



Method 8113

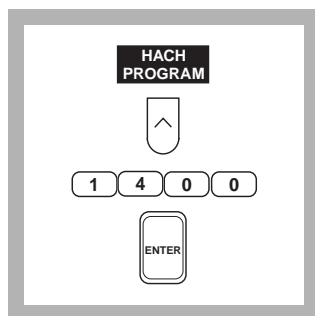
Mercuric Thiocyanate Method*

(0 to 25.00 mg/L Cl⁻)

Scope and Application: For water and wastewater.

The estimated detection limit for program number 1400 is 0.24 mg/L Cl⁻.

* Adapted from Zall, et. al., *Analytical Chemistry*, 28 (11) 1665 (1956)



1. Press the soft key under **HACH PROGRAM**.

Select the stored program number for chloride (Cl⁻) by pressing **1400** with the numeric keys.

Press: **ENTER**

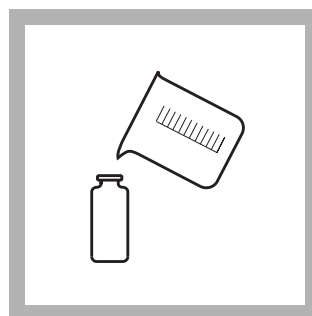
Note: If samples cannot be analyzed immediately, see *Sample Collection, Storage and Preservation* following these steps.

Note: The Flow Cell and Sipper Modules cannot be used with this procedure.



2. The display will show:
HACH PROGRAM: 1400 Chloride

The wavelength (λ), **455 nm**, is automatically selected.



3. Fill a sample cell with 25 mL of sample (the prepared sample).

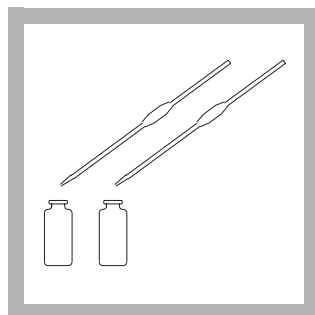
Note: Filter turbid samples through moderately rapid filter paper before analysis.

Note: For proof of accuracy, use a 10.0 mg/L chloride standard solution (see *Accuracy Check*) in place of the sample.

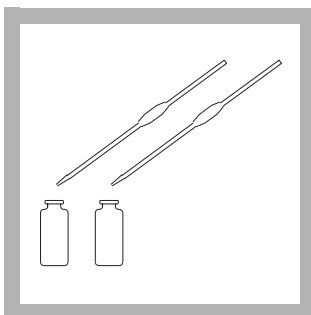
Note: For best results, determine a reagent blank for each new lot of reagent as follows. Prepare a reagent blank by repeating steps 3 through 10, using deionized water as the sample. Zero the instrument on deionized water by pressing the soft key under **ZERO**. Insert the reagent blank and the blank value will be displayed. Correct for the reagent blank by pressing the soft keys under **OPTIONS, (MORE)**, and then **BLANK:OFF**. Enter the reagent blank value and press **ENTER**. Repeat for each new lot of reagent.



4. Fill another sample cell with 25 mL of deionized water (the blank).

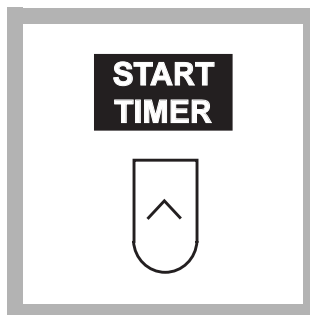


5. Pipet 2.0 mL of Mercuric Thiocyanate Solution into each sample cell. Swirl to mix.



6. Pipet 1.0 mL of Ferric Ion Solution into each sample cell. Swirl to mix.

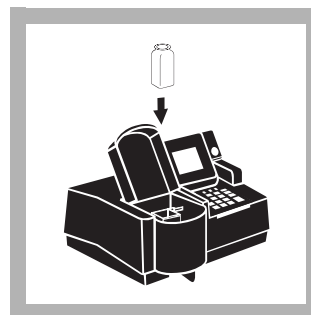
Note: An orange color will develop if chloride is present.



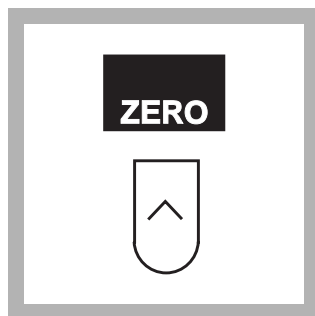
7. Press the soft key under **START TIMER**.

A 2-minute reaction period will begin.

Note: Read the sample within 5 minutes after the timer beeps.



8. Place the blank into the cell holder. Close the light shield.



9. Press the soft key under **ZERO**.

The display will show:

0.00 mg/L Cl⁻

Note: If you are using a reagent blank correction, the display will show the correction.

Note: For alternate concentration units, press the soft key under **OPTIONS**. Then press the soft key under **UNITS** to scroll through the available options. Press **ENTER** to return to the read screen.



10. Place the prepared sample into the cell holder. Close the light shield. Results in mg/L chloride (or chosen units) will be displayed.

Interferences

Table 1 Interfering Substances and Suggested Treatments

Interfering Substance	Interference Levels and Treatments
Extreme pH	<p>Should be about 2</p> <p>If the sample is strongly acidic or alkaline, adjust a portion of sample before testing to a pH of about 7. Use either 5.0 N Sodium Hydroxide Standard Solution or a 1:5 dilution of perchloric acid. Use pH paper, as most pH electrodes will contaminate the sample with chloride.</p>

Sample Collection, Storage and Preservation

Collect samples in glass or plastic containers. Samples can be stored for at least 28 days at room temperature.

Accuracy Check

Standard Additions Method

- Leave the unspiked sample in the sample compartment. Verify that the units displayed are in mg/L. Select standard additions mode by pressing the soft keys under **OPTIONS, (MORE)** and then **STD ADD**.
- Press **ENTER** to accept the default sample volume (mL), 25.
- Press **ENTER** to accept the default standard concentration (mg/L), 1000.
- Press the soft key under **ENTRY DONE**.
- Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of 1000-mg/L Chloride Standard Solution, respectively, to three 25-mL samples and mix each thoroughly.
- Analyze each standard addition sample as described above. Accept the standard additions reading by pressing the soft key under **READ** each time. Each addition should reflect approximately 100% recovery.
- After completing the sequence, the display will show the extrapolated concentration value and the “best-fit” line through the standard additions data points, accounting for matrix interferences.
- See Section 1.4.1 *Standard Additions* for more information.

Standard Solution Method

Prepare a 10.00-mg/L chloride standard solution by pipetting 5.00 mL of Chloride Standard Solution, 1000-mg/L, into a 500-mL volumetric flask and diluting to the mark with deionized water. Use Class A glassware. Perform the chloride procedure as described above.

To adjust the calibration curve using the reading obtained with the 10.00-mg/L standard solution, press the soft keys under **OPTIONS, (MORE)** then **STD: OFF**. Press **ENTER** to accept the displayed concentration, the value of which depends on the selected units. If an alternate concentration is used, enter the actual concentration and press **ENTER** to return to the read screen. See Section 1.5.5 *Adjusting the Standard Curve* for more information.

Method Performance

Precision

Standard: 10.00 mg/L Cl⁻

Program	95% Confidence Limits
1400	9.84–10.16 mg/L Cl ⁻

For more information on determining precision data and method detection limits, refer to Section 1.5.

Estimated Detection Limit

Program	EDL
1400	0.24 mg/L Cl ⁻

For more information on derivation and use of Hach's estimated detection limit, see Section 1.5.2. To determine a method detection limit (MDL) as defined by the 40 CFR part 136, Appendix B, see Section 1.5.1.

Sensitivity

Program Number: 1400

Portion of Curve:	ΔAbs	ΔConcentration
0.010 Abs	0.010	0.122 mg/L
12.50 mg/L	0.010	0.338 mg/L
22.50 mg/L	0.010	0.544 mg/L

See Section 1.5.3 *Sensitivity Explained* for more information.

Calibration Standard Preparation

To perform a chloride calibration using the mercuric thiocyanate method, prepare a 100.0-mg/L chloride stock solution by pipetting 50.00 mL of 1000-mg/L Chloride Standard Solution into a 500-mL volumetric flask using Class A glassware. Dilute to the mark with deionized water and mix thoroughly.

Prepare calibration standards containing 3.00, 6.00, 9.00, 12.00, 15.00, 18.00, and 20.00 mg/L Cl⁻ as follows:

- Into seven different 100-mL volumetric flasks, pipet 3.00, 6.00, 9.00, 12.00, 15.00, 18.00, and 20.00 mL of the 100.0-mg/L Cl⁻ stock solution using Class A glassware.
- Dilute to the mark with deionized water and mix thoroughly.
- Using the mercuric thiocyanate method and the calibration procedure described in the *User-Entered Programs* section in the *DR/4000 Spectrophotometer Instrument Manual*, generate a calibration curve from the standards prepared above.

Summary of Method

Chloride in the sample reacts with mercuric thiocyanate to form mercuric chloride and liberate thiocyanate ion. Thiocyanate ions react with the ferric ions to form an orange ferric thiocyanate complex. The amount of this complex is proportional to the chloride sample concentration. Chloride at these levels also can be determined directly using the Chloride Ion Selective Electrode (Cat. No. 50255-00).

Safety

Good safety habits and laboratory techniques should be used throughout the procedure. Consult the *Material Safety Data Sheet* for information specific to the reagents used. For additional information, refer to *Section 1*.

Pollution Prevention and Waste Management

Both the sample and the blank will contain mercury (D009) at a concentration regulated as a hazardous waste by the Federal RCRA. Do not pour these solutions down the drain. See *Section 3* for more information on proper disposal of these materials.

CHLORIDE, continued

REQUIRED REAGENTS AND STANDARDS

	Cat. No.
Chloride Reagent Set (50 Tests*).....	23198-00
Includes: (1) 22122-42, (1) 22121-29	

Description	Quantity Required		Unit	Cat. No.
	per test			
Ferric Ion Solution	2 mL	100	mL	22122-42
Mercuric Thiocyanate Solution	4 mL	200	mL	22121-29
Water, deionized	25 mL	4	liters	272-56

REQUIRED EQUIPMENT AND SUPPLIES

DR/4000 1-Inch Cell Adapter	1	each.....	48190-00
Pipet, volumetric, Class A, 1.00-mL	1	each.....	14515-35
Pipet, volumetric, Class A, 2.00-mL	1	each.....	14515-36
Pipet Filler, safety bulb.....	1	each.....	14651-00
<i>or</i>			
Pipet, TenSette, 0.1 to 1.0 mL	1	each.....	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	1	50/pkg.....	21856-96

OPTIONAL REAGENTS AND STANDARDS

Chloride Standard Solution, 1000-mg/L Cl ⁻	500 mL	183-49
Chloride Standard Solution, 2-mL Voluette Ampule, 12,500-mg/L Cl ⁻	20/pkg	14250-20
Perchloric Acid, ACS, 70%	680 g	757-65
Sodium Hydroxide Standard Solution, 5.0 N	50 mL DB	2450-26

OPTIONAL EQUIPMENT AND SUPPLIES

Combination Chloride Electrode	each	50255-00
DR/4000 Carousel Module Kit	each	48070-02
Filter Paper, folded, 12.5-cm	100/pkg	692-57
Flask, Erlenmeyer, 125-mL	each	505-43
Flask, volumetric, 100-mL, Class A	each	14574-42
Flask, volumetric, 100-mL, Class A	6/pkg	14574-72
Flask, volumetric, 500-mL, Class A, with glass stopper	each	14574-49
Funnel, analytical, filtering, polypropylene, 75-mm	each	1083-68
pH Paper, 1.0 to 11.0 pH	5 rolls/pkg	391-33

OPTIONAL EQUIPMENT AND SUPPLIES

Pipet, volumetric, Class A, 3.00-mL	each	14515-03
Pipet, volumetric, Class A, 5.00-mL	each	14515-37
Pipet, volumetric, Class A, 6.00-mL	each	14515-06
Pipet, volumetric, Class A, 9.00-mL	each	14515-09
Pipet, volumetric, Class A, 15.00-mL	each	14515-39
Pipet, volumetric, Class A, 20.00-mL	each	14515-20
Pipet, volumetric, Class A, 50.00-mL	each	14515-41

* 50 tests equals 25 samples and 25 blanks.



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