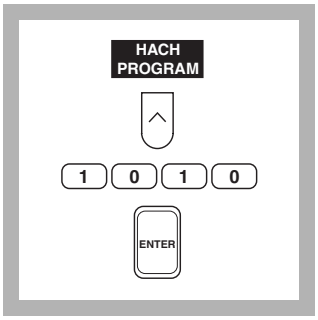
ALUMINUM

Method 8326 **Eriochrome Cyanine R Method***

Powder Pillows **(0 to 0.250 mg/L Al^{3+})**

Scope and Application: *For water. The estimated detection limit for program number 1010 is 0.002 mg/L Al^{3+}.*

* Adapted from *Standard Methods for the Examination of Water and Wastewater*



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

Select the stored program for aluminum (Al), ECR by pressing **1010** with the numeric keys.

Press: **ENTER**

Note: *If samples cannot be analyzed immediately, see following these steps. Adjust the pH of preserved samples before analysis.*

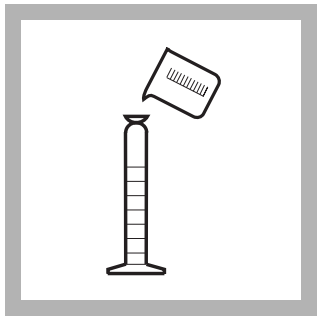
Note: *The Flow Cell and Sipper Modules cannot be used for this procedure.*

2. The display will show:

HACH PROGRAM: 1010 Aluminum, ECR

The wavelength (λ), **535 nm**, is automatically selected.

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 12, 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.*

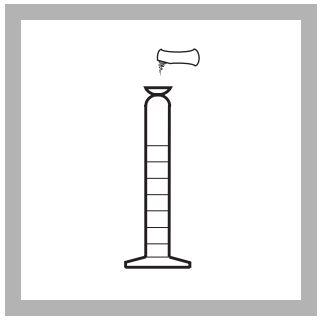


3. Fill a 25-mL graduated mixing cylinder to the 20-mL mark with sample.

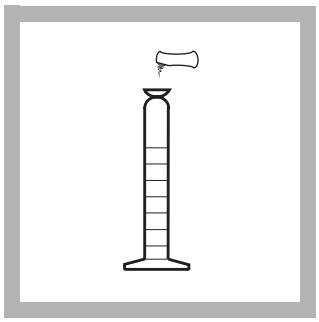
Note: *Rinse cylinder with 1:1 hydrochloric acid and deionized water before use to avoid errors due to contaminants absorbed on the glass.*

Note: *The sample temperature must be between 20-25 °C (68-77 °F) for accurate results.*

Note: *For proof of accuracy, use a 0.1 mg/L aluminum standard solution (preparation given in the Accuracy Check* section*) in place of the sample.*

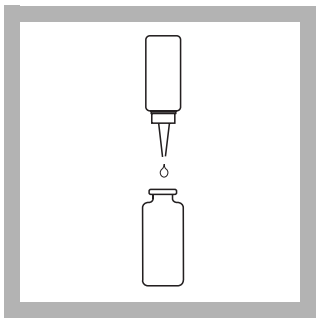


4. Add the contents of one ECR Reagent Powder Pillow for 20-mL sample size. Stopper. Invert several times to dissolve powder. Then press the soft key under ***START TIMER***. A 30-second reaction period will begin.



5. Add the contents of one Hexamethylenetetramine Buffer Reagent Powder Pillow for 20-mL sample size. Stopper. Invert repeatedly until the powder is dissolved.

Note: *A red-orange color will develop if aluminum is present.*

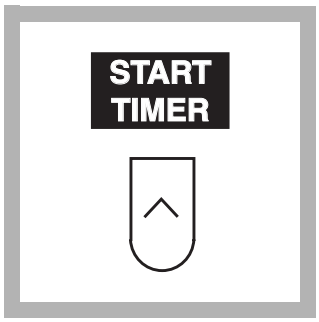


6. Put 1 drop of ECR Masking Reagent Solution into a clean sample cell. This will become the blank.

7. Pour 10 mL from the mixing cylinder into the sample cell with the ECR Masking Reagent (the blank). Swirl to mix.

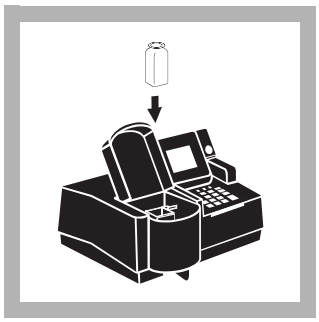
Note: *The solution will start to turn yellow.*

8. Fill a second sample cell to the 10-mL mark with the remaining solution in the cylinder (the prepared sample).

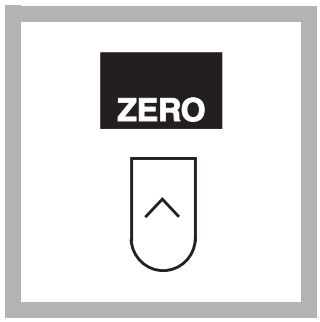


9. Press the soft key under ***START TIMER.***

A 5-minute reaction period will begin.



10. Within five minutes after the timer beeps, place the blank in the cell holder.
Close the light shield.



11. Press the softkey under ***ZERO.***

The display will show:

0.000 mg/L Al^{3+}

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 softkey under* ***UNITS*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*

12. Immediately place the prepared sample into the cell holder.
Close the light shield.
Results in mg/L aluminum (or chosen units) will be displayed.

Note: *If fluoride is present, it needs to be measured and the actual aluminum value determined from Table 2.*

Note: *The results can be expressed as mg/L aluminum oxide (Al_2O_3). Press the soft key under* ***OPTIONS****, then under* ***FORM:*** *to scroll through the available options. Press* **ENTER** *to return to the read screen.*

Interferences

Table 1 Interfering Substances and Suggested Treatments

Interfering Substance	Interference Levels and Treatments
Acidity	Greater than 62 mg/L as $CaCO_2$
Alkalinity	Greater than 750 mg/L as $CaCO_3$
Ca^{2+}	Greater than 1000 mg/L as $CaCO_3$
Cl^-	Greater than 1000 mg/L
Cr^{6+}	0.2 mg/L (error is -5% of reading)
Cu^{2+}	2 mg/L (error is -5% of reading)
Fe^{2+}	Greater than 4 mg/L (error is positive and = mg/L Fe^{2+} x 0.0075)
Fe^{3+}	Greater than 4 mg/L (error is positive and = mg/L Fe^{3+} x 0.0075)
F^-	See *Table 2*.
Hexameta-phosphate	0.1 mg/L as PO_4^{3-} (error is -5% of reading)
Mg^{2+}	Greater than 1000 mg/L as $CaCO_3$
Mn^{2+}	Greater than 10 mg/L
NO_2^-	Greater than 5 mg/L
NO_3^-	Greater than 20 mg/L
pH	2.9–4.9 or 7.5–11.5. A sample pH between about 4.9 and 7.5 causes dissolved aluminum to partially convert to colloidal and insoluble forms. This method measures much of that hard-to-detect aluminum without any pH adjusting pretreatment as is necessary in some other methods.
PO_4^{3-} (ortho)	4 mg/L (error is -5% of reading)
Polyphosphate	See procedure below.
SO_4^{2-}	Greater than 1000 mg/L
Zn^{2+}	Greater than 10 mg/L

Polyphosphate interference can be reduced by converting polyphosphate to orthophosphate by the following steps:

a. Rinse a 50-mL graduated mixing cylinder and a 125-mL erlenmeyer flask containing a magnetic stir bar with 6 N hydrochloric acid. Rinse again with deionized water. This will remove any aluminum present.

Note: *Rinse two Erlenmeyer flasks if a reagent blank is used; see Step b below.*

b. Measure 50 mL deionized water into the 125-mL erlenmeyer flask using the graduated cylinder. This is the reagent blank. Because of the test sensitivity, this step must be done only when any of the reagents used in the following pretreatment are replaced even if the new reagent has a matching lot number. When the pretreated sample has been analyzed, correct for the aluminum concentration of the reagent blank by pressing the soft keys under ***OPTIONS***, then ***(MORE)***, then ***BLANK:OFF***. Enter the reagent blank value using the numeric keys and press **ENTER**.

c. Measure 50 mL sample into the 125-mL erlenmeyer flask using the graduated cylinder. Use a small amount of deionized water to rinse the cylinder contents into the flask.

d. Add 4.0 mL of 5.25 N Sulfuric Acid Standard Solution.

e. Use a combination hot plate/stirrer to boil and stir the sample for at least 30 minutes. Add deionized water as needed to maintain a sample volume of 20-40 mL. Do not boil dry.

f. Cool the solution to near room temperature.

g. Add 2 drops of Bromphenol Blue Indicator Solution.

h. Add 1.5 mL of 12.0 N Potassium Hydroxide Standard Solution using the calibrated, plastic dropper provided. Swirl to mix. The solution color should be yellow or green but not purple. If the color is purple, begin with Step a again using an additional 1 mL Sulfuric Acid Standard Solution in Step d.

i. While swirling the flask, add 1.0 N Potassium Hydroxide Solution, a drop at a time, until the solution turns a dirty green color.

j. Pour the solution into the graduated cylinder. Rinse the flask contents into the graduated cylinder with deionized water to bring the total volume to 50 mL.

k. Use this solution in Step 3 of the ECR method.

Fluoride interference can be corrected by using *Table 2*.

An Example:
If the fluoride concentration is known to be 1.00 mg/L F^- and the ECR method gives a DR/4000 reading of 0.060 mg/L aluminum, what is the true mg/L aluminum concentration?

Note: *Intermediate values can be found by interpolation. Do not use correction graphs or charts found in other publications.*

Answer: 0.183 mg/L

Sample Collection, Storage and Preservation

Collect samples in a clean glass or plastic containers. Preserve samples by adjusting the pH to 2 or less with concentrated nitric acid (about 1.5 mL per liter). Preserved samples can be stored up to six months at room temperature. Before analysis, adjust the pH to 2.9–4.9 with 12.0 N Potassium Hydroxide Standard Solution and/or 1 N Potassium Hydroxide Solution. Correct the test result for volume additions; see Section *1.2.2 Correcting for Volume Additions*.

Accuracy Check

Standard Solution Method
Using Class A glassware, prepare a 0.100 mg/L aluminum standard solution by pipetting 1.00 mL of Aluminum Standard Solution, 100 mg/L as Al^{3+}, into a 1000-mL volumetric flask. Dilute to the mark with deionized water. Prepare this solution daily. Perform the aluminum procedure as described above.

Or, add 2.0 mL of solution from an Aluminum Voluette Ampule Standard Solution (50 mg/L as Al) into a 1000-mL volumetric flask. Dilute to volume with deionized water. Prepare this solution daily. Perform the aluminum procedure as described above.

To adjust the calibration curve using the reading obtained with the 0.100-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.

Table 2 True aluminum concentration (mg/L) vs. DR/4000 reading (mg/L) and fluoride concentration (mg/L) for Eriochrome Cyanine R method

DR/4000 Reading		Fluoride Concentration (mg/L)									
(mg/L)	0.00	0.20	0.40	0.60	0.80	1.00	1.20	1.40	1.60	1.80	2.00
0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000
0.010	0.010	0.019	0.030	0.040	0.052	0.068	0.081	0.094	0.105	0.117	0.131
0.020	0.020	0.032	0.046	0.061	0.077	0.099	0.117	0.137	0.152	0.173	0.193
0.030	0.030	0.045	0.061	0.077	0.098	0.124	0.146	0.166	0.188	0.214	0.243
0.040	0.040	0.058	0.076	0.093	0.120	0.147	0.174	0.192	0.222		
0.050	0.050	0.068	0.087	0.109	0.135	0.165	0.188	0.217			
0.060	0.060	0.079	0.100	0.123	0.153	0.183	0.210	0.241			
0.070	0.070	0.090	0.113	0.137	0.168	0.201	0.230				
0.080	0.080	0.102	0.125	0.152	0.184	0.219					
0.090	0.090	0.113	0.138	0.166	0.200	0.237					
0.100	0.100	0.124	0.150	0.180	0.215						
0.120	0.120	0.146	0.176	0.209	0.246						
0.140	0.140	0.169	0.201	0.238							
0.160	0.160	0.191	0.226								
0.180	0.180	0.213									
0.200	0.200	0.235									
0.220	0.220										
0.240	0.240	True Aluminum Concentration (mg/L) Al									

Method Performance

Precision

Standard: 0.100 mg/L Al^{3+}

Program	95% Confidence Limits
1010	0.098-0.102 mg/L Al^{3+}

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

Estimated Detection Limit

Program	EDL
1010	0.002 mg/L Al^{3+}

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: 1010

Portion of Curve	ΔAbs	ΔConcentration
0.010 Abs	0.010	0.0023 mg/L
0.125 mg/L	0.010	0.0015 mg/L
0.225 mg/L	0.010	0.0015 mg/L

See Section *1.5.3 Sensitivity Explained* for more information.

Calibration Standard Preparation

To perform an aluminum calibration using the ECR method, use a 10.0 mg/L Aluminum Standard Solution (Cat. No. 23058-42). Prepare calibration standards containing 0.01, 0.02, 0.04, 0.08, 0.12, 0.16, 0.200, 0.240 mg/L Al as follows:

a. Into eight different 1000-mL Class A volumetric flasks, pipet 1.00, 2.00, 4.00, 8.00, 12.00, 16.00, 20.00 and 24.00 mL of the 10 mg/L Al stock solution using Class A glassware.

b. Dilute to the mark with deionized water and mix thoroughly.

c. Using the ECR method and the calibration procedure described in the *User-Entered Programs* section of the *DR/4000 Spectrophotometer Instrument Manual*, generate a calibration curve from the standards prepared above.

Summary of Method

Eriochrome Cyanine R combines with aluminum in a sample to produce an orange-red color. The intensity of color is proportional to the aluminum concentration.

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

For information on pollution prevention and waste management, refer to Section *1*.

REQUIRED REAGENTS AND STANDARDS

	Cat. No.
Aluminum Reagent Set (100 Tests)	26037-00
Includes (1) 26038-49, (1) 26039-99, (1) 23801-23	

Description	Quantity Required per test	Unit	Cat. No.
ECR Reagent Powder Pillows	1 pillow	100/pkg	26038-49
Hexamethylenetetramine Buffer Reagent Powder Pillows	1 pillow	100/pkg	26039-99
ECR Masking Reagent Solution	1 drops	25 mL SCDB	23801-23

REQUIRED EQUIPMENT AND SUPPLIES

Cylinder, 25 mL, graduated mixing, with glass stopper	1	each	1896-40
DR/4000 1-Inch Cell Adapter	1	each	48190-00

OPTIONAL REAGENTS AND STANDARDS

Description	Unit	Cat. No.
Aluminum Standard Solution, 10 mg/L	100 mL	23058-42
Aluminum Standard Solution, 100 mg/L	100 mL	14174-42
Aluminum Standard Solution, 10-mL Voluette Ampule, 50 mg/L as Al, 10 mL	16/pkg	14792-10
Aluminum Standard Solution, 2-mL Voluette Ampule, 25 mg/L as Al, 2 mL	20/pkg	25571-20
Bromphenol Blue Indicator Solution	100 mL MDB	14552-32
Hydrochloric Acid Solution, 6 N (1:1)	500 mL	884-49
Nitric Acid, ACS	500 mL	152-49
Nitric Acid Solution, 1:1	500 mL	2540-49
Potassium Hydroxide Solution, 1 N	50 mL SCDB	23144-26
Potassium Hydroxide Standard Solution, 12.0 N	100 mL	230-32
Potassium Hydroxide Standard Solution, 12.0 N	500 mL	230-49
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449-32
Water, deionized	4 liters	272-56
Brush, test tube	each	690-00
DR/4000 Carousel Module Kit	each	48090-02
Flask, Erlenmeyer, 125-mL	each	505-43
Flask, volumetric, Class A, 100-mL	each	14574-42
Flask, volumetric, Class A, 1000-mL, with glass stopper	each	14574-53
Hot Plate/Stirrer, 120 V	each	23442-00
Hot Plate/Stirrer, 240 V	each	23442-02
Pad, cooling, 4 x 4 in.	each	18376-00
pH Paper, 1.0 to 11.0 pH	5 rolls/pkg	391-33
pH Meter, *sens**ion**™1*, portable	each	51700-00
Pipet Filler, safety bulb	each	14651-00
Pipet, serological, 2-mL	each	532-36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700-01
Pipet Tips, for 19700-01 TenSette Pipet	50/pkg	21856-96
Pipet, volumetric, Class A, 1.00-mL	each	14515-35
Pipet, volumetric, Class A, 2.00-mL	each	14515-36
Pipet, volumetric, Class A, 3.00-mL	each	14515-03
Pipet, volumetric, Class A, 4.00-mL	each	14515-04
Pipet, volumetric, Class A, 5.00-mL	each	14515-37
Pipet, volumetric, Class A, 6.00-mL	each	14515-06
Pipet, volumetric, Class A, 8.00-mL	each	14515-08
Pipet, volumetric, Class A, 20.00-mL	each	14515-20
Stir Bar, octagonal, 28.6 x 7.9 mm	each	20953-52
Thermometer, -10 to 110 °C	each	1877-01

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