommended to remove suspended matter in the sample by filtering or centrifuging prior to analysis.

4.2 The interference information stated below is from standard methods. Each laboratory is responsible for validating the method for respective sample types.

4.3 Sample color that absorbs at measurement wavelength interferes with the quantitation. When color is suspect, a test with true sample blank can be used. For true sample blank iron (III) nitrate is not added to the blank reagent. [4]

4.4 Sample pH outside 3 – 10 should be adjusted.[4]

4.5 Interference can arise from substances which reduce iron (III) to iron (II) and mercury (II) to mercury (I) such as sulfite and thiosulfate. [5]

4.6 Halides, e.g. bromide and iodide, also form strong complexes with mercuric ion and give positive interference. [4, 5]

4.7 Other possible interfering substances are thiocyanate, cyanides (including complex cyanides), sulphate, sulphide, and non-ionic detergents.[6]

5. Safety

5.1 General laboratory safe practices should be used in handling all samples,reagents and chemicals in this test method.

5.2 The toxicity and carcinogenicity of each reagent used in this method have not been fully established. Each chemical should be regarded as a potential health hazard and exposure should be as low as reasonably achievable.

5.3 The following chemicals are used in this method and have the potential to be toxic or hazardous. Consult MSDS (Material Safety Data Sheet) for details.

5.3.1 Mercuric thiocyanate ($Hg(SCN)_2$) (contained in Chloride R1) (CAS# 592-85-8). Note that pure $Hg(SCN)_2$ is toxic and even fatal if not handled properly.

5.3.2 Methanol (CH_3OH) (contained in Chloride R1) (CAS# 67-56-1)

5.3.3 Ferric nitrate ($Fe(NO_3)_3 \cdot 9\ H_2O$) (contained in Chloride R1) (CAS# 7782-61-8)

5.3.4 Nitric acid (HNO_3) (contained in Chloride R1) (CAS# 7697-37-2)

5.3.5 Sodium chloride (CAS# 7647-14-5)

6. Equipment and Supplies

6.1 Balance: Analytical, capable of accurately weighing to the nearest 0.0001 g.

6.2 Water purification system for producing suitable water. Refer to analyzer user manual.

6.3 Thermo Scientific Gallery (Gallery, Gallery Aqua Master, Gallery Plus, Gallery Plus Aqua Master), automated photometric discrete analyzer. Later referred as Gallery.

6.4 Filter, wavelength 480 nm.

6.5 DECACELL™ Cuvettes for Gallery. DECACELL cuvettes must always be used with Gallery. Cuvettes are for single use only. Ordering code 986540.

6.6 20 ml reagent bottles. Ordering code 981456 (16 pcs).

6.7 Washing solution 4.5 % hypochlorite solutionis used for daily analyzer cleansing. Ordering code 984030 (4 x 20 ml).

7. Reagents and Standards

	THERMO SCIENTIFIC ORDERING CODES
Reagents for Gallery:	984364 Chloride R1, 4 × 20 mL
	984365 Chloride R1L, 20 × 20 mL
Standards for Gallery:	984721 Chloride standard, 1000 ppm, 500 mL

7.1 Preparation of reagents needed in this method is described under. Also, ready to use reagents are available for this method.

7.2 Reagent water — Distilled or deionized water, aseptic and free of the analyte of interest and heavy metals. Water stored in bottles should be substituted by fresh water after one week.

7.3 Chloride R1 — Use ready to use reagent 984364/984365 or prepare reagent as follows. Dilute 75 ml of Mercuric Thiocyanate Stock solution (7.3.1) and 75 ml of Ferric Nitrate Stock solution (7.3.2) to 500 ml with deionized water. This self-made solution is stable for 1 month.

7.3.1 Mercuric Thiocyanate Stock Solution — Dissolve 4.16 g mercuric thiocyanate ($Hg(SCN)_2$) in 1000 ml of methanol. Mix and filter as necessary. This self-made solution is stable for 2 months.

7.3.2 Ferric Nitrate Stock Solution — Dissolve 202 g ferric nitrate ($Fe(NO_3)_3 \cdot 9H_2O$) in 800 ml deionized water. Carefully add 44.4 ml of concentrated nitric acid (HNO_3). Dilute to 1000 ml with deionized water. Store in an amber bottle. This self-made solution is stable for 2 months.

7.4 Chloride standard (stock), 1000 mg/L — Use commercial standard solutions or prepare a self-made standard (stock) solution by dissolving 1.6484 g of dried sodium chloride (NaCl) in 1000 mL of distilled water. The solution is stable unless evaporation occurs.

7.5 Chloride Calibration Solutions — Prepare an appropriate series of standards by diluting manually suitable volume of Chloride standard (stock) with deionized water or use the automated Gallery dilution feature.

7.6 Quality Control Solution (QCS) — A second source standard from an external source, e.g. 984721 Chloride Standard, 1000 ppm, is used. Do not use chloride calibration solutions as QCS-samples. Dilute suitable volumes of QCS stock solution with deionized water to get QCS samples of appropriate concentrations.

7.7 Laboratory Fortified Blank (LFB) — Commercial standard solution e.g. 984721 Chloride Standard, 1000 ppm, or a self-made standard solution is used. Dilute suitable volumes of LFB stock solution with deionized water to get LFB samples of appropriate concentrations. Do not use chloride calibration solutions as LFB-samples.

8. Sample Collection, Preservation, and Storage

8.1 Collect representative samples in clean, chemically resistant glass or plastic bottles. Volume collected should be sufficient to ensure a representative sample, allow for replicate analysis and minimize waste disposal.

8.2 Sample preservation and holding time requirements for samples.

8.2.1 No preservative is used.

8.2.2 No temperature requirements.

8.2.3 Analyze within 28 days.

9. Quality Control

9.1 Quality control (QC) program — Each laboratory using this method is required to operate a formal quality control (QC) program. The minimum requirements of this program consist of an initial demonstration of laboratory capability and the analysis of laboratory reagent blanks, continuing calibration check standards, fortified blanks, and fortified samples as duplicates as a continuing check on performance. The laboratory is required to maintain performance records that define the quality of the data generated.

9.2 Calibration and calibration verification — Prior to the analysis of samples, calibrate the test and verify the calibration with a second source standard. Recalibration is needed whenever a significant change in the instrument response is expected or observed.

9.2.1 Calibration — calibrate the instrument using a calibration solution diluted to at least five different concentrations that bracket the expected sample concentration. The coefficient of determination (r^2) must be 0.998 or greater and the recoveries of back-calculated values for calibrator levels must be within limits. If limits are not met, determine the problem, and recalibrate the test.

Note: The Gallery analyzer calculates two equations, linear and 2nd order, to fit the results of the analysis of each calibration standard versus the nominal concentration of the analyte in the calibration standards. The best fit is not always linear, so the user can choose a 2nd order equation instead.

Criteria for calibration:	$r^2 \geq 0.998$ % Recovery of back-calculated calibrator level results 90 – 110% or 75 – 125% when c ≤ 2 x Minimum Reporting Level (MRL, see 9.3.3).

9.2.2 Quality Control Sample (QCS) — Secondary, external source standard solution samples (QCS) are used for the verification of the calibration standards and acceptable analyzer performance. QCS´s must be run when beginning the use of this method, whenever new standard materials are used, on a quarterly basis or as required to meet data-quality needs. If the determined concentrations are not within limits, the performance of the determinative step of the method is unacceptable. The source of the problem must be identified and corrected before proceeding with the initial determination of capability or continuing with on-going analyses.

$$\%\text{Recovery} = \frac{C_s}{C} \text{ x } 100$$

where C_s = sample result concentration, mg/L
C = sample theoretical concentration, mg/L

Criteria for QCS %Recovery: 90 – 110 %

9.3 Initial demonstration of capability (IDC) — IDC is used to characterize analyzer performance in an individual laboratory by determination of the operational range and analysis of quality control samples (QCS). Determination of method detection limit (MDL), minimum reporting level (MRL) and the initial precision and recovery (IPR) are used for testing the laboratory performance.

9.3.1 Operational Range — Instrument operational range is to be determined initially and verified every six months or whenever a significant change in the instrument response is expected or observed. The initial demonstration of the operational range must employ a number of standards sufficient to ensure that the results are reproducible and statistically acceptable. The periodic verifications of the operational range must use a minimum of a blank and three standards. If any verification data exceeds the nominal value of the standard by ±10% (or ±25% when c ≤ 2 x MRL), the operational range must be re-established.

Criteria for operational range:	Recovery 90 - 110 % for operational range standard samples or 75 - 125 % when c ≤ 2 x MRL

9.3.2 Method Detection Limit (MDL) — MDL should be established based on a low concentration laboratory fortified blank (LFB) deviation or from laboratory reagent blank (LRB) deviation. First an MDL estimate is calculated as three times the standard deviation of replicate measurements of the reagent water:

$$MDL_{est} = 3 \times (SD_0)$$

where SD_0 = standard deviation of the replicate analyses (n = 10) of reagent water

A laboratory fortified blank sample (LFB) at a concentration which is from two to ten times the MDL_{est} is analyzed in seven replicates during three days. Each individual result must be within 50 – 150 % of the theoretical value and RSD% of results ≤20%. Calculate the MDL from LFB results as follows:

$$MDL_{LFB} = t \times SD$$

where t = Student's t-value for a 99 % confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for 7 replicates]
SD = standard deviation of the replicate analyses

For calculation of RSD%, use the following equation.

$$\%RSD = \frac{100}{\bar{X}} \times \sqrt{\sum_{i=1}^{n} \frac{(X_1 - \bar{X})^2}{n-1}}$$

where $\bar{X}$ = mean of replicate measurements
X_1 = measured value of the replicate
n = number of replicates

Analyze also a laboratory reagent blank (LRB) in seven replicates during three days. MDL value from blank is calculated as follows:

$$MDL_{LRB} = t \times SD$$

where t = Student's t-value for a 99 % confidence level and a standard deviation estimate with n-1 degrees of freedom [t = 3.14 for 7 replicates]
SD = standard deviation of the replicate analyses

Whichever MDL, MDL_{LFB} or MDL_{LRB}, is higher will be selected as method MDL.

MDL should be determined initially or whenever there is a significant change in the background or analyzer response. MDL should be verified quarterly with analysis of LFB at concentration originally used for MDL determination. MDL is verified when the recovery is 50 – 150%.

9.3.3 Minimum Reporting Level (MRL) Confirmation — The minimum concentration that can be reported by a laboratory as a quantified value. The MRL must be at or above the level of the lowest fortified calibrator, where it must meet the criteria set for MRL confirmation. It would also have to be considered that criteria for Laboratory Reagent Blank (LRB) must be met (LRB ≤ 1/2 x MRL).

Fortify and analyze seven replicate LFBs at the proposed MRL concentration. Calculate the mean (Mean) and standard deviation (SD) for these replicates. Determine the Half Range for the Prediction Interval of Results (HR_{PIR}) using the equation:

$$HR_{PIR} = 3.963 \text{ x } SD$$

where SD = standard deviation
3.963 = constant value for seven replicates

Calculate the upper and lower limits for the Prediction Interval of Results (PIR = Mean ± HR_{PIR}) from the results and confirm that the results meet the criteria. Accepted results confirm the verification of MRL.

$$\text{PIR Upper Limit} = \frac{\text{Mean} + HR_{PIR}}{\text{Fortified concentration}} \text{x100}$$

$$\text{PIR Lower Limit} = \frac{\text{Mean} - HR_{PIR}}{\text{Fortified concentration}} \text{x100}$$

Criteria for PIR Limits: The Upper PIR Limit must be ≤ 150 %.
The Lower PIR Limit must be ≥ 50 %

MRL is determined initially and verified with continues analysis of low-level Continuing Calibration Verification (CCV LL) sample at MRL. MRL is verified when the recovery is 75 – 125%. See also 9.4.3 for analyzing CCV. Redetermine MRL if LL CCV is out of limits on regular bases.

9.3.4 Initial Precision and Recovery (IPR) — For initial precision and recovery test the laboratory should analyze four replicate volumes of reagent water spiked with the analyte of interest (LFB). IPR is analyzed every time there are any modifications made to the method and every time a new analyst starts to use the method. If IPR is not within criteria, the source of the problem should be identified and resolved before continuing analyses.

Calculate accuracy as percent recovery with the following equation and precision as relative standard deviation (% RSD) as shown in section 9.3.2.

$$\text{Recovery\%} = \frac{C_s - C}{s}$$

where Cs = spiked sample concentration
C = sample background concentration
s = concentration equivalent of analyte added to sample

Criteria for IPR: Recovery 85 - 115 % or 80 - 120 % when c is ≤ 2 x MRL
% RSD ≤10%

9.4 Ongoing QC — Assessing laboratory performance with ongoing QC includes the use of Laboratory Reagent Blank (LRB) samples, Laboratory Fortified Blank (LFB) samples, Laboratory Fortified Matrix (LFM) samples and Continuing Calibration Verification (CCV) samples. Certified reference material (CRM) is used quarterly if applicable. Many of these QC procedures are done automatically by the analyzer.

9.4.1 Laboratory Reagent Blank (LRB) — The laboratory should analyze at least one LRB with each batch of samples and at minimum every twentieth sample. Data produced is used to assess possible contamination from the laboratory environment. The use of LRB is not relevant for the high concentration test (11.4).

Criteria for LRB: LRB ≤ 1/2 x MRL

9.4.2 On-going Precision and Recovery (OPR) — The laboratory should analyze at least one LFB with each batch of samples and at minimum every twentieth sample. LFB concentrations should be rotated to cover different parts of the used ranges.

Calculate accuracy as percent recovery as shown in section 9.2.2. If the recovery of the analyte falls outside the required control limits, the source of the problem should be identified and resolved before continuing analyses.

Also, the standard deviations (SD) should be monitored regularly and documented.

LFB analysis data is used to assess laboratory performance against the required control limits.

Criteria for OPR: Recovery 85 - 115% or 80 - 120% when c ≤ 2 x MRL

When enough data, preferably twenty or more results, from LFB samples is analyzed as part of method ongoing QC, the laboratory can assign its own control limits from the standard deviation and mean of the results:

Control limits = Mean ± 3 x SD

9.4.3 Continuing Calibration Verification (CCV) — For all determinations the laboratory should analyze a mid-range calibration verification standard (CCV MID) immediately following calibration, after every tenth sample and at the beginning and end of the sample run. Ongoing analyses of the CCV samples verify that the calibration is within limits. In addition, a low-level verification standard (CCV LL) at concentration of the MRL is analyzed daily with the low concentration test (11.3) to verify quantitation at MRL.

If the calibration cannot be verified within the limits specified in the test, the analyzer gives a message of outlier result. In such case reanalyze the CCV samples. If the second analysis of the CCV samples confirms calibration to be outside the limits, sample analysis must be discontinued, the cause determined and/or in the case of drift the analyzer recalibrated. All samples following the last acceptable CCV samples must be reanalyzed, even if the resumed CCV samples are acceptable.

Criteria for CCV: % Recovery 90 – 110% or 75 – 125 %, when c is ≤ 2 x MRL

9.4.4 Laboratory Fortified Matrix Sample (LFM) (also termed Matrix Spike, MS) — The laboratory must add a known amount of analyte to a minimum of 5 % of the tested samples or daily, whichever is more often. The spike sample is done in duplicates (LFMD or MSD) and from same source that was used for LFB.

The spiked sample concentration must not exceed the high calibration standard. Also, the original and spiked sample results should be at minimum two times the MRL. Ideally the new concentration should be at or below the midpoint of the calibration curve. It is preferred to use the same concentrations as for LFB samples to be able to separate the matrix's effect from laboratory performance. In addition, the spike concentration should be from one to five times the sample's original concentration so that the original sample result wouldn't affect too much on the spike recovery result.

If the results for LFM or LFMD are not within criteria, make corrective actions targeted to the sample in question, e.g. dilute, use different method or if reported, add information of crossing criteria.

Calculate the %Recovery for each spike as follows.

$$\text{LFM Recovery \%, R} = \frac{C_s - C \times f}{s} \times 100$$

where
- C_s = spiked sample concentration
- f = spike dilution correction (sample volume per total volume of the spiked sample)
- C = original sample concentration (sample without spike)
- s = concentration equivalent of analyte added to sample (spike)

Note: If the added spike volume is less than 1% of the total LFM sample volume, the factor f can be excluded.

The precision of the LFM determinations is assessed by measuring LFM samples as duplicates (LFMD, also termed Matrix Spike Duplicate or MSD). Precision is then calculated as follows:

$$\%\text{RPD} = 100 \times \frac{\text{LFM}-\text{LFMD}}{\frac{1}{2} \times (\text{LFM}+\text{LFMD})}$$

where LFM = analyte concentration measured in LFM sample
LFMD = analyte concentration measured in LFM duplicate

Criteria for LFM: %Recovery 85 – 115%
%RPD: ≤ 10%

9.4.5 Certified Reference material (CRM) — In order to verify the accuracy of the method, analyze a Certified Reference Material (CRM) as a regular sample (if practical) at least once per quarter in replicates. The concentration of the CRM should be in the concentration mid-range for the chosen method. The matrix of the CRM sample should be similar to the samples analyzed. Each replicate must be taken through the complete analytical test method including any sample preservation and pretreatment steps. Compare the results to the acceptance limits provided by the CRM manufacturer. Also, the method limits must be met.

Criteria for CRM: Limits from the CRM certificate
%Recovery: 85 - 115 % or 80 - 120 %, when c is ≤ 2 x MRL

10. Calibration and Standardization

10.1 Dilute Chloride Calibration Stock with deionized water to get a suitable chloride standard solution for calibration. Use the automated Gallery dilution feature for the calibration curve. Alternatively prepare a series of at least five standards covering the desired range for the calibration curve.

10.2 Process standards and blanks as described in Section 11 Procedure.

10.3 The Gallery analyzer automatically plots analyzer response against standard concentration. The user must accept this calibration curve before the analyzer starts to measure samples. The calibration correlation coefficient shall be equal to or greater than 0.998.

10.4 After the calibration has been established, it must be verified by the analysis of a suitable quality control sample (QCS) before analyzing samples. If measurements exceed ± 10 % of the established value, the analysis should be terminated, and the analyzer recalibrated.

10.5 Also, a low level CCV is analyzed after calibration and at the beginning of daily sample load to verify quantitation at MRL. Sample analysis can be started if the result for CCV LL is also within limits of ± 25 %.

10.6 Ongoing QC is done automatically by the analyzer, and it includes analyzing LRB, LFB and CCV samples with each batch of samples. In addition, LFM samples are to be done in duplicates from at least 5 % of samples or daily whichever is more often. CRM sample is recommended to be analyzed at least once per quarter.

11. Procedure

11.1 Preparation before analysis — Add all required reagents, samples, other consumables, and requests for tests following the analyzer and reagent instructions provided by the manufacturer.

11.2 The reagents and samples needed for the analysis are dispensed automatically according to the pre-defined test to single-use cuvettes, where all the reactions and measurements take place. Incubations are done at 37 °C.

11.3 Gallery Drinking Water Chloride Low test flow — 120 µl of Chloride R1 is dispensed to the cuvette and incubated for 4 minutes. After a blank measurement, 100 µL of sample is added and solution is mixed. After 4 minutes incubation, the absorbance is measured at 480 nm. Suggested test is shown in Appendix A.

11.4 Gallery Drinking Water Chloride High test flow — 120 µl of Chloride R1 is dispensed to the cuvette and incubated for 4 minutes. After a blank measurement, 80 µL of sample is added and solution is mixed. After 4 minutes incubation, the absorbance is measured at 480 nm. Suggested test is shown in Appendix A.

12. Data Analysis and Calculation

12.1 The Gallery analyzer automatically plots the analyzer responses against standard concentrations to create a calibration curve. The analyzer computes sample concentration by comparing sample response with the standard curve.

12.2 Results are reported in mg/L.

13. Method Performance

13.1 The results presented here are from a single laboratory study.

13.2 MDL for the Gallery Drinking Water Chloride method was 0.1 mg/L and MRL was confirmed to be 1.0 mg/L.

13.3 Calibration equation was done as second order and the coefficient of determination (r^2) was 1.000 for low and 0.999 for high calibration. QCS sample had recoveries of 96 - 104% for low and 98 – 105% for high test.

13.4 Initial precision was analyzed to be 0.1 – 2.7 %RSD and recovery 98 – 106 % at multiple concentrations between 2.0 and 300.0 mg/L.

13.5 Recovery for LFB samples from ongoing QC results was 94 -106 % at multiple concentrations between 2.0 and 300.0 mg/L and 94 - 99% at concentrations ≤2 mg/L

13.6 CCV LL standard at MRL 1.0 mg/L had recoveries 82 - 96 %, CCV MID 97 - 105 % and LRB was always below 1/2 of MRL – 0.2 mg/L at maximum.

13.7 Method limits for QCS recovery are 90 – 110% and for LFB and LFM samples 85 – 115 % (80 – 120 % when c is ≤ 2 x MRL) and maximum 10 % RSD or % RPD. For CCV mid-level 90 - 110 % Recovery limit is used and 75 – 125 % when c is ≤ 2 x MRL. LRB must be below or equal to one half of the MRL.

14. Pollution Prevention

14.1 The analyzer uses small amounts of reagents, which significantly reduces the quantity of wastes compared to manual methods or flow analyzers. The small packing size facilitates the use of reagents during their shelf lives and thus reduces disposal costs of unused materials.

14.2 If reagents are self-prepared in the laboratory, the used amounts should be as small as possible.

15. Waste Management

15.1 Excess reagents, samples and method process wastes should be characterized and disposed of in an acceptable manner according to local regulations.

15.2 Note! Mercuric thiocyanate is very toxic to aquatic life with long lasting effects. The final concentration of Mercuric thiocyanate in the Chloride reagent is 0.063 %

15.3 The containers for cuvette and liquid waste must be emptied and rinsed with water at the end of the day.

16. References

1. 4500-Cl- B. Chloride /Argentometric Method. Standard Methods for the Examination of Water and Wastewater, 23rd Edition, American Public Health Association (APHA), 2017.

2. Code of Federal Regulations: Title 40 Appendix A to Subpart C of Part 141, Alternative Testing Methods for Contaminants Listed at 40 CFR 143.4(b)

3. Code of Federal Regulations 40 § 143.4. Inorganic chemical sampling and analytical requirements.

4. ISO 15682:2000(E) – Water Quality – Determination of chloride by flow analysis (CFA and FIA) and photometric or potentiometric detection.

5. Standard Methods for the Examination of Water and Wastewater - Part 4500-Cl^-: Chloride (2017).

6. Standing Committee of Analysts (SCA) blue books - Chloride in Waters, Sewage and Effluents (1981) ISBN 0117516260.Code of Federal Regulations 40 § Appendix B to Part 136 — Definition and Procedure for the Determination of the Method Detection Limit – Revision 1.11.

7. 4020 Quality Assurance/Quality Control. Standard Methods for the Examination of Water and Wastewater, 23rd Edition, American Public Health Association (APHA), 2017.

8. 1020-B. Quality Assurance/Quality Control. Standard Methods for the Examination of Water and Wastewater, 23rd Edition, American Public Health Association (APHA), 2017.

9. Winslow, S. D.; Pepich, B. V.; Martin, J. J.; Hallberg, G. R.; Munch, D. J.; Frebis, C. P.; Hedrick, E. J.; Krop, R. A. "Statistical Procedures for Determination and Verification of Minimum Reporting Levels for Drinking Water Methods." Environmental Science & Technology 2006, 40, 281.

17. Test protocols and performance data

17.1 Method performance tests were done with a Gallery test following this method. See chapter 11.

17.2 Method performance data

Method performance study was done in a single laboratory using reagent water based standard samples and tap water samples. Results of this study are presented in the following tables and graphs. All acceptance criteria of the method were met.

Notes: Although Thermo Fisher Scientific publishes method performance data, including MDL and precision, we cannot guarantee that each laboratory will be capable of meeting such performance. Individual laboratory and instrument conditions play a major role in determining method performance. This support data serves as a guide to the potential method performance. Some laboratories may not be able to reach this level of performance for various reasons, while other laboratories may exceed it.

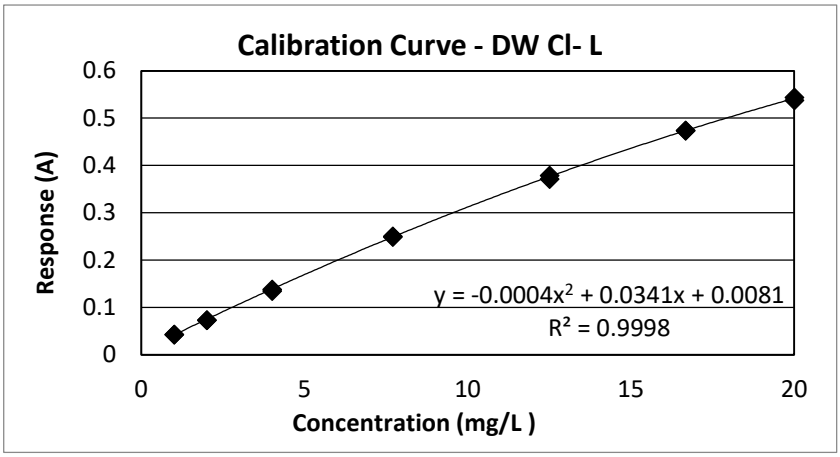


Figure 1A. Calibration curve for DW Cl- L -test.

Table 1. Results for QCS samples after calibration of DW Cl- L -test.

QCS-sample	Result (mg/L)	% Recovery
Cl- QCS 4	3.9	97 %
Cl- QCS 18	17.7	98 %

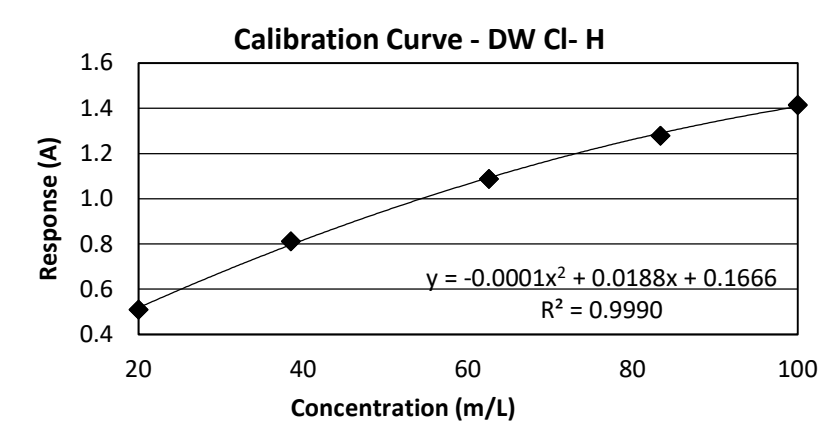


Figure 1B. Calibration curve for DW Cl- H -test.

Table 1B. Results for QCS samples after calibration of DW Cl- H -test.

QCS-sample	Result (mg/L)	% Recovery
Cl- QCS 30	31.4	105 %
Cl- QCS 90	87.8	98 %

Table 2. MDL results for DW CL- Method. MDL was tested according to 40 CFR Part 136 Appendix B [4].

Sample:	Results (mg/L) 0.4 mg/l LFB	Results (mg/L) LRB
Average	0.41	0.13
Min	0.37	0.09
Max	0.43	0.16
n	7	7
std. deviation (SD)	0.02	0.02
MDL (LFB / LRB)	**0.07**	**0.06**

Table 3. Results for MRL confirmation for Drinking Water Chloride Method.

Sample	Result (mg/L)	% Recovery	
LFB 1.0 mg/L	0.94	94 %	
LFB 1.0 mg/L	0.92	92 %	
LFB 1.0 mg/L	0.93	93 %	
LFB 1.0 mg/L	0.93	93 %	
LFB 1.0 mg/L	0.93	93 %	
LFB 1.0 mg/L	0.94	94 %	
LFB 1.0 mg/L	0.93	93 %	
Average	0.93	93 %	
n	7		
Std. deviation (SD)	0.004		
HR_{PIR}	0.018		
Upper PIR Limit	**95 %**	**≤ 150 %**	**MRL 1.0 mg/L confirmed**
Lower PIR Limit	**91 %**	**≥ 50 %**	**MRL 1.0 mg/L confirmed**

Criteria for PIR Limits: The Upper PIR Limit must be ≤ 150 %.
The Lower PIR Limit must be ≥ 50 %

Table 4. Results for operational range study.

Calibration range 0 - 20 mg/L			All samples were analyzed in triplicates. Also individual %Recoveries were within acceptable limits.		
Nominal value, mg/L	**Result, mg/L**	**Average Recovery**			
0*	0.4				
0.9*	0.9	**99 %**			
1.0	1.0	**97 %**			
2.0	1.8	**92 %**			
5.0	5.0	**99 %**			
10.0	10.1	**101 %**			
15.0	14.9	**99 %**			
18.0	18.0	**100 %**			
20.0	20.0	**100 %**			
30*	29.4	**98 %**			
Calibration range 20 - 100 mg/L			**Extended range 100 - 500 mg/L**		
Nominal value, mg/L	**Result, mg/L**	**Average Recovery**	**Nominal value, mg/L**	**Result, mg/L**	**Average Recovery**
18.0*	17.3	**96 %**	100	98	**98 %**
20.0	19.5	**97 %**	110	116	**105 %**
30.0	30.8	**103 %**	250	260	**104 %**
70.0	69.9	**100 %**	400	401	**100 %**
100.0	100.5	**100 %**	500	505	**101 %**
110.0*	116.7	**106 %**	550*	559	**102 %**

*) Above / below range limits

Criteria for operational range:	90 - 110 %Recovery for operational range standard samples or 75 - 125 % when c ≤ 2 x MRL

Table 5. IPR Results for DW Cl- L and DW Cl- H tests. n = 4 per sample.

Sample	Test	Average Recovery	Min. Recovery	Max. Recovery	RSD
Cl- LFB 2	DW Cl- L	101 %	100 %	101 %	0.5 %
Cl- LFB 18	DW Cl- L	99 %	98 %	101 %	1.3 %
Cl- LFB 30	DW Cl- H	102 %	102 %	103 %	0.1 %
Cl- LFB 90	DW Cl- H	104 %	100 %	106 %	2.7 %
Cl- LFB 300 (dil. 1+4)	DW Cl- H	102 %	99 %	103 %	1.9 %

Criteria for IPR: Recovery 85 - 115 % or 80 - 120 % when c is ≤ 2 x MRL
% RSD ≤10%

Table 6. OPR Results for DW CL- method.

Sample	Average Recovery	Min. Recovery	Max. Recovery	n	RSD
Cl- LFB 2	96 %	94 %	99 %	22	1.2 %
Cl- LFB 4	97 %	94 %	98 %	7	1.8 %
Cl- LFB 18	100 %	97 %	102 %	33	1.3 %
Cl- LFB 30	104 %	101 %	106 %	23	1.5 %
Cl- LFB 90	101 %	98 %	104 %	20	1.9 %
Cl- LFB 300 (dil. 1+4)	103 %	102 %	103 %	4	0.2 %

Criteria for OPR: Recovery 85 - 115 % or 80 - 120 % when c ≤ 2 x MRL
%RSD ≤ 10%

Table 7. LRB result summary.

Sample: LRB	Results (mg/L)
Avg. Result	0.10
Min. Result	0.03
Max. Result	0.23
n	31
Limit LRB ≤ 1/2 x MRL	≤ 0.5

Criteria for LRB: ≤ 1/2 x MRL

Table 8. CCV result summary.

Sample	Average Recovery	Min. Recovery	Max. Recovery	n	RSD
Cl- L-CCC LL (1 mg/L)	90 %	82 %	96 %	31	3.8 %
Cl- L-CCC MID (10 mg/l)	101 %	97 %	103 %	33	1.6 %
Cl- H-CCC MID (50 mg/l)	102 %	98 %	105 %	18	1.9 %

Criteria for CCV: % Recovery 90 – 110% or 75 – 125 %, when c is ≤ 2 x MRL

Table 9. LFM results for DW Cl- tests. D = duplicate sample.

Sample*	Application	Results, mg/L	Theoretical value, mg/l corrected for spike volume	Spike Recovery	RPD
Tap water 1	DW Cl- L	5.0			
Tap water 1 +10	DW Cl- L	14.9	15.0	**99 %**	**0.6 %**
Tap water 1+10 D	DW Cl- L	14.8	15.0	**98 %**	
Tap water 1 +50	DW Cl- H	56.3	54.8	**103 %**	**1.2 %**
Tap water 1 +50 D	DW Cl- H	55.6	54.8	**102 %**	
Tap water 2	DW Cl- H	125.8			
Tap water 2 +10	DW Cl- H	134.4	135.8	**98 %**	**0.4 %**
Tap water 2 +10 D	DW Cl- H	135.0	135.8	**104 %**	
Tap water 2 +50	DW Cl- H	175.8	169.9	**112 %**	**0.5 %**
Tap water 2 +50 D	DW Cl- H	174.8	169.9	**111 %**	
Tap water 3	DW Cl- H	27.3			
Tap water 3 +10	DW Cl- H	37.7	37.3	**107 %**	**0.5 %**
Tap water 3 +10 D	DW Cl- H	37.9	37.3	**109 %**	
Tap water 3 +50	DW Cl- H	77.7	76.0	**104 %**	**0.7 %**
Tap water 3 +50 D	DW Cl- H	77.2	76.0	**103 %**	

Criteria for LFM: %Recovery 85 – 115%
%RPD: ≤ 10%

*) Samples: Treated drinking water sample from surface water source (Tap water 1), treated drinking water sample from ground water source with high hardness of 254 mg $CaCO_3$ / L (Tap water 2) and treated drinking water sample from surface water source with high total organic carbon (TOC) of 2.3 mg/L (Tap water 3).

Table 10. CRM results. n = 4 per sample

Sample	**ERA CRM 698**	
Nominal value, mg/L	118	
Application	**DW Cl- L**	**DW Cl- H**
Dilution, 1+	10.79	1.36
Average, mg/L	114	119
RSD	1.0 %	0.3 %
Recovery	**97 %**	**100 %**

Criteria for CRM: Limits from the CRM certificate 104 – 133 mg/L
%Recovery: 85 - 115 % or 80 - 120 %, when c is ≤ 2 x MRL

APPENDIX A.

DW Chloride Low test for the Gallery analyzers:

thermo scientific

Test parameters

DW Cl- L Version number 1.1

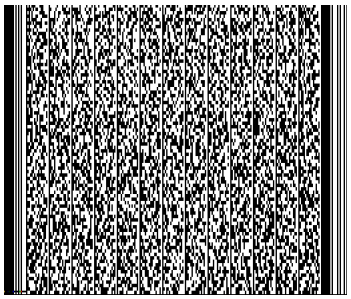
Gallery™ * NSDWR application
Thermo Fisher Scientific Oy
Prior to change

Date 19.6.2023
Time 14.27.38 **Software version:8.1.0.0**

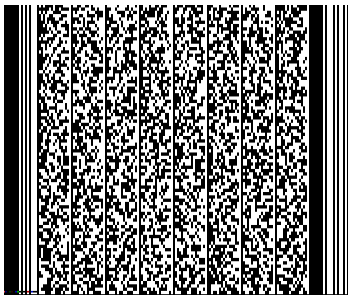
Info

Tag	INT001
Last time changed	19.6.2023 14.23
User name	Test designer
Full name	DW Chloride Low
In use	No
Type	Photometric
Online name	
Acceptance	Manual
Result unit	mg/l
Number of decimals	2
Correction factor	1
Correction bias	0

Barcode 1



Barcode 2



Sample type

Flow

Blank type Yes Primary dilution 1 + 0 Dispensed volume 220

Reagent	Reagent	Volume (µl)	Dispense with	Extra volume (µl)	Syringe speed	Replacing reagent
	Chloride R1	120	Extra	40	Normal	None
	Barcode ID	Alarm limit (ml)	Onboard stability (days)			
	A03	2,0	5			
Incubate	Time (sec)	Actual time (sec)				
	240	234				
End-point blank	Blank resp. min.(A)	Blank resp. max.(A)				
	*	*				
Sample	Volume (µl)	Dispense with	Extra volume (µl)	Extra wash		
	100	Extra	40	No		
Incubate	Time (sec)	Actual time (sec)				
	240	234				
End-point measurement	Main wavelength (nm)	Side wavelength (nm)	Residual net abs. (A)			
	480	None	0			

*) Gallery™ includes Gallery, Gallery Aqua Master, Gallery Plus and Gallery Plus Aqua Master

Test parameters

DW Cl- L Version number 1.1

Gallery™ * NSDWR application
Thermo Fisher Scientific Oy
Prior to change

Date 19.6.2023
Time 14.27.38 **Software version:8.1.0.0**

Dilution

Dilution with	Water
Primary dilution 1 +	0

Limits

	Measuring range (mg/l) Min	Max		Next dilution ratio (1+) Low	High
Primary dilution	*	*		*	*
2nd dilution	*	*		*	*
3rd dilution	*	*		*	*
4th dilution	*	*		*	*
Test limit	*	20,000	mg/l		
Critical limit	*	*	mg/l		
Init. abs.	*	2,5	A		

Calibration

Calibration type	2nd order
Repeat time (days)	1
Points/calibrator	Duplicate
Acceptance	Manual
Calibration order	Ascending

Abs. error (A)	*
Rel. error (%)	*
Factor limit min.	*
Factor limit max.	*

Nbr	Calibrator	Current lot	Concentration	Dilution 1 +
1	Cl- Low-cal	Default	100,000	4
2	Cl- Low-cal	Default	100,000	5
3	Cl- Low-cal	Default	100,000	7
4	Cl- Low-cal	Default	100,000	12
5	Cl- Low-cal	Default	100,000	24
6	Cl- Low-cal	Default	100,000	49
7	Cl- Low-cal	Default	100,000	99

Coeff. of det. min.	0,998
RSE max. (%)	*

QC

*) Gallery™ includes Gallery, Gallery Aqua Master, Gallery Plus and Gallery Plus Aqua Master

Test parameters

DW Cl- L Version number 1.1

Gallery™ * NSDWR application
Thermo Fisher Scientific Oy
Prior to change

Date 19.6.2023
Time 14.27.38
Software version:8.1.0.0

Procedure	Cal QC	QC profile	Cl- Cal QC
Interval type		In use	Yes
Requests		Acceptance	Manual
Time (hh:mm)	0.00	Trigger	Manual,Calibration

Procedure	CCV LL	QC profile	Cl- CCV LL
Interval type		In use	Yes
Requests		Acceptance	Manual
Time (hh:mm)	0.00	Trigger	Manual,Start of run

Procedure	Ongoing QC	QC profile	Cl- L
Interval type	Requests	In use	Yes
Requests	20	Acceptance	Manual
Time (hh:mm)	0.00	Trigger	Manual,Interval,Reagent lot change,Reagent vial change,Start of run,End of run

Procedure	Control	Current Lot	Conc.	SD	Req. count	Run group
Cal QC	Cl- L CCV M	Default	10,00	0,500	1	All
Cal QC	Cl- CCV LL	Default	1,00	0,125	1	All
Cal QC	Cl- QCS 18	Default	18,00	0,900	1	All
Cal QC	Cl- QCS 4	Default	4,00	0,200	1	All
CCV LL	Cl- CCV LL	Default	1,00	0,125	1	All
Ongoing QC	Cl- L CCV M	Default	10,00	0,500	1	All
Ongoing QC	LRB	Default	0,00	0,250	1	All
Ongoing QC	Cl- LFB 2	Default	2,00	0,200	1	1
Ongoing QC	Cl- LFB 18	Default	18,00	1,350	1	2

Procedure	Nbr of controls	SD multiplier
Cal QC	1	2
CCV LL	1	2
Ongoing QC	1	2

*) Gallery™ includes Gallery, Gallery Aqua Master, Gallery Plus and Gallery Plus Aqua Master

DW Chloride High test for the Gallery analyzers:

thermo scientific

Test parameters

DW Cl- H Version number 1.1

Gallery™ * NSDWR application

Thermo Fisher Scientific Oy

Prior to change

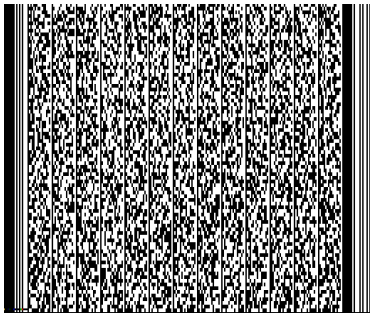
Date 19.6.2023

Time 14.28.03 **Software version:8.1.0.0**

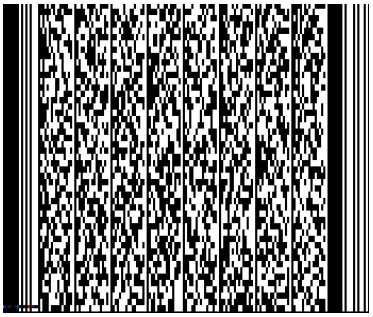
Info

Tag	INT002
Last time changed	19.6.2023 14.24
User name	Test designer
Full name	DW Chloride High
In use	No
Type	Photometric
Online name	
Acceptance	Manual
Result unit	mg/l
Number of decimals	2
Correction factor	1
Correction bias	0

Barcode 1



Barcode 2



Sample type

Flow

Blank type Yes Primary dilution 1 + 0 Dispensed volume 200

Reagent	Reagent	Volume (µl)	Dispense with	Extra volume (µl)	Syringe speed	Replacing reagent
	Chloride R1	120	Extra	40	Normal	None
	Barcode ID	Alarm limit (ml)	Onboard stability (days)			
	A03	2,0	5			
Incubate	Time (sec)	Actual time (sec)				
	240	234				
End-point blank	Blank resp. min.(A)	Blank resp. max.(A)				
	*	*				
Sample	Volume (µl)	Dispense with	Extra volume (µl)	Extra wash		
	80	Extra	50	No		
Incubate	Time (sec)	Actual time (sec)				
	240	234				
End-point measurement	Main wavelength (nm)	Side wavelength (nm)	Residual net abs. (A)			
	480	None	0			

*) Gallery™ includes Gallery, Gallery Aqua Master, Gallery Plus and Gallery Plus Aqua Master

thermo scientific

Test parameters

DW Cl- H Version number 1.1

Gallery™ * NSDWR application
Thermo Fisher Scientific Oy
Prior to change

Date 19.6.2023
Time 14.28.03

Software version:8.1.0.0

Dilution

Dilution with	Water
Primary dilution 1 +	0

Limits

	Measuring range (mg/l) Min	Max		Next dilution ratio (1+) Low	High
Primary dilution	*	100,000		*	4,0
2nd dilution	*	*		*	*
3rd dilution	*	*		*	*
4th dilution	*	*		*	*
Test limit	20,000	500,000	mg/l		
Critical limit	*	*	mg/l		
Init. abs.	*	2,5	A		

Calibration

Calibration type	2nd order
Repeat time (days)	1
Points/calibrator	Duplicate
Acceptance	Manual
Calibration order	Ascending

Abs. error (A)	*
Rel. error (%)	*
Factor limit min.	*
Factor limit max.	*

Nbr	Calibrator	Current lot	Concentration	Dilution 1 +
1	Cl- High-cal	Default	500,000	24
2	Cl- High-cal	Default	500,000	12
3	Cl- High-cal	Default	500,000	7
4	Cl- High-cal	Default	500,000	5
5	Cl- High-cal	Default	500,000	4

Coeff. of det. min. 0,998

RSE max. (%) *

QC

*) Gallery™ includes Gallery, Gallery Aqua Master, Gallery Plus and Gallery Plus Aqua Master

thermo scientific

Test parameters

DW Cl- H Version number 1.1

Gallery™ * NSDWR application
Thermo Fisher Scientific Oy
Prior to change

Date 19.6.2023
Time 14.28.03

Software version:8.1.0.0

Procedure	Cal QC	QC profile	Cl- Cal QC
Interval type		In use	Yes
Requests		Acceptance	Manual
Time (hh:mm)	0.00	Trigger	Manual,Calibration

Procedure	Ongoing QC	QC profile	Cl- H
Interval type	Requests	In use	Yes
Requests	20	Acceptance	Manual
Time (hh:mm)	0.00	Trigger	Manual,Interval,Reagent lot change,Reagent vial change,Start of run,End of run

Procedure	Control	Current Lot	Conc.	SD	Req. count	Run group
Cal QC	Cl- H CCV M	Default	50,00	2,500	1	All
Cal QC	Cl- QCS 30	Default	30,00	1,500	1	All
Cal QC	Cl- QCS 90	Default	90,00	4,500	1	All
Ongoing QC	Cl- H CCV M	Default	50,00	2,500	1	All
Ongoing QC	Cl- LFB 30	Default	30,00	2,250	1	1
Ongoing QC	Cl- LFB 90	Default	90,00	6,750	1	2

Procedure	Nbr of controls	SD multiplier
Cal QC	1	2
Ongoing QC	1	2

*) Gallery™ includes Gallery, Gallery Aqua Master, Gallery Plus and Gallery Plus Aqua Master