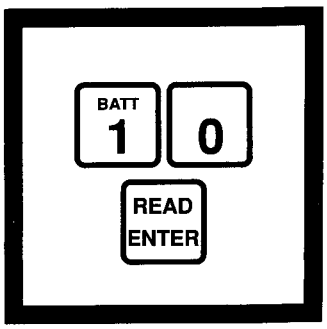
ALUMINUM (0 to 0.80 mg/L)

Aluminon Method*



1. Enter the stored program number for aluminum (Al).

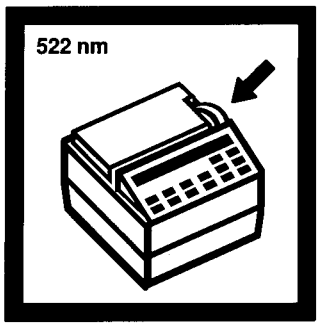
Press: **1 0 READ/ENTER**

The display will show:
DIAL nm TO 522

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

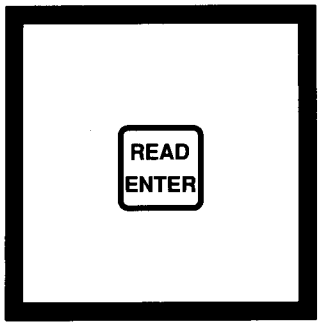
Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

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



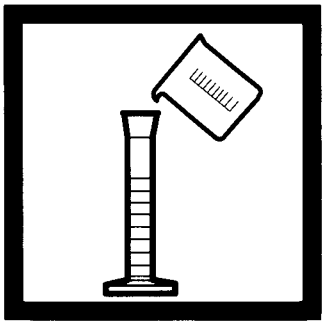
2. Rotate the wavelength dial until the small display shows:
522 nm

Note: *Total aluminum determination needs a prior digestion; use any of the three procedures given in* Digestion (Section I).



3. Press: **READ/ENTER**

The display will show:
mg/l Al



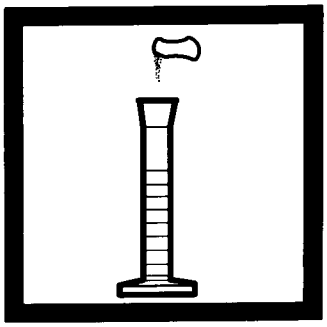
4. Fill a 50–mL graduated mixing cylinder to the 50–mL mark with sample.

Note: *Rinse cylinder with 1:1 Hydrochloric Acid and demineralized water before use to avoid errors due to contaminants absorbed on the glass.*

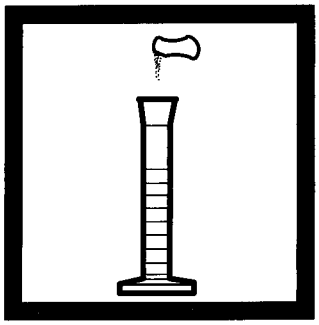
Note: *The sample temperature must be between 20–25 °C (68–77 °F) for accurate results.*

Note: *For proof of accuracy, use a 0.4 mg/L aluminum standard solution (preparation given in the* Accuracy Check*) in place of the sample.*

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



5. Add the contents of one Ascorbic Acid Powder Pillow. Stopper. Invert several times to dissolve powder.

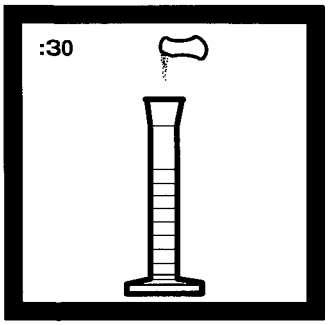


6. Add the contents of one AluVer 3 Aluminum Reagent Powder Pillow. Stopper. Invert repeatedly for one minute to dissolve.

Note: A red–orange color develops if aluminum is present.

Note: Inconsistent results will be obtained if any powder is undissolved.

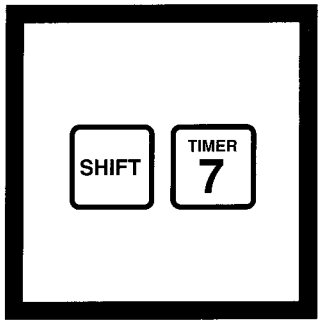
7. Pour 25 mL of mixture into a 25–mL sample cell (the prepared sample).



8. Add contents of one Bleaching 3 Reagent Powder Pillow to the remaining 25 mL in the graduated mixing cylinder. Stopper. Vigorously shake for 30 seconds.

Note: This solution should turn a light to medium orange upon bleaching. It will not become colorless.

9. Pour the remaining 25 mL of mixture in the cylinder into a second 25–mL sample cell (the blank).

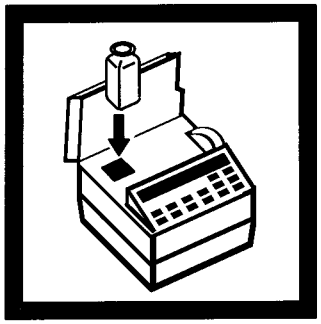


10. Press: **SHIFT TIMER**

A 15–minute reaction period will begin.

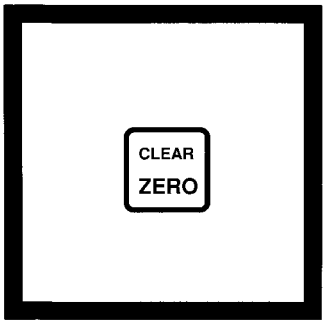
When the timer beeps, the display will show:

mg/l Al



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

Note: The Pour–Thru Cell can be used if rinsed well with demineralized water between the blank and prepared sample.



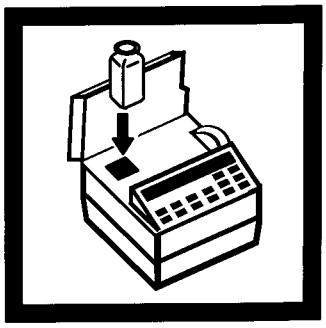
12. Press: **ZERO**

The display will show:

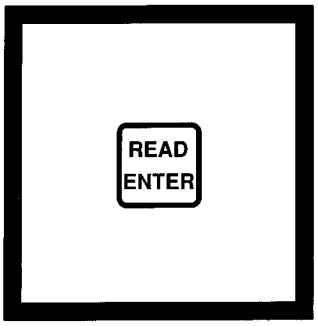
WAIT

then:

0.00 mg/l Al



13. Immediately place the prepared sample into the cell holder. Close the light shield.



14. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L aluminum will be displayed.

Note: *Clean the graduated cylinder and sample cells with soap and brush immediately following the test.*

Note: *For most accurate results, analyze a reagent blank (demineralized water) and subtract the amount determined on each lot of AluVer 3 Aluminum Reagent from the sample reading.*

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

SAMPLING AND STORAGE

Collect samples in a cleaned glass or plastic container. Preserve the sample by adjusting the pH to 2 or less with 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 3.5 to 4.5 with 5.0 N Sodium Hydroxide. Correct the test result for volume additions *(see Correction for Volume Additions in Section I).*

ACCURACY CHECK

Standard Additions Method

a) Snap the neck off an Aluminum Voluette Ampule Standard Solution, 50 mg/L Al.

b) Use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively, to three 50–mL samples. Mix each thoroughly.

c) Analyze each sample as described above. The aluminum concentration should increase 0.1 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Prepare a 0.4–mg/L aluminum standard solution by pipetting 1.00 mL of Aluminum Standard Solution,

100 mg/L as Al^{3+}, into a 250–mL volumetric flask. Dilute to the mark with demineralized water. Prepare this solution daily. Perform the aluminum procedure as described above. The mg/L Al reading in Step 14 should be 0.4 mg/L Al.

Or, using the TenSette Pipet, add 0.8 mL of solution from an Aluminum Voluette Ampule Standard Solution (50 mg/L as Al) into a 100–mL volumetric flask. Dilute to volume with demineralized water.

PRECISION

In a single laboratory, using a standard solution of 0.2 mg/L Al and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ± 0.016 mg/L Al.

INTERFERENCES

The following do not interfere up to the indicated concentrations.

Alkalinity	1000 mg/L as $CaCO_3$
Iron	20 mg/L
Phosphate	50 mg/L

Interferences from higher alkalinity concentrations can be eliminated by the following pretreatment.

a) Add one drop of m–Nitrophenol Indicator Solution to the sample taken in Step 4. A yellow color indicates excessive alkalinity.

b) Add one drop of 5.25 N Sulfuric Acid Standard Solution. Stopper the cylinder. Invert to mix. If the yellow color persists, repeat until the sample changes to colorless. Continue with the test.

Polyphosphate interferes at all levels by causing negative errors and must not be present. Before running the test polyphosphate must be converted to orthophosphate by acid hydrolysis as described under the phosphorus procedure.

Acidity interferes at greater than 300 mg/L as $CaCO_3$. Samples with greater than 300 mg/L acidity as $CaCO_3$ must be treated as follows:

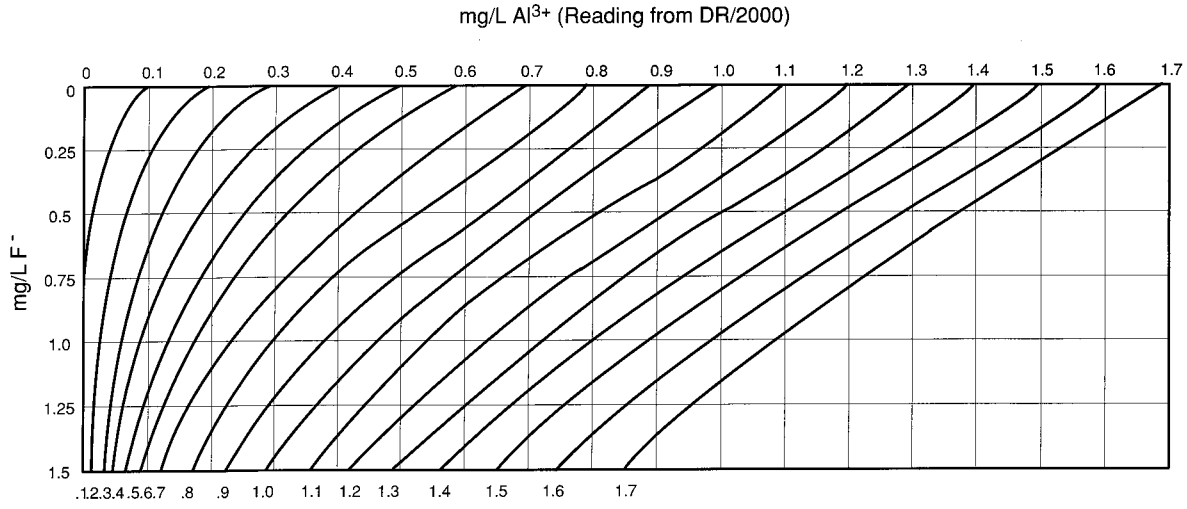
a) Add one drop of m–Nitrophenol Indicator Solution to the sample taken in Step 4.

b) Add one drop of 5.0 N Sodium Hydroxide Standard Solution. Stopper the cylinder. Invert to mix. Repeat as often as necessary until the color changes from colorless to yellow.

c) Add one drop of 5.25 N Sulfuric Acid Standard Solution to change the solution from yellow back to colorless. Continue with the test.

Calcium does not interfere.

Fluoride interferes at all levels by complexing with aluminum. The actual aluminum concentration can be determined using the Fluoride Interference Graph when the fluoride concentration is known. To use the fluoride interference graph, select the vertical grid line along the top of the graph that represents the aluminum reading obtained in Step 14. Locate the point of the line where it intersects with the horizontal grid line that indicates how much fluoride is present



FLUORIDE INTERFERENCE GRAPH

in the sample. Extrapolate the true aluminum concentration by following the curved lines on either side of the intersect point down to the true aluminum concentration. For example, if the aluminum test result was 0.7 mg/L Al and the fluoride present in the sample was 1 mg/L F^-, the point where the 0.7 grid line intersects with the 1 mg/L F^- grid line falls between the 1.2 and 1.3 mg/L Al curves. In this case, the true aluminum content would be 1.27 mg/L.

SUMMARY OF METHOD

Aluminon indicator combines with aluminum in the sample to form a red–orange color. The intensity of color is proportional to the aluminum concentration. Ascorbic acid is added to remove iron interference. The AluVer 3 Aluminum Reagent, packaged in powder form, shows exceptional stability and is applicable for fresh water samples.

REQUIRED REAGENTS

	Cat. No.
Aluminum Reagent Set (100 Tests)	22420–00
Includes: (4) 14290–68, (1) 14577–99, (1) 14294–99	

Description	Quantity Required Per Test	Unit	Cat. No.
AluVer 3 Aluminum Reagent Powder Pillow	1 pillow	25/pkg	14290–68
Ascorbic Acid Powder Pillow	1 pillow	100/pkg	14577–99
Bleaching 3 Reagent Powder Pillow	1 pillow	100/pkg	14294–99

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968–00
Cylinders, graduated mixing, 50 mL	1	each	1896–41

OPTIONAL REAGENTS

Aluminum Standard Solution, 100 mg/L	105 mL	14174–42
Aluminum Standard Solution, Voluette ampule, 50 mg/L as Al, 10 mL	16/pkg	14792–10
Hydrochloric Acid Solution, 6 N (1:1)	500 mL	884–49
m–Nitrophenol Indicator Solution, 10 g/L	100 mL MDB	2476–32
Nitric Acid, ACS	500 mL	152–49
Nitric Acid Solution, 1:1	500 mL	2540–49
Sodium Hydroxide Standard Solution, 5.0 N	100 mL MDB	2450–32
Sodium Hydroxide Standard Solution, 5.0 N	59 mL	2450–26
Sulfuric Acid Standard Solution, 5.25 N	100 mL MDB	2449–32
Water, demineralized	4 L	272–56

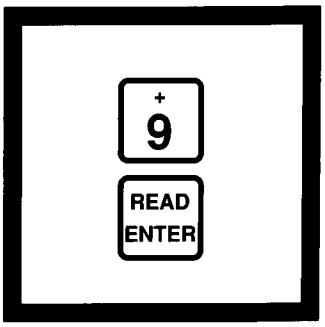
OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968-00
Brush	each	690–00
Flask, volumetric, 250 mL	each	547–46
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391–33
pH Meter, EC10, portable	each	50050–00
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, 1 mL	each	515–35
Pour–Thru Cell Assembly Kit	each	45215–00
Thermometer, –20° to 105°C	each	1877–01

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

ALUMINUM (0 to 0.220 mg/L)

Eriochrome Cyanine R Method*



1. Enter the stored program number for aluminum (Al), Eriochrome Cyanine R (ECR) method.

Press: **9 READ/ENTER**

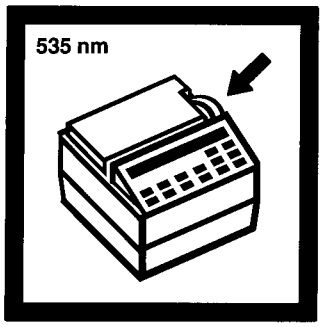
The display will show:
DIAL nm TO 535

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

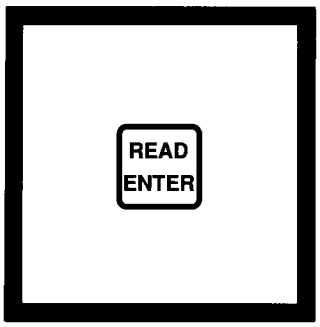
Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

Note: *If your software version is 2.0 or less, see* Instrument Setup *following these steps.*

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

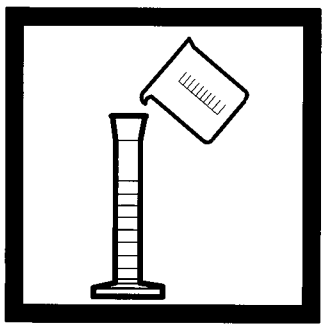


2. Rotate the wavelength dial until the small display shows:
535 nm



3. Press: **READ/ENTER**

The display will show:
mg/l Al ECR



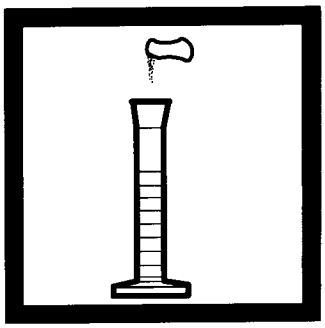
4. Fill a 50–mL graduated mixing cylinder to the 50–mL mark with sample.

Note: *Rinse cylinder with 1:1 Hydrochloric Acid and demineralized water before use to avoid errors due to contaminants adsorbed on the glass.*

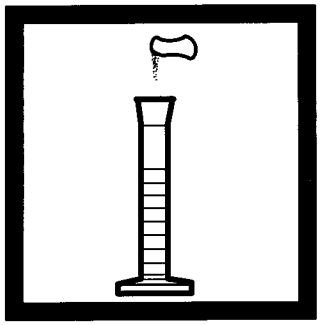
Note: *The sample temperature must be 20–25 °C (68–77 °F) for accurate results.*

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

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



5. Add the contents of one ECR Reagent Powder Pillow. Stopper. Invert several times to dissolve powder, then wait 30 seconds.



6. Add the contents of one Hexamethylenetetramine Buffer Reagent Powder Pillow. Stopper. Invert several times to dissolve powder.

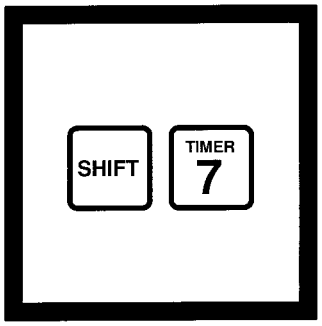
Note: An orange to purple color develops if aluminum is present.

7. Put 2 drops of ECR Masking Reagent Solution into a 25–mL sample cell.

8. Pour 25 mL from the graduated mixing cylinder into the 25–mL sample cell. Swirl to mix and thus make the blank.

Note: The solution will start to turn yellow.

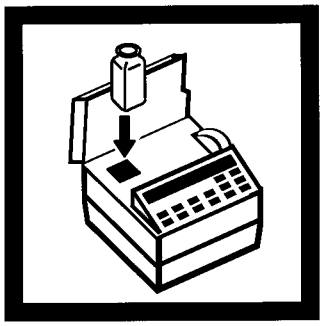
9. Pour the remaining 25 mL of mixture into a second 25–mL sample cell to make the prepared sample.



10. Press: **SHIFT TIMER**

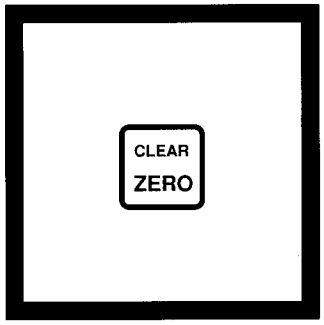
A 5–minute reaction period will begin.

Note: When the timer beeps, the display will show:
mg/l Al ECR



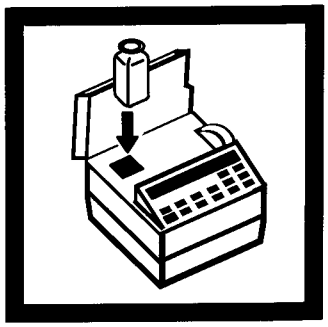
11. Within five minutes after the timer beeps, place the blank into the cell holder. Close the light shield.

Note: The Pour–Thru Cell cannot be used.

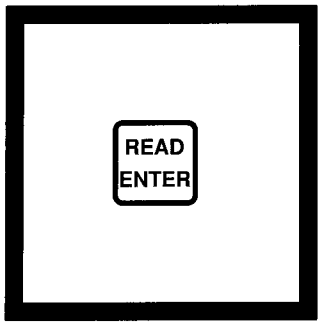


12. Press: **ZERO**

The display will show:
WAIT
then:
0.000 mg/l Al ECR



13. Immediately, place the prepared sample into the cell holder. Close the light shield.



14. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L aluminum will be displayed.

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

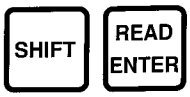
Note: *If fluoride (F^-) is present, it needs to be measured and the actual value determined,* (see Table 2).

Instrument Setup

For a DR/2000 with software versions 1.261 and 1.27, enter the following calibration information as an operator–programmed calibration. Refer to the Operation section of the *DR/2000 Instrument Manual.* Store the method information as follows:

nm = 535
Decimal = 0.000
Units = mg/l
Symbol = Al ECR
TIMER 1 = 05:00

With software versions 1.261 and 1.27, the calibration is first entered as a "flat" curve, then the absorbance values of 0.000 are edited to the correct values. To do this, do not place anything in the sample cell compartment. Begin by storing standards #0 through #6 as concentrations of 0.000, 0.027, 0.144, 0.164, 0.184, 0.206, and 0.228, respectively. Accept 0.000 Abs as the value for each standard. Store the calibration by pressing these keys:



To edit the absorbence values of 0.000 to the correct values, refer to the *Operation* section of the *DR/2000 Instrument Manual.*

Standard	Concentration	Absorbence
0	0.000	0.000
1	0.027	0.125
2	0.144	0.875
3	0.164	1.000
4	0.184	1.125
5	0.206	1.250
6	0.228	1.375

This method is now stored as an operator–stored method with a method number between 950 and 999. Record the method number for future reference when using this method.

For a DR/2000 with software version 2.0, which does not already have the Aluminum ECR method (Stored Method 9), enter the method as a Hach–entered program as follows:

1) Press: 

2) Press: SHIFT CONFIG METH

3) Press: + 9 READ ENTER

4) Within 3 seconds, press:

SHIFT PROG 3 CONFIG METH

The display will show:
ENTER nm

If the display returns to the METHOD prompt, repeat the sequence.

5) Press: ABS 5 PROG 3 ABS 5 READ ENTER

The display will show:
DECIMAL? 00.00

6) Use the arrow keys to correctly position the decimal point. For this method, press the **LEFT/UP ARROW** key once. The display will show:
DECIMAL? 0.000

7) When the decimal point is correctly positioned, press: **READ/ENTER.** The display will show:
UNITS?

8) Use the arrow keys to select the appropriate unit of measure. For this method, press the **DOWN ARROW** key twice. The display will show:
mg/l

9) With the proper unit of measure displayed, press **READ/ENTER**. The display will show:
SYMBOL?

10) Use the arrow keys to construct the correct symbol display. For this method, press the **DOWN ARROW** key repeatedly until you see:
mg/l a

11) Press **SHIFT** to make the "a" uppercase. The display will show:
mg/l A

12) Press the **READ/ENTER** key to accept the capital A.

13) Continue to construct the display:
mg/l Al ECR
The space is the "character" displayed after one press of the **DOWN ARROW** key.

14) When the last character of the symbol is accepted with the **READ/ENTER** key, press the **READ/ENTER** key again. The display will show:
TIMER?

15) Press: SHIFT TIMER 7

The display will show:
MM:SS TIME 1 ?

16) Select 5 minutes by pressing:

0 ABS 5 0 0

The display will show:
05:00 TIME 1 ?

17) Press: **READ/ENTER.** The display will show:
MM:SS TIME 2 ?

There are no more timer values for this method, so press **READ/ENTER.** The display will show:
 # 1 Data

18) Enter the following 12 numbers as shown. Complete each number with the **READ/ENTER** key.

# 1 DATA	**0**
# 2 DATA	**6931**
# 3 DATA	**5140**
# 4 DATA	**4884**
# 5 DATA	**4884**
# 6 DATA	**5142**
# 7 DATA	**5887**
# 8 DATA	**65535**
# 9 DATA	**65535**
# 10 DATA	**13107**
# 11 DATA	**512**
# CHECKSUM	**19051**

The final number is a check value which is used to determine if the data sequence was entered correctly. If an error is made during number entry, the display will return to the prompt for data number 1 and the entire sequence must be re–entered. If all the numbers are correctly entered, the display will return to the method prompt and is ready for use.

SAMPLING AND STORAGE

Collect samples in a clean glass or plastic container. Preserve samples by adjusting the pH to 2 or less with 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 to 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 Corrections for Volume Additions in Section I).*

ACCURACY CHECK

Standard Solution Method

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 demineralized water. Prepare this solution daily. Perform the aluminum procedure as described above. The mg/L Al reading in Step 14 should be 0.10 mg/L Al.

Or, using the TenSette Pipet, add 0.2 mL of solution from an Aluminum Voluette Ampule Standard Solution (50 mg/L as Al) into a 100–mL volumetric flask. Dilute to volume with demineralized water.

PRECISION

In a single laboratory, using a standard solution of 0.100 mg/L Al and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ± 0.004 mg/L Al.

INTERFERENCES

Table 1 lists common interferences and the amount of interference that can be expected.

Table 1. Common Interferences with the Eriochrome Cyanine R Method

Constituent	Concentration	Error
Acidity	0–62 mg/L as $CaCO_3$	0%
Alkalinity	0–750 mg/L as $CaCO_3$	0%
Ca^{2+}	0–1000 mg/L as $CaCO_3$	0%
Cl^-	0–1000 mg/L	0%
Cr^{6+}	0.2 mg/L	–5% of reading
Cu^{2+}	2 mg/L	–5% of reading
Fe^{2+}	0–4 mg/L	+ mg/L Fe^{2+} X 0.0075
Fe^{3+}	0–4 mg/L	+ mg/L Fe^{3+} X 0.0075
F^-	see Table 2	
Hexameta-phosphate	0.1 mg/L as PO_4^{3-}	–5% of reading
Mg^{2+}	0–1000 mg/L as $CaCO_3$	0%
Mn^{2+}	0–10 mg/L	0%
NO_2^-	0–5 mg/L	0%

Table 1. (continued)

Constituent	Concentration	Error
NO_3^-	0–20 mg/L	0%
pH	2.9–4.9	0%
	7.5–11.5	0%
PO_4^{3-} (ortho)	4 mg/L	–5% of reading
SO_4^{2-}	0–1000 mg/L	0%
Zn^{2+}	0–10 mg/L	0%

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.

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 demineralized water. These rinses will remove any aluminum present.

Note: *Rinse two erlenmeyer flasks if a reagent blank is used* (see Step b below).

b) Measure 50 mL of demineralized 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, subtract the aluminum concentration of the reagent blank from the sample results.

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

d) Add 4.0 mL of Sulfuric Acid Solution, 5.25 N.

e) Use a combination hot plate/stirrer to stir and boil the sample for at least 30 minutes. Add demineralized 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 of Sulfuric Acid 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 demineralized water to bring the total volume to 50 mL.

k) Use this solution in Step 5 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/2000 reading of 0.060 mg/L aluminum, what is the true mg/L aluminum concentration?

Answer: 0.183 mg/L

Table 2. True aluminum concentration (mg/L) vs. DR/2000 reading (mg/L) and fluoride concentration (mg/L) when the Eriochrome Cyanine R method is used.

DR/2000 Reading (mg/L)	Fluoride Concentration (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	0.153	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)

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

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.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Aluminum Reagent Set (100 tests)			24434–00
Includes (4) 23802–68, (4) 1878–68, (1) 23801–23			
ECR Reagent Powder	1 pillow	25/pkg	23802–68
Hexamethylenetetramine Buffer Reagent	1 pillow	25/pkg	1878–68
ECR Masking Reagent Solution	2 drops	29 mL	23801–23

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968–00
Cylinder, graduated mixing, 50 mL	1	each	1896–41

OPTIONAL REAGENTS

Aluminum Standard Solution, 100 mg/L	100 mL	14174–42
Aluminum Standard Solution, Voluette ampule, 50 mg/L as Al, 10 mL	16/pkg	14792–10
Bromphenol Blue Indicator Solution	100 mL	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	59 mL	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	2449–32
Water, demineralized	4 L	272–56

OPTIONAL APPARATUS

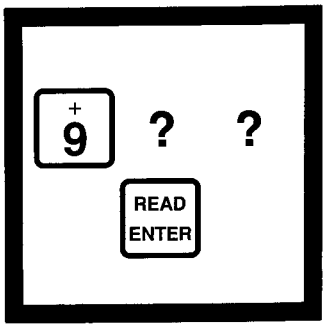
Ampule Breaker Kit	each	21968-00
Brush	each	690–00
Flask, erlenmeyer, glass, 125 mL	each	505–43
Flask, volumetric, 100 mL	each	14574–42
Flask, volumetric, 1000 mL	each	14574–53
Hot Plate, Stirrer, 120 V	each	23442–00
Hot Plate, Stirrer, 240 V	each	23442–02
Pad, cooling, 4" x 4"	each	18376–00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391–33
pH Meter, EC10, portable	each	50050–00
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 mL	each	14515–35
Stir Bar, Octagonal, 25.4 x 7.9 mm	each	20953–52
Thermometer, –20° to 105 °C	each	1877–01

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

ARSENIC (0 to 0.200 mg/L)

For water, wastewater and seawater

Silver Diethyldithiocarbamate Method*, USEPA accepted for reporting wastewater and drinking water analysis (distillation required)**



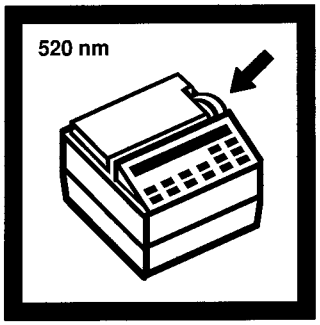
1. Enter the user stored program number for arsenic (As).

Press: **9 ? ? READ/ENTER**

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

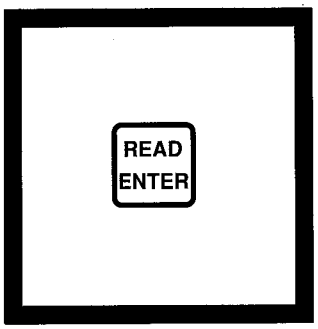
Note: *Due to potential variation between lots of arsenic absorber solution, it is necessary to perform a new calibration for each lot of this reagent. Prepare and store the calibration as directed under* Calibration *below, then use the following procedure.*



2. Rotate the wavelength dial until the small display shows:

520 nm

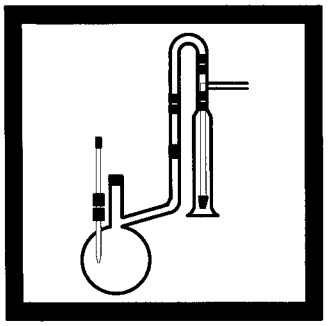
Note: *If samples cannot be analyzed immediately, see* Sampling and Storage *below.*



3. Press: **READ/ENTER**

The display will show:

mg/l As

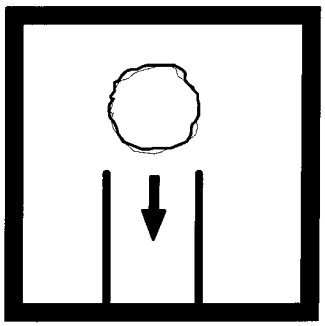


4. Prepare the distillation apparatus for arsenic recovery. Place it under a fume hood to vent toxic fumes.

Note: *See the* Hach Distillation Manual *for assembly instructions.*

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

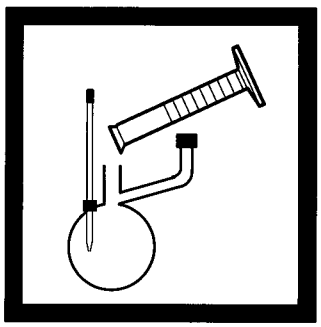
**Procedure is equivalent to USEPA method 206.4 for wastewater and Standard Methods 3500–As for drinking water.



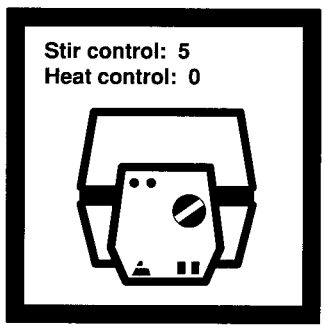
5. Dampen a cotton ball with 10% Lead Acetate Solution. Place it in the gas scrubber. Be certain the cotton seals against the glass.

6. Measure 25 mL of prepared arsenic absorber solution into the cylinder/gas bubbler assembly with a graduated cylinder. Attach it to the distillation apparatus.

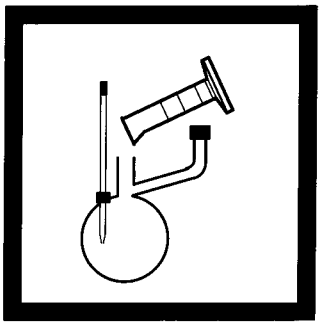
Note: *Prepare the arsenic absorber solution as directed under* Reagent Preparation *below.*



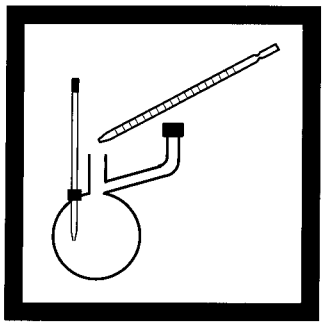
7. Measure 250 mL of sample into the distillation flask using a graduated cylinder.



8. Turn on the power switch. Set the stir control to 5. Set the heat control to 0.

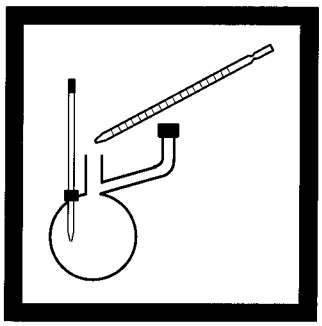


9. Measure 25 mL of hydrochloric acid, ACS, into the flask using a graduated cylinder.



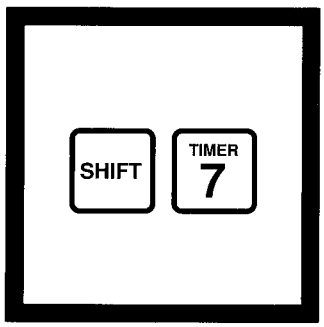
10. Measure 1 mL of Stannous Chloride Solution into the flask.

Note: *Use a serological pipet to measure the solution.*



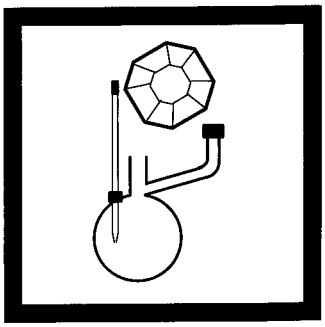
11. Add 3 mL of Potassium Iodide Solution to the flask. Cap.

Note: *Use a serological pipet to measure the solution.*

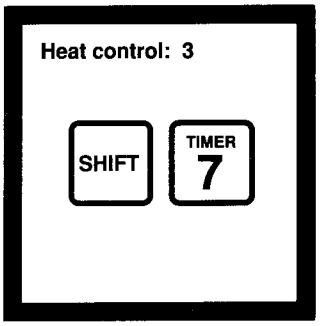


12. Press: **SHIFT TIMER**

A 15–minute reaction period will begin.



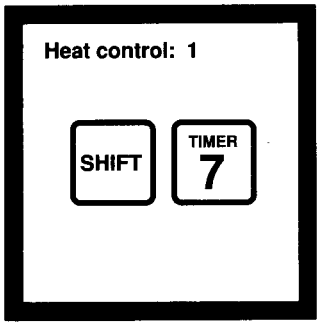
13. When the timer beeps, add 6.0 g of 20–mesh zinc to the flask. Cap immediately.



14. Set the heat control to 3.

Press: **SHIFT TIMER**

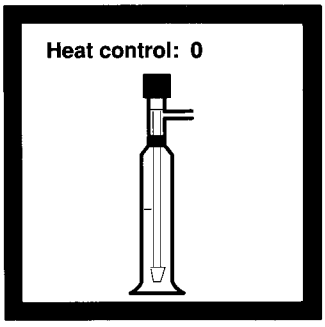
A second 15–minute reaction period will begin.



15. When the timer beeps, set the heat control to 1.

Press: **SHIFT TIMER**

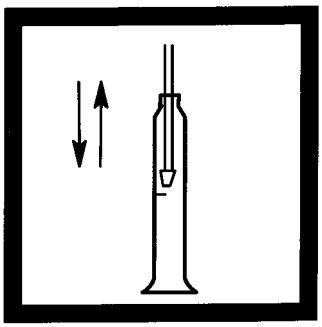
A third 15–minute reaction period will begin.



16. When the timer beeps, the display will show:

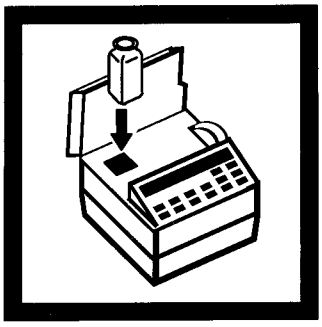
mg/l As

Turn off the heater. Remove the cylinder/gas bubbler assembly as a unit.



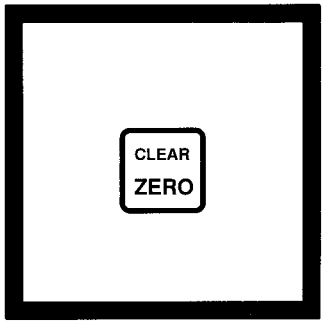
17. Rinse the gas bubbler by moving it up and down in the arsenic absorber solution.

18. Fill a dry sample cell with unreacted arsenic absorber solution (the blank). Stopper.



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

Note: *The Pour–Thru Cell cannot be used with this procedure.*



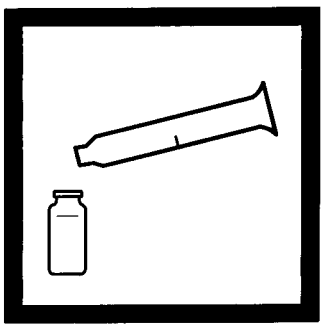
20. Press: **ZERO**

The display will show:

WAIT

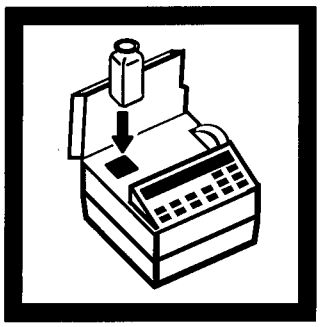
then:

0.000 mg/l As

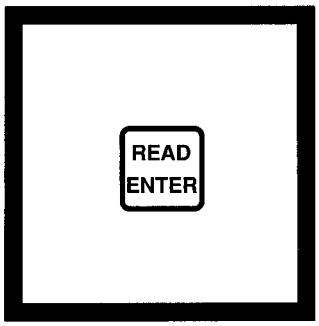


21. Pour the reacted arsenic absorber solution into a sample cell (the prepared sample). Stopper.

Note: If the solution volume is less than 25 mL, add pyridine to bring the volume to exactly the 25–mL mark. Swirl to mix.



22. Place the prepared sample into the cell holder. Close the light shield.



23. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L arsenic (As) will be displayed.

Note: In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

REAGENT PREPARATION

Prepare the arsenic absorber solution as follows:

1. Weigh 1.00 g of silver diethyldithiocarbamate on an analytical balance.

2. Transfer the powder to a 200–mL volumetric flask. Dilute to volume with pyridine. (Use pyridine only in a fume hood.)

3. Mix well to dissolve. Store the reagent, tightly sealed, in an amber bottle. The reagent is stable for one month if stored in this manner. Larger volumes of reagent can be prepared if the reagent is used within one month.

CALIBRATION

Perform a new calibration for each lot of arsenic absorber solution prepared as follows:

a) Prepare a 10.0–mg/L arsenic working standard by pipetting 1.00 mL of Arsenic Standard Solution, 1000 mg/L As, into a 100–mL volumetric flask. Dilute to volume with demineralized water.

b) Prepare standards of 0.04, 0.08, 0.12, and 0.16 mg/L arsenic by diluting 1.0, 2.0 3.0 and 4.0 mL, respectively, of the working standard into four 250–mL volumetric flasks. Dilute to volume with demineralized water.

c) Store the calibration in the instrument memory using the procedure in the *Operation* section of the *DR/2000 Instrument Manual*. Store units as mg/L As, the decimal position as 0.000, the wavelength as 520 nm and three timer intervals of 15:00. (The instrument must be in the constant–on mode, because the calibration will require a long time period.)

d) Perform Steps 4 through 17 of the above procedure on the first standard, using unreacted arsenic absorber solution for the zero calibration. Enter the arsenic concentration of the next standard (0.04 mg/L), measure and enter the absorbance as prompted by the instrument. Distill, measure and enter the remaining standards.

e) Use this stored program number in the procedure above. Prepare a new calibration for each new lot of absorber solution. Use the same stored program number.

SAMPLING AND STORAGE

Collect samples in acid washed glass or plastic bottles. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Preserved samples may be stored up to six months at room temperature. Correct the test result for volume additions *(see Correction for Volume Additions in Section I).*

INTERFERENCES

Antimony salts may interfere with color development.

SUMMARY OF METHOD

Arsenic is reduced to arsine gas by a mixture of zinc, stannous chloride, potassium iodide and hydrochloric acid in a specially equipped distillation apparatus. The arsine is passed through a scrubber containing cotton saturated with lead acetate and then into an absorber tube containing silver diethyldithiocarbamate in pyridine. The arsenic reacts to form a red complex which is read colorimetrically. This procedure requires a manual calibration.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Arsenic Standard Solution, 1000 mg/L As	varies	100 mL	14571–42
Hydrochloric Acid, ACS	25 mL	500 mL	134–49
Lead Acetate Solution, 10%	1 mL	100 mL	14580–42
Potassium Iodide Solution, 20%	3 mL	100 mL	14568–42
Pyridine, ACS	50 mL	500 mL	14469–49
Silver Diethyldithiocarbamate, ACS	1 g	25 g	14476–24
Stannous Chloride Solution	1 mL	100 mL	14569–42
Zinc, 20–mesh, ACS	6 g	454 g	795–01

REQUIRED APPARATUS

Balance, analytical	1	each	22310–00
Balls, cotton	1	100/pkg	2572–01
Boat, weighing	2	500/pkg	21790–00
Bottle, amber, 237 mL	1	6/pkg	7144–41
Cap, polypropylene	1	6/pkg	21667–06
Cylinder, graduated, 25 mL	2	each	508–40
Cylinder, graduated, 250 mL	1	each	508–46
Distillation Apparatus Arsenic Accessories	1	set	22654–00
Distillation Apparatus General Purpose Accessories	1	set	22653–00
Flask, volumetric, 100 mL	1	each	14574–42
Flask, volumetric, 200 mL	1	each	14574–45
Flask, volumetric, 250 mL	4	each	14574–46
Pipet Filler, safety bulb	1	each	14651–00
Pipet, serological, 5 mL	2	each	532–37
Pipet, volumetric, Class A, 1 mL	2	each	14515–35
Pipet, volumetric, Class A, 2 mL	1	each	14515–36
Pipet, volumetric, Class A, 3 mL	1	each	14515–03
Pipet, volumetric, Class A, 4 mL	1	each	14515–04
Stopper, hollow, poly, No. 0	2	6/pkg	14480–00

Select one based on available voltage:

Distillation Apparatus Heater, 115 Vac, 60 Hz		each	22744–00
Distillation Apparatus Heater, 230 Vac, 50 Hz		each	22744–02

OPTIONAL REAGENTS

Hydrochloric Acid, ACS	2.8 kg	134–06
Nitric Acid, ACS	500 mL	152–49
Nitric Acid Solution, 1:1	500 mL	2540–49
Pyridine	4 L	14469–17
Water, demineralized	4 L	272–56

OPTIONAL APPARATUS

pH Meter, EC10, portable	each	50050–00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391–33
Pipet, serological, 2 mL	each	532–36

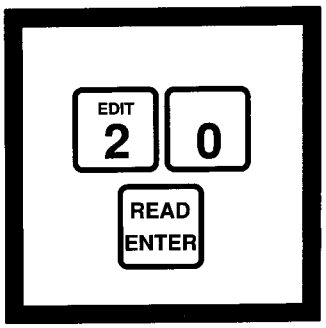
For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

BARIUM (0 to 100 mg/L)

For water, wastewater, oil-field water and seawater

Turbidimetric Method* (Powder Pillows or AccuVac Ampuls)

USING POWDER PILLOWS



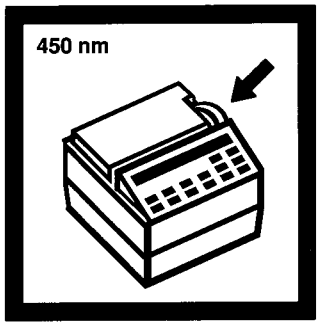
1. Enter the stored program number for barium (Ba).

Press: **2 0 READ/ENTER**

The display will show:
DIAL nm TO 450

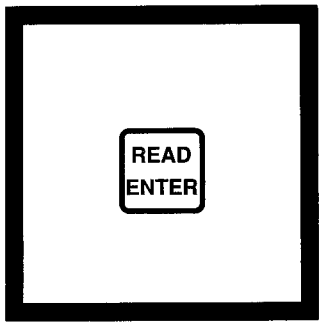
Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*



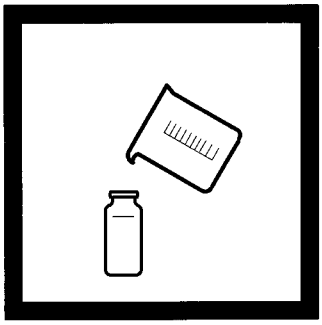
2. Rotate the wavelength dial until the small display shows:
450 nm

Note: *If sample cannot be analyzed immediately, see* Sampling and Storage *below. Adjust the pH of stored samples before analysis.*



3. Press: **READ/ENTER**

The display will show:
mg/l Ba



4. Fill a sample cell with 25 mL of sample.

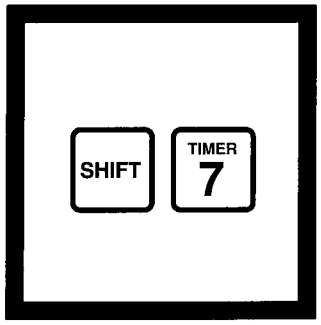
Note: *Filter highly colored or turbid water samples using labware listed under* Optional Apparatus. *Large amounts of color or turbidity will interfere and cause high readings. Use the filtered sample in Steps 4 and 7.*

Note: *For proof of accuracy, use a 100 mg/L barium standard solution (preparation given in the* Accuracy Check*) in place of the sample.*

Turbidimetric Method* (Powder Pillows or AccuVac Ampuls)
*Adapted from Snell and Snell, *Colorimetric Methods of Analysis, Vol. II,* 769 (1959)

5. Add the contents of one BariVer 4 Barium Reagent Powder Pillow to the cell (the prepared sample). Swirl to mix.

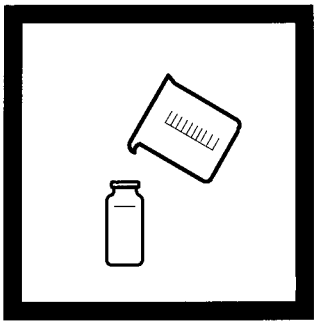
Note: *A white turbidity will develop if barium is present.*



6. Press: **SHIFT TIMER**

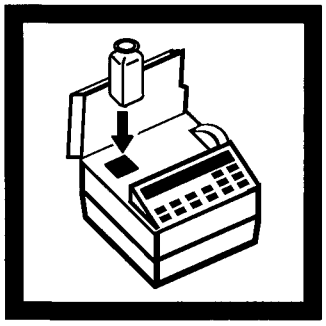
A 5–minute reaction period will begin.

Note: *The sample should not be disturbed during the five–minute turbidity development period. If the BariVer 4 Barium Reagent does not dissolve readily in the sample, use a 25–mL graduated mixing cylinder. Mix the reagent with the sample in the cylinder before pouring it into the sample cell.*



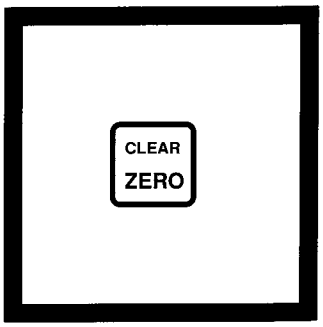
7. Fill another sample cell (the blank) with 25–mL of sample.

Note: *The Pour–Thru Cell cannot be used with this procedure.*



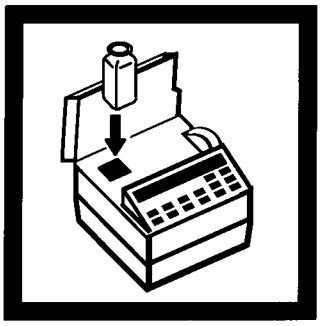
8. When the timer beeps, the display will show:
mg/l Ba

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

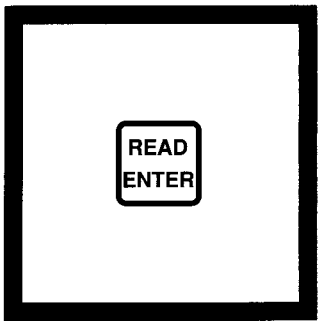


9. Press: **ZERO**

The display will show:
WAIT
then:
0. mg/l Ba



10. Within 10 minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ/ENTER**

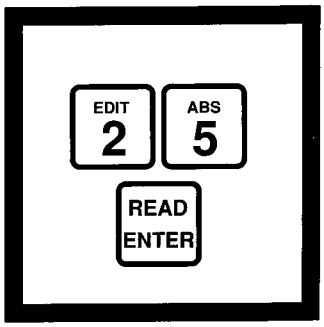
The display will show:
WAIT
then the result, in mg/L barium will be displayed.

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

Note: *If more than five minutes elapse after the timer beeps, ZERO SAMPLE will appear. Remove the prepared sample, insert the blank and press: ZERO. Insert the prepared sample and press: READ/ENTER.*

Note: *Immediately after each test the sample cell should be cleaned with soap, water, and a brush to prevent a film of barium sulfate from developing on the inside of the sample cell.*

USING ACCUVAC AMPULS



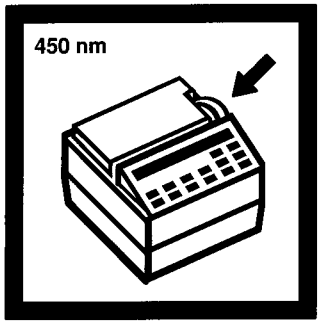
1. Enter the stored program number for barium using AccuVac ampuls.

Press: **2 5 READ/ENTER**

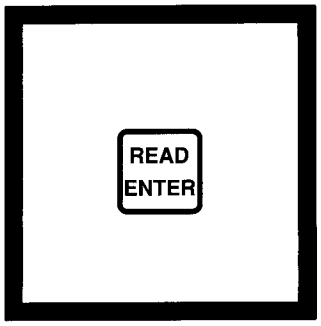
The display will show:
DIAL nm TO 450

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

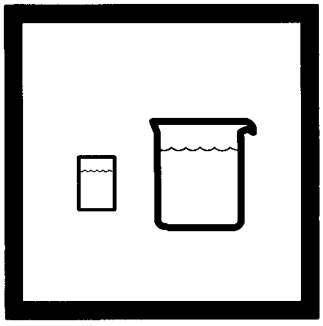


2. Rotate the wavelength dial until the small display shows:
450 nm



3. Press: **READ/ENTER**

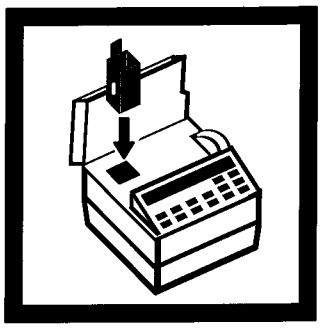
The display will show:
mg/l Ba AV



4. Fill a zeroing vial with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50–mL beaker.

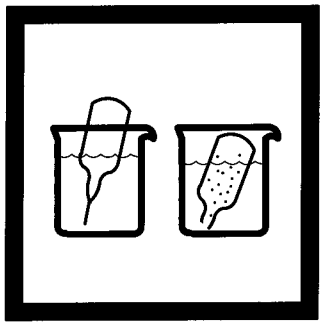
Note: *Filter highly colored or turbid samples using labware listed under* Optional Apparatus.

Note: *For proof of accuracy, use a 100 mg/L Barium standard solution (preparation given in the* Accuracy Check*) in place of the sample.*



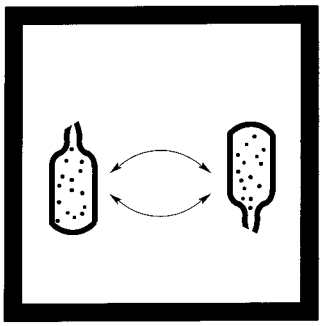
5. Place the AccuVac Vial Adapter into the cell holder of the instrument.

Note: *Place the grip tab at the rear of the cell holder.*



6. Fill a Barium AccuVac Ampul with sample (the prepared sample).

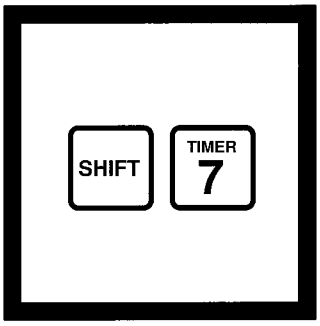
Note: *Keep the tip immersed while the ampul fills completely.*



7. Quickly invert the ampul several times to mix, then wipe off any liquid or fingerprints.

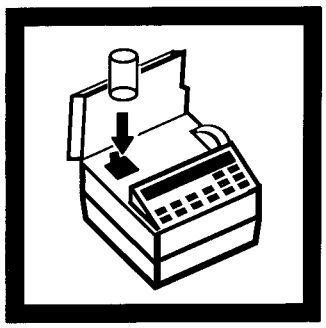
Note: *A white turbidity will develop if barium is present.*

Note: *The sample should not be disturbed during the five minute turbidity–development period.*



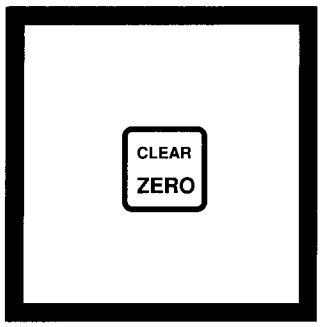
8. Press: **SHIFT TIMER**

A five–minute reaction period will begin.



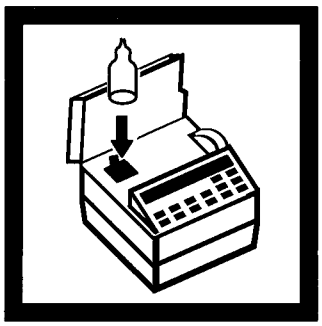
9. When the timer beeps, the display will show:
mg/l Ba AV

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



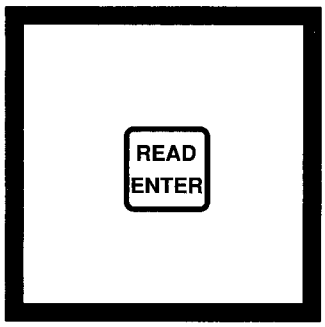
10. Press: **ZERO**

The display will show:
WAIT
then:
0. mg/l Ba AV



11. Place the prepared sample into the cell holder. Close the light shield.

Note: *Take reading within 5 minutes after beeper sounds.*



12. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L barium will be displayed.

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

SAMPLING AND STORAGE

Collect samples in an acid cleaned glass or plastic container. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Preserved samples can be stored up to six months at room temperature. Adjust the pH to 5 with 5.0 N sodium hydroxide before analysis. Correct the test result for volume additions *(see Correction for Volume Additions in Section I).*

ACCURACY CHECK

Standard Additions Method

a) Snap the neck off a Barium Voluette Ampule Standard, 5000 mg/L Ba.

b) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively to three 25–mL samples and mix each thoroughly (for AccuVac ampuls, use 50–mL beakers).

c) Analyze each sample as described above. The barium concentration should increase 20 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

A 100.0–mg/L barium standard solution can be prepared by pipetting 2.00 mL of Barium Voluette Ampule Standard, 5000 mg/L, into a 100–mL volumetric flask and diluting to the mark with demineralized water. This solution should be prepared daily. Perform the barium procedure as described above. The mg/L barium reading should be 100 mg/L.

PRECISION

In a single laboratory using a standard solution of 100 mg/L barium and two representative lots of reagents with the DR/2000, a single operator obtained a standard deviation of ± 1 mg/L barium.

In a single laboratory using a standard solution of 100 mg/L barium and two representative lots of AccuVac ampuls with the DR/2000, a single operator obtained a standard deviation of ± 1.5 mg/L barium.

INTERFERENCES

The following may interfere when present in concentrations exceeding those listed below:

Silica	500 mg/L
Sodium Chloride	130,000 mg/L as NaCl
Magnesium	100,000 mg/L as $CaCO_3$
Calcium	10,000 mg/L as $CaCO_3$
Strontium	Interferes at any level

If strontium is known to be present, the total concentration between barium and strontium may be expressed as a PS (Precipitated by Sulfate). While this

does not distinguish between barium and strontium, it gives an accurate indication of scaling tendency.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment *(see pH Interference in Section I).*

SUMMARY OF METHOD

The BariVer 4 Barium Reagent Powder combines with barium to form a barium sulfate precipitate, which is held in suspension by a protective colloid. The amount of turbidity present caused by the fine white dispersion of particles is directly proportional to the amount of barium present.

REQUIRED REAGENTS AND APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
BariVer 4 Barium Reagent Powder Pillows	1 pillow	50/pkg	12064–66
Clippers, for opening powder pillows	1	each	968–00

REQUIRED REAGENTS (Using AccuVac Ampuls)

BariVer 4 Barium Reagent AccuVac Ampuls	1 ampul	25/pkg	25130–25

REQUIRED APPARATUS (Using AccuVac Ampuls)

Adapter, AccuVac Vial	1	each	43784–00
Beaker, 50 mL	1	each	500–41
Zeroing vial	1	each	21228–00

OPTIONAL REAGENTS

Barium Standard Solution, 50 mg/L Ba	500 mL	1951–49
Nitric Acid, ACS	500 mL	152–49
Nitric Acid Solution, 1:1	500 mL	2540–49
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450–53
Water, demineralized	4 L	272–56

OPTIONAL APPARATUS

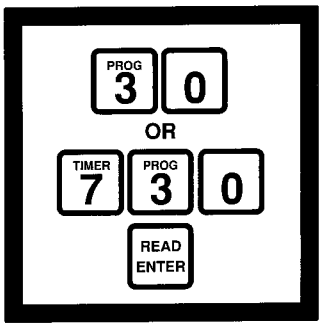
Brush	each	690–00
Filter Paper, folded, 12.5 cm	100/pkg	1894–57
Funnel, poly, 65 mm	each	1083–67
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391–33
pH Meter, EC10, portable	each	50050–00
Pipet, serological, 2 mL	each	532–36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700–01
Pipet Tips, for 19700–01 TenSette Pipet	50/pkg	21856–96
Pipet Filler, safety bulb	each	14651–00
Sample Cell, with 25–mark, matched pair	each pair	20950–00
Sample Cell, 1-inch, polystyrene, disposable	12/pkg	24102–12

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

BENZOTRIAZOLE OR TOLYLTRIAZOLE (0 to 16.0 mg/L)

For cooling or boiler water

UV Photolysis Method*



1. Enter the stored program number for benzotriazole (0 to 16.0 mg/L).

Press: **3 0 READ/ENTER**

OR

Enter the stored program number for tolyltriazole (0 to 20.0 mg/L).

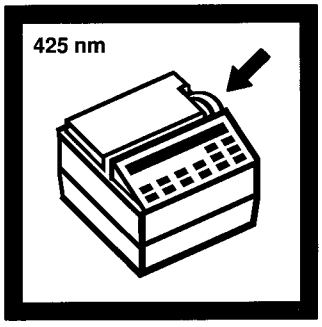
Press: **7 3 0 READ/ENTER**

The display will show:
DIAL nm TO 425

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

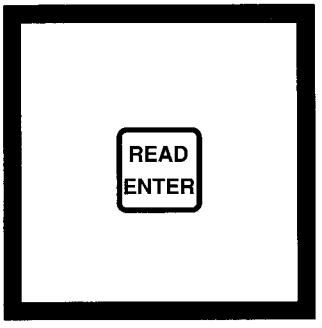
Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

Note: *If samples cannot be analyzed immediately, see* Sampling and Storage *below.*



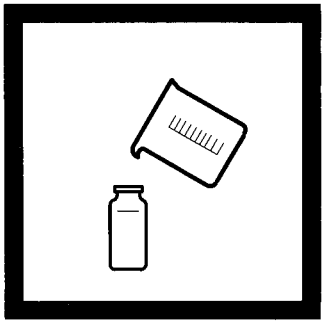
2. Rotate the wavelength dial until the small display shows:

425 nm



3. Press: **READ/ENTER**

The display will show:
mg/l BENZOTRIAZ.
OR
mg/l TOLYLTRIAZ.



4. Fill a sample cell with 25 mL of sample.

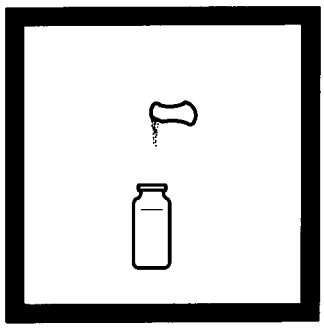
Note: *For proof of accuracy, use a 5.0 mg/L benzotriazole standard solution (preparation given in the* Accuracy Check*) in place of the sample.*

Note: *Sample temperature should be between 20–25 °C (68–78 °F).*

Note: *If sample contains nitrite or borax (sodium borate), adjust the pH to between 4 to 6 with 1 N sulfuric acid.*

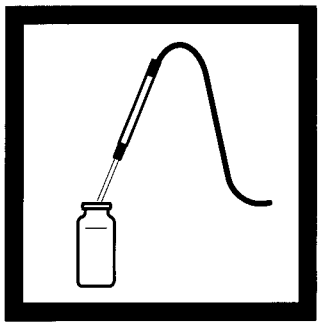
*Adapted from Harp, D., *Proceedings 45th International Water Conference,* 299 (October 22–24, 1984)

BENZOTRIAZOLE OR TOLYLTRIAZOLE, continued



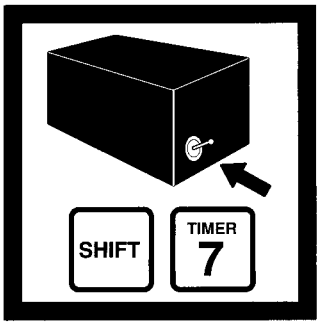
5. Add the contents of one Triazole Reagent Powder Pillow. Swirl to dissolve completely.

Note: *If the sample contains more than 500 mg/L hardness (as $CaCO_3$), add 10 drops of Rochelle Salt Solution.*



6. Insert the ultraviolet lamp into the sample cell.

Note: *UV safety goggles should be worn while the lamp is on.*

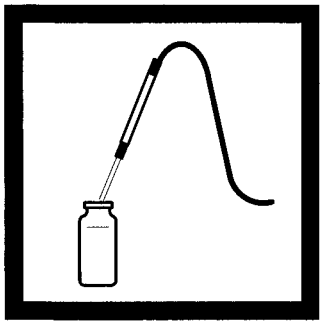


7. Turn the UV lamp ON and press: **SHIFT TIMER**

A 5–minute reaction period will begin.

Note: *A yellow color will form if triazole is present.*

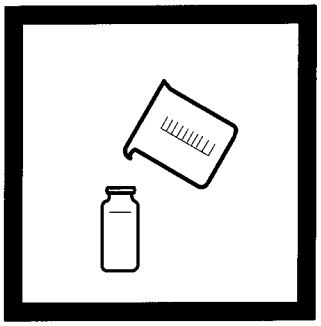
Note: *The Pour–Thru Cell can be used with this procedure.*



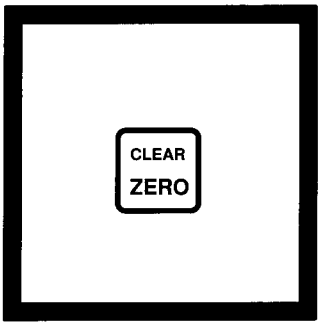
8. When the timer beeps, turn the lamp off. Remove the lamp from the cell (the prepared sample). Swirl the cell to mix thoroughly.

Note: *Low results will occur if photolysis (lamp ON) takes place for more or less than five minutes.*

Note: *Avoid fingerprints on the quartz surface of the lamp. Rinse the lamp and wipe with a soft, clean tissue between tests.*

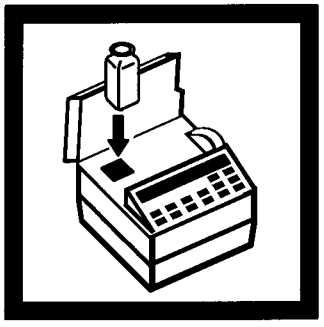


9. Fill another sample cell with 25 mL of sample (the blank). Place the blank into the cell holder. Close the light shield.

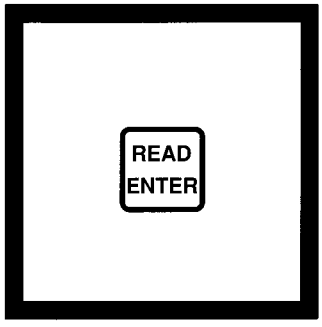


10. Press: **ZERO**

The display will show:
WAIT
then:
0.0 mg/l BENZOTRIAZ
OR
0.0 mg/l TOLYLTRIAZ



11. Place the prepared sample into the cell holder. Close the light shield.



12. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L benzotriazole or mg/L tolyltriazole will be displayed.

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

SAMPLING AND STORAGE
The most reliable results are obtained when samples are analyzed as soon as possible after collection.

ACCURACY CHECK
Standard Additions Method
a) Use the TenSette pipet to add 0.1, 0.2 and 0.3 mL of standard solution, 500 mg/L benzotriazole, to three 25–mL samples. Perform the test according to the above procedure.

Note: The test will not distinguish between benzotriazole and tolyltriazole.

b) Each addition of 0.1 mL of standard solution should increase the benzotriazole reading by 2 mg/L over the reading of an unspiked sample.

c) If these increases are not obtained see *Standard Additions* in *Section I* for more information.

UV Lamp Check
To verify the ultraviolet lamp (normal life equals 5000 hours) is working properly, perform the following test:

a) Prepare a 5.0 mg/L benzotriazole standard solution by pipetting 10.0 mL of benzotriazole standard solution, 500 mg/L benzotriazole, into a 1–L volumetric flask. Dilute to volume.

b) Analyze according to the above procedure. If the result is significantly below 5.0 mg/L, replace the lamp.

PRECISION
In a single laboratory, using a standard solution of 10.0 mg/L benzotriazole and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ± 0.15 mg/L.

In a single laboratory, using a standard solution of 10.0 mg/L tolyltriazole and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ± 0.15 mg/L.

INTERFERENCES
The following may interfere when present in concentrations exceeding those listed below:

Acrylates (as methyl acrylate)	50 mg/L
Alum	400 mg/L
Borate (as sodium tetraborate)	4000 mg/L
Chlorine (as Cl_2)	20 mg/L
Chromium (as chromate)	12 mg/L
Copper	10 mg/L
Hardness	500 mg/L as $CaCO_3$
Iron	20 mg/L
Lignosulfonates	40 mg/L
Magnesium	300 mg/L as $CaCO_3$
Molybdenum (as molybdate)	200 mg/L
Nitrite	4000 mg/L
Phosphonates (AMP or HEDP)	100 mg/L
Sulfate	200 mg/L
Zinc	80 mg/L

Strong oxidizing or reducing agents present in the sample will interfere directly.

SUMMARY OF METHOD
Benzotriazole or tolyltriazole, used in many applications as corrosion inhibitors for copper and copper alloys, are determined by a proprietary catalytic ultraviolet (UV) photolysis procedure requiring less than 10 minutes to perform.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Triazole Reagent Powder Pillows	1 pillow	50/pkg	21412–66

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968–00
UV Safety Goggles	1	each	21134–00

Select one based on available voltage:

Lamp, UV, with power supply, 115 Vac, 60 Hz	each	20828–00
Lamp, UV, with power supply, 230 Vac, 50 Hz	each	20828–02

BENZOTRIAZOLE OR TOLYLTRIAZOLE, continued

OPTIONAL REAGENTS

Benzotriazole Standard Solution, 500 mg/L	105 mL	21413–42
Rochelle Salt Solution	29 mL* DB	1725–33
Sulfuric Acid Standard Solution, 1.0 N	100 mL* MDB	1270–32

OPTIONAL APPARATUS

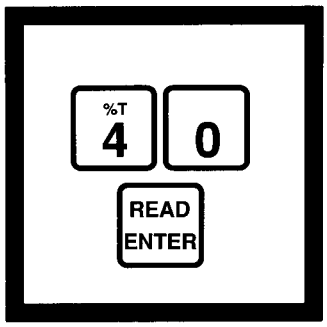
Flask, volumetric, 1000 mL	each	14574–53
Lamp, UV, (lamp only)	each	20823–00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391–33
Pipet Filler, safety bulb	each	14651–00
Pipet, volumetric, Class B, 10 mL	each	515–38
Pour–Thru Cell Assembly Kit	each	45215–00
Single to dual UV lamp cord adapter	each	19485–00
Stopwatch	each	14645–00
Timer, interval, 1 second to ten hours	each	23480–00

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

*Contact Hach for larger sizes.

BORON (0 to 14.0 mg/L)

Carmine Method*



1. Enter the stored program number for boron (B).

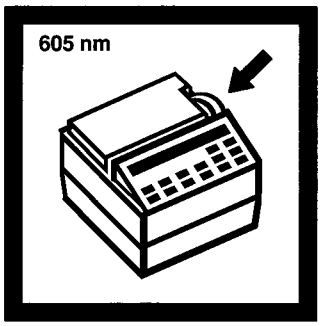
Press: **4 0 READ/ENTER**

The display will show:
DIAL nm TO 605

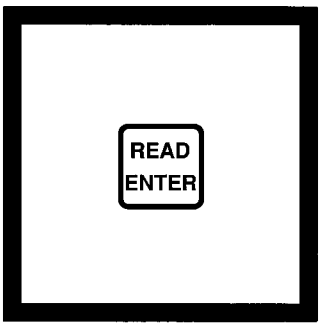
Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

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

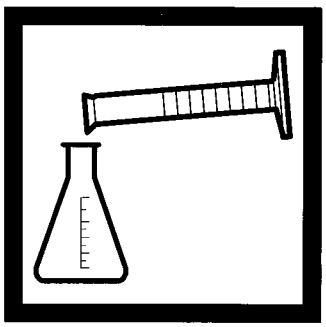


2. Rotate the wavelength dial until the small display shows:
605 nm



3. Press: **READ/ENTER**

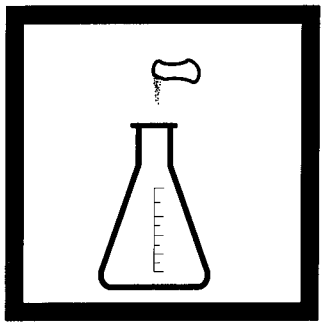
The display will show:
mg/l B



4. Measure 75.0 mL of sulfuric acid, ACS, using a 100–mL graduated cylinder, into a 300–mL erlenmeyer flask.

Note: *All glassware must be completely dry. Excess water will cause low results.*

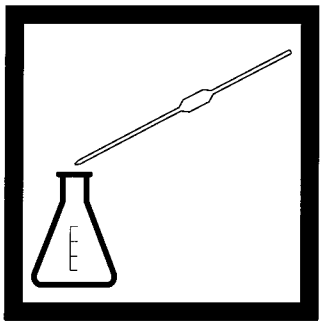
Warning: Do not use a stoppered or capped vessel to complete Steps 4 and 5.



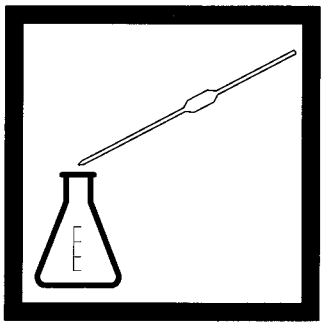
5. Add the contents of one BoroVer 3 Reagent Powder Pillow to the flask. Swirl to mix.

Note: *The powder will dissolve within five minutes.*

Note: *Use adequate ventilation; see* Reagent Preparation *below.*

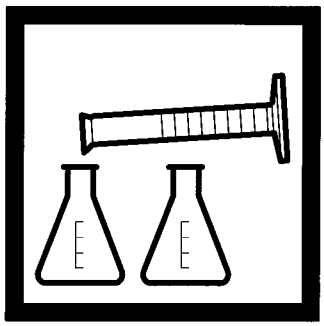


6. Accurately pipet 2.0 mL of demineralized water into a 125–mL erlenmeyer flask (the blank).



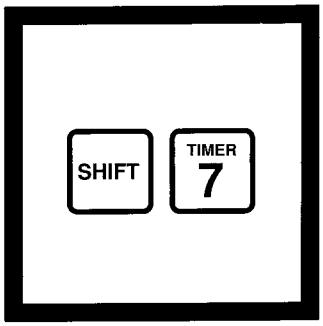
7. Accurately pipet 2.0 mL of sample into another 125–mL erlenmeyer flask (the prepared sample).

Note: *For proof of accuracy, use a 4.0 mg/L boron standard solution (preparation given in the* Accuracy Check*) in place of the sample.*



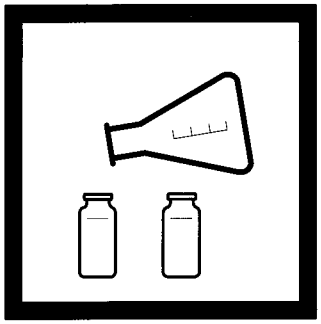
8. Add 35 mL of the BoroVer 3/sulfuric acid reagent solution to each erlenmeyer flask using a 50–mL graduated cylinder. Swirl to mix completely.

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



9. Press: **SHIFT TIMER**

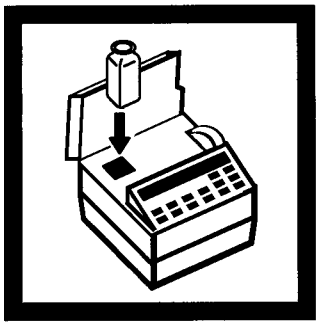
A 25–minute reaction period will begin.



10. When the timer beeps, the display will show:

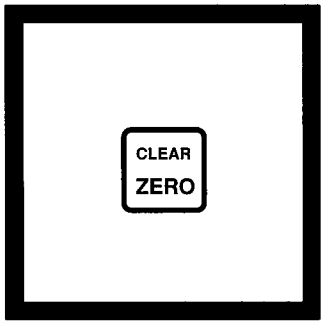
mg/l B

Pour 25 mL from each flask into individual sample cells and label blank and prepared sample.



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

Note: *The Pour–Thru Cell cannot be used with this procedure.*



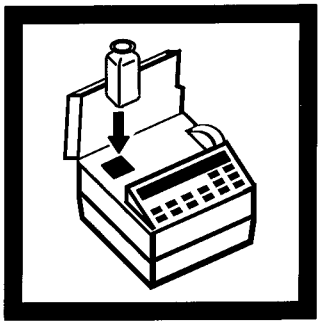
12. Press: **ZERO**

The display will show:

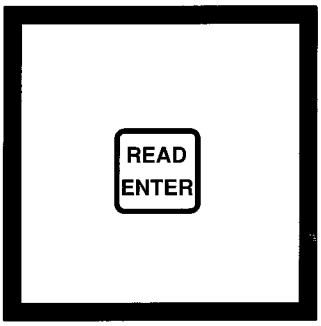
WAIT

then:

0.0 mg/l B



13. Place the prepared sample into the cell holder. Close the light shield.



14. Press: **READ/ENTER**

The display will show:

WAIT

then the result in mg/L boron will be displayed.

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

SAMPLING AND STORAGE

Collect samples in polyethylene bottles or alkali–resistant boron–free glass.

REAGENT PREPARATION

Prepare additional BoroVer 3/sulfuric acid solution by mixing one BoroVer 3 Reagent Powder Pillow per 75 mL of sulfuric acid, ACS, adding the powder pillows individually with stirring. Preparation of this solution generates gaseous HCl when the indicator pillow is added to the concentrated sulfuric acid. **Use of a fume hood or other well–ventilated lab area is strongly advised.** This solution will be stable for up to 48 hours if stored in plastic containers. It should not be stored in Pyrex or Kimax (borosilicate) vessels for longer than one hour because the solution will leach boron from these containers. Use soft glass or polyethylene containers for storage.

ACCURACY CHECK

Standard Additions Method

a) Snap the neck off a Boron Voluette Ampule Standard, 250 mg/L B.

b) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard to three 25–mL portions of sample.

c) Perform the above procedure. The boron concentration reading should increase 1 mg/L for each 0.1 mL of standard solution added.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Check the accuracy of the test using Boron Standard Solution, 4 mg/L as B, listed under Optional Reagents, below. Or, prepare this solution as follows:

a) Pipet 4.00 ml of the Boron Voluette Ampule Standard, 250 mg/L B, into a 250–mL volumetric flask.

b) Dilute to volume with demineralized water. Swirl to mix.

Analyze according to the above procedure using either of these solutions as the sample.

PRECISION

In a single laboratory, using a standard solution of 10 mg/L boron and one representative lot of reagent with the DR/2000, a single operator obtained a standard deviation of ±0.20 mg/L boron.

SUMMARY OF METHOD

Boron is determined by its reaction with carminic acid in the presence of sulfuric acid to produce a reddish to bluish color. The amount of color is directly proportional to the boron concentration.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
BoroVer 3 Boron Reagent Powder Pillows	1 pillow	50/pkg	14170–66
Sulfuric Acid, ACS	75 mL	4 Kg	979–09
Water, demineralized	2.0 mL	4 L	272–56

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968–00
Cylinder, graduated, 50 mL	1	each	508–41
Cylinder, graduated, 100 mL	1	each	508–42
Flask, erlenmeyer, 125 mL	2	each	505–43
Flask, erlenmeyer, 300 mL	1	each	505–47
Pipet, volumetric, Class A, 2.0 mL	2	each	14515–36

OPTIONAL REAGENTS

Boron Standard Solution, 4 mg/L as B	500 mL	1963–49
Boron Standard Solution, Voluette ampule, 250 mg/L B, 10 mL	16/pkg	14249–10

OPTIONAL APPARATUS

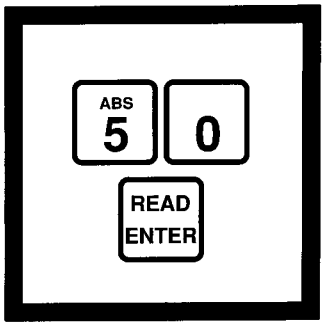
Ampule Breaker Kit	each	21968-00
Cylinder, graduated, 500 mL	each	20885–49
Flask, erlenmeyer, 1000 mL	each	505–53
Pipet, TenSette, 0.1 to 1.0 mL	each	19700–01
Pipet Tips, for 19700–01 TenSette Pipet	50/pkg	21856–96
Pipet, volumetric, 4.00 mL, Class A	each	14515–04
Pipet Filler, safety bulb	each	14651–00
Sample cell, with 25–mL mark	each pair	13537–02

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

BROMINE (0 to 4.50 mg/L)

DPD Method* (Powder Pillows or AccuVac Ampuls)

USING POWDER PILLOWS



1. Enter the stored program number for bromine (Br_2)–powder pillows.

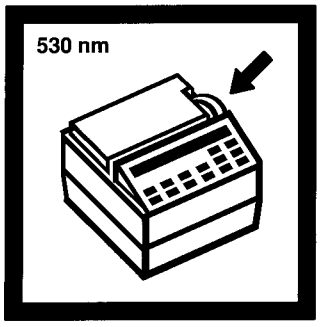
Press: **5 0 READ/ENTER**

The display will show:
DIAL nm TO 530

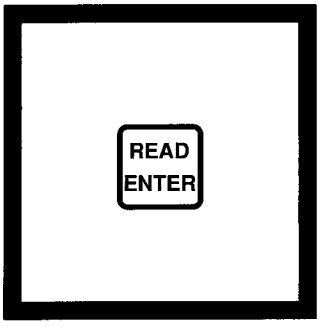
Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

Note: Samples must be analyzed immediately and cannot be preserved for later analysis.

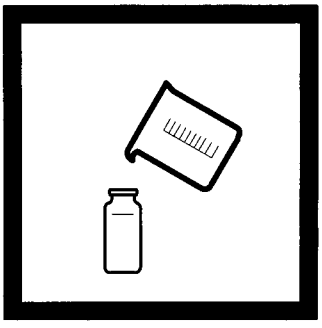


2. Rotate the wavelength dial until the small display shows:
530 nm



3. Press: **READ/ENTER**

The display will show:
mg/l Br_2



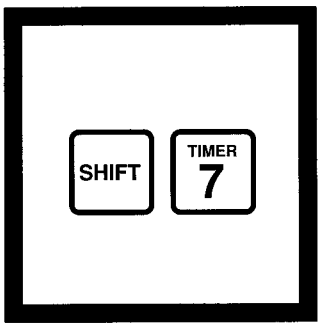
4. Fill a sample cell with 25 mL of sample.

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

5. Add the contents of one DPD Total Chlorine Powder Pillow to the sample cell (the prepared sample). Swirl to mix.

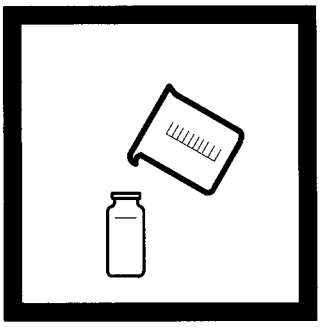
Note: A pink color will develop if bromine is present.

Note: Accuracy is not affected by undissolved powder.



6. Press: **SHIFT TIMER**

A 3–minute reaction period will begin.

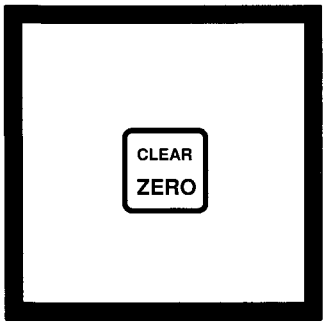


7. When the timer beeps, the display will show:

mg/l Br_2

Fill a second sample cell (the blank) with 25 mL of sample. Place it into the cell holder.

Note: The Pour–Thru Cell can be used with this procedure if it is rinsed shortly after each analysis with demineralized water.



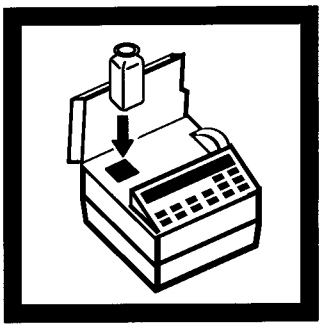
8. Press: **ZERO**

The display will show:

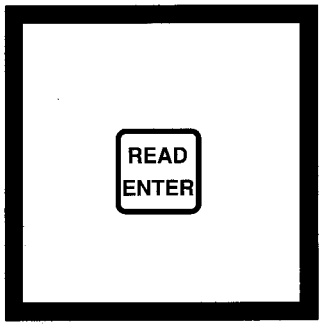
WAIT

then:

0.00 mg/l Br_2



9. Within three minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.



10. Press: **READ/ENTER**

The display will show:

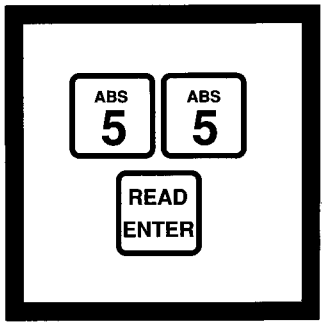
WAIT

then the result in mg/L Br_2 will be displayed.

Note: If the sample temporarily turns yellow after reagent addition, or shows OVER–RANGE, dilute a fresh sample and repeat the test. A slight loss of bromine may occur because of the dilution. Multiply the result by the appropriate dilution factor (see Sample Dilution Techniques in Section I).

Note: In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

USING ACCUVAC AMPULS



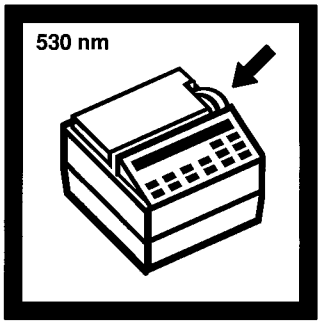
1. Enter the stored program number for bromine (Br_2)–AccuVac ampuls.

Press: **5 5 READ/ENTER**

The display will show:
DIAL nm TO 530

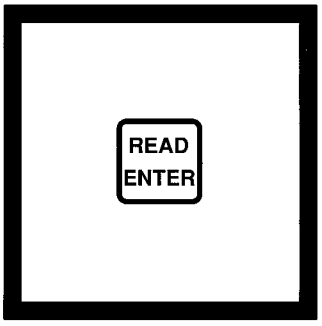
Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*



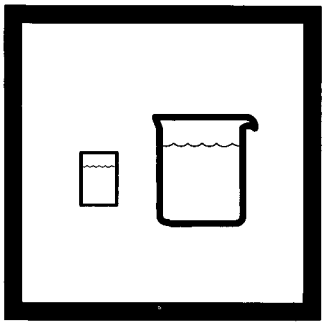
2. Rotate the wavelength dial until the small display shows:
530 nm

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

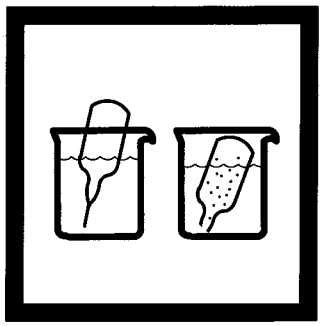


3. Press: **READ/ENTER**

The display will show:
mg/l Br_2 AV

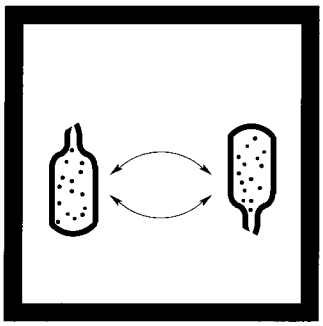


4. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50–mL beaker.



5. Fill a DPD Total Chlorine Reagent AccuVac Ampul with sample.

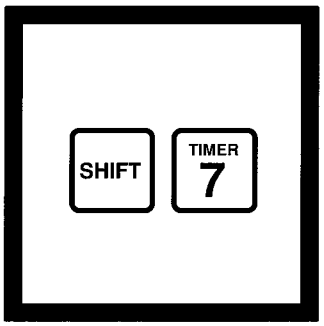
Note: *Keep the tip immersed while the ampul fills completely.*



6. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

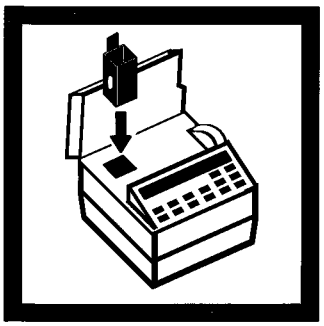
Note: *A pink color will form if bromine is present.*

Note: *Accuracy is not affected by undissolved powder.*



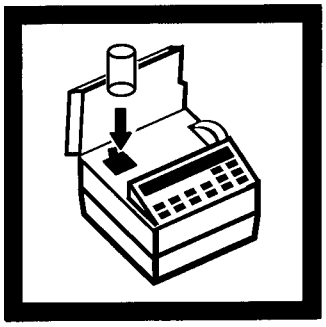
7. Press: **SHIFT TIMER**

A 3–minute reaction period will begin.

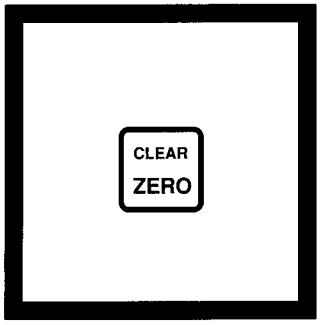


8. Place the AccuVac Vial Adapter into the cell holder.

Note: Place the grip tab at the rear of the cell holder.

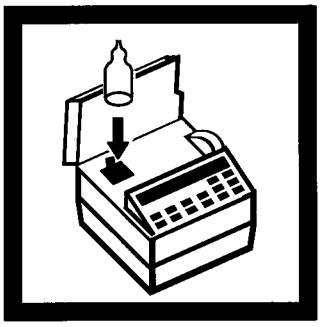


9. When the timer beeps, the display will show:
mg/l Br_2 AV
Place the blank into the cell holder. Close the light shield.

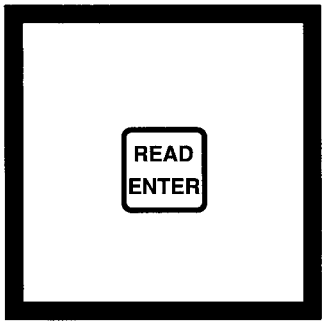


10. Press: **ZERO**

The display will show:
WAIT
then:
0.00 mg/l Br_2 AV



11. Within three minutes after the timer beeps, place the AccuVac Ampul into the cell holder. Close the light shield.



12. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L Br_2 will be displayed.

Note: *If the sample temporarily turns yellow after sample addition, or shows OVER–RANGE, dilute a fresh sample and repeat the test. A slight loss of bromine may occur because of the dilution. Multiply the result by the appropriate dilution factor* (see Sample Dilution Techniques in Section I).

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

ACCURACY CHECK

Standard Additions Method

a) Snap the top off a Chlorine Voluette Ampule Standard Solution.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 ml of standard to three 25–mL samples. Swirl gently to mix. (For AccuVac Ampuls, use 50–mL beakers.)

c) Analyze each sample as described above. Each 0.1 mL of standard will cause an incremental increase in bromine, the exact value of which depends on the chlorine concentration in the Voluette. Check the certificate enclosed with the Voluettes for the incremental chlorine value; then multiply by 2.25 to obtain the value for bromine.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

PRECISION

In a single laboratory, using standard solutions of 1.00 mg/L chlorine (equivalent to 2.25 mg/L bromine) and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ±0.012 mg/L chlorine. This is equivalent to ±0.027 mg/L bromine.

In a single laboratory, using a standard solution of 1.00 mg/L chlorine (equivalent to 2.48 mg/L bromine) and two representative lots of AccuVac ampuls with the DR/2000, a single operator obtained a standard deviation of ±0.009 mg/L chlorine. This is equivalent to ±0.019 mg/L bromine.

INTERFERENCES

Samples containing more than 300 mg/L alkalinity or 150 mg/L acidity as $CaCO_3$ may not develop the full amount of color, or it may instantly fade. Neutralize these samples to a pH of 6 to 7 with 1 N sulfuric acid or 1 N sodium hydroxide. Determine the amount required on a separate 25 mL sample. Add the same amount to the sample to be tested. Correct the test result for volume additions *(see Correction for Volume Additions in Section I).*

Chlorine, iodine, ozone and oxidized forms of manganese and chromium also may react and show as bromine. Compensate for the effects of manganese (Mn^{4+}) or chromium (Cr^{6+}), by adjusting the pH to 6 to 7 as described above. Add 3 drops of 30–g/L potassium iodide to 25 mL of sample, mix and wait one minute. Add 3 drops of 5 g/L Sodium Arsenite and mix. Analyze this sample as described above. (If chromium is present, allow exactly the same reaction period with DPD for both analyses.) Subtract the result of this test from the original analysis to obtain the accurate bromine result. DPD Total Chlorine Reagent Powder Pillows and AccuVac Ampuls contain a buffer formulation which will withstand high (>1000 mg/L) levels of hardness without interference.

SUMMARY OF METHOD

Bromine reacts with DPD (N,N–diethyl–p–phenylenediamine) to form a red color which is proportional to the total bromine concentration.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Total Chlorine ReagentPowder Pillows	1 pillow	100/pkg	14064–99

REQUIRED REAGENTS (Using AccuVac Ampuls)

DPD Total Chlorine Reagent AccuVac Ampuls	1 ampul	25/pkg	25030–25

REQUIRED APPARATUS (Using Powder Pillows)

Clippers, for opening powder pillows	1	each	968–00

REQUIRED APPARATUS (Using AccuVac Ampuls)

Adapter, AccuVac vial	1	each	43784–00
Beaker, 50 mL	1	each	500–41
Vial, zeroing	1	each	21228–00

OPTIONAL REAGENTS

Chlorine Standard Solution, Voluette ampule, 50–75 mg/L, 10 mL	16/pkg	14268–10
Potassium Iodide Solution, 30 g/L	100 mL* MDB	343–32
Sodium Arsenite, 5 g/L	100 mL* MDB	1047–32
Sodium Hydroxide Standard Solution, 1 N	100 mL* MDB	1045–32
Sulfuric Acid Standard Solution, 1 N	100 mL* MDB	1270–32
Water, demineralized	4 L	272–56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052–00
Ampule Breaker Kit	each	21968–00
Cylinder, graduated, 25 mL, poly	each	1081–40
Graph Paper, linear	100/pkg	22313–00
pH Meter, EC10, portable	each	50050–00

OPTIONAL APPARATUS (continued)

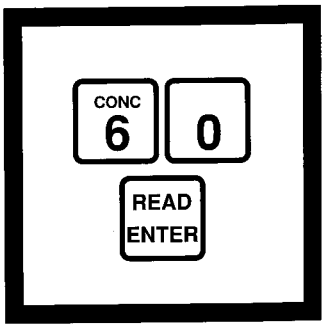
Pipet, TenSette, 0.1 to 1.0 mL	each	19700–01
Pipet Tips, for 19700–01 TenSette Pipet	50/pkg	21856–96
Pour–Thru Cell Assembly Kit	each	45215–00
Sample Cells, 1–inch, polystyrene, disposable	12/pkg	24102–12

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

*Contact Hach for larger sizes

CADMIUM (0 to 80 µg/L)

Dithizone Method*



1. Enter the stored program number for cadmium (Cd).

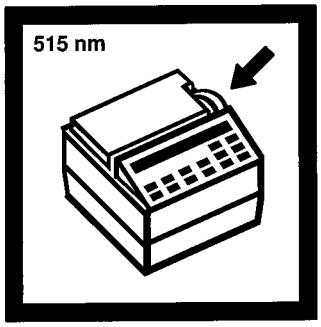
Press: **6 0 READ/ENTER**

The display will show:
DIAL nm TO 515

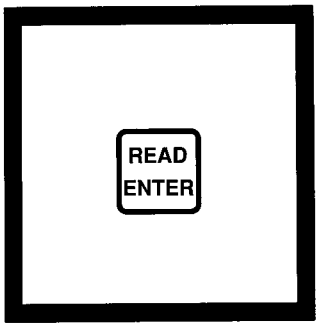
Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

Note: *If sample cannot be analyzed immediately, see* Sampling and Storage, *following these steps. Adjust the pH of stored samples before analysis.*



2. Rotate the wavelength dial until the small display shows:
515 nm

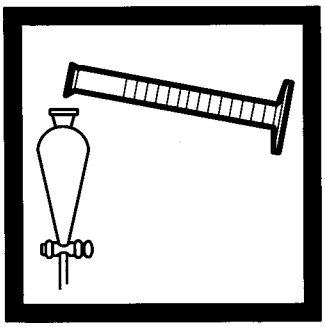


3. Press: **READ/ENTER**

The display will show:
µg/l Cd

Note: *Total cadmium determination requires a prior digestion; use one of the three procedures given in* Digestion (Section I).

Note: *For proof of accuracy, use a 40 µg/L cadmium standard solution (preparation given in the* Accuracy Check*) in place of the sample.*



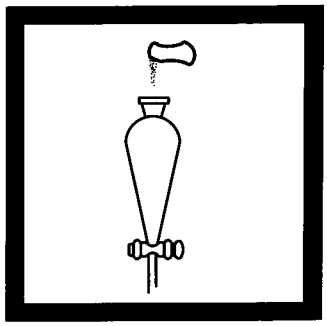
4. Fill a 250–mL graduated cylinder to the 250–mL mark with sample. Pour the sample into a 500–mL separatory funnel.

Note: *Clean all glassware with Nitric Acid Solution, 1:1. Rinse with demineralized water.*

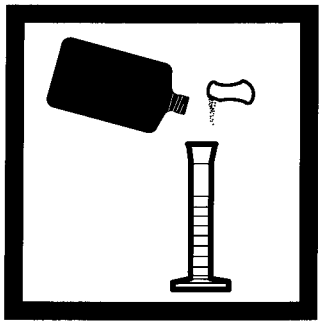
Note: *Cloudy and turbid samples may require filtering before running test. Report results as µg/L soluble cadmium. Use glass membrane type filter to avoid loss of cadmium by adsorption on filter paper.*

Note: *A reagent blank should be determined to obtain the most accurate results. Use demineralized water in place of the sample in Step 4. The amount of reagent blank determined on each lot of DithiVer Metals Reagent Powder Pillow is then subtracted from the reading obtained in Step 15.*

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

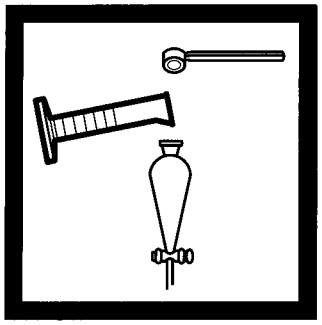


5. Add the contents of one Buffer Powder Pillow, citrate type for heavy metals. Stopper the funnel and shake to dissolve.



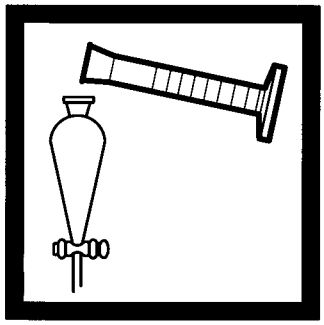
6. Add 30 mL of chloroform to a 50–mL graduated mixing cylinder. Add the contents of one DithiVer Metals Reagent Powder Pillow. Stopper the cylinder. Invert several times to mix (this is DithiVer solution).

Note: *Use adequate ventilation. The DithiVer powder will not all dissolve in the chloroform. For further notes see* DithiVer Solution Preparation and Storage.

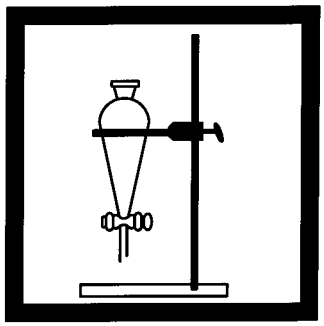


7. Add 20 mL of 50% Sodium Hydroxide Solution and then a 0.1–g scoop of potassium cyanide to the funnel. Shake vigorously for 15 seconds. Remove the stopper and let stand for one minute.

Note: *Spilled reagent will affect test accuracy and is hazardous to skin and other materials*

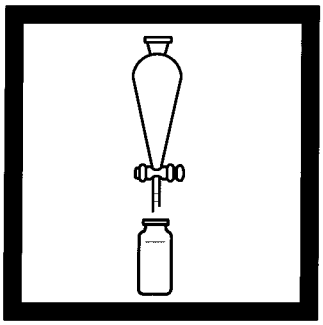


8. Add 30 mL of the DithiVer solution to the 500–mL separatory funnel. Stopper, invert, and open stopcock to vent. Close the stopcock and shake funnel once or twice; vent again. Close the stopcock and shake the funnel vigorously for 60 seconds.



9. Let the funnel stand undisturbed for roughly one minute.

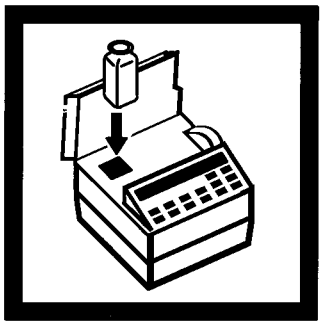
Note: *The bottom (chloroform) layer will be pink if cadmium is present.*



10. Insert a cotton plug the size of a pea into the delivery tube of the funnel and slowly drain the bottom (chloroform) layer into a dry 25–mL sample cell (the prepared sample). Cap.

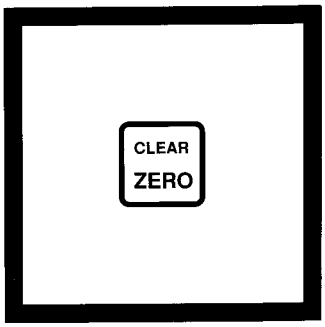
Note: *The cadmium–dithizone complex is stable for hours if the sample cell is kept tightly capped and out of direct sunlight.*

11. Fill a dry 25–mL sample cell with chloroform (the blank). Cap.



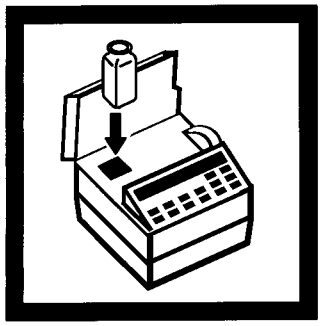
12. Place the blank into the cell holder. Close the light shield.

Note: *The Pour–Thru Cell cannot be used.*

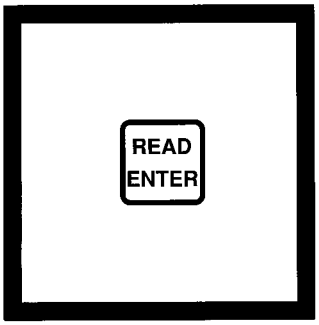


13. Press: **ZERO**

The display will show:
WAIT
then:
0. µg/l Cd



14. Place the prepared sample into the cell holder. Close the light shield.



15. Press: **READ/ENTER**

The display will show:
WAIT
then the result in µg/L cadmium will be displayed.

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

SAMPLING AND STORAGE

Collect samples in an acid–cleaned glass or plastic container. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Store preserved samples up to six months at room temperature. Adjust the pH to 2.5 with 5.0 N sodium hydroxide before analysis. Correct the test result for volume additions *(see Correction for Volume Additions in Section I).*

DITHIVER SOLUTION PREPARATION AND STORAGE

Store DithiVer powder pillows away from light and heat. A convenient way to prepare this solution is to add the contents of 16 DithiVer Metals Reagent Powder Pillows to a pint bottle of chloroform and invert several times until well mixed (carrier powder may not dissolve). Store dithizone solution in an amber glass bottle. This solution is stable for 24 hours.

ACCURACY CHECK

Standard Additions Method

a) Snap the neck off a Cadmium Voluette Ampule Standard Solution, 25 mg/L Cd.

b) Use the TenSette Pipet to add 0.1 mL, 0.2 mL, and 0.3 mL of standard, respectively, to three 250–mL samples. Mix each thoroughly.

c) Analyze each sample as described above. The cadmium concentration should increase 10 µg cadmium/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Prepare a 5.0–mg cadmium/L standard solution by pipetting 5.00 mL of Cadmium Standard Solution, 100–mg/L Cd, into a 100–mL volumetric flask. Dilute to the mark with demineralized water. Prepare this solution daily. Pipet 2.00 mL of the 5.0–mg/L cadmium standard solution into 248 mL of demineralized water in a 500–mL separatory funnel. This is a 40 µg cadmium/L solution. Perform the cadmium test as described in Steps 4 to 16.

PRECISION

In a single laboratory, using a standard solution of 61 µg/L cadmium and two representative lots of reagents with the DR/2000, a single operator obtained a standard deviation of ±0.9 µg/L cadmium.

INTERFERENCES

The following do not interfere:

Aluminum
Antimony
Arsenic
Calcium
Chromium
Cobalt
Iron
Lead
Magnesium
Manganese
Nickel
Tin
Zinc

The following interfere causing high results when present in concentrations exceeding those listed below:

Copper	2 mg/L
Bismuth	80 mg/L
Mercury	all levels
Silver	2 mg/L

Eliminate interference from these metals by the following treatment, beginning after Step 6.

a) Measure about 5 mL of the DithiVer solution into the separatory funnel. Stopper the funnel, invert and open the stopcock to vent. Close the stopcock and shake the solution vigorously for 15 seconds. Allow the funnel to stand undisturbed until the layers separate (about 30 seconds). A yellow, red, or bronze color in the bottom (chloroform) layer confirms the presence of interfering metals. Draw off and discard the bottom (chloroform) layer.

b) Repeat extraction with fresh 5 mL portions of the DithiVer solution (discarding the bottom layer each time) until the bottom layer shows a pure dark green color for three successive extracts. Extractions can be repeated several times without appreciably affecting the amount of cadmium in the sample.

c) Extract the solution with several 2 or 3 mL portions of pure chloroform to remove any remaining DithiVer, again discarding the bottom layer each time.

d) Continue with Step 7.

e) In Step 8, substitute 28.5 mL of DithiVer solution for the 30 mL.

f) Continue with Step 9.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment *(see pH Interference in Section I).*

WASTE MANAGEMENT

Collect all cyanide–containing waste for proper disposal. To prevent release of hydrogen cyanide gas, store cyanide wastes in a strong solution of sodium hydroxide. In the event of a spill or release, clean up the area by following the steps:

a) Use a fume hood or supplied–air or self–contained breathing apparatus.

b) While stirring, add the waste to a beaker containing a strong solution of sodium hydroxide and calcium hypochlorite or sodium hypochlorite (household bleach).

c) Maintain a strong excess of hydroxide and hypochlorite. Let the solution stand for 24 hours.

d) Neutralize and flush the solution down the drain with a large excess of water.

SUMMARY OF METHOD

The dithizone method is designed for the determination of cadmium in water and wastewater. The DithiVer metals reagent is a stable powder form of dithizone. Cadmium ions in basic solution react with dithizone to form a pink to red cadmium–dithizonate complex, which is extracted with chloroform.

REQUIRED REAGENTS

	Cat. No.
Cadmium Reagent Set (68 Tests)	22422–00

Includes: (1) 14202–99, (1) 14458–17, (4) 12616–68, (1) 767–14, (4) 2180–49

Description	Quantity Required Per Test	Unit	Cat. No.
Buffer Powder Pillows, citrate for heavy metals	1 pillow	100/pkg	14202–99
Chloroform, ACS	30 mL	500 mL	14458–49
DithiVer Metals Reagent Powder Pillows	1 pillow	25/pkg	12616–68
Potassium Cyanide, ACS	0.1 g	113 g	767–14
Sodium Hydroxide Solution, 50%	20 mL	500 mL	2180–49
Cotton Balls, absorbent	1	100/pkg	2572–01

REQUIRED APPARATUS

Clippers, for opening pillows	1	each	968–00
Cylinder, graduated, 25 mL	1	each	508–40
Cylinder, graduated, 250 mL	1	each	508–46
Cylinder, mixing, graduated, 50 mL	1	each	1896–41
Funnel, separatory, 500 mL	1	each	520–49
Spoon, measuring, 0.1 g	1	each	511–00
Support Ring, 4"	1	each	580–01
Support Stand, 5" X 8"	1	each	563–00

OPTIONAL REAGENTS

Cadmium Standard Solution, 100 mg/L as Cd	100 mL	14024–42
Cadmium Standard Solution, Voluette ampule, 25 mg/L Cd, 10 mL	16/pkg	14261–10
Nitric Acid Solution, 1:1	500 mL	2540–49
Sodium Hydroxide Standard Solution, 5.0 N	100 mL	2450–32
Sodium Hydroxide Standard Solution, 5.0 N	59 mL	2450–26
Water, demineralized	4 L	272–56

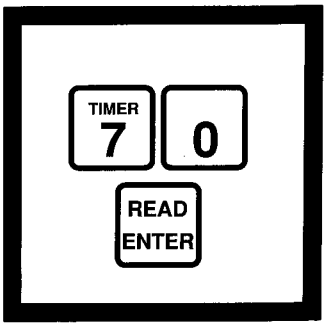
OPTIONAL APPARATUS

Ampule Breaker Kit	each	21968–00
Cylinder, graduated, 5 mL	each	508–37
Filter Discs, glass, 47 mm	100/pkg	2530–00
Flask, erlenmeyer, 500 mL	each	505–49
Flask, filtering, 500 mL	each	546–49
Flask, volumetric, 100 mL	each	547–42
Hot Plate, 3 1/2" diameter, 120 Vac	each	12067–01
Hot Plate, 3 1/2" diameter, 240 Vac	each	12067–02
Membrane Filter Holder, graduated, 500 mL, for 47 mm filter	each	2340–00
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391–33
pH Meter, EC10, portable	each	50050–00
Pipet, serological, 2 mL	each	532–36
Pipet, TenSette, 0.1 to 2.0 mL	each	19700–01
Pipet Tips, for 19700–01 TenSette Pipet	50/pkg	21856–96
Pipet, volumetric, 2.00 mL	each	515–36
Pipet Filler, safety bulb	each	14651–00
Sample Cell, with 25–mL mark, matched pair	each	20950–00
Stopper, hollow, poly, Size No. 0	6/pkg	14480–00
Tongs, crucible	each	569–00

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

CHLORIDE (0 to 20.0 mg/L Cl^-)

Mercuric Thiocyanate Method*



1. Enter the stored program number for Chloride (Cl^-).

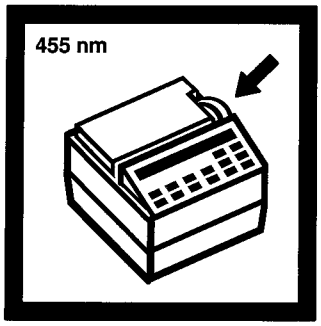
Press: **7 0 READ/ENTER**

The display will show:
DIAL nm TO 455

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

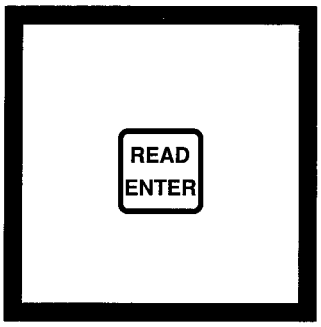
Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

Note: *Samples can be stored for at least 28 days at room temperature in glass or plastic bottles.*



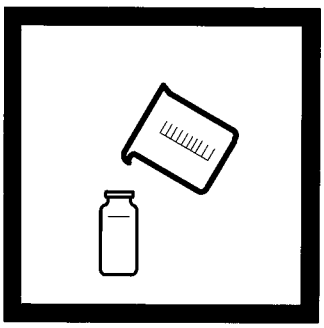
2. Rotate the wavelength dial until the small display shows:
455 nm

Note: *Approach the wavelength setting from higher to lower values.*



3. Press: **READ/ENTER**

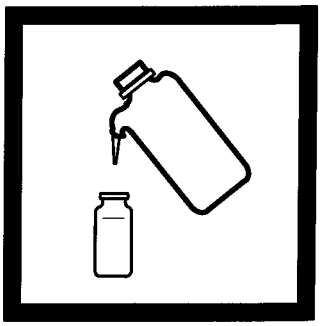
The display will show:
mg/l Cl^-



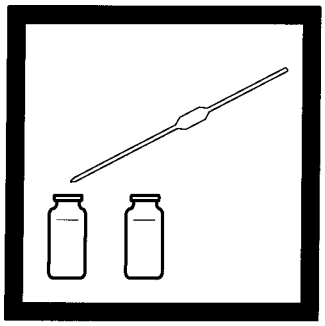
4. Fill a sample cell with 25 mL of sample (the prepared sample).

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

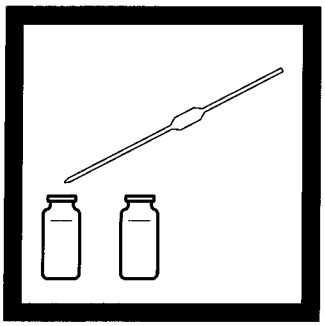
Note: *For proof of accuracy, use a 10.0 mg/L chloride standard solution (preparation given in the* Accuracy Check*) in place of the sample.*



5. Fill another sample cell with 25 mL of demineralized water (the blank).

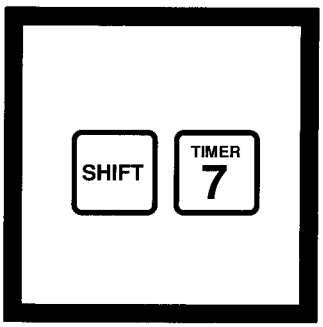


6. Pipet 2.0 mL of Mercuric Thiocyanate Solution into each sample cell. Swirl to mix.



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

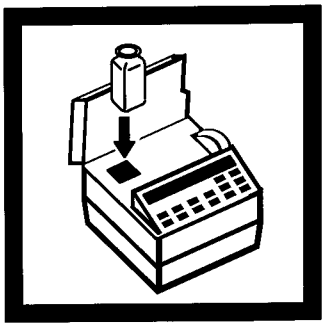
Note: *An orange color will develop if chloride is present.*



8. Press: **SHIFT TIMER**

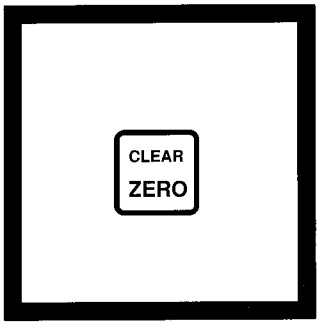
A 2–minute reaction period will begin.

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



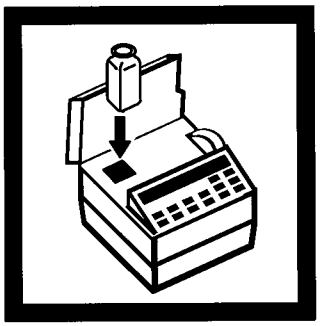
9. When the timer beeps, the display will show:
mg/l Cl^-
Place the blank into the cell holder. Close the light shield.

Note: The Pour–Thru Cell can be used with this procedure.

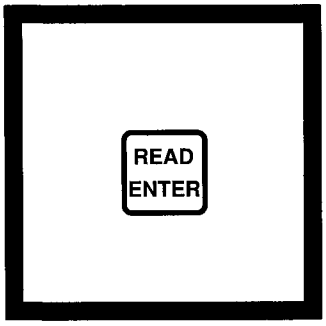


10. Press: **ZERO**

The display will show:
WAIT
then:
0.0 mg/l Cl^-



11. Place the prepared sample into the cell holder. Close the light shield.



12. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L chloride (Cl^-) will be displayed.

***Note:** In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the results.*

ACCURACY CHECK

Standard Additions Method

a) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of Chloride Standard Solution, 1000 mg/L as Cl^-, to each of three 25–mL water samples. Mix each thoroughly.

b) Analyze each sample as described above.

c) The chloride concentration should increase 4.0 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Prepare a 10.0 mg/L chloride standard solution by diluting 5.00 mL of Chloride Standard Solution, 1000 mg/L to 500 mL with demineralized water.

PRECISION

In a single laboratory, using a standard solution of 10 mg/L chloride and two lots of reagent with the DR/2000, a single operator obtained a standard deviation of ±0.3 mg/L chloride.

INTERFERENCES

The pH of the sample after addition of reagents should be about 2. If the sample is strongly acid 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.

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 concentration. Chloride at these levels also can be determined directly using the Chloride Ion Selective Electrode (Cat. No. 44510–71)

REQUIRED REAGENTS

	Cat. No.
Chloride Reagent Set (50 Tests*)	23198–00
Includes: (1) 22122-42, (1) 22121-31	

Description	Quantity Required Per Test	Unit	Cat. No.
Ferric Ion Solution	2 mL	100 mL	22122–42
Mercuric Thiocyanate Solution	4 mL	236 mL	22121–31
Water, demineralized	25 mL	4 L	272–56

REQUIRED APPARATUS

Pipet, volumetric, 1.0 mL	1	each	515–35
Pipet, volumetric, 2.0 mL	1	each	515–36
Pipet Filler, safety bulb	1	each	14651–00
OR			
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

Chloride Standard Solution, 1000 mg/L as Cl	500 mL	183–49
Perchloric Acid, ACS, 70%	680 g	757–65
Sodium Hydroxide Standard Solution, 5.0 N	59 mL SCDB	2450–26

OPTIONAL APPARATUS

Filter Paper, folded, mod. rapid, 12.5 cm	100/box	692–57
Flask, erlenmeyer, 125 mL	each	505–43
Flask, volumetric, 500 mL	each	547–49
Funnel, filtering, polypropylene, 75 mm	each	1083–68
pH Paper, 1 to 11 pH	5 rolls/pkg	391–33
Pipet, volumetric, Class A, 5 mL	each	14515–37
Pour–Thru Cell Assembly Kit	each	45215–00

Chloride at these levels can be determined directly using the Chloride Ion Selective Electrode (Cat. No. 44510–71)

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

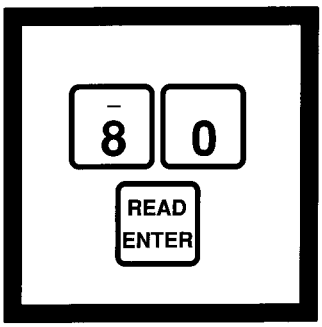
*50 tests equals 25 samples and 25 blanks.

CHLORINE, FREE (0 to 2.00 mg/L)

For water, wastewater and seawater

DPD Method* (Powder Pillows or AccuVac Ampuls), USEPA accepted for reporting wastewater and drinking water analysis**

USING POWDER PILLOWS



1. Enter the stored program number for free and total chlorine (Cl_2)–powder pillows.

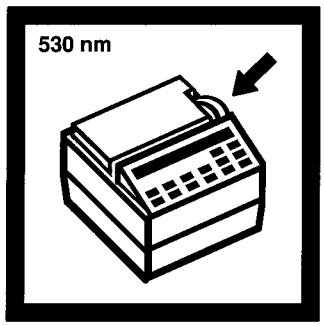
Press: **8 0 READ/ENTER**

The display will show:
DIAL nm TO 530

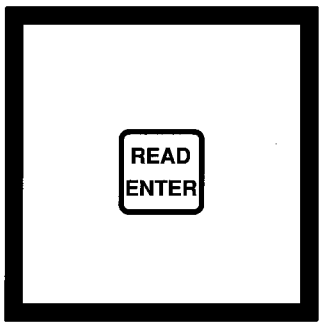
Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

Note: Samples must be analyzed immediately and cannot be preserved for later analysis.

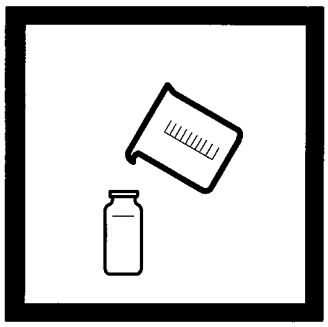


2. Rotate the wavelength dial until the small display shows:
530 nm



3. Press: **READ/ENTER**

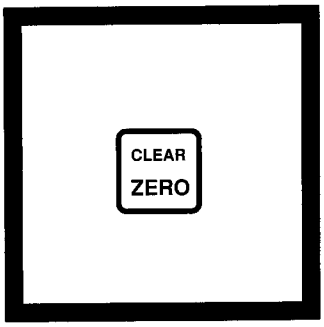
The display will show:
mg/l Cl_2



4. Fill a sample cell with 25 mL of sample (the blank). Place it into the cell holder.

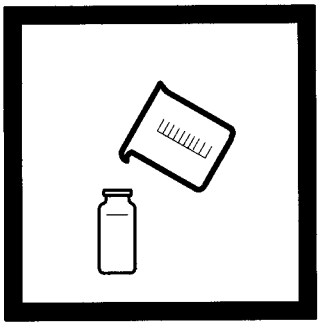
*Adapted from *Standard Methods for the Examination of Water and Wastewater.*

**Procedure is equivalent to USEPA method 330.5 for wastewater and Standard Method 4500–Cl G for drinking water.

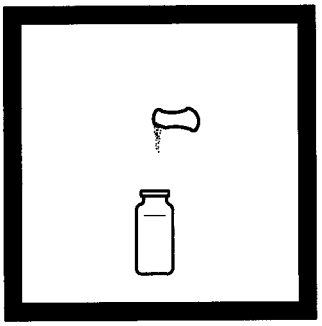


5. Press: **ZERO**

The display will show:
WAIT
then:
0.00 mg/l Cl_2



6. Fill another cell with 25 mL of sample.

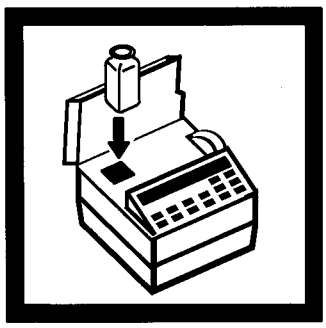


7. Add the contents of one DPD Free Chlorine Powder Pillow to the sample cell (the prepared sample). Stopper the sample cell and shake for 20 seconds. Remove stopper.

Note: *A pink color will develop if free chlorine is present.*

Note: *Accuracy is not affected by undissolved powder.*

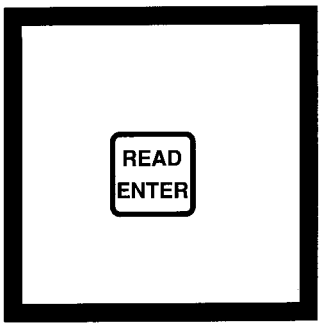
Note: *Shaking the cell dissipates bubbles which may form in samples containing dissolved gases.*



8. Immediately (within one minute of reagent addition) place the prepared sample into the cell holder. Close the light shield.

Note: *The Pour–Thru Cell can be used with this procedure if it is rinsed shortly after each analysis with demineralized water.*

Note: *Do not push SHIFT TIMER. Proceed immediately to Step 9.*



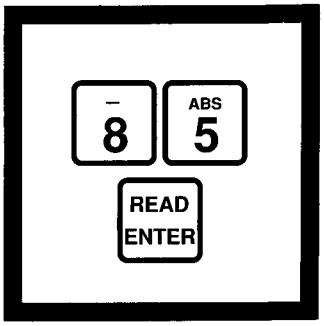
9. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L chlorine (Cl_2) will be displayed.

Note: *If the sample temporarily turns yellow after reagent addition, or shows OVER–RANGE, dilute a fresh sample and repeat the test. A slight loss of chlorine may occur because of the dilution. Multiply the result by the appropriate dilution factor* (see Sample Dilution Techniques in Section I).

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

USING ACCUVAC AMPULS



1. Enter the stored program number for free and total chlorine (Cl_2)–AccuVac ampuls.

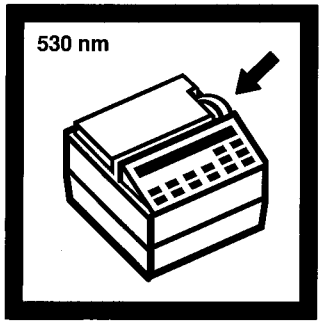
Press: **8 5 READ/ENTER**

The display will show:
DIAL nm to 530

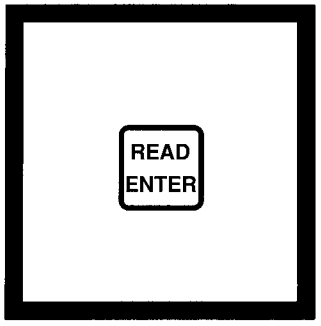
Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

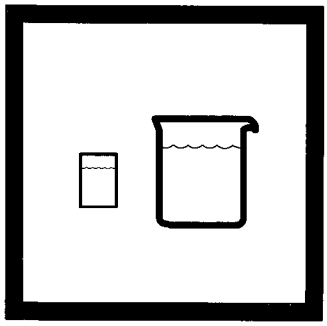


2. Rotate the wavelength dial until the small display shows:
530 nm

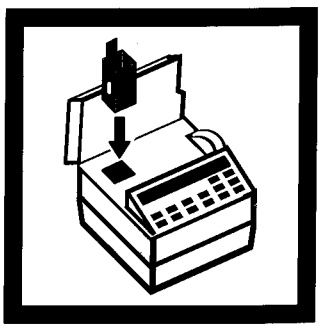


3. Press: **READ/ENTER**

The display will show:
mg/l Cl_2 AV

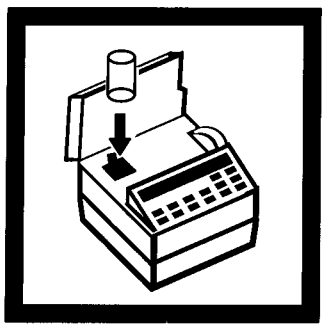


4. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50–mL beaker.

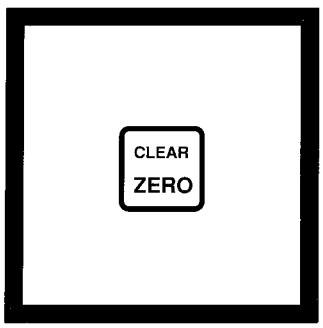


5. Place the AccuVac Vial Adapter into the cell holder of the instrument.

Note: *Place the grip tab at the rear of the cell holder.*

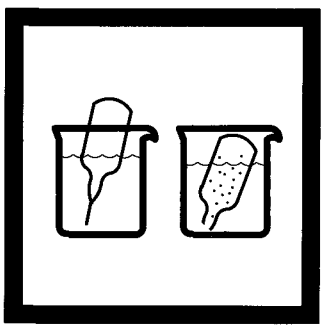


6. Place the blank into the cell holder. Close the light shield.



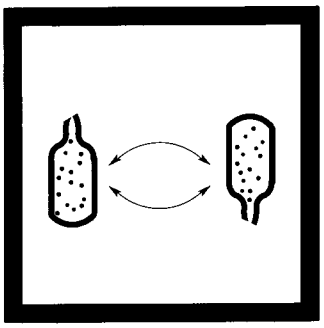
7. Press: **ZERO**

The display will show:
WAIT
then:
0.00 mg/l Cl_2 AV



8. Fill a DPD Free Chlorine Reagent AccuVac Ampul with sample.

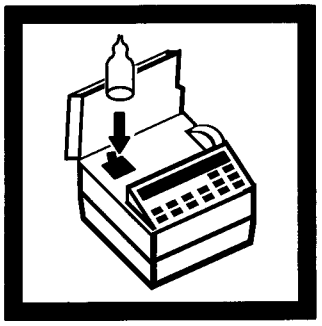
Note: *Keep the tip immersed while the ampul fills completely.*



9. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

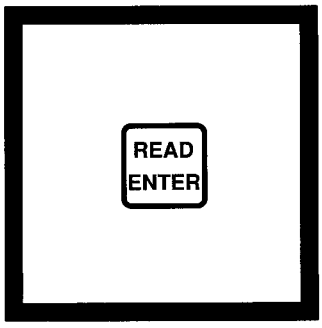
Note: A pink color will form if free chlorine is present.

Note: Accuracy is not affected by undissolved powder.



10. Immediately (within one minute of sample addition) place the AccuVac ampul into the cell holder. Close the light shield.

Note: Do not press SHIFT TIMER. Proceed immediately to Step 11.



11. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L Cl_2 will be displayed.

Note: If the sample temporarily turns yellow after sample addition, or shows OVER–RANGE, dilute a fresh sample and repeat the test. A slight loss of chlorine may occur due to the dilution. Multiply the result by the appropriate dilution factor (see Sample Dilution Techniques in Section I).

Note: In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

ACCURACY CHECK

Standard Additions Method

a) Snap the top off a Chlorine Voluette Ampule Standard Solution.

b) Use the TenSette Pipet to add 0.1, 0.2 and 0.3 mL of standard to three 25–mL samples. Swirl gently to mix. (For AccuVac ampuls, use 50–mL beakers.)

c) Analyze each sample as described above. Each 0.1 mL of standard will cause an incremental increase in chlorine, the exact value of which depends on the concentration in the Voluette. Check the certificate enclosed with the Voluettes for this value.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

PRECISION

In a single laboratory, using a standard solution of 1.00 mg/L chlorine and two representative lots of reagents with the DR/2000, a single operator obtained standard deviations of ± 0.012 mg/L chlorine.

In a single laboratory, using a standard solution of 1.10 mg/L chlorine and two representative lots of AccuVac ampuls with the DR/2000, a single operator obtained a standard deviation of ± 0.009 mg/L chlorine.

INTERFERENCES

Samples containing more than 250 mg/L alkalinity or 150 mg/L acidity as $CaCO_3$ may not develop the full amount of color, or it may instantly fade. Neutralize these samples to a pH of 6 to 7 with 1 N sulfuric acid, or 1 N sodium hydroxide. Determine the amount required on a separate 25–mL sample; then add the same amount to the sample to be tested.

Samples containing monochloramine will cause a gradual drift to higher chlorine readings. When read within one minute of reagent addition, 3.0 mg/L monochloramine will cause an increase of less than 0.1 mg/L in the free chlorine reading.

Bromine, iodine, ozone and oxidized forms of manganese and chromium also may react and show as chlorine. To compensate for the effects of manganese (Mn^{4+}) or chromium (Cr^{6+}), adjust pH to 6 to 7 as described above, then add 3 drops of potassium iodide, 30 g/L, to 25 mL of sample, mix and wait 1 minute. Add 3 drops of sodium arsenite, 5 g/L, and mix. Analyze this sample as described above. (If chromium is present, allow exactly the same reaction period with the DPD for both analyses.) Subtract the result of this test from the original analysis to obtain the accurate chlorine result.

DPD Free Chlorine Reagent Powder Pillows and AccuVac Ampuls contain a buffer formulation which will withstand high (at least 1000 mg/L) levels of hardness without interference.

SUMMARY OF METHOD

Chlorine in the sample as hypochlorous acid or hypochlorite ion (free chlorine or free available chlorine) immediately reacts with DPD (N,N–diethyl–p–phenylenediamine) indicator to form a red color which is proportional to the chlorine concentration.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Free Chlorine Reagent Powder Pillows, 25 mL	1 pillow	100/pkg	14070–99

REQUIRED REAGENTS (Using AccuVac Ampuls)

DPD Free Chlorine Reagent AccuVac Ampuls	1 ampul	25/pkg	25020–25

REQUIRED APPARATUS (Using Powder Pillows)

Clippers, for opening powder pillows	1	each	968–00
Stopper, rubber, No 2	1	12/pkg	2118–02

REQUIRED APPARATUS (Using AccuVac Ampuls)

Adapter, AccuVac vial	1	each	43784–00
Beaker, 50 mL	1	each	500–41
Vial, Zeroing	1	each	21228–00

OPTIONAL REAGENTS

Chlorine Standard Solution, Voluette ampule, 50–75 mg/L, 10 mL	16/pkg	14268–10
Potassium Iodide Solution, 30 g/L	100 mL* MDB	343–32
Sodium Arsenite, 5 g/L	100 ml* MDB	1047–32
Sodium Hydroxide Standard Solution, 1.000 N	100 mL* MDB	1045–32
Sulfuric Acid Standard Solution, 1.000 N	100 mL* MDB	1270–32
Water, demineralized	4 L	272–56

OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052–00
Ampule Breaker Kit	each	21968–00
Cylinder, graduated, 25 mL, poly	each	1081–40
Graph Paper, linear	100/pkg	22313–00
pH Meter, EC10 portable	each	50050–00
Pipet, Tensette, 0.1 to 1.0 mL	each	19700–01
Pipet Tips, for 19700–01 TenSette Pipet	50/pkg	21856–96
Pour–Thru Cell Assembly Kit	each	45215–00

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

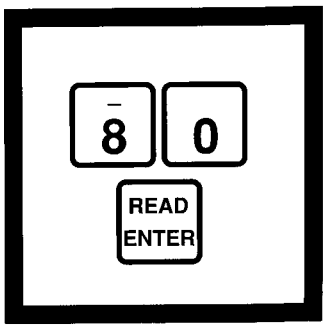
[k]Contact Hach for larger sizes.

CHLORINE, TOTAL (0 to 2.00 mg/L)

For water, wastewater and seawater

DPD Method* (Powder Pillows or AccuVac Ampuls), USEPA accepted for reporting drinking water analysis**

USING POWDER PILLOWS



1. Enter the stored program number for free and total chlorine (Cl_2)–powder pillows.

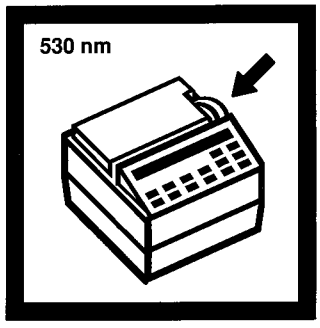
Press: **8 0 READ/ENTER**

The display will show:
DIAL nm TO 530

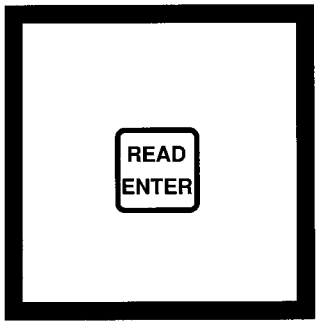
Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

Note: Samples must be analyzed immediately and cannot be preserved for later analysis.

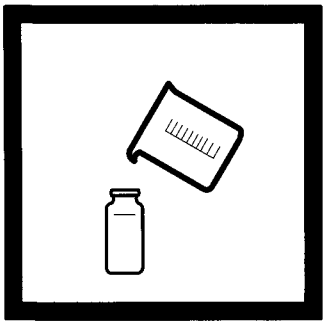


2. Rotate the wavelength dial until the small display shows:
530 nm



3. Press: **READ/ENTER**

The display will show:
mg/l Cl_2



4. Fill a sample cell with 25 ml of sample.

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

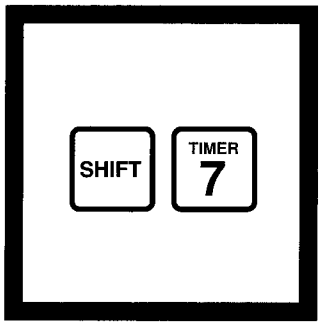
**Procedure is equivalent to USEPA method 330.5 for wastewater and Standard Method 4500–Cl G for drinking water.

5. Add the contents of one DPD Total Chlorine Powder Pillow to the sample cell (the prepared sample). Stopper the sample cell and shake for 20 seconds. Remove stopper.

Note: A pink color will develop if chlorine is present.

Note: Accuracy is not affected by undissolved powder.

Note: Shaking the cell dissipates bubbles which may form in samples containing dissolved gases.



6. Press: **SHIFT TIMER**

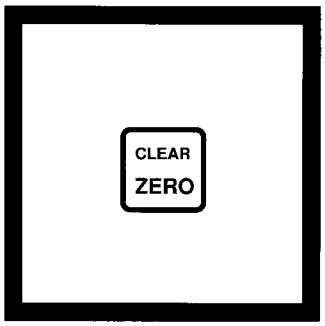
A 3–minute reaction period will begin.

7. When the timer beeps, the display will show:

mg/l Cl_2

Fill another sample cell (the blank) with 25 mL of sample. Place it into the cell holder.

Note: The Pour–Thru Cell can be used with this procedure if it is rinsed shortly after each analysis with demineralized water.



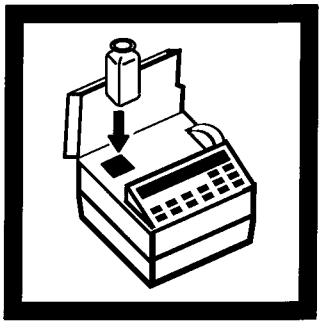
8. Press: **ZERO**

The display will show:

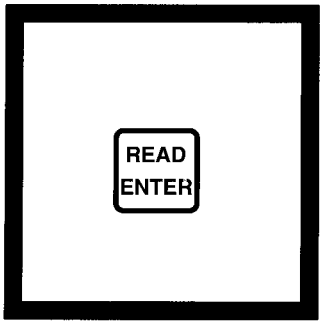
WAIT

then:

0.00 mg/l Cl_2



9. Within three minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.



10. Press: **READ/ENTER**

The display will show:

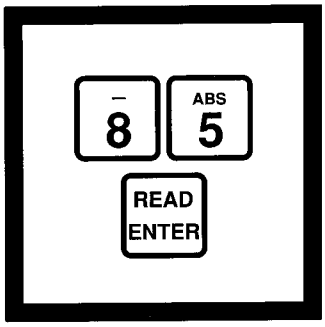
WAIT

then the result in mg/L chlorine (Cl_2) will be displayed.

Note: If the sample temporarily turns yellow after sample addition, or shows OVER–RANGE, dilute a fresh sample and repeat the test. A slight loss of chlorine may occur because of the dilution. Multiply the result by the appropriate dilution factor (see Sample Dilution Techniques in Section I).

Note: In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

USING ACCUVAC AMPULS



1. Enter the stored program number for free and total chlorine (Cl_2)–AccuVac ampuls.

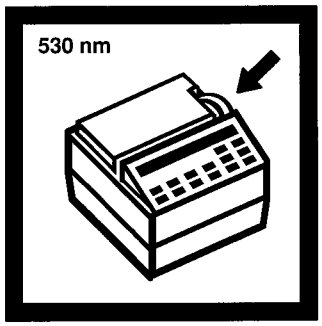
Press: **8 5 READ/ENTER**

The display will show:
DIAL nm TO 530

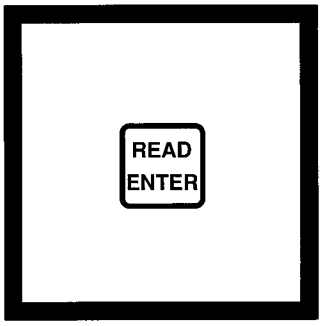
Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

Note: *Samples must be analyzed immediately and cannot be preserved for later analysis.*

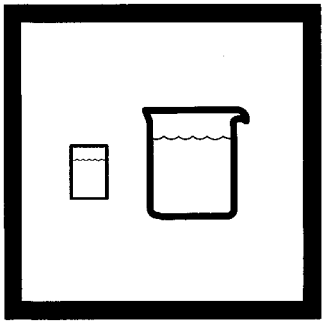


2. Rotate the wavelength dial until the small display shows:
530 nm

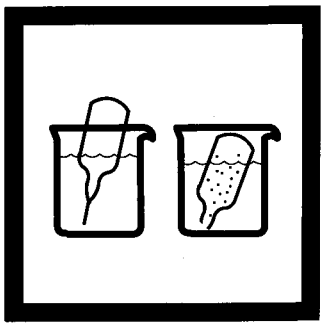


3. Press: **READ/ENTER**

The display will show:
mg/l Cl_2 AV

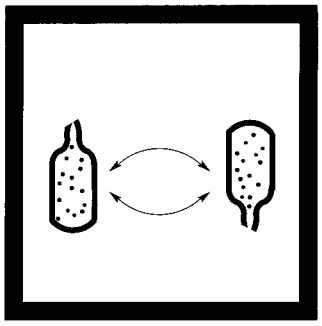


4. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50–mL beaker.



5. Fill a DPD Total Chlorine Reagent AccuVac Ampul with sample.

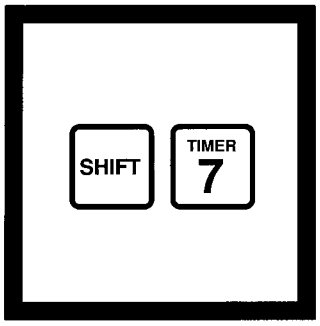
Note: Keep the tip immersed while the ampul fills completely.



6. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

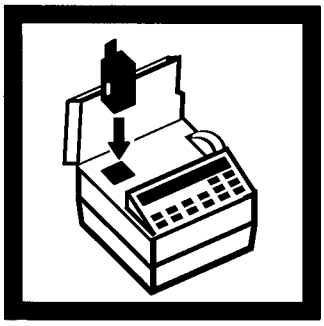
Note: A pink color will form if chlorine is present.

Note: Accuracy is not affected by undissolved powder.



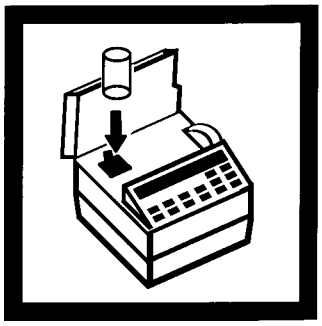
7. Press: **SHIFT TIMER**

A 3–minute reaction period will begin.



8. Place the AccuVac Vial Adapter in the cell holder of the instrument.

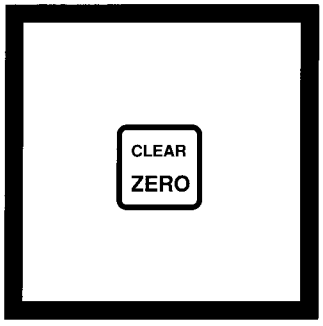
Note: Place the grip tab at the rear of the cell holder.



9. When the timer beeps, the display will show:

mg/l Cl_2 AV

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



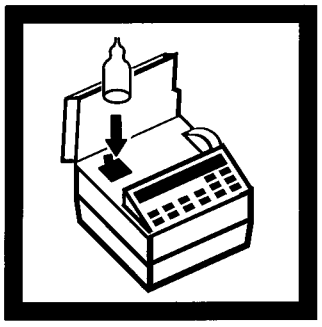
10. Press: **ZERO**

The display will show:

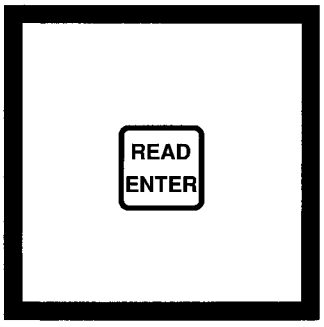
WAIT

then:

0.00 mg/l Cl_2 AV



11. Within three minutes after the timer beeps, place the AccuVac ampul into the cell holder. Close the light shield.



12. Press: **READ/ENTER**

The display will show:

WAIT

then the result in mg/L chlorine (Cl_2) will be displayed.

Note: If the sample temporarily turns yellow after sample addition, or shows OVER–RANGE, dilute a fresh sample and repeat the test. A slight loss of chlorine may occur because of the dilution. Multiply the result by the appropriate dilution factor (see Sample Dilution Techniques in Section I).

Note: In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

ACCURACY CHECK

Standard Additions Method

a) Snap the top off the Chlorine Voluette Ampule Standard Solution.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to three 25–mL samples. Swirl gently to mix. (For AccuVac Ampuls, use 50–mL beakers.)

c) Analyze each sample as described above. Each 0.1 mL of standard will cause a incremental increase in chlorine, the exact value of which depends of the concentration in the Voluette. Check the certificate enclosed with the Voluettes for this value.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

PRECISION

In a single laboratory, using a standard solution of 1.00 mg/L chlorine and two lots of reagents with the DR/2000, a single operator obtained standard deviations of ±0.012 mg/L chlorine.

In a single laboratory, using a standard solution of 1.10 mg/L chlorine and two representative lots of AccuVac ampuls with the DR/2000, a single operator obtained a standard deviation of ±0.009 mg/L chlorine.

INTERFERENCES

Samples containing more than 300 mg/L alkalinity or 150 mg/L acidity as $CaCO_3$ may not develop the full amount of color, or it may instantly fade. Neutralize these samples to a pH of 6 to 7 with 1 N sulfuric acid, or 1 N sodium hydroxide. Determine the amount required on a separate 25 mL sample. Add the same amount to the sample to be tested. Correct for volume additions.

Bromine, iodine, ozone and oxidized forms of manganese and chromium also may react and read as chlorine. To compensate for the effects of manganese (Mn^{4+}) or chromium (Cr^{6+}), adjust the pH to 6 to 7 as described above; then add 3 drops of potassium iodide, 30 g/L, to 25 mL of sample, mix and wait one minute. Add 3 drops of sodium arsenite, 5 g/L, and mix. Analyze this sample as described above. (If chromium is present, allow exactly the same reaction period with the DPD for both analyses.) Subtract the result of this test from the original analysis to obtain the accurate chlorine result.

DPD Total Chlorine Reagent Powder Pillows and AccuVac Ampuls contain a buffer formulation which will withstand high levels of hardness (at least 1000 mg/L) without interference.

SUMMARY OF METHOD

Chlorine can be present in water as free available chlorine and as combined available chlorine. Both forms can exist in the same water and be determined together as the total available chlorine. Free chlorine is present as hypochlorous acid and/or hypochlorite ion. Combined chlorine exists as monochloramine, dichloramine, nitrogen trichloride and other chloroderivatives. The combined chlorine oxidizes iodide in the reagent to iodine. The iodine reacts with DPD (N, N–diethyl–p–phenylenediamine) along with free chlorine present in the sample to form a red color which is proportional to the total chlorine concentration. To determine the concentration of combined chlorine, run a free chlorine test. Subtract the results from the results of the total chlorine test to obtain combined chlorine.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
DPD Total Chlorine Reagent Powder Pillows	1 pillow	100/pkg	14064–99

REQUIRED REAGENTS (Using AccuVac Ampuls)

DPD Total Chlorine Reagent AccuVac Ampuls	1 ampul	25/pkg	25030–25

REQUIRED APPARATUS (Using Powder Pillows)

Clippers, for opening powder pillows	1	each	968–00
Stopper, rubber, No. 2	1	12/pkg	2118–02

REQUIRED APPARATUS (Using AccuVac Ampuls)

Adapter, AccuVac vial	1	each	43784–00
Beaker, 50 mL	1	each	500–41
Vial, zeroing	1	each	21228–00

OPTIONAL REAGENTS

Chlorine Standard Solution, Voluette ampule, 50–75 mg/L, 10 mL	16/pkg	14268–10
Potassium Iodide Solution, 30 g/L	100 mL* MDB	343–32
Sodium Arsenite, 5 g/L	100 mL* MDB	1047–32
Sodium Hydroxide Standard Solution, 1 N	100 mL* MDB	1045–32
Sulfuric Acid Standard Solution, 1 N	100 mL* MDB	1270–32
Water, demineralized	4 L	272–56

OPTIONAL APPARATUS

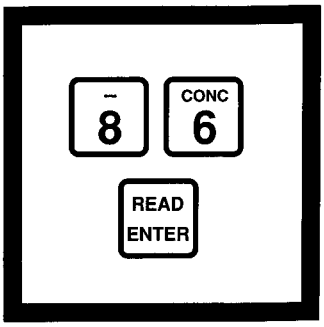
AccuVac Snapper Kit	each	24052–00
Ampule Breaker Kit	each	21968–00
Cylinder, graduated, 25 mL, poly	each	1081–40
Graph Paper, linear	100/pkg	22313–00
pH Meter, EC10, portable	each	50050–00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700–01
Pipet Tips, for 19700–01 TenSette Pipet	50/pkg	21856–96
Pour–Thru Cell Assembly Kit	each	45215–00

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

*Contact Hach for larger sizes.

CHLORINE, TOTAL, ULTRA LOW RANGE (0 to 500 µg/L) For clean water

DPD Method* – USEPA accepted for drinking water analysis**



1. Enter the stored program number for the Ultra Low Range Chlorine method.

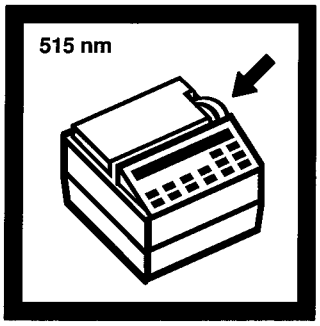
Press: **8 6 READ/ENTER**

The display will show:
DIAL nm to 515

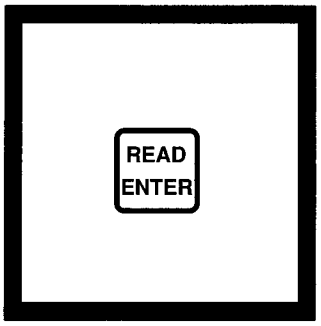
Note: *Or use the UP/DOWN Arrow keys to scroll to the operator–programmed number and press: READ/ENTER.*

Note: *See* Instrument Setup *following these steps for calibration information used in the operator–programmed method.*

Note: *Samples should be analyzed immediately after collection as chlorine is not stable in aqueous solution.*

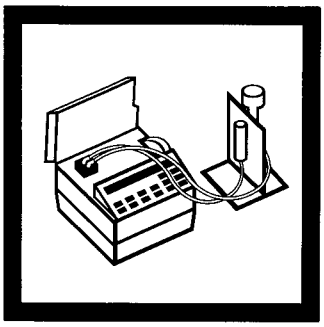


2. Rotate the wavelength dial until the small display shows:
515 nm



3. Press: **READ/ENTER**

The display will show:
µg/l Cl_2 ULR

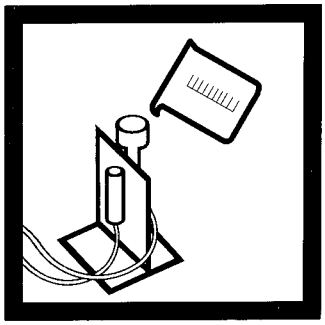


4. Install the Pour–Thru Cell on the instrument. Flush it with 50 mL of demineralized water.

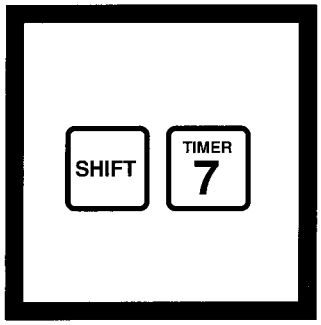
Note: *See Analysis Labware section for more information on cleaning labware.*

Note: *The Pour–Thru Cell must be used* (see Summary of Method section).

*U.S. Patent Number 5,362,650
**Procedure is equivalent to Standard Method 4500–C1G for drinking water.



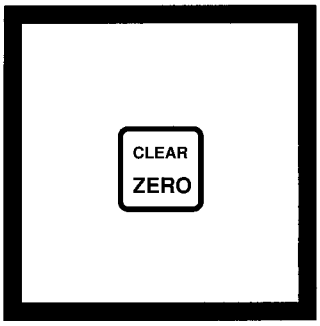
5. Pour at least 50 mL of sample into the Pour–Thru Cell.



6. After the flow stops, begin a 3–minute period by pressing:

SHIFT TIMER

Note: *The 3 minute period allows any turbidity or solids in the sample to settle. This ensures a stable reading before zeroing the instrument.*



7. When the timer beeps, the display will show:

µg/l Cl_2 ULR

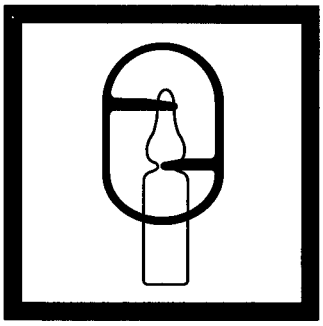
Press: **ZERO**

The display will show:

WAIT

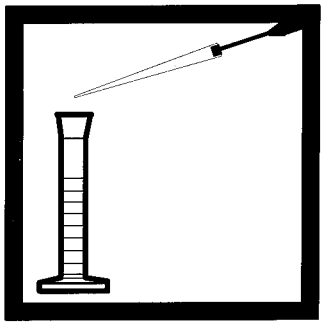
then:

0 µg/l Cl_2 ULR



8. Break open 1 ampule of ULR Chlorine Buffer Solution.

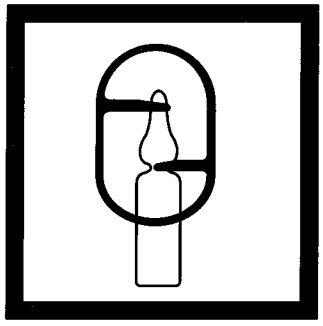
Note: *If the Buffer Reagent gets cold, the contents may precipitate. If this occurs, place the ampul in a 40–45 °C drying oven for one hour. Allow to cool to room temperature before use.*



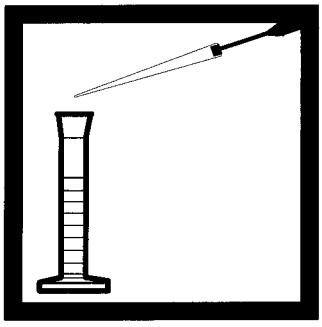
9. Using a TenSette Pipet and clean tip, transfer 1.0 mL of buffer from the ampule to a clean, treated 50–mL graduated mixing cylinder.

Note: *See* Treating Analysis Labware *following these steps for cleaning glassware.*

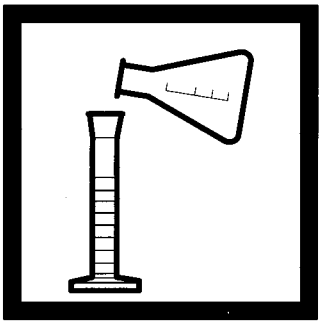
Note: *The ampules contain more than 1.0 mL of solution for ease of reagent transfer. Discard any excess reagent in the ampul.*



10. Break open 1 ampule of DPD Indicator Solution for Ultra Low–Range Chlorine.

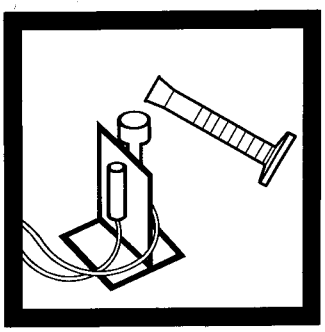


11. Using a TenSette Pipet and clean tip, transfer 1.0 mL of indicator from the ampule to the graduated mixing cylinder. Swirl to mix the reagents. Proceed with Step 12 within 1 minute.



12. Avoiding extra agitation, carefully fill the cylinder to the 50–mL mark with sample. Stopper the cylinder. Gently invert it twice to mix (the prepared sample).

Note: *When collecting the sample, allow the sample stream to flow a few minutes before sampling.*

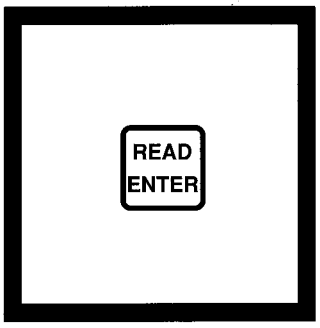


13. Pour the contents of the graduated mixing cylinder into the Pour–Thru Cell.

14. Press: **SHIFT TIMER**

A 3–minute reaction time will begin.

Note: Measure the sample 3–4 minutes after mixing the sample and reagents. If less than 3 minutes elapses, reaction with chloramines may be incomplete. A reading after 4 minutes may result in higher reagent blank values.



15. When the timer beeps, press

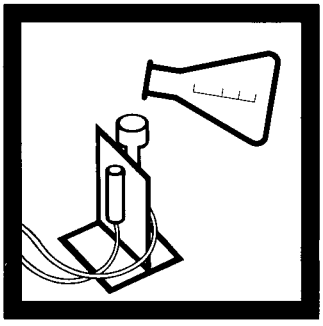
READ/ENTER

The display will show:

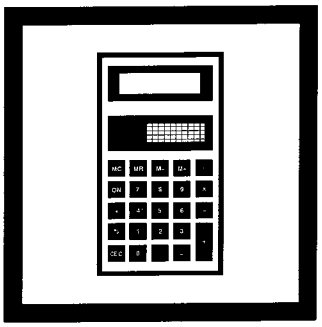
WAIT

then the result in µg/L Cl_2 will be displayed.

Note: It is not necessary to press the READ/ENTER key when in the "CONSTANT ON" mode.



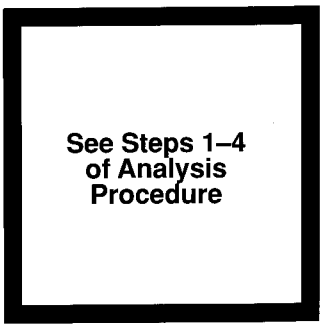
16. Flush the Pour–Thru Cell with at least 50 mL of demineralized water immediately after use.



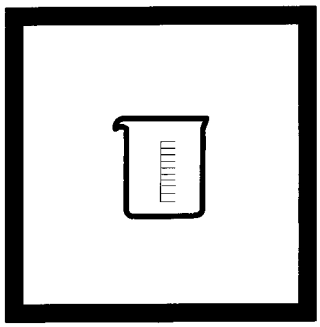
17. Determine the reagent blank using the procedure following these steps. Subtract the reagent blank value (in µg/L) from the value obtained in Step 15.

Note: Determine the reagent blank value for a combined lot of Indicator/Buffer reagent solutions at least once a day. If sample color or turbidity fluctuates frequently during the day, determine a reagent blank for each sample.

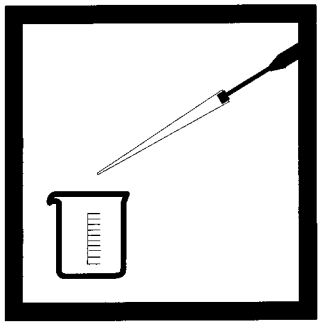
DETERMINING THE REAGENT BLANK VALUE



1. Set up the DR/2000 Spectrophotometer as described in Steps 1–4 of the procedure.

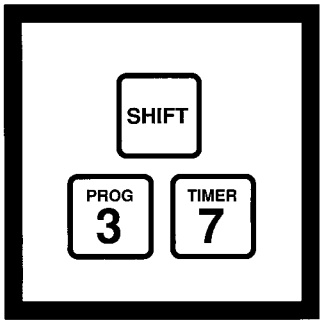


2. Collect about 100 mL of tap water or deionized water in a clean 250–mL beaker.



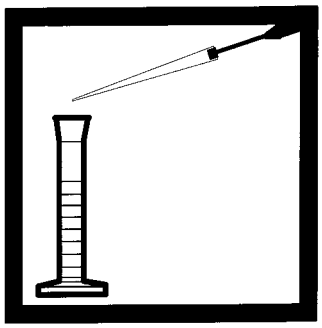
3. Using a TenSette Pipet, add 1.0 mL of Blanking Reagent to the beaker. Swirl several times to mix.

Note: The Blanking Reagent removes chlorine from the water.



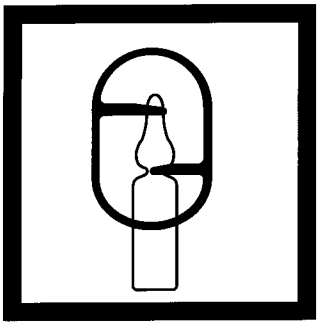
4. Press:
SHIFT PROG TIMER

Then press:
READ/ENTER
then
0500

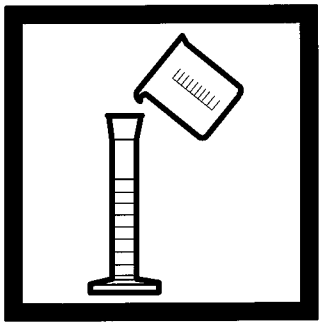


5. After the 5–minute period, break open 1 ampule of ULR Chlorine Buffer Solution. Using a TenSette Pipet and clean tip, transfer 1.0 mL of buffer from the ampule to a clean 50–mL mixing graduated cylinder.

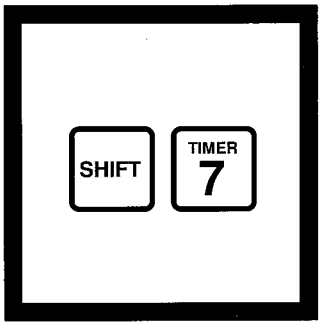
Note: If theBuffer Reagent gets cold, the contents may precipitate. If this occurs, place the ampule in a 40 – 45 °C drying oven for one hour. Allow to cool to room temperature before use.



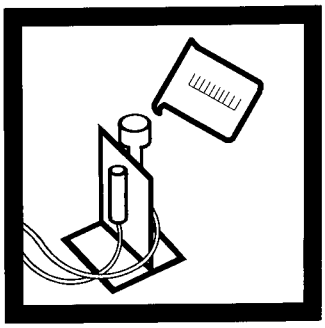
6. Break open 1 ampule of DPD Indicator Solution for Ultra Low–Range Chlorine. Using a TenSette Pipet and clean tip, transfer 1.0 mL of indicator from the ampule to the cylinder. Swirl to mix the reagents. Proceed with Step 7 within 1 minute.



7. Fill the cylinder to the 50–mL mark with the dechlorinated water from Step 3. Cap and invert twice to mix. Save the remaining water for Step 9.



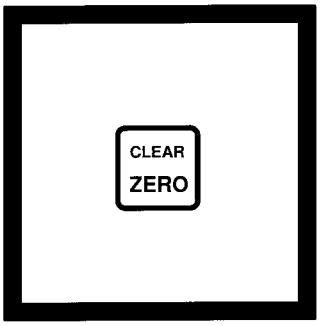
8. Press: **SHIFT TIMER** to begin a 3–minute reaction period



9. When the timer beeps, the display will show:

µg/l Cl_2 ULR

Flush the Pour–Thru Cell with the remainder of the original dechlorinated water from Step 7.



10. When the flow stops,

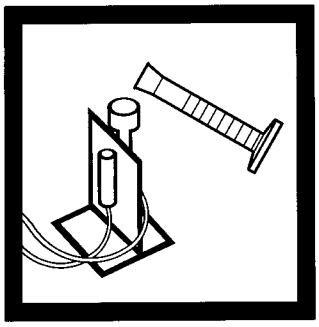
Press: **ZERO**

The display will show:

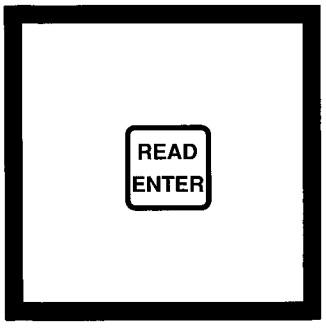
WAIT

then:

0 µg/l Cl_2 ULR



11. Pour the contents of the cylinder into the Pour–Thru Cell.



12. After the flow stops, press

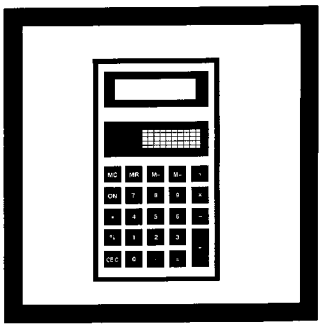
READ/ENTER

The display will show:

WAIT

then the reagent blank value in µg/L Cl_2 will be displayed.

Note: *It is not necessary to press the READ/ENTER key when in the "CONSTANT ON" mode.*



13. Use this value to correct the sample result obtained in the procedure.

Note: *The reagent blank value is normally less than 5 µg/L. If the value is greater than 5 µg/L, an interfering substance may be present in the blanking water or the DPD Indicator may be developing some color. Blanks of up to 5 µg/L may be used successfully.*

INSTRUMENT SETUP

For DR/2000s with software versions 1.261 and 1.27

Enter the following calibration as an operator–programmed calibration. Follow these steps in the *Operation* section of the *DR/2000 Instrument Manual* under User Methods. Store the method as follows:

nm = 515
Decimal = 0000.
Units = µg/l
Symbol = Cl_2 ULR
Timer 1 = 03:00
Timer 2 = 03:00

Enter the calibration with 0.000 absorbance values for the #0 and #1 standards. To do this, leave the sample cell compartment empty. Begin by storing #0 and #1 standard as the concentrations shown in the table below (with nothing in the sample cell compartment). Accept 0.000 Abs as the value for all standards. Store the calibration by pressing **SHIFT READ/ENTER**.

Next, edit the absorbance values for the standards to the values given in the table below. Follow the steps in the *Operations* section of the *DR/2000 Instrument Manual.*

Standard	Concentration	Absorbance
#0	0	0.000
#1	500	0.334

The method is now stored as an operator–programmed method with a method number between 950 and 999. Record the method number for future reference when using this method.

DR/2000 with Software Versions 2.0 and 2.2.

Enter the calibration as an update to Hach stored programs.

1. Press: [I/O]

2. Press: [SHIFT] [CONFIG METH]

3. Press: [-/8] [CONC/6] [READ/ENTER]

4. Within 3 seconds, press:

[SHIFT] [PROG/3] [CONFIG METH]

The display will show:

ENTER nm

5. Press: [ABS/5] [BATT/1] [ABS/5]

Press: **READ/ENTER**

Note: If you make an error, press SHIFT CLEAR and re–enter the number. When the number is correct, press READ/ENTER.

The display will show:

DECIMAL? 00.00

6. Use the arrow keys to correctly position the decimal point. Press the **DOWN ARROW** key twice. The display will show:

DECIMAL? 0000.

Press: **READ/ENTER**

7. The display will show:

UNITS?

8. Use the arrow keys to select the appropriate unit of measure. Press the **DOWN ARROW** key twice. The display will show:

ug/l

9. Press **READ/ENTER** when the correct unit of measure is displayed. The display will show:

SYMBOL?

10. Construct the correct symbol display:

Cl_2 ULR

a. Select letters and regular numbers by scrolling to the correct symbol with the arrow keys.
b. To make a letter or number uppercase, press the **SHIFT** key.
c. To enter subscript numbers, enter the digit with the numeric keypad.
d. To enter superscript numbers, enter the digit with the numeric keypad, then make it subscript by pressing **SHIFT**.
e. The space is the character displayed after one press of the **DOWN ARROW** key.
f. Accept each symbol by pressing **READ/ENTER**.
g. To end symbol entry, press **READ/ENTER** a second time after accepting the last character.

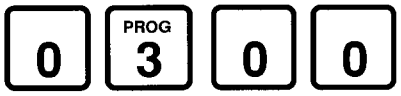
11. When the instrument is out of symbol entry mode, the display will show:

TIMER?

12. This method has two timed step, so press **SHIFT TIMER**. The display will show:

MM:SS TIME 1?

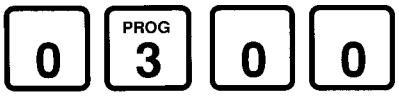
13. Enter a timer value of 3 minutes. Press:



14. Press **READ/ENTER** to accept the timer value. The display will show:

MM:SS TIME 2?

15. Enter another timer value of 3 minutes:



16. Press **READ/ENTER** to accept the timer value. The display will show:

MM:SS TIME 3?

17. Press **READ/ENTER** to complete the timer entry. The display will show:

#1 Data

18. Enter the following 12 numbers as shown. Complete each number entry by pressing the **READ/ENTER** key.

# 1 Data	**0**
# 2 Data	**24157**
# 3 Data	**24157**
# 4 Data	**24157**
# 5 Data	**65535**
# 6 Data	**65535**
# 7 Data	**65535**
# 8 Data	**65535**
# 9 Data	**65553**
#10 Data	**6553**
#11 Data	**1088**
Checksum	**50965**

The final number is a check value which determines if the data sequence was correctly entered. If an error was made during number entry, the display will return to the prompt for data # 1 and the entire sequence must be re–entered. If all numbers are correctly entered, the display will return to the method prompt and is ready for use.

DR/2000 with Software Version 3.0 and 3.1

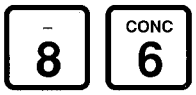
1. Turn the instrument on. Press **SHIFT METHOD** to enter configuration mode. The display will show:

MOMENTARY or CONSTANT ON

2. Press the **UP ARROW** key twice to select HACH UPDATE. Press **READ/ENTER**. The display will show:

ENTER #:

3. Press:



Then press **READ/ENTER**. The display will show:

P86 ENTER nm

4. Press:

Press: **READ/ENTER**

Note: If you make an error, press SHIFT CLEAR and re–enter the number. When the number is correct, press READ/ENTER.

The display will show:

P86 DECIMAL? 00.00

5. Use the arrow keys to correctly position the decimal point. Press the **DOWN ARROW** key twice. The display will show:

DECIMAL? 0000.

Press **READ/ENTER**. The display will show:

P86 UNITS?

6. Use the arrow keys to select the appropriate unit of measure. Press the **DOWN ARROW** key twice. The display will show:

P86 µg/l

7. Press **READ/ENTER** when the correct unit of measure is displayed. The display will show:

P86 µg/l _

8. Construct the display to read the correct symbol. The symbol must be entered EXACTLY as shown including dashes and spaces between characters.

Cl_2 ULR

a. Select letters and numbers by scrolling to the correct character with the arrow keys.
b. To make a letter or number uppercase, press the **SHIFT** key.
c. Make a number or sign superscript, subscript or regular by pressing **SHIFT** until the symbol is correct.
d. The space is the character displayed after one press of the **DOWN ARROW** key.

e. Make sure to enter the display line EXACTLY as shown, including all spaces. Do not enter trailing spaces.
f. Accept each symbol by pressing **READ/ENTER**.
g. To end symbol entry, press **READ/ENTER** a second time after accepting the last character.

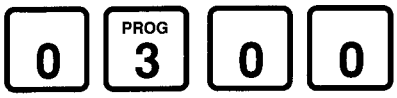
9. When the instrument is out of symbol entry mode, the display will show:

P86 TIMER?

10. This method has two timed step, so press **SHIFT TIMER**. The display will show:

MM:SS TIME 1?

11. Enter a timer value of 3 minutes. Press:



12. Press **READ/ENTER** to accept the timer value. The display will show:

MM:SS TIME 2?

13. Enter a timer value of 3 minutes. Press: **0 3 0 0**

14. Press **READ/ENTER** to accept the timer value. The display will show:

MM:SS TIME 3?

15. Press **READ/ENTER** to complete the timer entry. The display will show:

#0 STANDARD

16. Press **READ/ENTER** to display the zero data pair. The display will show:

0.000 Abs 0000. µg/l

Press **READ/ENTER**. The display will show:

#1 STANDARD

17. Press **READ/ENTER**. The display will prompt for entry of the first concentration point:

 # 1 0000. µg/l

18. Enter concentration point #1 from the table below by pressing **0500** so that the display shows:

 # 1 0500. µg/l

19. Press **READ/ENTER**. The display will prompt for entry of the first absorbance point:

 # 1 0.000 Abs

20. Enter absorbance point #1 from the table below by pressing **0334** so that the display shows:

 # 1 0.334 Abs

21. Press **READ/ENTER**. The display will show the first data pair:

0.334 Abs 0500. µg/l

22. Press **READ/ENTER** to accept the first data pair. The display will show:

 # 2 STANDARD

23. The data pair values from the table below are now entered.

Standard	Concentration	Absorbance
# 0	[0] µg/l	[0.000] Abs
# 1	[500] µg/l	[0.334] Abs

24. When the last point pair is entered the display will show:

 # 2 STANDARD

25. Press **SHIFT READ/ENTER** to complete data point entry The display will show:

#:

26. Enter the validation number: **2265** so that the display shows:

#: 2265

27. Press **READ/ENTER**. The display will show:

COMPLETED

then:

P86 µg/l Cl_2 ULR

Note: If the display shows:

INCORRECT #

then prompts again for the validation number you may have made an error during data entry. Make sure the validation number is correct. If so, then the error occurred during some other portion of the method entry. You must press METH and respond to the ABORT? message by pressing READ/ENTER then re-enter the method.

The instrument is now ready for use with method 86.

TREATING ANALYSIS LABWARE

Glassware and demineralized water used in this test must be chlorine demand–free. Treat all glassware with a dilute solution of chlorine bleach prepared by adding 0.5 mL of commercial bleach to 1 liter of water. Soak glassware in this solution at least one hour. After soaking, rinse the glassware with copious amounts of demineralized water and allow to dry before use.

Treat the Pour–Thru Cell similarly with dilute bleach and let stand for several minutes and then rinse several times with demineralized water.

CLEANING THE POUR–THRU CELL

The Pour–Thru Cell may accumulate a buildup of color reaction products, especially if the reacted solutions are allowed to remain in the cell for long periods after measurement. Remove the buildup by rinsing the cell with 5.25N sulfuric acid followed by several rinsings with demineralized water.

PRECISION

In a single laboratory, using a standard solution of 9 µg/L chlorine and one lot of reagents, a single operator obtained a standard deviation of ± 0.4 µg/L.

MINIMUM DETECTION LEVEL

Based on the USEPA's procedure for estimating the method detection limit (40 CFR, Pt. 136, App. B, 7–1–96), the detection limit, using the procedure as written, is less than 2 µg/L chlorine.

INTERFERENCES

Oxidized manganese reacts directly with DPD. The apparent chlorine result is about 3 µg/L per every µg/L Mn^{7+}. Mn^{2+} does not interfere up to 5000 µg/L.

Copper (Cu^{2+}) and iron (Fe^{3+}) do not interfere up to 1000 µg/L each.

Nitrite (uncommon in pure water) causes a positive interference which varies with the nitrite concentration:

mg/L Nitrite	Apparent µg/L Chlorine
2.0 mg/L	3 mg/L
5.0	5
10.0	7
15.0	16
20.0	18

Bromine, iodine, ozone, and other strong oxidizing agents may also interfere.

SUMMARY OF METHOD

This method is designed for clean water, low in color and turbidity. The main applications include monitoring for trace chlorine breakthrough of activated carbon beds and feedwater to reverse osmosis membranes or ion–exchange resins.

Several modifications to the normal DPD chlorine method are necessary to measure trace levels of chlorine. The 1–inch Pour–Thru Cell must be used in the spectrophotometer. Liquid reagents are also required. The reproducible optics of the Pour–Thru Cell gives more stable readings than is possible with movable sample cells, resulting in more stable measurements.

The reagents are packaged in ampules and sealed under argon gas to ensure stability. Use of liquid reagents eliminates any slight turbidity that might be caused by using powdered reagents. Due to the possible oxidation of the reagents (which could give a positive chlorine reading in the blank), a reagent blank should be determined at least once a day for each lot of reagent used. This reagent blank value is subtracted from the sample result and the corrected value is the actual chlorine concentration.

REQUIRED REAGENTS

	Cat. No.
ULR Chlorine Reagent Set (about 20 tests)	25630–00
Includes: (1) 24930–23, (1) 24931–20, (1) 24932–20	

Description	Quantity Required Per Test	Unit	Cat. No.
ULR Chlorine Buffer	1 mL	20/pkg	24931–20
DPD Indicator Solution for ULR Chlorine	1 mL	20/pkg	24932–20
Blanking Reagent for ULR Chlorine	1 mL	29 mL	24930–23

REQUIRED APPARATUS

Description	Quantity Required Per Test	Unit	Cat. No.
Beaker, 250 mL	1	each	500–46
Cylinder, mixing, graduated, 50 mL	1	each	1896–41
Pipet Tips, for 19700–01 TenSette Pipet	2	50/pkg	21856–96
Pour–Thru Cell Assembly Kit	1	each	45215–00
TenSette Pipet, 0.1 to 1.0 mL	1	each	19700–01

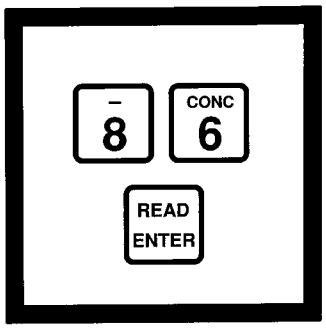
OPTIONAL REAGENTS

Sulfuric Acid Solution, 5.25 N	1 L	2449–53
Demineralized Water	4 L	272–56

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

CHLORINE, TOTAL, ULTRA LOW RANGE*(0 to 500 µg/L) For treated wastewater

DPD Method* – USEPA accepted for reporting wastewater analysis**



1. Enter the stored program number for the Ultra Low Range Chlorine method.

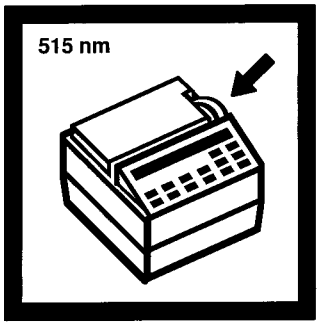
Press: **8 6 READ/ENTER**

The display will show:
DIAL nm to 515

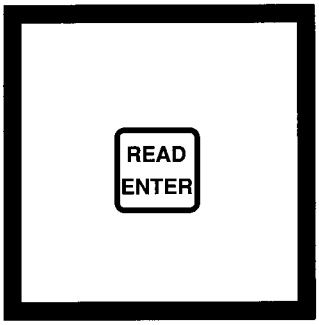
Note: *Or use the UP/DOWN Arrow keys to scroll to the operator–programmed number and press: READ/ENTER.*

Note: *See* Instrument Setup *following these steps for calibration information used in the operator–programmed method.*

Note: *Samples should be analyzed immediately after collection as chlorine is not stable in aqueous solution.*

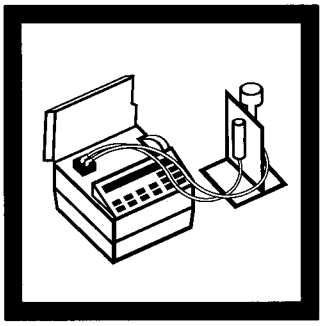


2. Rotate the wavelength dial until the small display shows:
515 nm



3. Press: **READ/ENTER**

The display will show:
µg/l Cl_2 ULR

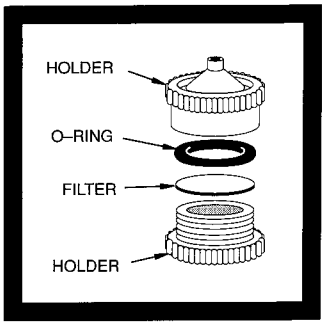


4. Install the Pour–Thru Cell and flush with at least 50 mL of demineralized water.

Note: *The Pour–Thru cell must be cleaned and treated for chlorine demand. See* Analysis Labware *section for more information on cleaning labware.*

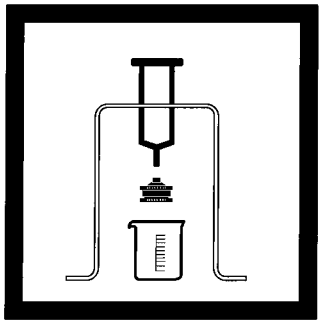
Note: *The Pour–Thru cell must be used. See* Summary of Method *section.*

*U.S. Patent Number 5,362,650.
**Procedure is equivalent to Standard Method 4500–C1–D for wastewater.



5. Unscrew the filter holder assembly and install a new 3 micron membrane filter into the filter holder. Be sure the O–ring is properly seated on top of the membrane. Reassemble and hand–tighten the holder assembly.

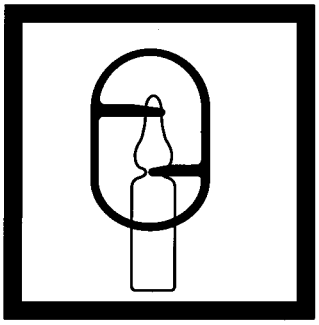
Note: *Use a new filter for each test. Use only the filter disc specified. The use of a membrane filter not specified for the test may result in low analysis results or inability to filter the required sample volume.*



6. Couple the filter holder containing the membrane filter to a clean 60–cc syringe barrel, without the plunger. Mount the syringe/filter holder assembly on the support stand. Place a 100 mL beaker underneath the filter holder.

Note: *The filter holder side labeled "OUTLET" should point down towards the beaker.*

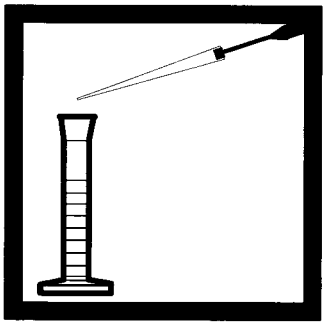
Note: *The syringe and filter holder should be used only for chlorine testing to minimize cross contamination.*



7. Break open 1 ampule of ULR Chlorine Buffer Solution.

Note: *The Ampule Breaker (shown) is a convenient way to open ampules.*

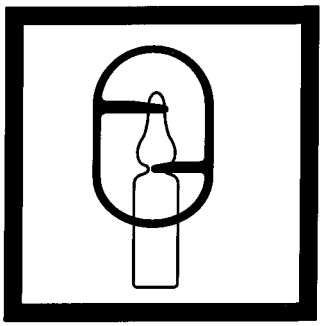
Note: *If the Buffer Reagent gets cold, the contents may precipitate. If this occurs, place the ampule in a 40 – 45 °C drying oven for one hour. Allow to cool to room temperature before use.*



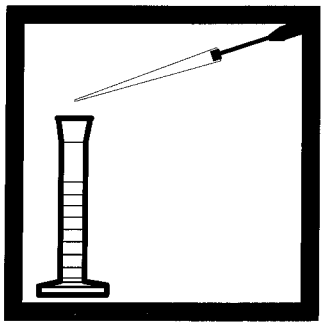
8. Using a TenSette pipet with a clean pipet tip, transfer 1.0 mL buffer from the ampule to a clean, treated 50–mL mixing graduated cylinder.

Note: *See* Treating Analysis Labware *following these steps for cleaning glassware.*

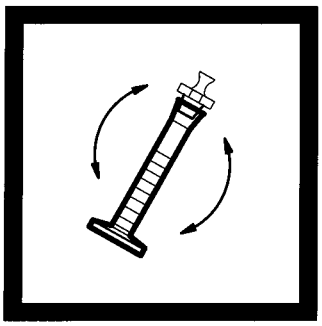
Note: *The ampules contain more than 1.0 mL for ease of reagent transfer. Discard any excess reagent remaining in the ampul.*



9. Break open 1 ampul of DPD Indicator Reagent Solution for Ultra Low Range Chlorine.

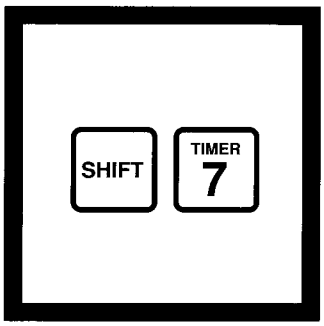


10. Using the TenSette pipet with a clean tip, transfer 1.0 mL indicator from the ampule to the cylinder. Swirl to mix the reagents. Proceed with Step 11 within one minute.



11. Avoiding extra agitation, carefully fill the cylinder to the 50–mL mark with sample. Stopper the cylinder. Gently invert twice to mix (the prepared sample).

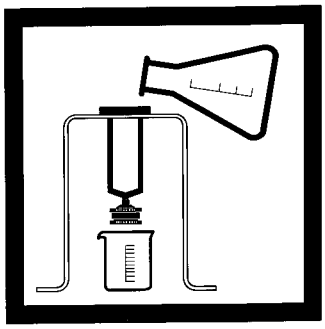
Note: *When collecting the sample, allow the sample stream to flow a few minutes before sampling.*



12. Press: **SHIFT TIMER**

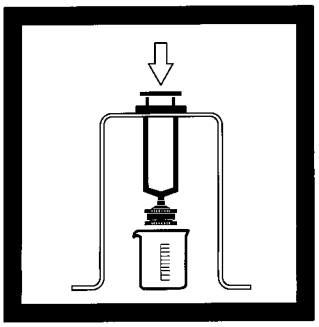
A three–minute reaction period will begin.

Note: *Make the sample measurement between 3 to 6 minutes after sample is added to mixed reagents. If the reading is made less than three minutes, reaction with chloramines may be incomplete. If readings are made in excess of six minutes, the reagent blank value may be more significant.*



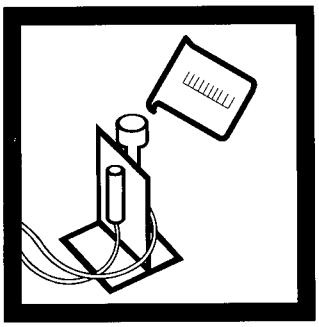
13. During the three minute reaction period, pour a second 50–mL portion of the original sample into the syringe/filter holder assembly.

Note: *Perform Steps 13–18 during the three–minute reaction period.*

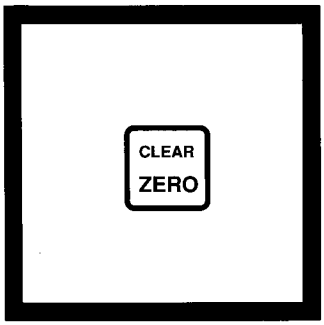


14. Insert the plunger into the top of the syringe and slowly push the plunger down with even pressure, forcing the sample through the filter assembly into the beaker.

Note: *Filter at least 30 mL sample.*



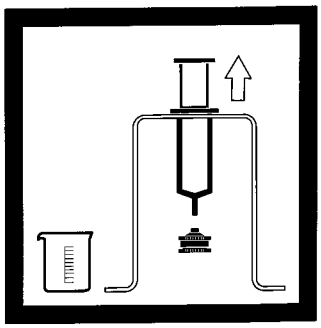
15. Pour the filtered sample from the beaker into the Pour–Thru Cell.



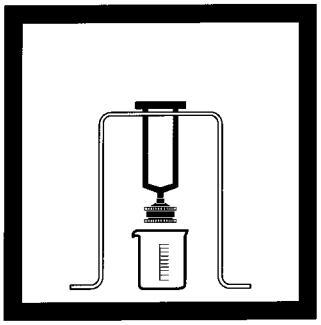
16. After the flow stops, Press: **ZERO**

The display will show:
WAIT

then:
0 µg/l Cl_2 ULR



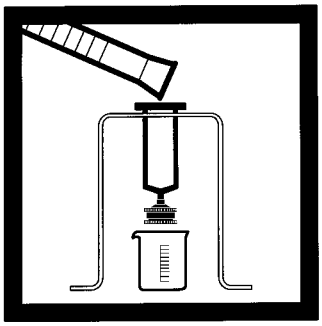
17. Remove the filter holder from the syringe. Remove the plunger from the syringe, discarding any remaining unfiltered sample.



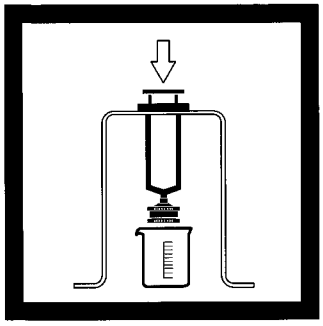
18. Couple the filter holder back on the syringe barrel (without plunger) and mount on the support stand. Place a clean 100 mL beaker underneath the syringe/filter holder assembly.

Note: *For extremely turbid samples, a new membrane filter may need to be installed. Alternatively, use a second, clean filter holder assembly with a new membrane filter installed.*

Note: *The filter holder side labeled "OUTLET" should point down towards the beaker.*

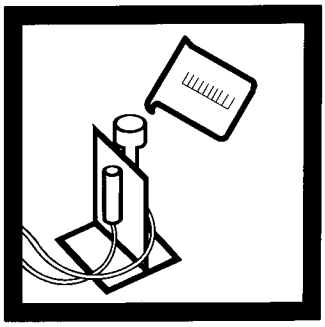


19. When the timer beeps, pour the contents of the mixing graduated cylinder into the syringe/filter holder assembly.

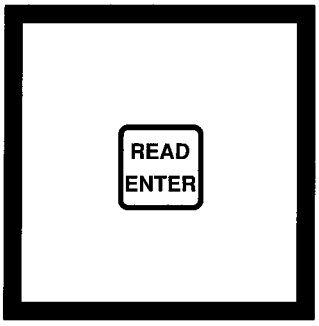


20. Insert the plunger into the top of the syringe and slowly push the plunger down with even pressure, forcing the sample through the filter assembly into the beaker.

Note: *At least 30 mL of filtered reacted sample is required.*



21. Pour the filtered, reacted sample from the beaker into the Pour–Thru Cell.



22. After the flow stops, press

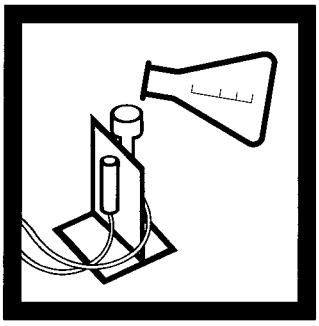
READ/ENTER

The display will show:

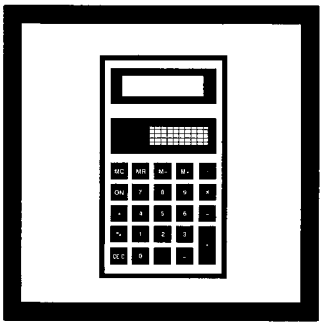
WAIT

then the result in µg/L Cl_2 will be displayed. Record the result.

***Note:** It is not necessary to press the READ/ENTER key when in the "CONSTANT ON" mode.*



23. Flush the Pour–Thru Cell with at least 50 mL of demineralized water immediately after use.

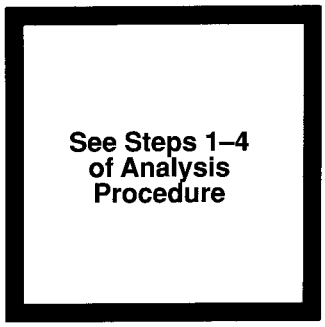


24. Determine the reagent blank using the procedure following these steps. Subtract the determined reagent blank value (in µg/L) from the value obtained in Step 22.

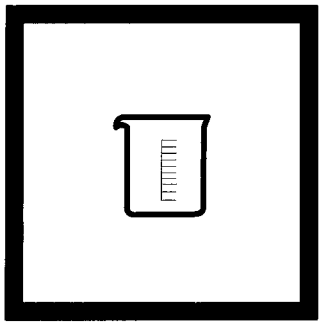
***Note:** Determine the reagent blank value for a combined lot of Indicator/Buffer reagent solutions at least once per day.*

***Note:** If a dechlorination agent such as sulfite or sulfur dioxide is present in the sample, the sample result, corrected for the reagent blank, will read "0" or a slightly negative value.*

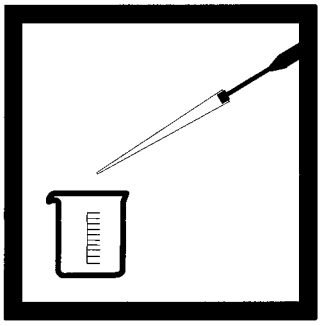
DETERMINATION OF THE REAGENT BLANK VALUE



1. Set up the DR/2000 spectrophotometer as described in Steps 1–4 of the procedure.

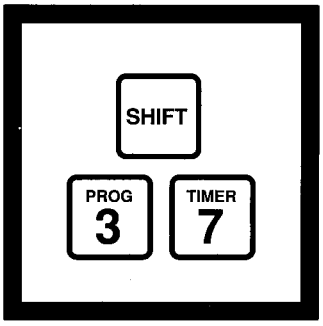


2. Collect about 100 mL deionized or tap water in a clean 250 mL beaker.



3. Using a Tensette Pipet, add 1.0 mL Blanking Reagent to the beaker. Swirl several times to mix.

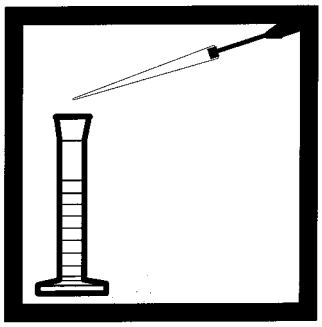
Note: The Blanking Reagent removes chlorine from the water.



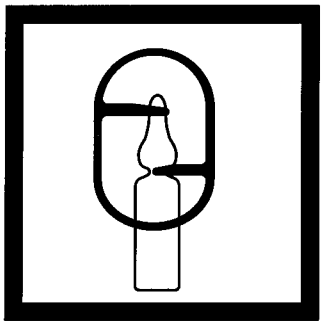
4. Press:
SHIFT PROG TIMER

Then press
READ/ENTER,
then
0500,
then
READ/ENTER.

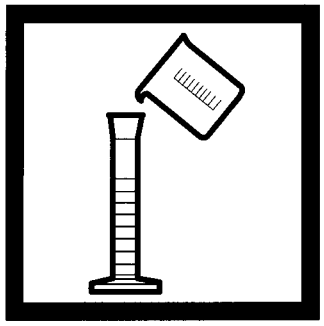
For software version 2.2 and lower, press
0500
then
SHIFT TIMER.



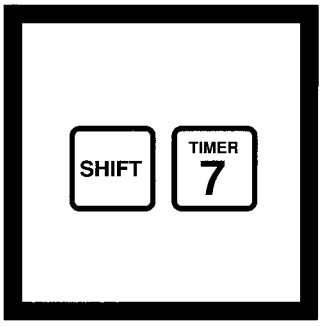
5. After the timer beeps, break open one ampule of ULR Chlorine Buffer Solution. Using a TenSette Pipet and clean tip, transfer 1.0 mL of buffer from the ampule to a clean 50–mL mixing graduated cylinder.



6. Break open one ampule of ULR DPD Indicator Reagent Solution. Using a TenSette Pipet and clean tip, transfer 1.0 mL of indicator from the ampule to the cylinder. Swirl to mix the reagents. Proceed with Step 7 within 1 minute.

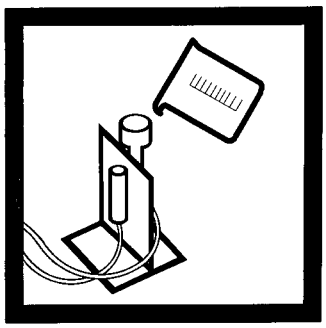


7. Fill the cylinder to the 50–mL mark with the dechlorinated water from Step 3. Cap and invert twice to mix. Save the remaining water for Step 9.

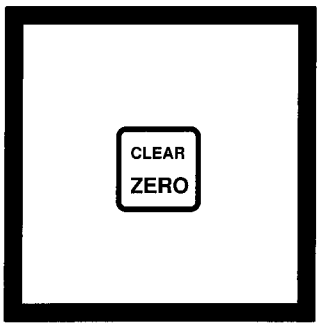


8. Press: **SHIFT TIMER**

A three–minute reaction period will begin.



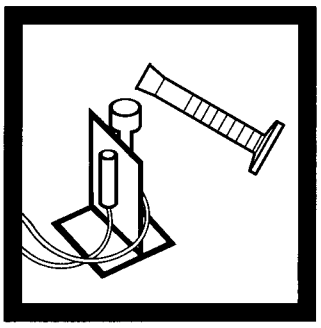
9. During the reaction period, flush the Pour–Thru Cell with the remainder of the original dechlorinated water from Step 7.



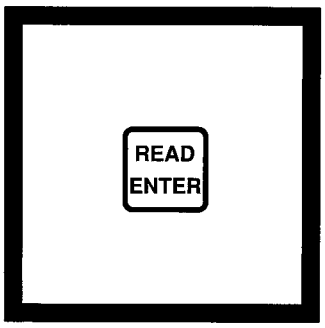
10. When the sample flow stops,
Press: **ZERO**

The display will show:
WAIT

then:
0 µg/l Cl_2 ULR



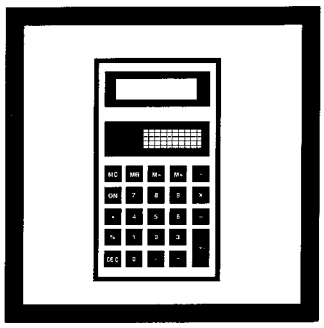
11. When the timer beeps, pour the contents of cylinder into the Pour–Thru Cell.



12. After the flow stops, press
READ/ENTER

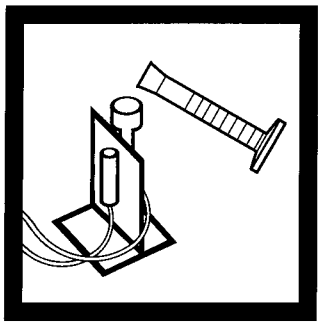
The display will show:
WAIT
then the reagent blank value in µg/L Cl_2 will be displayed.

Note: *It is not necessary to press the READ/ENTER key when in the "CONSTANT ON" mode.*



13. Use this value to correct the sample result obtained in the procedure.

Note: *The reagent blank value is normally less than 5 µg/L. If the reagent blank value is greater than 5 µg/L, an interfering substance may be present in the blanking water or the DPD Indicator may be developing some reagent color. Blanks of up to 5 µg/L may be used successfully.*



14. Flush the Pour–Thru Cell with at least 50 mL demineralized water immediately after use.

INSTRUMENT SETUP

For DR/2000s with software versions 1.261 and 1.27
Enter the following calibration as an operator–programmed calibration. Follow these steps in the *Operation* section of the *DR/2000 Instrument Manual* under *User Methods*. Store the method as follows:

nm = 515
Decimal = 0000.
Units = µg/l
Symbol = Cl_2 ULR
Timer 1 = 03:00
Timer 2 = 03:00

Enter the calibration with 0.000 absorbance values for the #0 and #1 standards. To do this, leave the sample cell compartment empty. Begin by storing #0 and #1 standard as the concentrations shown in the table below (with nothing in the sample cell compartment). Accept 0.000 Abs as the value for all standards. Store the calibration by pressing **SHIFT READ/ENTER**.

Next, edit the absorbance values for the standards to the values given in the table below. Follow the steps in the *Operations* section of the *DR/2000 Instrument Manual.*

Standard	Concentration	Absorbance
#0	0	0.000
#1	500	0.334

The method is now stored as an operator–programmed method with a method number between 950 and 999. Record the method number for future reference when using this method.

DR/2000 with Software Versions 2.0 and 2.2.
Enter the calibration as an update to Hach stored programs.

1. Press: 

2. Press: 

3. Press: 

4. Within 3 seconds, press:


The display will show:
ENTER nm

5. Press: 

Press: **READ/ENTER**

Note: If you make an error, press SHIFT CLEAR and re–enter the number. When the number is correct, press READ/ENTER.

The display will show:
DECIMAL? 00.00

6. Use the arrow keys to correctly position the decimal point. Press the **DOWN ARROW** key twice. The display will show:
DECIMAL? 0000.

Press: **READ/ENTER**

7. The display will show:
UNITS?

8. Use the arrow keys to select the appropriate unit of measure. Press the **DOWN ARROW** key twice. The display will show:
ug/l

9. Press **READ/ENTER** when the correct unit of measure is displayed. The display will show:
SYMBOL?

10. Construct the correct symbol display:
Cl_2 ULR

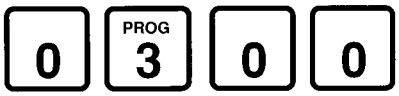
a. Select letters and regular numbers by scrolling to the correct symbol with the arrow keys.
b. To make a letter or number uppercase, press the **SHIFT** key.
c. To enter subscript numbers, enter the digit with the numeric keypad.
d. To enter superscript numbers, enter the digit with the numeric keypad, then make it subscript by pressing **SHIFT**.
e. The space is the character displayed after one press of the **DOWN ARROW** key.
f. Accept each symbol by pressing **READ/ENTER**.
g. To end symbol entry, press **READ/ENTER** a second time after accepting the last character.

11. When the instrument is out of symbol entry mode, the display will show:
TIMER?

12. This method has two timed step, so press **SHIFT TIMER**. The display will show:

MM:SS TIME 1?

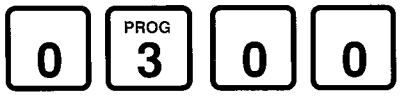
13. Enter a timer value of 3 minutes. Press:



14. Press **READ/ENTER** to accept the timer value. The display will show:

MM:SS TIME 2?

15. Enter another timer value of 3 minutes:



16. Press **READ/ENTER** to accept the timer value. The display will show:

MM:SS TIME 3?

17. Press **READ/ENTER** to complete the timer entry. The display will show:

#1 Data

18. Enter the following 12 numbers as shown. Complete each number entry by pressing the **READ/ENTER** key.

# 1 Data	**0**
# 2 Data	**24157**
# 3 Data	**24157**
# 4 Data	**24157**
# 5 Data	**65535**
# 6 Data	**65535**
# 7 Data	**65535**
# 8 Data	**65535**
# 9 Data	**65553**
#10 Data	**6553**
#11 Data	**1088**
Checksum	**50965**

The final number is a check value which determines if the data sequence was correctly entered. If an error was made during number entry, the display will return to the prompt for data # 1 and the entire sequence must be re–entered. If all numbers are correctly entered, the display will return to the method prompt and is ready for use.

DR/2000 with Software Version 3.0 and Above

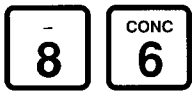
1. Turn the instrument on. Press **SHIFT METHOD** to enter configuration mode. The display will show:

MOMENTARY or CONSTANT ON

2. Press the **UP ARROW** key twice to select HACH UPDATE. Press **READ/ENTER**. The display will show:

ENTER #:

3. Press:



Then press **READ/ENTER**. The display will show:

P86 ENTER nm

4. Press:

Press: **READ/ENTER**

Note: If you make an error, press SHIFT CLEAR and re–enter the number. When the number is correct, press READ/ENTER.

The display will show:

P86 DECIMAL? 00.00

5. Use the arrow keys to correctly position the decimal point. Press the **DOWN ARROW** key twice. The display will show:

DECIMAL? 0000.

Press **READ/ENTER**. The display will show:

P86 UNITS?

6. Use the arrow keys to select the appropriate unit of measure. Press the **DOWN ARROW** key twice. The display will show:

P86 µg/l

7. Press **READ/ENTER** when the correct unit of measure is displayed. The display will show:

P86 µg/l _

8. Construct the display to read the correct symbol. The symbol must be entered EXACTLY as shown including dashes and spaces between characters.

Cl_2 ULR

a. Select letters and numbers by scrolling to the correct character with the arrow keys.
b. To make a letter or number uppercase, press the **SHIFT** key.
c. Make a number or sign superscript, subscript or regular by pressing **SHIFT** until the symbol is correct.
d. The space is the character displayed after one press of the **DOWN ARROW** key.

e. Make sure to enter the display line EXACTLY as shown, including all spaces. Do not enter trailing spaces.
f. Accept each symbol by pressing **READ/ENTER**.
g. To end symbol entry, press **READ/ENTER** a second time after accepting the last character.

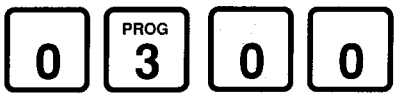
9. When the instrument is out of symbol entry mode, the display will show:

P86 TIMER?

10. This method has two timed step, so press **SHIFT TIMER**. The display will show:

MM:SS TIME 1?

11. Enter a timer value of 3 minutes. Press:



12. Press **READ/ENTER** to accept the timer value. The display will show:

MM:SS TIME 2?

13. Enter a timer value of 3 minutes. Press: **0 3 0 0**

14. Press **READ/ENTER** to accept the timer value. The display will show:

MM:SS TIME 3?

15. Press **READ/ENTER** to complete the timer entry. The display will show:

#0 STANDARD

16. Press **READ/ENTER** to display the zero data pair. The display will show:

0.000 Abs 0000. µg/l

Press **READ/ENTER**. The display will show:

#1 STANDARD

17. Press **READ/ENTER**. The display will prompt for entry of the first concentration point:

 # 1 0000. µg/l

18. Enter concentration point #1 from the table below by pressing **0500** so that the display shows:

 # 1 0500. µg/l

19. Press **READ/ENTER**. The display will prompt for entry of the first absorbance point:

 # 1 0.000 Abs

20. Enter absorbance point #1 from the table below by pressing **0334** so that the display shows:

 # 1 0.334 Abs

21. Press **READ/ENTER**. The display will show the first data pair:

0.334 Abs 0500. µg/l

22. Press **READ/ENTER** to accept the first data pair. The display will show:

 # 2 STANDARD

23. The data pair values from the table below are now entered.

Standard	Concentration	Absorbance
# 0	[0] µg/l	[0.000] Abs
# 1	[500] µg/l	[0.334] Abs

24. When the last point pair is entered the display will show:

 # 2 STANDARD

25. Press **SHIFT READ/ENTER** to complete data point entry The display will show:

#:

26. Enter the validation number: **2265** so that the display shows:

#: 2265

27. Press **READ/ENTER**. The display will show:

COMPLETED

then:

P86 µg/l Cl_2 ULR

Note: *If the display shows:*

INCORRECT #

then prompts again for the validation number you may have made an error during data entry. Make sure the validation number is correct. If so, then the error occurred during some other portion of the method entry. You must press METH and respond to the ABORT? message by pressing READ/ENTER then re–enter the method.

The instrument is now ready for use with method 86.

TREATING ANALYSIS LABWARE

Glassware used in the test must be chlorine demand–free. Treat all glassware with a dilute solution of chlorine bleach prepared by adding 0.5 mL of a commercial bleach solution to 1 liter of water. Soak glassware in this solution at least one hour. After soaking, rinse the glassware with several rinsings of demineralized water and allow to dry before use.

Treat the Pour–Thru Cell similarly with dilute bleach and let stand for several minutes and then rinse several times with demineralized water.

CLEANING THE POUR–THRU CELL

The Pour–Thru Cell may accumulate a buildup of colored reaction products, especially if the reacted solutions are allowed to stand in the cell for long periods after measurements. Remove the buildup by rinsing the cell with 5.25 N sulfuric acid followed by several rinsings with demineralized water.

PRECISION

In a single laboratory using a standard solution of 9 µg/L chlorine and one lot of reagents, a single operator obtained a standard deviation of ± 0.4 µg/L.

MINIMUM DETECTION LEVEL

Based on the USEPA's procedure for estimating the method detection limit (40 CFR, Pt. 136, App. B, 7–1–96), the detection limit, using the procedure as written, is less than 2 µg/L chlorine.

INTERFERENCES

Oxidized manganese will interfere with an apparent chlorine result of about 3 µg/L chlorine per mg/L Mn^{+7}. Manganese (+2) does not interfere up to 5000 µg/L.

Nitrite causes a positive interference which varies according to the following table:

mg/L Nitrite	Apparent µg/L Chlorine
2.0 mg/L	3 µg/L
5.0	5
10.0	7
15.0	16
20.0	18

Bromine, iodine, ozone, and other strong oxidizing agents may also interfere.

SUMMARY OF METHOD

Several modifications to the normal DPD chlorine method are necessary to measure trace levels of chlorine in treated wastewaters. The 1–inch Pour–Thru Cell must be used in the spectrophotometer. Liquid reagents are also required.

The reproducible optics of the Pour–Thru Cell give more consistent readings than is possible with movable sample cells, resulting in more stable readings.

The reagents are packaged in ampules and sealed under argon gas to ensure stability. Use of liquid reagents eliminates any slight turbidity that might be caused by using powdered reagents. Due to the possible oxidation of the reagents (which could give a positive chlorine reading in the blank), a reagent blank must be determined at least once per day for each lot of reagents used. This reagent blank is subtracted from the sample result and the corrected value is the actual chlorine concentration.

It is essential that interfering sample turbidity be removed using a 3 micron membrane filter. To avoid loss of chlorine, the filtration is perform after reaction of DPD with chlorine in the sample. The filter used in the test has been specifically selected as to not retain the colored reaction product. Sample color is compensated by zeroing the spectrophotometer on a filtered sample.

REQUIRED REAGENTS

	Cat. No.
ULR Chlorine Reagent Set (about 20 tests)	25630–00
Includes: (1) 24930–23, (1) 24931–20, (1) 24932–20	
ULR Chlorine Aparatus Set	25956–00
Includes: (1) 25940–25, (1) 2468–00, (1) 25939–00, (1) 23764–00, (1) 30327–00, (1) 1080–42	

Description	Quantity Required Per Test	Unit	Cat. No.
ULR Chlorine Buffer	1 mL	20/pkg	24931–20
DPD Indicator Solution	1 mL	20/pkg	24932–20
Blanking Reagent Solution	1 mL	29 mL	24930–23

REQUIRED APPARATUS

Beaker, 250 ml	1	each	500–46
Beaker, 100 mL, poly	2	each	1080–42
Cylinder, mixing, grad., 50 mL	1	each	1896–41
Filter Holder Assembly	1	each	2468–00
Membrane Filters, 3–micron	1	25/pkg	25940–25

REQUIRED APPARATUS (continued)

Description	Quantity Required Per Test	Unit	Cat. No.
Pipet Tips, for TenSette Pipet	2	50/pkg	21856–96
Plunger, Syringe	1	each	23764–00
Pour–Thru Cell Assembly Kit	1	each	45215–00
Support Stand	1	each	30327–00
Syringe, 60 cc	1	each	25939–00
TenSette Pipet, 0.1 to 1.0 mL	1	each	19700–01

OPTIONAL REAGENTS

Sulfuric Acid Solution, 5.25N		1 L	2449–53
Water, demineralized		4 L	272–56

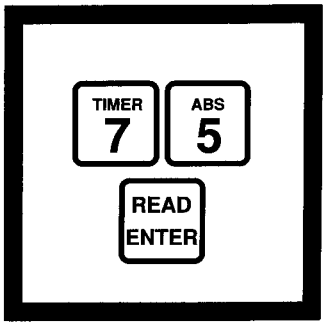
OPTIONAL APPARATUS

Ampul Breaker	1	each	24846–00
Membrane Filters, 3–micron	1	25/pkg	25940–25

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

CHLORINE DIOXIDE, HR (0 to 700 mg/L)

Direct Reading Method



1. Enter the stored program number for chlorine dioxide (ClO_2), high range.

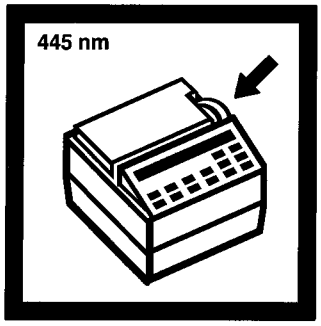
Press: **7 5 READ/ENTER**

The display will show:
Dial nm TO 445

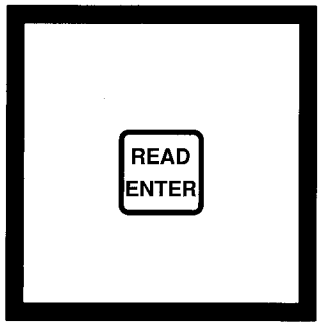
Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software version 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

Note: *Analyze samples immediately. See* Sampling and Storage *following these steps.*



2. Rotate the wavelength dial until the small display shows:
445 nm

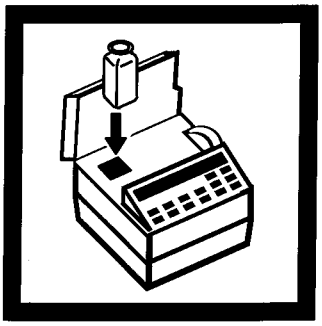


3. Press: **READ/ENTER**

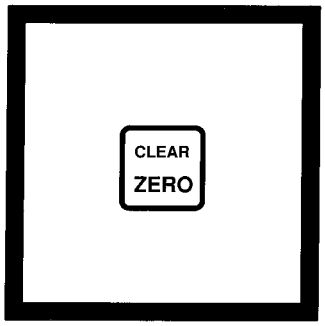
The display will show:
mg/l ClO_2 H

4. Fill a sample cell (the blank) with 25 mL of demineralized water.

Note: *The Pour–Thru Cell can be used with this procedure.*

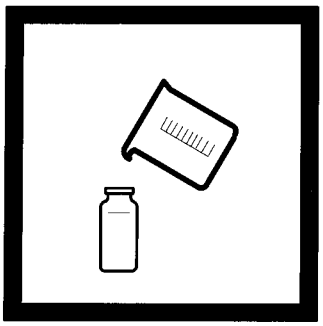


5. Place the blank into the cell holder.

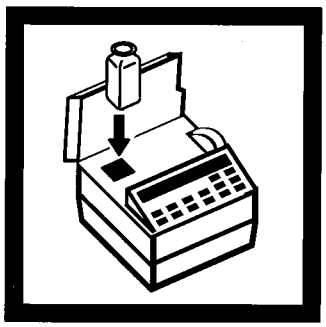


6. Press: **ZERO**

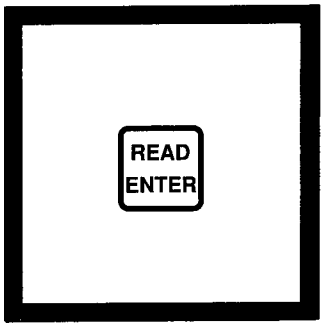
The display will show:
WAIT
then:
0. mg/l ClO_2 H



7. Fill another sample cell with sample (the prepared sample).



8. Place the prepared sample into the cell holder.



9. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L chlorine dioxide (ClO_2) will be displayed.

Note: In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

SAMPLING AND STORAGE

Collect samples in clean plastic or glass bottles. The most reliable results are obtained when samples are analyzed as soon as possible after collection. If prompt analysis is not possible, use sealed glass bottles, and fill them completely. Store the sealed bottle in a refrigerator at 4 °C (39 °F).

SUMMARY OF METHOD

Chlorine dioxide, a yellow gas, can be measured directly in a water solution. This method uses a wavelength of 445 nm to increase the range of the test.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Unit	Cat. No.
Water, demineralized	25 mL	4 L	272–56

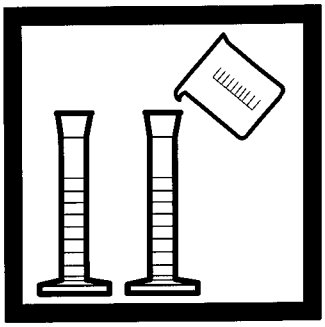
OPTIONAL APPARATUS

Pour–Thru Cell Assembly Kit	each	45215–00

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

CHLORINE DIOXIDE, LR (0 to 1.00 mg/L)

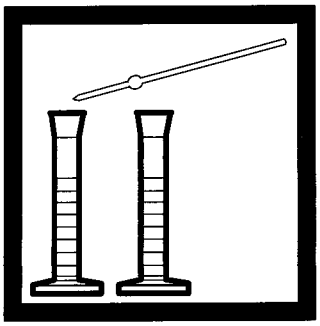
Chlorophenol Red Method*



1. Fill two 50–mL graduated mixing cylinders with sample to the 50–mL mark.

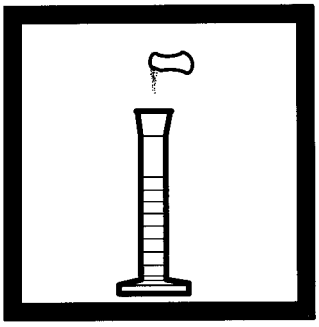
Note: Analyze samples immediately because of the instability and volatility of chlorine dioxide.

Note: For most accurate results, analyze each portion at the same sample temperature.

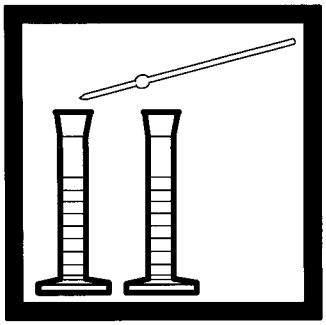


2. Add 1.0 mL of Chlorine Dioxide Reagent 1 to each cylinder. Stopper. Invert several times to mix.

Note: Use a volumetric pipet and pipet filler to add all reagents.

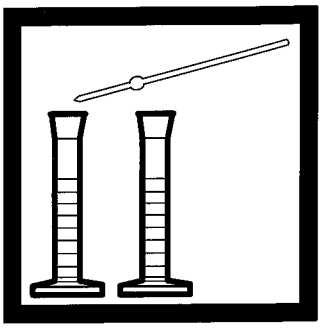


3. Add the contents of one Dechlorinating Reagent Powder Pillow to one cylinder. Invert several times until dissolved. This solution will become the blank. The other solution is the prepared sample.

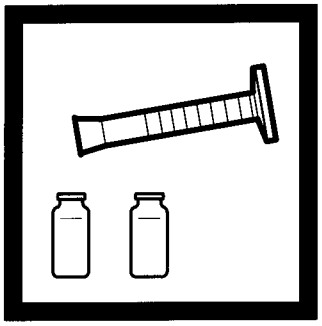


4. Add exactly 1.00 mL Chlorine Dioxide Reagent 2 to each cylinder. Stopper. Invert several times to mix.

Note: Use a Class A pipet to measure this reagent accurately.

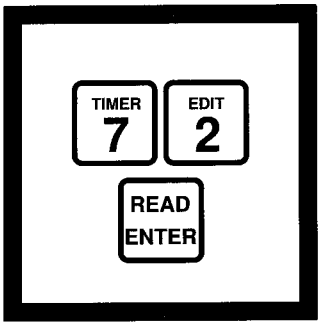


5. Add 1.0 mL of Chlorine Dioxide Reagent 3 to each cylinder. Stopper. Invert several times to mix.



6. Pour 25 mL from each cylinder into respective sample cells.

Note: The Pour–Thru Cell can be used with this procedure if it is rinsed shortly after each analysis with demineralized water.



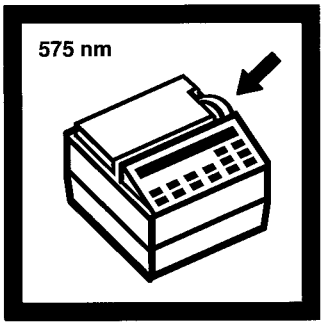
7. Enter the stored program number for chlorine dioxide (ClO_2), low range.

Press: **7 2 READ/ENTER**

The display will show:
DIAL nm TO 575

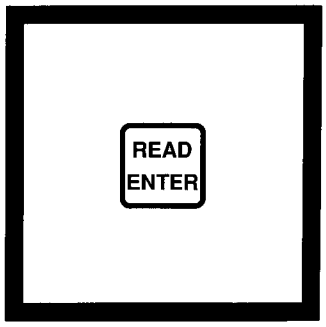
Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

Note: Instruments with software version 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 9. Proceed with Step 10.



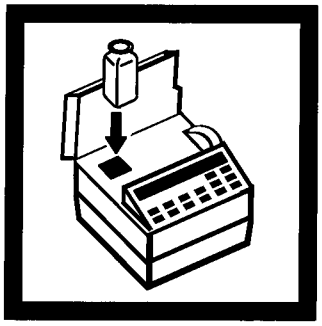
8. Rotate the wavelength dial until the small display shows:
575 nm

*Adapted from Harp, Klein, and Schoonover, *Jour. Amer. Water Works Assn.*, 73 387–388 (1981)

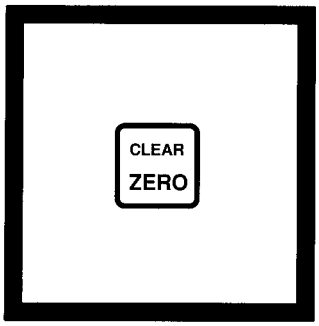


9. Press: **READ/ENTER**

The display will show:
mg/l ClO_2 L

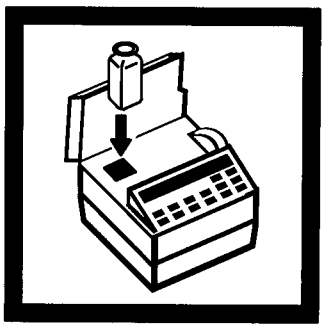


10. Place the blank into the cell holder. Close the light shield.



11. Press: **ZERO**

The display will show:
WAIT
then:
0.00 mg/l ClO_2 L



12. Place the prepared sample into the cell holder.

Press: **READ/ENTER**

The display will show
WAIT
then the results in mg/L ClO_2 will be displayed.

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

SAMPLING AND STORAGE

Collect samples in clean plastic or glass bottles. Fill completely and cap tightly. Avoid excessive agitation and exposure to light, especially sunlight. Samples must be analyzed immediately upon collection and cannot be preserved or stored for later analysis.

PRECISION

In a single laboratory, using a standard solution of 0.45 mg/L ClO_2 and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ±0.014 mg/L ClO_2.

INTERFERENCES

For highly acidic or alkaline water, 2.0 mL each of Chlorine Dioxide Reagent 1 and Chlorine Dioxide Reagent 3 may be required instead of 1.0 mL.

Ozone interferes at 0.5 mg/L

The following do not interfere at or below these concentrations:

ClO^-	5.5 mg/L
ClO_2^-	6 mg/L
ClO_3^-	6 mg/L
CrO_4^{2-}	3.6 mg/L
Fe^{3+}	5 mg/L
Hardness	1000 mg/L
Turbidity	1000 NTU

SUMMARY OF METHOD

Chlorine Dioxide (ClO_2) is determined by its combination with chlorophenol red at pH 5.2 to form a colorless complex. The net effect is bleaching of the color in an amount proportional to the chlorine dioxide concentration. The method is specific for ClO_2 and is unreactive to other active chlorine or moderate oxidizing compounds.

REQUIRED REAGENTS

	Cat No.
Chlorine Dioxide Reagent Set (100 Tests)	22423–00
Includes: (2) 20700–42, (2) 20701–42, (2) 20702–42, (1) 14363–69	

Description	Quantity Required Per Test	Unit	Cat. No.
Chlorine Dioxide Reagent 1	2 mL	100 mL	20700–42
Chlorine Dioxide Reagent 2	2 mL	100 mL	20701–42
Chlorine Dioxide Reagent 3	2 mL	100 mL	20702–42
Dechlorinating Reagent Powder Pillows	1 pillow	100/pkg	14363–69

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968–00
Cylinder, mixing, graduated, 50 mL	2	each	1896–41
Pipet, volumetric, Class A, 1.00 mL	3	each	14515–35
Pipet Filler, safety bulb	1	each	14651–00

OPTIONAL APPARATUS

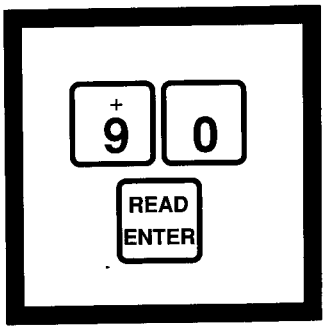
Pour–Thru Cell Assembly Kit	each	45215–00

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

CHROMIUM, HEXAVALENT (0 to 0.60 mg/L Cr^{6+}) For water and wastewater

1, 5-Diphenylcarbohydrazide Method* (Powder Pillows or AccuVac Ampuls), USEPA accepted for reporting wastewater analysis**

USING POWDER PILLOWS



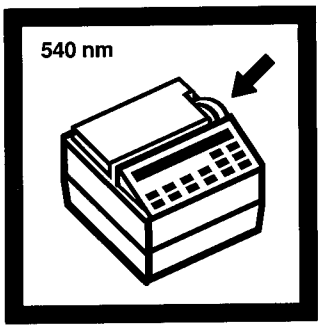
1. Enter the stored program number for hexavalent chromium (Cr^{6+}).

Press: **9 0 READ/ENTER**

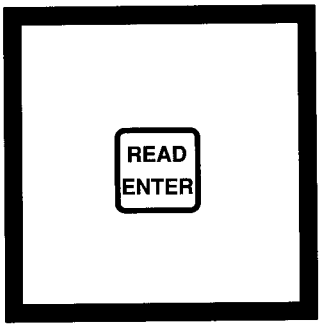
The display will show:
DIAL nm TO 540

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

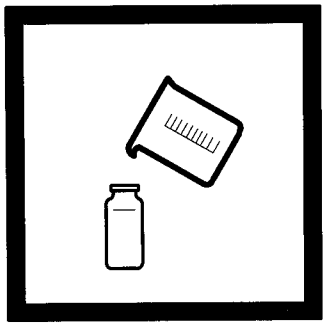


2. Rotate the wavelength dial until the small display shows:
540 nm



3. Press: **READ/ENTER**

The display will show:
mg/l Cr^{6+}



4. Fill a sample cell with 25 mL of sample.

Note: *For proof of accuracy, use a 0.25 mg/L hexavalent chromium standard solution (preparation given in the* Accuracy Check*) in place of the sample.*

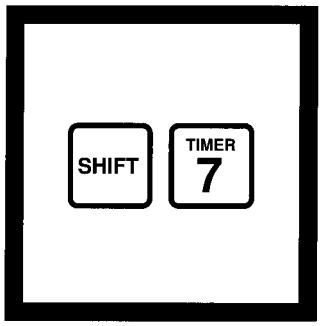
*Adapted from *Standard Methods for the Examination of Water and Wastewater*

**Procedure is equivalent to USGS method I–1230–85 for wastewater

5. Add the contents of one ChromaVer 3 Reagent Powder Pillow to the sample cell (the prepared sample). Swirl to mix.

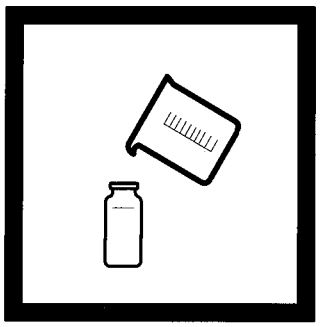
Note: A purple color will form if hexavalent chromium is present.

Note: At high chromium levels a precipitate will form. Dilute sample according to Sample Dilution Techniques *(Section I).*



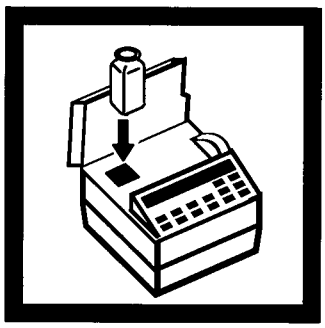
6. Press: **SHIFT TIMER**

A 5–minute reaction period will begin.



7. Fill another sample cell with 25 mL of sample (the blank).

Note: For turbid samples, treat the blank with the contents of one Acid Reagent Powder Pillow. This will ensure any turbidity dissolved by the acid in the ChromaVer 3 Chromium Reagent also will be dissolved in the blank.

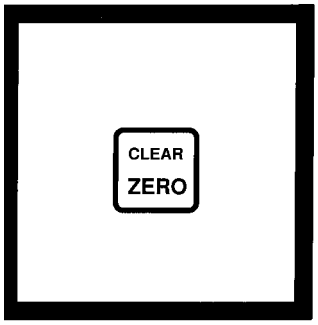


8. When the timer beeps, the display will show:

mg/l Cr^{6+}

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

Note: The Pour–Thru Cell can be used with this procedure.



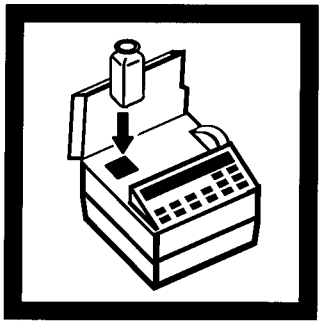
9. Press: **ZERO**

The display will show:

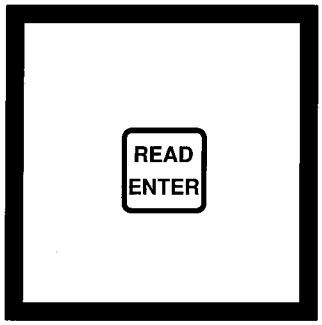
WAIT

then:

0.00 mg/l Cr^{6+}



10. Place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ/ENTER**

The display will show

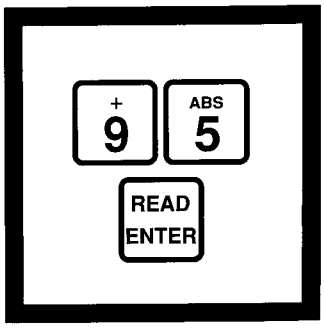
WAIT

then the results in mg/L hexavalent chromium will be displayed.

Note: The results can be expressed as mg/L chromate (CrO_4^{2-}) or mg/L sodium chromate (Na_2CrO_4) by multiplying the mg/L hexavalent chromium by 2.23 or 3.12, respectively.

Note: In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

USING ACCUVAC AMPULS



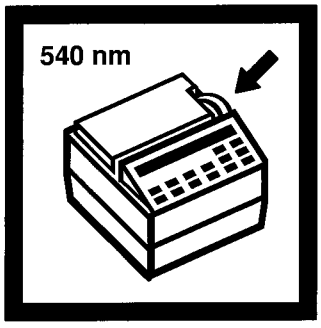
1. Enter the stored program number for hexavalent chromium.

Press: **9 5 READ/ENTER**

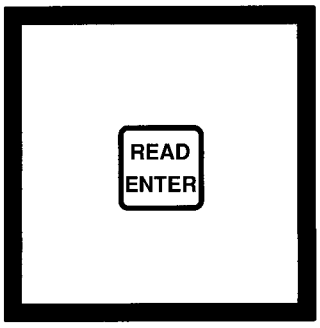
The display will show:
DIAL nm TO 540

Note: *DR/2000s with software version 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software version 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

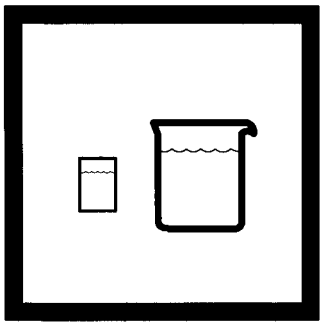


2. Rotate the wavelength dial until the small display shows:
540 nm



3. Press: **READ/ENTER**

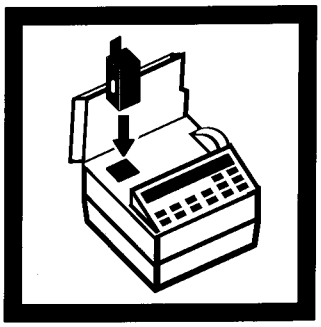
The display will show:
mg/l Cr^{6+} AV



4. Fill the zeroing vial with at least 10 mL of sample (the blank). Collect at least 40 mL of sample in a 50–mL beaker.

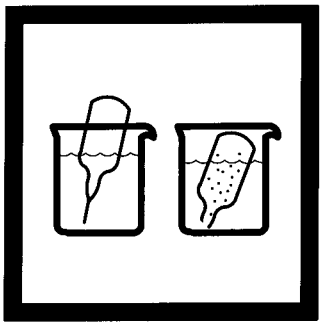
Note: *For turbid samples, treat 25 mL of the blank with the contents of one Acid Reagent Powder Pillow. This will ensure any turbidity dissolved by the acid in the ChromaVer 3 Chromium Reagent also will be dissolved in the blank.*

Note: *For proof of accuracy, use a 0.25 mg/L hexavalent chromium standard solution (preparation given in the* Accuracy Check*) in place of the sample.*



5. Place the AccuVac Vial Adapter into the cell holder.

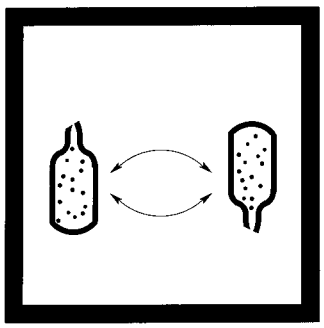
Note: *Place the grip tab at the rear of the cell holder.*



6. Fill a ChromaVer 3 Reagent AccuVac Ampul (the prepared sample) with sample.

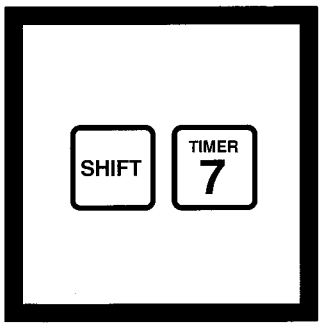
Note: *Keep the tip immersed while the ampul fills completely.*

Note: *ChromaVer 3 should be white to tan in color. Replace if it is brown or green.*



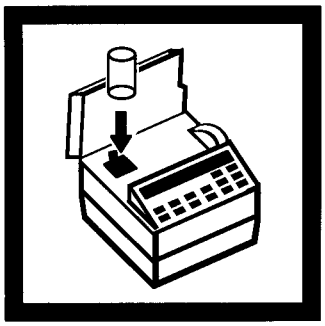
7. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

Note: *A purple color will form if hexavalent chromium is present.*



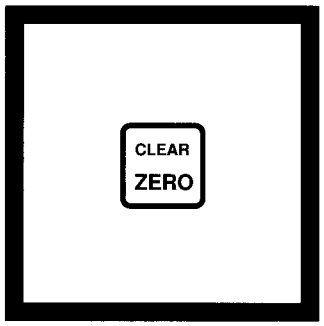
8. Press: **SHIFT TIMER**

A 5–minute reaction period will begin.



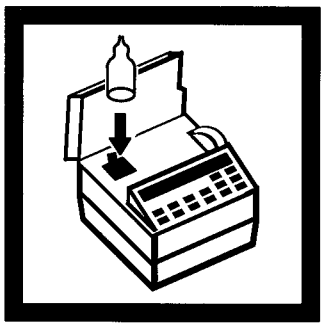
9. When the timer beeps the display will show:
mg/l Cr^{6+} AV

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

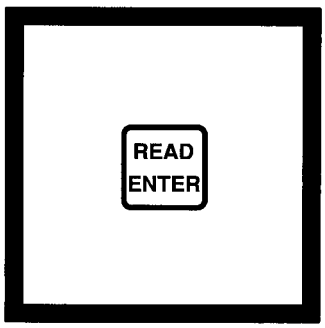


10. Press: **ZERO**

The display will show:
WAIT
then:
0.00 mg/l Cr^{6+} AV



11. Place the prepared sample into the cell holder. Close the light shield.



12. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L hexavalent chromium will be displayed.

Note: *The results can be expressed as mg/L chromate (CrO_4^{2-}) or mg/L sodium chromate (Na_2CrO_4) by multiplying the mg/L hexavalent chromium (Cr^{6+}) by 2.23 or 3.12, respectively.*

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

SAMPLING AND STORAGE

Collect samples in a cleaned glass or plastic container. Store at 4 °C (39 °F) up to 24 hours. Samples must be analyzed within 24 hours.

ACCURACY CHECK

Standard Additions Method

a) Snap the neck off a Chromium Voluette Ampule Standard, 12.5 mg/L Cr^{6+}.

b) Use the TenSette pipet to add 0.1 mL, 0.2 mL and 0.3 mL of standard, respectively to three 25–mL samples. Mix each thoroughly.

c) Analyze each sample as described above. The Chromium concentration should increase 0.05 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Prepare a 0.25–mg/L Cr^{6+} by pipetting 5.00 mL of hexavalent chromium standard solution, 50.0 mg/L Cr^{6+}, into a 1000–mL volumetric flask and diluting to the mark with demineralized water. Prepare this solution daily. Perform the chromium procedure as described above. The mg/L Cr^{6+} reading should be 0.25 mg/L Cr^{6+}.

PRECISION

In a single laboratory, using a standard solution of 0.4 mg/L Cr^{6+} and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ±0.003 mg/L Cr^{6+}.

In a single laboratory, using a standard solution of 0.4 mg/L Cr^{6+} and two representative lots of AccuVac ampuls with the DR/2000, a single operator obtained a standard deviation of ±0.001 mg/L Cr^{6+}.

INTERFERENCES

The following do not interfere in the test up to the following concentration:

Mercurous & Mercuric Ions	Interferes Slightly
Iron	1 mg/L
Vanadium	1 mg/L

Vanadium interference can be overcome by waiting ten minutes before reading.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment *(see pH interfernce in Section I).*

SUMMARY OF METHOD

Hexavalent chromium is determined by the 1,5–diphenylcarbohydrazide method using a single dry powder formulation called ChromaVer 3 Chromium Reagent. This reagent contains an acidic buffer combined with 1,5–diphenylcarbohydrazide, which reacts to give a purple color when hexavalent chromium is present.

REQUIRED REAGENTS AND APPARATUS (Using Powder Pillows)

Description	Quantity Required Per Test	Unit	Cat. No.
ChromaVer 3 Chromium Reagent Powder Pillows	1 pillow	100/pkg	12066–99
Clippers, for opening pillows	1	each	968–00

REQUIRED REAGENTS AND APPARATUS (Using AccuVac Ampuls)

ChromaVer 3 AccuVac ampuls	1 ampul	25/pkg	25050–25
Adapter, AccuVac Vial	1	each	43784–00
Beaker, 50 mL	1	each	500–41
Sample Cell, 25 x 54 mm, 10 mL, with cap	1	each	21228–00

OPTIONAL REAGENTS

Acid Reagent Powder Pillows	50/pkg	2126–66
Chromium, Hexavalent, Standard Solution, 50 mg/L Cr^{6+}	100 mL	810–42
Chromium, Hexavalent, Solution,Voluette ampule, 12.5 mg/L Cr^{6+}, 10 mL	16/pkg	14256–10
Nitric Acid, ACS	500 mL	152–49
Nitric Acid Solution, 1:1	500 mL	2540–49
Sodium Hydroxide Solution, 5.0 N	59 mL* SCDB	2450–26
Water, demineralized	4 L	272–56

OPTIONAL APPARATUS

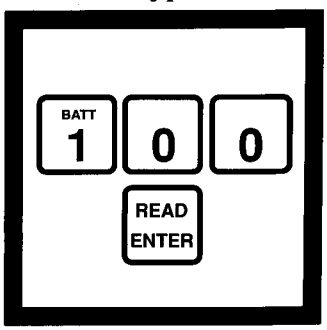
AccuVac Snapper Kit	each	24052–00
Ampule Breaker Kit	each	21968–00
Flask, volumetric, Class A, 25 mL	each	14574–40
Flask, volumetric, Class A, 1000 mL	each	14574–53
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391–33
pH Meter, EC10, portable	each	50050–00
Pipet, serological, 2 mL	each	532–36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700–01
Pipet Tips, for 19700–01 TenSette Pipet	50/pkg	21856–96
Pipet, volumetric, 5.00 mL, Class A	each	14515–37
Pipet Filler, safety bulb	each	14651–00
Pour–Thru Cell Assembly Kit	each	45215–00
Sample cell, with 25–mL mark, matched pair	each pair	20950–00

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

*Contact Hach for larger sizes.

CHROMIUM, TOTAL (0 to 0.60 mg/L)

Alkaline Hypobromite Oxidation Method*



1. Enter the stored program number for total chromium (Cr).

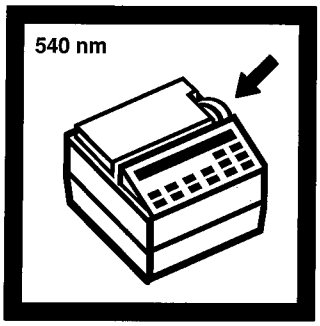
Press: **1 0 0 READ/ENTER**

The display will show:
DIAL nm TO 540

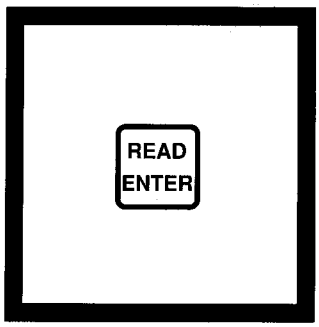
Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

Note: *If sample cannot be analyzed immediately, see* Sampling and Storage *below. Adjust the pH of stored samples before analysis.*



2. Rotate the wavelength dial until the small display shows:
540 nm

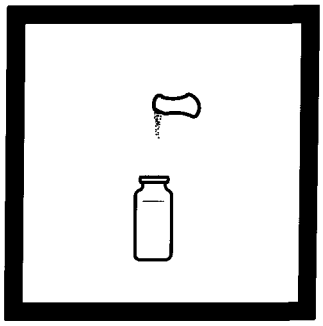


3. Press: **READ/ENTER**

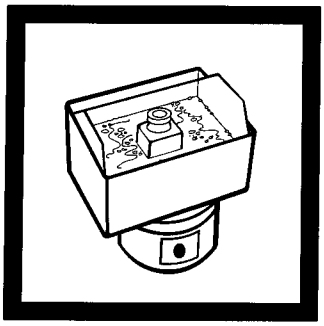
The display will show:
mg/l Cr

4. Fill a clean sample cell with 25 mL of sample.

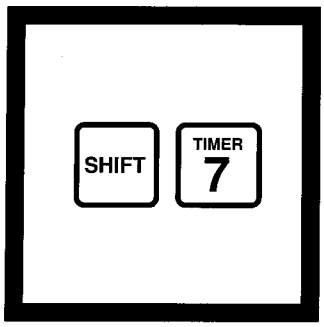
Note: *For proof of accuracy, use a 0.25 mg/L trivalent chromium standard solution (preparation given in the* Accuracy Check*) in place of the sample.*



5. Add the contents of one Chromium 1 Reagent Powder Pillow (the prepared sample). Swirl to mix.

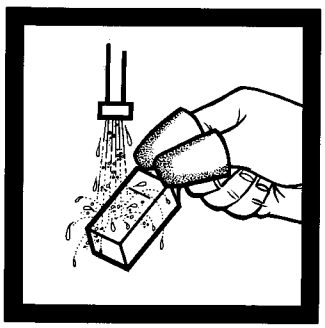


6. Place the prepared sample into a boiling water bath.



7. Press: **SHIFT TIMER**

A 5–minute reaction period will begin.

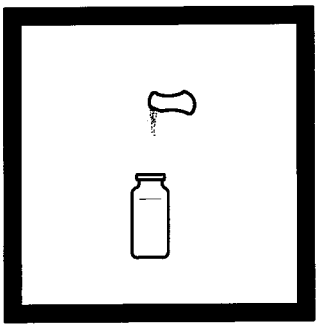


8. When the beeper sounds, remove the prepared sample. Using running tap water, cool the cell to 25 °C.

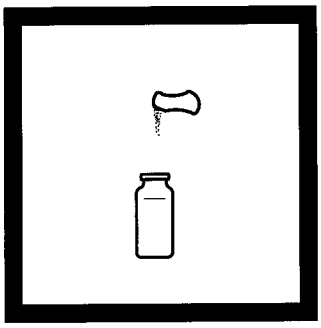
Note: *Use finger cots to handle the hot sample cell.*

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

9. Add the contents of one Chromium 2 Reagent Powder Pillow. Swirl to mix.



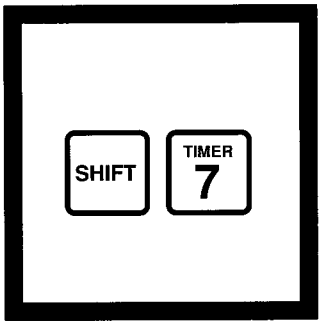
10. Add the contents of one Acid Reagent Powder Pillow. Swirl to mix.



11. Add the contents of one ChromaVer 3 Chromium Reagent Powder Pillow. Swirl to mix.

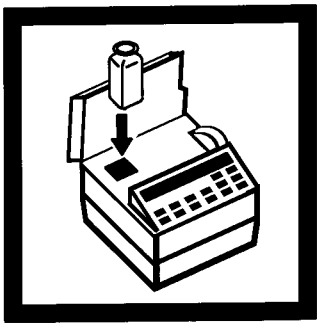
Note: *A purple color will form if chromium is present.*

Note: *The color of ChromaVer 3 should be white to tan. If the color is brown or green, replace the powder. Undissolved powder does not affect accuracy.*



12. Press: **SHIFT TIMER**

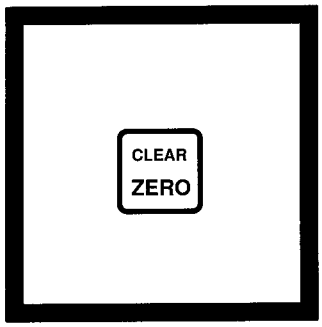
A 5–minute reaction period will begin.



13. When the timer beeps, fill another sample cell with 25 mL of sample (the blank). Place it into the cell holder. Close the light shield.

Note: *For turbid samples, treat the blank as described in Steps 4 through 10.*

Note: *The Pour–Thru Cell can be used with this procedure.*



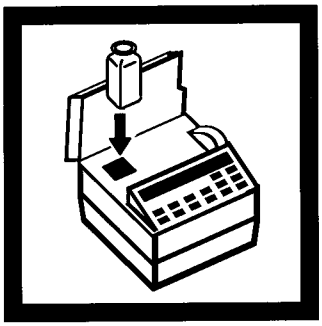
14. Press: **ZERO**

The display will show:

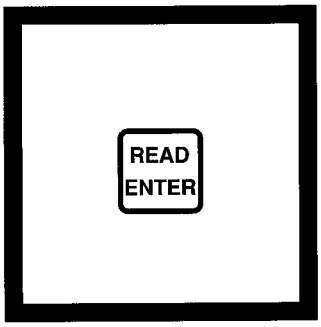
WAIT

then:

0.00 mg/l Cr



15. Place the prepared sample into the cell holder. Close the light shield.



16. Press: **READ/ENTER**

The display will show:

WAIT

then the result in mg/L chromium will be displayed.

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

Note: *Determine a reagent blank for each new lot of ChromaVer 3 reagent as follows: Repeat Steps 11 to 16, using demineralized water as the sample. Subtract this value from each result obtained with this lot of reagent.*

SAMPLING AND STORAGE
Collect samples in acid–washed glass or plastic containers. Store samples at 4 °C (39 °F) up to 24 hours. Samples must be analyzed within 24 hours.

ACCURACY CHECK
Standard Additions Method
a) Snap the top off a Trivalent Chromium Voluette Ampule Standard, 12.5 mg/L as Cr^{3+}.

b) Use the TenSette pipet to add 0.1, 0.2, and 0.3 m/L of standard to three 25–mL water samples. Mix each thoroughly.

c) Analyze each sample as described above. The chromium concentration should increase 0.05 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method
Prepare a 0.25 mg/L trivalent chromium standard by diluting 5.00 mL of chromium standard solution, 50 mg/L as Cr^{3+}, to 1000 mL with demineralized water. Prepare this solution daily.

PRECISION
In a single laboratory, using a standard solution of 0.4 mg/L chromium and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ±0.025 mg/L chromium.

INTERFERENCES
Large amounts of organic material may inhibit complete oxidation of trivalent chromium. If high levels of organic material are present, see *Digestion* in *Section I* for instruction on sample digestion. Perform the analysis as described on the digested sample.

Iron does not interfere.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment; see *Interferences, pH (Section I)*.

SUMMARY OF METHOD
Trivalent chromium in the sample is oxidized to the hexavalent form by hypobromite ion under alkaline conditions. The sample is acidified. The total chromium content is determined by the 1,5–diphenylcarbohydrazide method. Determine trivalent chromium by subtracting the results of a separate hexavalent chromium test from the results of the total chromium test.

REQUIRED REAGENTS

	Cat. No.
Total Chromium Reagent Set (100 Tests)	22425–00
Includes: (2) 2126–66, (2) 12066–66, (1) 2043–99, (1) 2044–99	

Description	Quantity Required Per Test	Unit	Cat. No.
Acid Reagent Powder Pillows	1 pillow	50/pkg	2126–66
ChromaVer 3 Chromium Reagent Powder Pillows	1 pillow	50/pkg	12066–66
Chromium 1 Reagent Powder Pillows	1 pillow	100/pkg	2043–99
Chromium 2 Reagent Powder Pillows	1 pillow	100/pkg	2044–99

REQUIRED APPARATUS

Clippers, for opening pillows	1	each	968–00
Water bath and rack (use with hot plate)	1	each	1955–55

Select one based on available voltage:

Hot plate, 3 1/2" diameter, 120 Vac	each	12067–01
Hot plate, 3 1/2" diameter, 240 Vac	each	12067–02

OPTIONAL REAGENTS

Chromium, trivalent, standard solution, 50 mg/L Cr^{3+}	100 mL	14151–42
Chromium, trivalent, standard solution, Voluette ampule, 12.5 mg/L Cr^{3+}, 10 mL	16/pkg	14257–10
Nitric Acid, ACS	500 mL	152–49
Nitric Acid Solution 1:1	500 mL	2540–49
Sodium Hydroxide Solution 5.0 N	59 mL* DB	2450–26
Water, demineralized	4 L	272–56

OPTIONAL APPARATUS

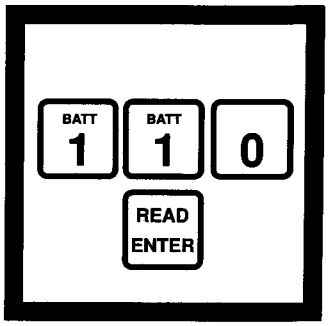
Ampul Breaker Kit	each	21968-00
Cylinder, graduated, polypropylene, 25 mL	each	1081–40
Flask, volumetric, 1000 mL	each	547–53
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391–33
pH Meter, EC10, portable	each	50050–00
Pipet, serological, 2 mL	each	532–36
Pipet, TenSette, 0.1 to 1.0 mL	each	19700–01
Pipet Tips for 19700–01 TenSette Pipet	50/pkg	21856–96
Pipet, volumetric, 5.00 mL, Class A	each	14515–37
Pipet Filler, safety bulb	each	14651–00
Pour–Thru Cell Assembly Kit	each	45215–00

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

*Contact Hach for larger sizes.

COBALT (0 to 2.00 mg/L)

1-(2-Pyridylazo)-2-Naphthol (PAN) Method*



1. Enter the stored program number for cobalt (Co).

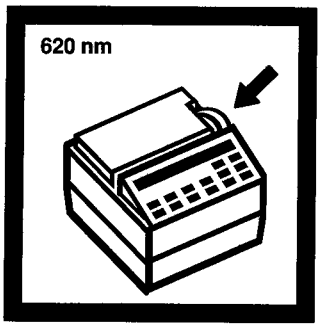
Press: **1 1 0 READ/ENTER**

The display will show:
DIAL nm TO 620

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

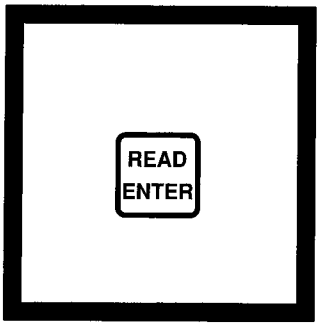
Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

Note: *If sample cannot be analyzed immediately, see* Sampling and Storage *below. Adjust the pH of stored samples before analysis.*



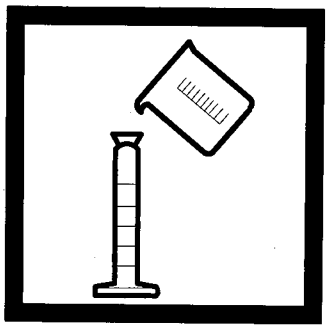
2. Rotate the wavelength dial until display shows:
620 nm

Note: *Total recoverable cobalt needs a prior digestion; use one of the three procedures given in* Digestion (Section I). *If EDTA is present, use the vigorous digestion.*



3. Press: **READ/ENTER**

The display will show:
mg/l Co

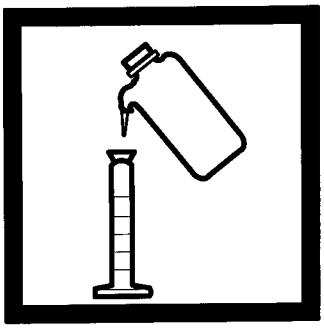


4. Measure 25 mL of sample in a 25–mL graduated mixing cylinder (the prepared sample).

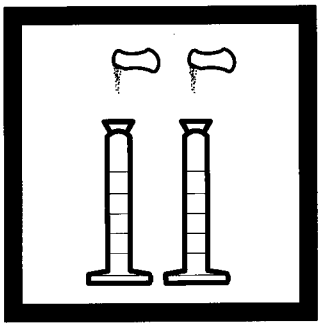
Note: *If sample is less than 10 °C (50 °F), warm to room temperature prior to analysis.*

Note: *For proof of accuracy, use a 1.0 mg/L cobalt standard solution (preparation given in the* Accuracy Check*) in place of the sample.*

*Adapted for Watanbe, H., *Talanta*, 21 295 (1974)

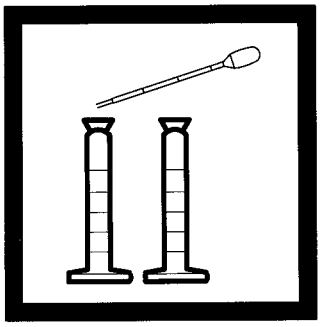


5. Measure 25 mL of demineralized water in a second cylinder (the blank).



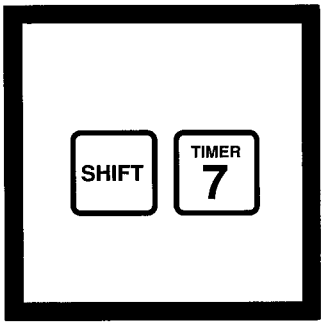
6. Add the contents of one Phthalate–Phosphate Reagent Powder Pillow to each cylinder. Stopper. Immediately shake to dissolve.

Note: *If sample contains iron (Fe^{3+}), it is important that all of the powder be dissolved completely before continuing with Step 7.*



7. Add 1.0 mL of 0.3% PAN Indicator Solution to each cylinder. Stopper. Invert several times to mix.

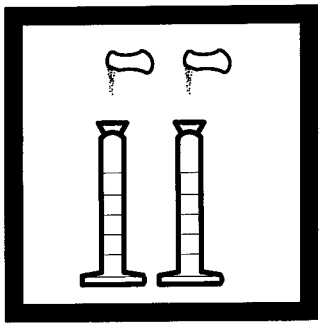
Note: *Use plastic dropper provided.*



8. Press: **SHIFT TIMER**

A 3–minute reaction period will begin.

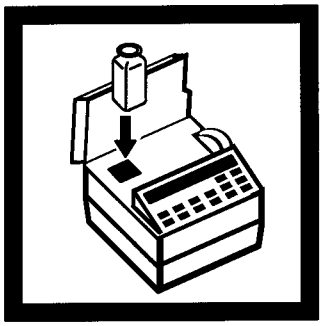
Note: *During color development, the sample solution color may vary from green to dark red, depending on the chemical make–up of the sample. The demineralized water blank should be yellow.*



9. When the timer beeps, the display will show:

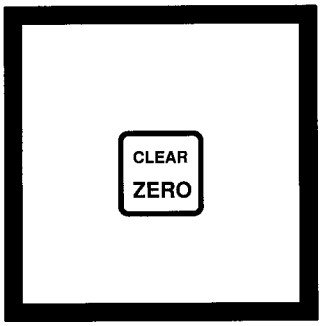
mg/l Co

Add the contents of one EDTA Reagent Powder Pillow to each cylinder. Stopper. Shake to dissolve.



10. Fill a sample cell with the blank. Place it into the cell holder. Close the light shield.

Note: *The Pour–Thru Cell can be used if rinsed well with demineralized water after use.*



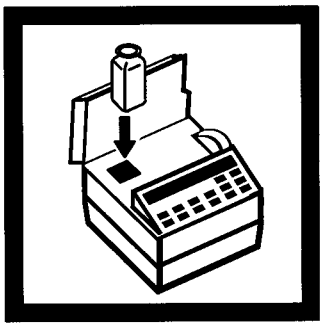
11. Press: **ZERO**

The display will show:

WAIT

then:

0.00 mg/l Co



12. Fill a second cell with the prepared sample. Place it into the cell holder. Close the light shield.

Press: **READ/ENTER**

The display will show:

WAIT

then the cobalt result in mg/L Co.

Note: *If the sample contains nickel refer to Stored Procedure No. 340 for Nickel, (PAN).*

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

SAMPLING AND STORAGE

Collect samples in acid–washed plastic bottles. Adjust the sample pH to 2 or less with nitric acid (about 5 mL per liter). Preserved samples can be stored up to six months at temperature. Adjust the sample pH between 3 and 8 with 5.0 N Sodium Hydroxide Standard Solution just before analysis. Do not exceed pH 8 as this may cause some loss of cobalt as a precipitate. Correct test results for volume additions *(see Correction for Volume Additions in Section I).*

ACCURACY CHECK

Standard Solution Method

Prepare 1.0 mg/L cobalt standard solution by diluting 10.0 mL of a 10 mg/L working stock solution to 100 mL in a volumetric flask. The working stock solution should be prepared daily by diluting 10.00 mL of Cobalt Standard Solution, 1000 mg/L as Co, to 1000 mL with demineralized water. This is a 10 mg/L cobalt standard solution.

PRECISION

In a single laboratory, using standard solutions of 0.75 mg/L cobalt and two representative lots of reagents with the DR/2000, a single operator obtained a standard deviation of ±0.001 mg/L cobalt.

INTERFERENCES

The following may interfere in concentrations exceeding those listed at right.

AL^{3+}	32 mg/L
Ca^{2+}	1000 mg/L as ($CaCO_3$)
Cd^{2+}	20 mg/L
Cl^{-}	8000 mg/L
Cr^{3+}	20 mg/L
Cr^{6+}	40 mg/L
Cu^{2+}	15 mg/L
F^{-}	20 mg/L
Fe^{2+}	interferes directly and must not be present.
Fe^{3+}	10 mg/L
K^{+}	500 mg/L
Mg^{2+}	400 mg/L
Mn^{2+}	25 mg/L
Mo^{6+}	60 mg/L
Na^{+}	5000 mg/L
Pb^{2+}	20 mg/L
Zn^{2+}	30 mg/L

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment *(see pH Interference in Section I).*

SUMMARY OF METHOD

After buffering the sample and masking any Fe^{3+} with pyrophosphate, the cobalt is reacted with 1–(2–Pyridylazo)–2–Naphthol indicator. The indicator forms complexes with most metals present. After color development, EDTA is added to destroy all metal–PAN complexes except nickel and cobalt. Both nickel and cobalt can be determined on the same sample.

REQUIRED REAGENTS

	Cat. No.
Cobalt Reagent Set (100 Test)	22426–00
Includes: (2) 7005–49, (4) 21501–66, (2) 21502–32	

Description	Quantity Required Per Test	Unit	Cat. No.
EDTA Reagent Powder Pillows	2 pillows	100/pkg	7005–99
Phthalate–Phosphate Reagent Powder Pillows	2 pillows	50/pkg	21501–66
PAN Indicator Solution, 0.3%	2 mL	100 mL	21502–32
Water, demineralized	25 mL	4 L	272–56

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968–00
Cylinder, mixing, graduated, 25 mL	2	each	20886–40

OPTIONAL REAGENTS

Cobalt Standard Solution, 1000 mg/L Co	100 mL	21503–42
Nitric Acid, ACS	500 mL	152–49
Nitric Acid Solution, 1:1	500 mL	2540–49
Sodium Hydroxide Standard Solution, 5.0 N	100 mL	2450–32
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450–53

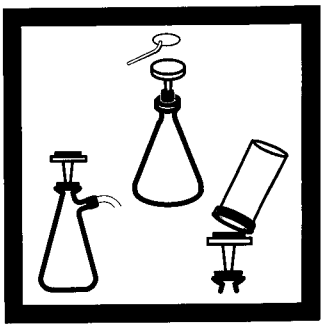
OPTIONAL APPARATUS

Flask, volumetric, Class A, 100 mL	each	14574–42
Flask, volumetric, Class A, 1000 mL	each	14574–53
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391–33
pH Meter, EC10, portable	each	50050–00
Pipet, serological, 1 mL	each	532–35
Pipet, serological, 5 mL	each	532–37
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, 10.0 mL	each	14515–38
Pipet Filler, safety bulb	each	14651–00
Pour–Thru Cell Assembly Kit	each	45215–00

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

COLOR, TRUE AND APPARENT (0 to 500 units) For water, wastewater and seawater

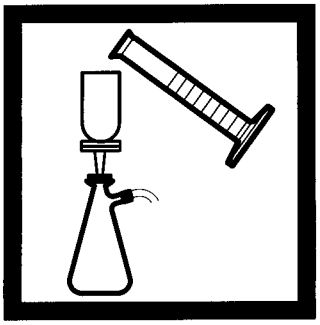
Platinum-Cobalt Standard Method*



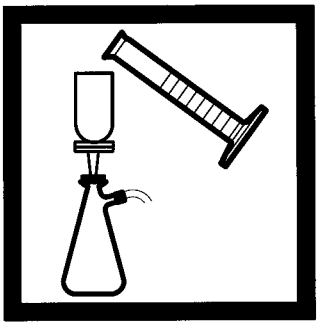
1. Assemble the filtering apparatus (membrane filter, filter holder, filter flask, and aspirator).

Note: *To test for apparent color, do not filter; omit Steps 1 to 3.*

Note: *If sample cannot be analyzed immediately, see* Sampling and Storage *below.*



2. Rinse the filter by pouring about 50 mL of demineralized water through the filter. Discard the rinse water.

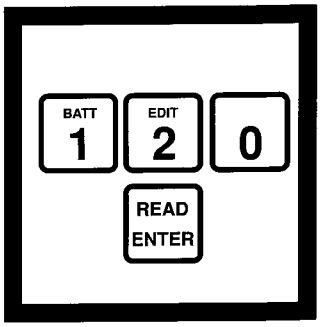


3. Pour another 50 mL of demineralized water through the filter.

4. Fill a sample cell (the blank) with 25 mL of filtered demineralized water. Discard the excess.

Note: *For apparent color use unfiltered demineralized water.*

Note: *The Pour–Thru Cell can be used with this procedure.*



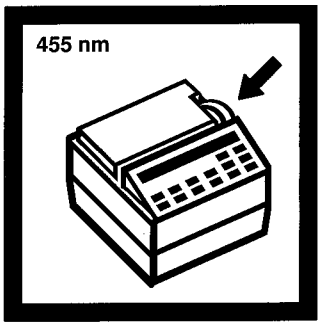
5. Enter the stored program number for true color.

Press: **1 2 0 READ/ENTER**

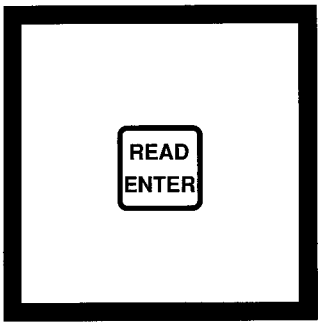
The display will show:
DIAL nm TO 455

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 7. Proceed with Step 8.*

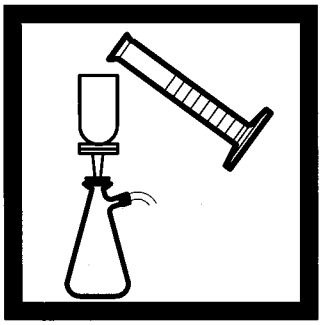


6. Rotate the wavelength dial until the small display shows:
455 nm



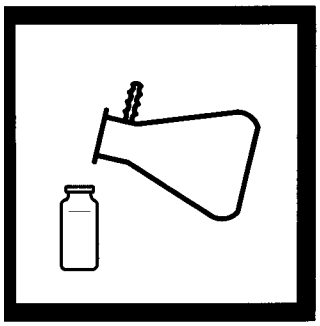
7. Press: **READ/ENTER**

The display will show:
UNITS PtCo COLOR



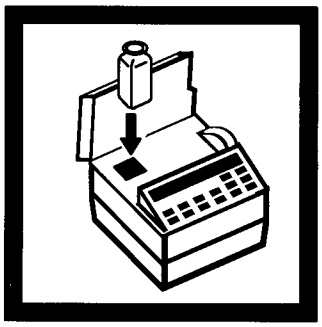
8. Pour about 50 mL of sample through the filter.

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

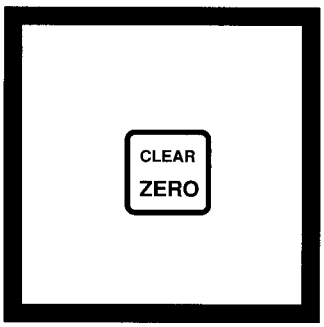


9. Fill a second sample cell (the prepared sample) with 25 mL of filtered sample.

Note: For proof of accuracy, use a 250–unit platinum–cobalt color standard solution preparation given in the Accuracy Check *in place of the filtered sample.*

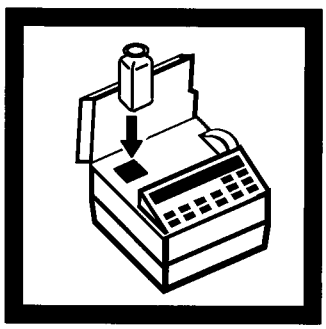


10. Place the blank into the cell holder. Close the lights shield.



11. Press: **ZERO**

The display will show:
WAIT
then:
0. UNITS PtCo COLOR



12. Place the prepared sample into the cell holder. Close the light shield.

Press: **READ/ENTER**

The display will show:
WAIT
and then the result in platinum–cobalt units will be displayed.

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the results.*

SAMPLING AND STORAGE

Collect samples in clean plastic or glass bottles. Most reliable results are obtained when samples are analyzed as soon as possible after the collection. If prompt analysis is impossible, fill bottles completely and cap tightly. Avoid excessive agitation or prolonged contact with air. Sample can be stored for 24 hours by cooling to 4 °C (39 °F). Warm to room temperature before running the test.

ACCURACY CHECK

Standard Solution Method

A 500 platinum–cobalt units color standard solution is available under Optional Reagents for checking test accuracy. A 250 platinum–cobalt units standard can be made by pipetting 50.0 mL of the 500 platinum–cobalt units standard into a 100–mL volumetric flask and diluting to volume with demineralized water.

SUMMARY OF METHOD

Color may be expressed as "apparent" or "true" color. The apparent color includes that from dissolved materials plus that from suspended matter. By filtering or centrifuging out the suspended materials, the true color can be determined. The procedure describes true color analysis. If apparent color is desired, it can be determined by measuring an unfiltered water sample. The stored program is used for both forms of color. The stored program is calibrated in color units based on the APHA–recommended standard of 1 color unit being equal to 1 mg/L platinum as chloroplatinate ion.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Units	Cat. No.
Water, demineralized	50 mL	4 L	272–56

REQUIRED APPARATUS

Aspirator, vacuum	1	each	2131–00
Filter Holder, 47 mm, 300 mL, graduated	1	each	13529–00
Filter, membrane, 47 mm, 0.45 microns	1	100/pkg	13530–00
Flask, filtering, 500 mL	1	each	546–49
Stopper, No 7, one hole	1	6/pkg	2119–07
Tubing, rubber	1	12 ft	560–19

OPTIONAL REAGENTS

Color Standard Solution, 500 platinum–cobalt units		1 L	1414–53

OPTIONAL APPARATUS

Flask, volumetric, Class A, 100 mL		each	14574–42
Pipet, volumetric, Class A, 50 mL		each	14515–41
Pour–Thru Cell Assembly Kit		each	45215–00

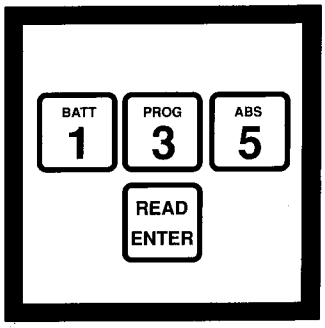
For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

COPPER (0 to 5.00 mg/L)

For water, wastewater and seawater **

Bicinchoninate Method* (Powder Pillows or AccuVac Ampuls);
USEPA approved for reporting wastewater analysis* – (digestion required; *See Section I*)**

USING POWDER PILLOWS



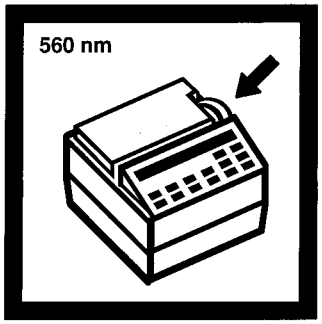
1. Enter the stored program number for copper (Cu), bicinchoninate–powder pillows

Press: **1 3 5 READ/ENTER**

The display will show:
DIAL nm TO 560

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

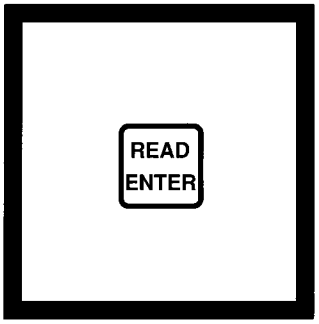
Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*



2. Rotate the wavelength dial until the small display shows:
560 nm

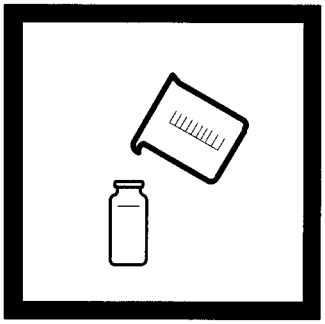
Note: *Determination of total copper needs a prior digestion (see* Digestion *in* Section I *for digestion procedures).*

Note: *If samples cannot be analyzed immediately, see* Sampling and Storage *following these steps. Adjust pH of stored samples before analysis.*



3. Press: **READ/ENTER**

The display will show:
mg/l Cu Bicn



4. Fill a sample cell with 25 mL of sample.

Note: *The Pour–Thru Cell can be used with this procedure.*

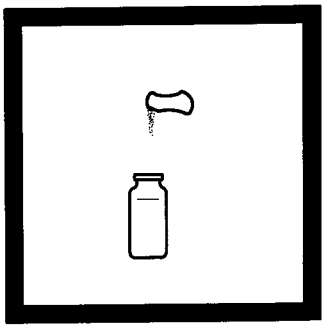
Note: *For proof of accuracy, use a 1.00 mg/L copper standard solution (preparation given in the* Accuracy Check*) in place of the sample.*

Note: *Determine a reagent blank for each new lot of reagent. Repeat Steps 4 to 10, using demineralized water as the sample. Subtract this value from each result obtained with this lot of reagent.*

*Adapted from Nakano, S., Yakugaku Zasshi, 82 486–491 (1962) [*Chemical Abstracts*, 58 3390e (1963)]

**Pretreatment required; see *Interferences (Using Powder Pillows)*

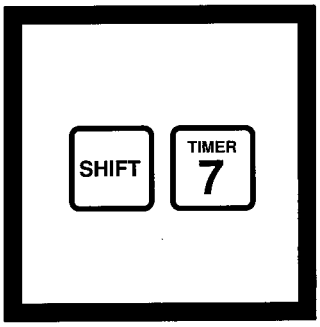
***Powder Pillows only: *Federal Register*, 45 (105) 36166 (May 29, 1980)



5. Add the contents of one CuVer 1 Copper Reagent Powder Pillow to the sample cell (the prepared sample). Swirl to mix.

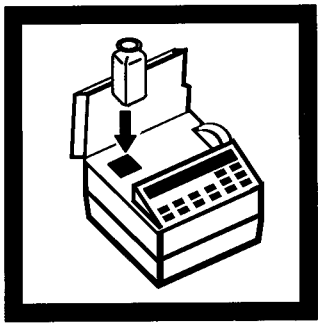
Note: A purple color will develop if copper is present.

Note: Accuracy is not affected by undissolved powder.



6. Press: **SHIFT TIMER**

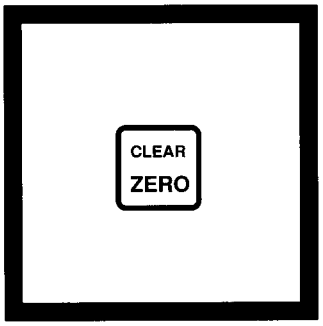
A 2–minute reaction period will begin.



7. When the timer beeps, the display will show:

mg/l Cu Bicn

Fill the second sample cell (the blank) with 25 mL of sample. Place the blank into the cell holder.



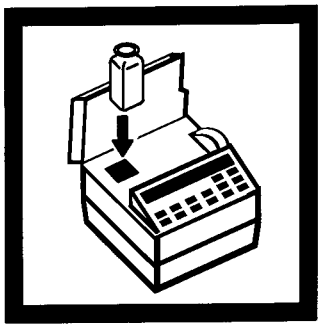
8. Press: **ZERO**

The display will show

WAIT

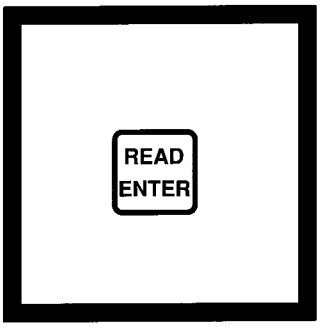
then:

0.00 mg/l Cu Bicn



9. Within thirty minutes after the timer beeps, place the prepared sample into the cell holder. Close the light shield.

Note: If more than five minutes elapse after the timer beeps, ZERO SAMPLE may appear. If so, remove the prepared sample. Insert the blank. Press: ZERO. Insert the prepared sample.



10. Press: **READ/ENTER**

The display will show:

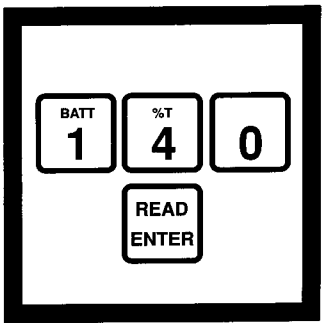
WAIT

then the result in mg/L copper will be displayed.

Note: In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

USING ACCUVAC AMPULS

Method 8026



1. Enter the stored program number for copper (Cu), bicinchoninate–AccuVac ampuls.

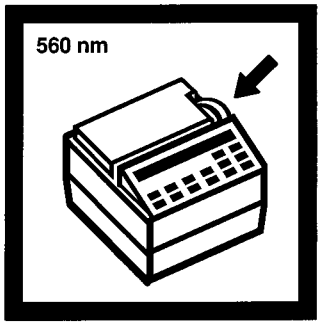
Press: **1 4 0 READ/ENTER**

The display will show:
DIAL nm TO 560

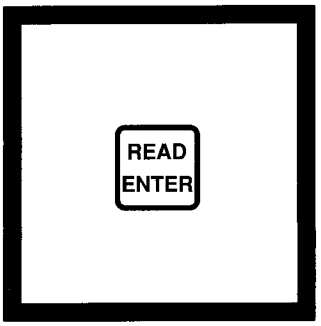
Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

Note: *If samples cannot be analyzed immediately, see* Sampling and Storage *following these steps. Adjust pH of stored samples before analysis.*

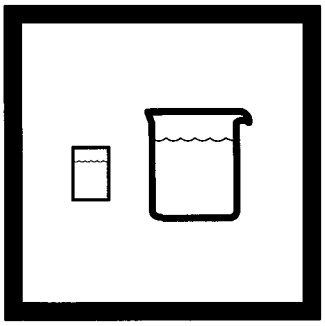


2. Rotate the wavelength dial until the small display shows:
560 nm



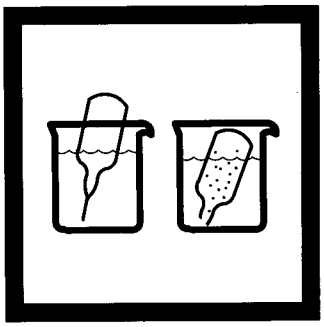
3. Press: **READ/ENTER**

The display will show:
mg/l Cu Bicn AV



4. Fill a zeroing vial (the blank) with at least 10 mL of sample. Collect at least 40 mL of sample in a 50–mL beaker.

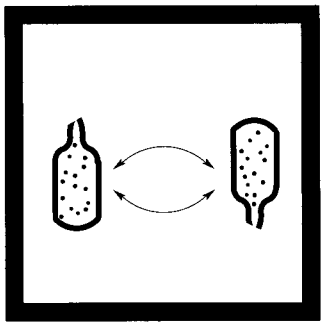
Note: *Determine a reagent blank for each new lot of reagent. Repeat Steps 4 to 12, using demineralized water as the sample. Subtract this value from each result obtained with this lot of reagent.*



5. Fill a CuVer 2 AccuVac Ampul with sample.

Note: Keep the tip immersed while the ampul fills completely.

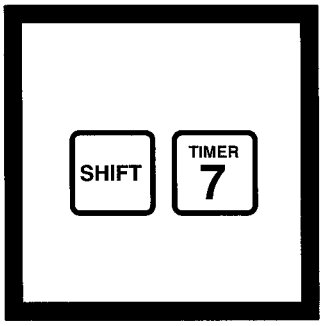
Note: For proof of accuracy, use a 1.00 mg/L copper standard solution (preparation given in the Accuracy Check*) in place of the sample.*



6. Quickly invert the ampul several times to mix. Wipe off any liquid or fingerprints.

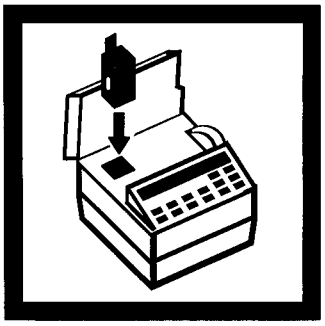
Note: A purple color will form if copper is present.

Note: Accuracy is not affected by undissolved powder.



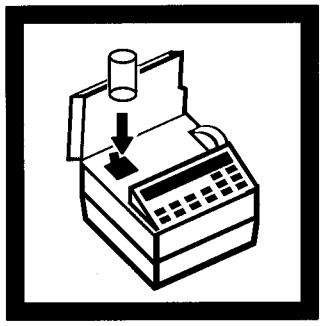
7. Press: **SHIFT TIMER**

A 2–minute reaction period will begin.

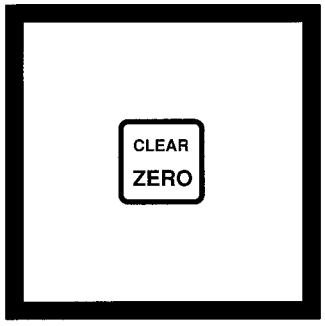


8. Place the AccuVac Vial Adapter into the cell holder.

Note: Place the grip tab at the rear of the cell holder.

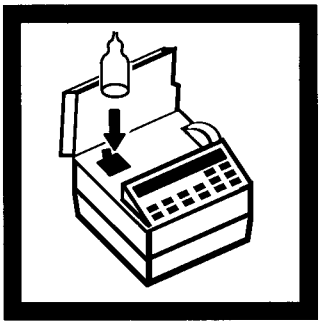


9. When the timer beeps, the display will show:
mg/l Cu Bicn AV
Place the blank into the cell holder. Close the light shield.



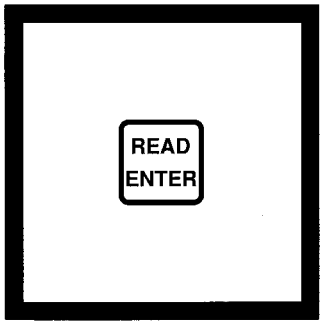
10. Press: **ZERO**

The display will show:
WAIT
then:
0.00 mg/l Cu Bicn AV



11. Within thirty minutes after the timer beeps, place the AccuVac ampul into the cell holder. Close the light shield.

Note: If more than five minutes elapse after the timer beeps, ZERO SAMPLE may appear. If so, remove the prepared sample. Insert the blank. Press: ZERO. Insert the prepared sample.



12. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L copper will be displayed.

SAMPLING AND STORAGE

Collect samples in acid–cleaned glass or plastic containers. Adjust the pH to 2 or less with nitric acid (about 2 mL per liter). Store preserved samples up to six months at room temperature. Before analysis, adjust the pH to 4 to 6 with 8 N potassium hydroxide. Do not exceed pH 6, as copper may precipitate. Correct the test result for volume additions *(see Correction for Volume Additions in Section I)*. If only dissolved copper is to be determined, filter the sample before acid addition using the labware listed under *Optional Apparatus*.

ACCURACY CHECK

Standard Additions Method

a) Snap the neck off the Copper Voluette Ampule Standard Solution, 75 mg/L.

b) Use the TenSette Pipet to add 0.1, 0.2, and 0.3 mL of standard to three 25–mL samples. Mix each thoroughly. (For AccuVac Ampuls, use 50–mL beakers.)

c) Analyze each sample as described above. The copper concentration should increase 0.3 mg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Addition* in *Section I* for more information.

Standard Solution Method

Prepare a 1.00 mg/L copper standard by diluting 1.00 mL of Copper Standard Solution, 100 mg/L as Cu, to 100 mL with demineralized water. Prepare this solution daily.

PRECISION

In a single laboratory, using a standard solution of 2.00 mg/L Cu and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ±0.007 mg/L Cu.

In a single laboratory, using a standard solution of 2.00 mg/L Cu and two representative lots of AccuVac ampuls with the DR/2000, a single operator obtained a standard deviation of ±0.007 mg/L Cu.

INTERFERENCES (Using Powder Pillows)

If the sample is extremely acidic (pH 2 or less) a precipitate may form. Add 8 N Potassium Hydroxide Standard Solution drop–wise while swirling to dissolve the turbidity. Read the mg/L Cu. If the turbidity remains and turns black, silver interference is likely. Eliminate silver interference by adding of 10 drops of saturated Potassium Chloride Solution to 75 mL of sample, followed by filtering through a fine or highly retentive filter. Use the filtered sample in the procedure. Cyanide interferences prevent sufficient color development but can be overcome by adding 0.5 mL of formaldehyde to the sample. Wait four minutes before taking the reading. Multiply the test results by 1.02 to correct for sample dilution by the formaldehyde.

To test samples such as seawater containing high levels of hardness, iron, or aluminum, follow the powder pillow procedure above, but substitute a CuVer 2 Copper Reagent Powder Pillow for the CuVer 1 Pillow used in Step 5. Results obtained will include total dissolved copper (free and complexed).

To differentiate free copper from that complexed to EDTA or other complexing agents, use a Free Copper Reagent Powder Pillow in place of the CuVer 1 pillow in Step 5. Results in Step 10 will be free copper only. Add a Hydrosulfite Reagent Powder Pillow to the same sample and re–read the result. This result will include the total dissolved copper (free and complexed).

INTERFERENCES (Using AccuVac Ampuls)

The CuVer 2 Reagent contained in the AccuVac Ampuls is formulated to withstand high levels of calcium, iron and aluminum without interference. Unlike CuVer 1 Reagent, CuVer 2 reacts directly with copper which is complexed by chelants such as EDTA. If free copper is to be determined separately from complexed copper, see the Powder Pillow Interference section above. If the sample is very acidic it should be adjusted to a pH greater than 4 before analysis. If a turbidity forms and turns black, silver interference is likely. This can be eliminated by adding 10 drops of saturated Potassium Chloride Solution to 75 mL of sample, followed by filtration through a fine filter using the labware listed under Optional Apparatus. Use the filtered sample in the procedure. Cyanide interferences prevent sufficient color development but can be overcome by adding 0.5 mL of formaldehyde to the sample. Wait four minutes before taking the reading.

SUMMARY OF METHOD

Copper in the sample reacts with a salt of bicinchoninic acid contained in CuVer 1 or 2 Copper Reagent to form a purple colored complex in proportion to the copper concentration. This method includes procedures for both powder pillow and AccuVac reagents.

REQUIRED REAGENTS (Using Powder Pillows)

Description	Quantity Required Per Test	Units	Cat. No.
CuVer 1 Copper Reagent Powder Pillows	1 pillow	50/pkg	14188–66

REQUIRED REAGENTS (Using AccuVac Ampuls)

CuVer 2 Copper Reagent AccuVac Ampuls	1 ampul	25/pkg	25040–25

REQUIRED APPARATUS (Using Powder Pillows)

Clippers, for opening powder pillows	1	each	968–00

REQUIRED APPARATUS (Using AccuVac Ampuls)

Adapter, AccuVac vial	1	each	43784–00
Beaker, 50 mL	1	each	500–41
Vial, zeroing	1	each	21228–00

OPTIONAL REAGENTS

Copper Standard Solution, 100 mg/L	100 mL	128–42
Copper Standard Solution, Voluette ampule, 75 mg/L	16/pkg	14247–10
CuVer 2 Reagent Powder Pillows	25/pkg	21882–68
Formaldehyde, 37%	100 mL* MDB	2059–32
Free Copper Reagent Powder Pillows	100/pkg	21186–69
Hydrochloric Acid Solution, 6 N	500 mL	884–49
Hydrosulfite Reagent Powder Pillows	100/pkg	21188–69
Nitric Acid, ACS	500 mL	152–49
Nitric Acid Solution, 1:1	500 mL	2540–49
Potassium Chloride Solution, saturated	59 mL SCDB	765–26
Potassium Hydroxide Standard Solution, 8.0 N	100 mL* MDB	282–32
Sodium Hydroxide Solution, 5.0 N	100 mL* MDB	2450–32
Water, demineralized	4 L	272–56

OPTIONAL APPARATUS

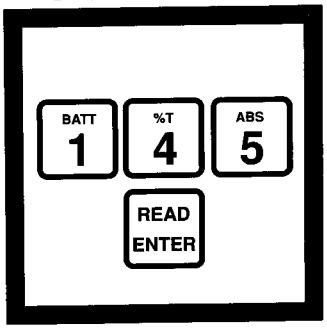
AccuVac Snapper Kit	each	24052–00
Ampule Breaker Kit	each	21968–00
Cylinder, graduated, polypropylene, 25 mL	each	1081–40
Cylinder, graduated, 100 mL	each	508–42
Filter Paper, folded, 12.5 cm	100/pkg	1894–57
Filter Pump	each	2131–00
Flask, volumetric, 100 mL	each	547–42
Funnel, polypropylene, 65 mm	each	1083–67
Hot Plate, 3 1/2" diameter, 120 Vac	each	12067–01
Hot Plate, 3 1/2" diameter, 240 Vac	each	12067–02
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391–33
pH Meter, EC10, portable	each	50050–00
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 Filler, safety bulb	each	14651–00
Pour–Thru Cell Assembly Kit	each	45215–00
Sample Cells, 1–inch, polystyrene, disposable	12/pkg	24102–12

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

*Contact Hach for larger sizes.

COPPER (0 to 210.0 µg/L)

Porphyrin Method*



1. Enter the stored program number for copper (Cu), porphyrin method.

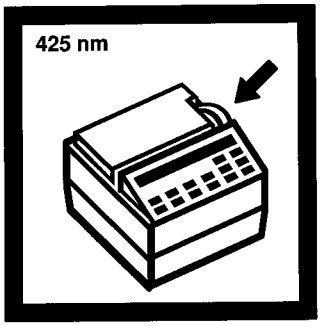
Press: **1 4 5 READ/ENTER**

The display will show:
DIAL nm TO 425

Note: *DR/2000s with software versions 3.0 and greater will not display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

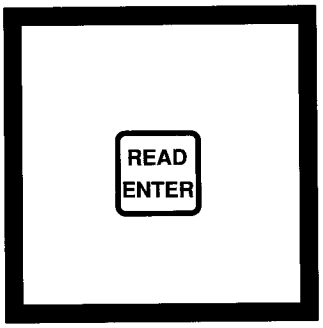
Note: *If samples cannot be analyzed immediately, see* Sampling and Storage *following these steps. Adjust pH of stored samples before analysis.*



2. Rotate the wavelength dial until the small display shows:
425 nm

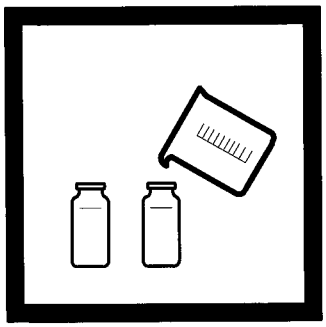
Note: *Total copper determination needs a prior digestion; use either the Digesdahl or vigorous digestion* (Section I).

Note: *This test is sensitive to the wavelength setting. The 425 nm wavelength should always be set by approaching from high to low values.*



3. Press: **READ/ENTER**

The display will show:
µg/l Cu Porph



4. Fill two sample cells with 25 mL of sample.

Note: *Wash all glassware with detergent. Rinse with tap water. Rinse again with Nitric Acid Solution, 1:1. Rinse a third time with copper-free, demineralized water.*

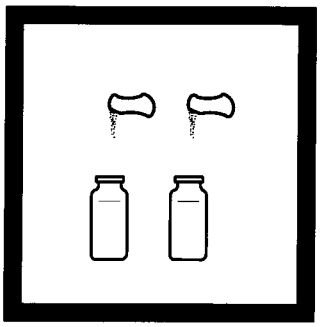
Note: *For proof of accuracy, use a 100 µg/L copper standard solution (preparation given in the* Accuracy Check*) in place of the sample.*

Note: *For most accurate results, run a blank using copper-free demineralized water. Subtract the value obtained in Step 12 from all following tests. Repeat for each new lot of reagents.*

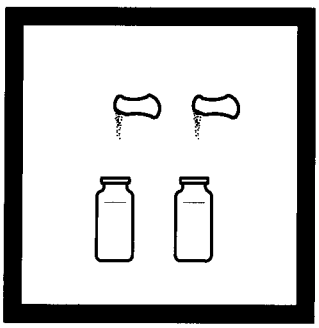
*Adapted from Ishii and Koh, Bunseki Kagaku, 28 473 (1979)

5. Add the contents of one Copper Masking Reagent Powder Pillow to one of the sample cells (the blank). Swirl to dissolve.

Note: *The other sample cell is the prepared sample.*

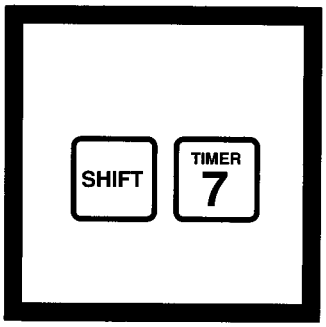


6. Add the contents of one Porphyrin 1 Reagent Powder Pillow to each sample cell. Swirl to dissolve.



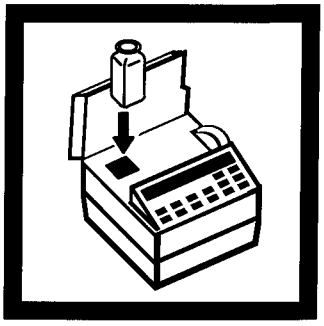
7. Add the contents of one Porphyrin 2 Reagent Powder Pillow to each sample cell. Swirl to dissolve.

Note: *The yellow color will turn blue momentarily. If any copper is present, the sample will return to yellow.*



8. Press: **SHIFT TIMER**

A 3–minute reaction period will begin.

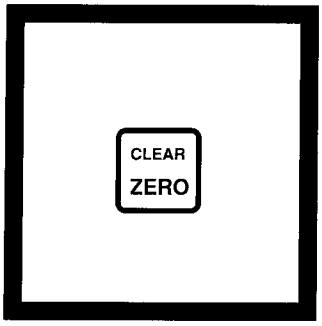


9. When the timer beeps, the display will show:

µg/l Cu Porph

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

Note: *The Pour–Thru Cell can be used if rinsed well with demineralized water between the blank and prepared sample.*



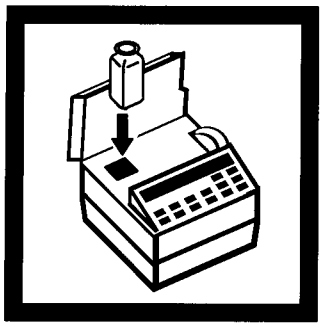
10. Press: **ZERO**

The display will show:

WAIT

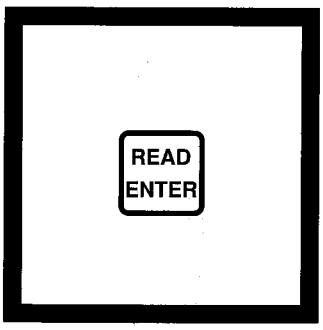
then:

0.0 µg/l Cu Porph



11. Place the prepared sample into the cell holder. Close the light shield.

Note: *If samples with high levels of metal are analyzed, a slight metallic deposit or yellow buildup may appear on the sample cell wall. Remove by rinsing with nitric acid.*



12. Press: **READ/ENTER**

The display will show:

WAIT

then the result in µg/L copper will be displayed.

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stablizes, read the result.*

SAMPLING AND STORAGE

Collect samples in acid–washed plastic bottles. To preserve, adjust the pH to 2 or less with nitric acid (about 5 mL per liter). Store preserved samples up to six months at room temperature.

Before testing, adjust the pH of the sample to between 2 and 6. If the sample is too acidic, adjust the pH with 5.0 N Sodium Hydroxide Standard Solution. Correct test results for volume additions *(see Correction for Volume Additions in Section I).*

ACCURACY CHECK

Standard Additions Method

a) Using a TenSette Pipet, add 0.1 mL of Copper Standard Solution, 10.0 mg/L Cu, to two sample cells containing 25 mL of sample.

b) Repeat, using 0.2 mL and 0.3 mL additions of standard.

c) Analyze the samples as described above. The copper concentration reading should increase by 40 µg/L for each 0.1 mL of standard added.

d) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

To assure the accuracy of the test, prepare a 100 µg/L copper standard:

a) Pipet 1.00 mL of copper standard solution, 10.0 mg/L Cu, into a 100–mL volumetric flask.

b) Dilute to volume with copper–free, reagent–grade water.

c) Use this standard in place of the sample in the procedure.

d) Prepare this solution daily.

PRECISION

In a single laboratory, using standard solutions of 100 µg/L copper and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ±0.31 µg/L copper.

INTERFERENCES

The following may interfere when present in concentrations exceeding those listed below:

Aluminum	60 mg/L
Cadmium	10 mg/L
Calcium	1,500 mg/L
Chloride	90,000 mg/L
Chromium (Cr^{6+})	110 mg/L
Cobalt	100 mg/L
Fluoride	30,000 mg/L
Iron	6 mg/L
Lead	3 mg/L
Magnesium	10,000 mg/L
Manganese	140 mg/L
Mercury	3 mg/L
Molybdenum	11 mg/L
Nickel	60 mg/L
Potassium	60,000 mg/L
Sodium	90,000 mg/L
Zinc	9 mg/L

Chelating agents, such as EDTA, interfere at all levels unless either the vigorous or Digesdahl digestion (*Section I*) is performed.

Highly buffered samples or extreme sample pH may exceed the buffering capacity of the reagents and require sample pretreatment *(see pH Interference in Section I).*

SUMMARY OF METHOD

The porphyrin method is very sensitive to trace amounts of free copper. The method is free from most interferences and does not require any sample extraction or preconcentration. Interferences from other metals are eliminated by the copper masking reagent. The porphyrin indicator forms an intense, yellow–colored complex with any free copper present in sample.

REQUIRED REAGENTS

	Cat. No.
Copper Reagent Set (100 Tests)	22427–00
Includes: (2) 21873–66, (4) 21874–99, (2) 21875–69	

Description	Quantity Required Per Test	Units	Cat. No.
Copper Masking Reagent Powder Pillows	1 pillow	50/pkg	21873–66
Porphyrin 1 Reagent Powder Pillows	2 pillows	50/pkg	21874–66
Porphyrin 2 Reagent Powder Pillows	2 pillows	100/pkg	21875–69

REQUIRED APPARATUS

Clipper, for opening powder pillows	1	each	968–00

OPTIONAL REAGENTS

Copper Standard Solution, 10 mg/L Cu	100 mL MDB	129–32
Hydrochloric Acid Solution, 1:1 (6 N)	500 mL	884–49
Nitric Acid, ACS	500 mL	152–49
Nitric Acid Solution, 1:1	500 mL	2540–49
Sodium Hydroxide Standard Solution, 5 N	1 L	2450–53
Water, demineralized	4 L	272–56

OPTIONAL APPARATUS

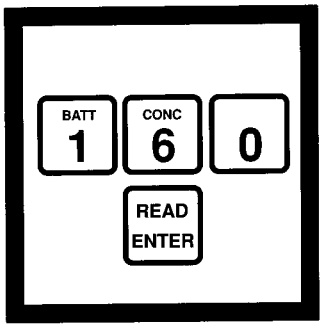
Beaker, 100 mL	each	500–42
Flask, volumetric, Class A, 50 mL	each	14574–41
Flask, volumetric, Class A, 100 mL	each	14574–42
Hot Plate, 7" x 7", 120 Vac	each	23441–00
Hot Plate, 7" x 7", 240 Vac	each	23441–02
pH Indicator Paper, 1 to 11 pH	5 rolls/pkg	391–33
Pipet, Mohr, 5 mL	each	20934–37
Pipet, TenSette, 0.1 to 1.0 mL	each	14515–35
Pipet Tips, for 19700-01 TenSettes Pipet	50/pkg	21856–96
Pipet, volumetric, Class A, 1 mL	each	14515–35
Pipet, volumetric, Class A, 50 mL	each	14515–41
Pipet Filler, safety bulb	each	14651–00
Pour–Thru Cell Assembly Kit	each	45215–00
Watch Glass	each	578–70

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

CYANIDE (0 to 0.200 mg/L)

For water, wastewater and seawater

Pyridine-Pyrazalone Method*



1. Enter the stored program number for cyanide (CN^-).

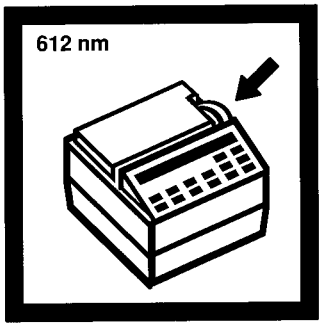
Press: **1 6 0 READ/ENTER**

The display will show:
DIAL nm TO 612

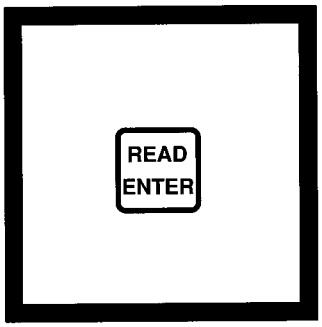
Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

Note: *If samples cannot be analyzed immediately, see* Sampling and Storage *following these steps. Adjust pH of stored samples before analysis.*



2. Rotate the wavelength dial until the small display shows:
612 nm

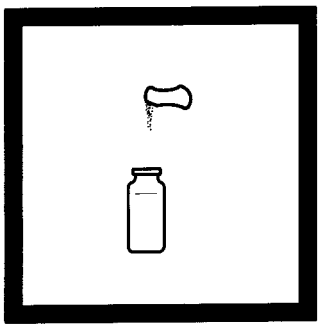


3. Press: **READ/ENTER**

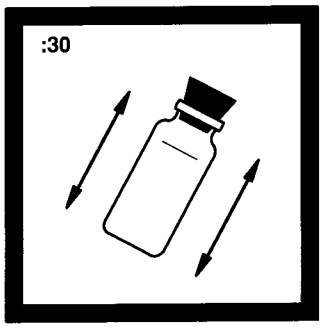
The display will show:
mg/l CN^-

4. Using a graduated cylinder, pour 25 mL of sample into a sample cell.

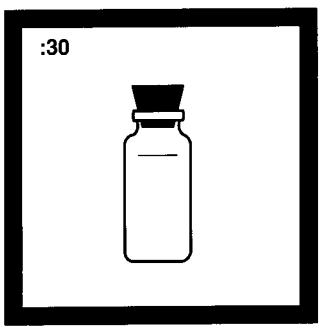
Note: *For proof of accuracy, use a 0.10 mg/L cyanide standard solution (preparation given in the* Accuracy Check*) in place of the sample.*



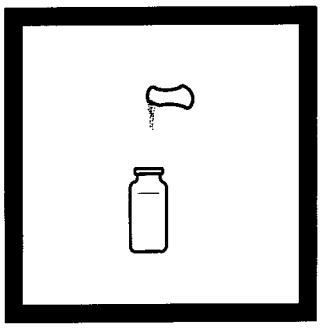
5. Add the contents of one CyaniVer 3 Cyanide Reagent Powder Pillow. Stopper the sample cell.



6. Shake the sample cell for 30 seconds.

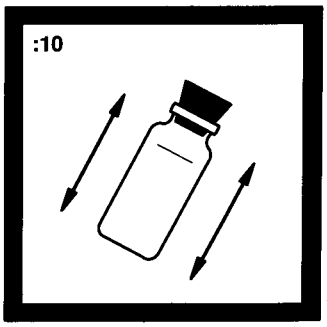


7. Wait an additional 30 seconds while the sample cell is undisturbed.



8. Add the contents of one CyaniVer 4 Cyanide Reagent Powder Pillow. Stopper the sample cell.

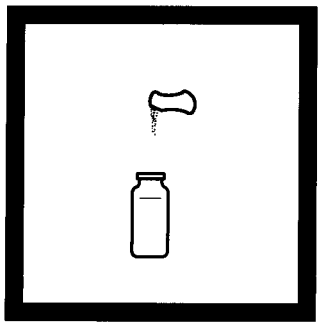
*Adapted from Epstein, Joseph, *Anal. Chem.* 19 (4), 272 (1947)



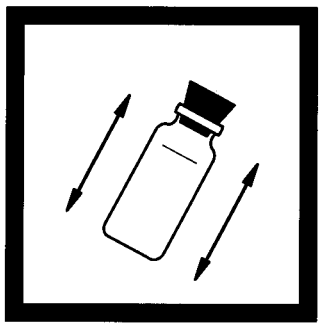
9. Shake the sample cell for ten seconds. Immediately proceed with Step 10.

Note: *Delaying the addition of the CyaniVer 5 Cyanide Reagent Powder for more than 30 seconds after the addition of the CyaniVer 4 Cyanide Reagent Powder will give lower test results.*

Note: *Accuracy is not affected by undissolved CyaniVer 4 Cyanide Reagent Powder.*

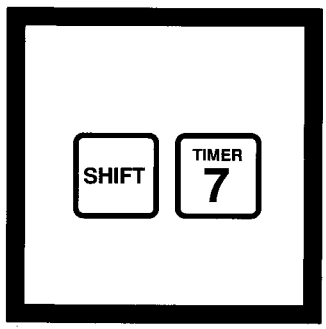


10. Add the contents of one CyaniVer 5 Cyanide Reagent Powder Pillow. Stopper the cell.



11. Shake vigorously to completely dissolve the CyaniVer 5 Cyanide Reagent Powder (the prepared sample).

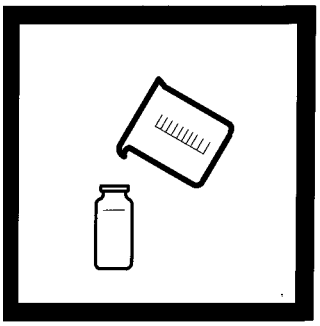
Note: *If cyanide is present, a pink color will develop which then turns blue after a few minutes.*



12. Press: **SHIFT TIMER**

A 30–minute reaction period will begin.

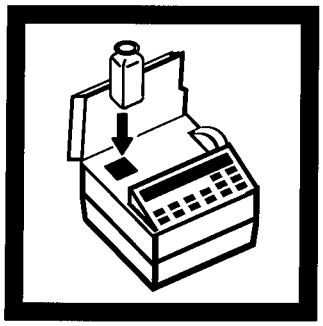
Note: *Samples at less than 25 °C require longer reaction time and samples at greater than 25 °C give low test results.*



13. When the timer beeps, the display will show:

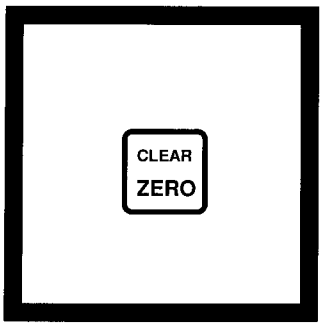
mg/l CN^-

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



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

Note: *The Pour–Thru Cell can be used with this procedure.*



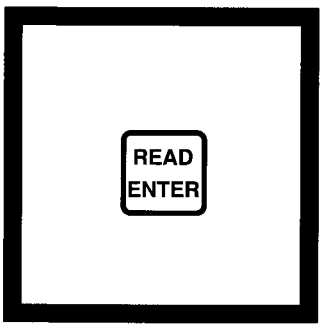
15. Press: **ZERO**

The display will show:

WAIT

then:

0.000 mg/l CN^-



16. Remove the stopper. Place the prepared sample into the cell holder. Close the light shield.

Press: **READ/ENTER**

The display will show:

WAIT

then the result in mg/L cyanide will be displayed.

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

SAMPLING AND STORAGE

Samples collected in glass or plastic bottles should by analyzed as quickly as possible.

The presence of oxidizing agents, sulfides and fatty acids can cause the loss of cyanide during sample storage. Samples containing these substances must be pretreated as described in the following procedures before preservation with sodium hydroxide. If the sample contains sulfide and is not pretreated, it must be analyzed within 24 hours.

Preserve the sample by adding 4.0 mL of 5.0 N Sodium Hydroxide Standard Solution to each liter (or quart) of sample, using a glass serological pipet and pipet filler. Check the sample pH. Four mL of sodium hydroxide is usually enough to raise the pH of most water and wastewater samples to 12. Add more 5.0 N sodium hydroxide if necessary. Store the samples at 4 °C (39 °F) or less. Samples preserved in this manner can be stored for 14 days.

Before testing, samples preserved with 5.0 N sodium hydroxide or samples that are highly alkaline due to chlorination treatment processes or sample distillation procedures should be adjusted to approximately pH 7 with 2.5 N Hydrochloric Acid Standard Solution. Where significant amounts of preservative are used, a volume correction should be made *(see Correction for Volume Additions in Section I).*

Oxidizing Agents

Oxidizing agents such as chlorine decompose cyanide during storage. To test for their presence and to eliminate their effect, pretreat the sample as follows:

a) Take a 25–mL portion of the sample and add one drop of m–Nitrophenol Indicator Solution, 10 g/L. Swirl to mix.

b) Add 2.5 N Hydrochloric Acid Standard Solution drop–wise until the color changes from yellow to colorless. Swirl the sample thoroughly after the addition of each drop.

c) Add two drops of 30 g/L Potassium Iodide Solution and two drops of Starch Indicator Solution to the sample. Swirl to mix. The solution will turn blue if oxidizing agents are present.

d) If Step c suggests the presence of oxidizing agents, add two level 1–g measuring spoonfuls of ascorbic acid per liter of sample.

e) Withdraw a 25–mL portion of sample treated with ascorbic acid and repeat Steps a to c. If the sample turns blue, repeat Steps d and e.

f) If the 25–mL sample remains colorless, preserve the remaining sample to pH 12 for storage with 5 N Sodium Hydroxide Standard Solution (usually 4 mL/L).

g) Perform the procedure given under *Interferences, Reducing Agents*, to eliminate the effect of excess ascorbic acid, before following the cyanide procedure.

Sulfides

Sulfides will quickly convert cyanide to thiocyanate (SCN). To test for the presence of sulfide and eliminate its effect, pretreat the sample as follows:

a) Place a drop of sample on a disc of hydrogen sulfide test paper that has been wetted with pH 4 Buffer Solution.

b) If the test paper darkens, add a 1–g measuring spoon of lead acetate to the sample. Repeat Step a.

c) If the test paper continues to turn dark, keep adding lead acetate until the sample tests negative for sulfide.

d) Filter the lead sulfide precipitate through filter paper and a funnel. Preserve the sample for storage with 5 N Sodium Hydroxide Standard Solution or neutralize to a pH of 7 for analysis.

Fatty Acids

Caution— *perform this operation in a hood as quickly as possible.*

When distilled, fatty acids will pass over with cyanide and form soaps under the alkaline conditions of the absorber. If the presence of fatty acid is suspected, do not preserve samples with sodium hydroxide until the following pretreatment is performed. The effect of fatty acids can be minimized as follows:

a) Acidify 500 mL of sample to pH 6 or 7 with Acetic Acid Solution.

b) Pour the sample into a 1000–mL separatory funnel and add 50 mL of hexane.

c) Stopper the funnel and shake for one minute. Allow the layers to separate.

d) Drain off the sample (lower) layer into a 600–mL beaker. If the sample is to be stored, add 5 N Sodium Hydroxide Standard Solution to raise the pH to above 12.

ACCURACY CHECK

Standard Solution Method

Caution— *Cyanides and their solutions, and the hydrogen cyanide liberated by acids, are very poisonous. Both the solutions and the gas can be absorbed through the skin.*

To assure the accuracy of the test, prepare the following standard solutions:

Prepare a 100 mg/L cyanide stock solution weekly by dissolving 0.1884 grams of sodium cyanide in demineralized water and diluting to 1000 mL.

Immediately before use prepare a 0.10 mg/L cyanide working solution by diluting 1.00 mL of the 100 mg/L stock solution of 1000 mL using demineralized water.

PRECISION

In a single laboratory, using a standard solution of 0.095 mg/L CN^- and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ±0.0043 mg/L CN^-.

INTERFERENCES

Turbidity

Large amounts of turbidity will interfere and cause high readings. If the water sample is highly turbid, it should first be filtered before use in Steps 4 and 13. Filter using the labware listed under *Optional Apparatus*. The test results should then be recorded as soluble cyanide.

Oxidizing and Reducing Agents

Large amounts of chlorine in the sample will cause a milky white precipitate after the addition of the CyaniVer 5 Reagent. If chlorine or other oxidizing agents are known to be present, or if reducing agents (such as sulfide or sulfur dioxide) are known to be present, pretreat the sample before testing as follows using adequate ventilation:

Oxidizing Agents

a) Adjust a 25–mL portion of the alkaline sample to between pH 7 and 9 with 2.5 N Hydrochloric Acid Standard Solution. Count the number of drops of acid added.

b) Add two drops of Potassium Iodide Solution and two drops of Starch Indicator Solution to the sample. Swirl to mix. The sample will turn blue if oxidizing agents are present.

c) Add Sodium Arsenite Solution drop–wise until the sample turns colorless. Swirl the sample thoroughly after each drop. Count the number of drops.

d) Take another 25–mL sample and add the total number of drops of Hydrochloric Acid Standard Solution counted in Step a.

e) Subtract one drop from the amount of Sodium Arsenite Solution added in Step c. Add this amount to the sample and mix thoroughly.

f) Continue with Step 5 of the cyanide procedure.

Reducing Agents

a) Adjust a 25–mL portion of the alkaline sample to between pH 7 and 9 with 2.5 N Hydrochloric Acid Standard Solution. Count the number of drops added.

b) Add four drops of Potassium Iodide Solution and four drops of Starch Indicator Solution to the sample. Swirl to mix. The sample should be colorless.

c) Add Bromine Water drop–wise until a blue color appears. Swirl the sample thoroughly after each addition. Count the number of drops.

d) Take another 25 mL sample and add the total number of drops of Hydrochloric Acid Standard Solution counted in Step a.

e) Add the total number of drops of Bromine Water counted in Step c to the sample and mix thoroughly.

f) Continue with Step 5 of the cyanide procedure.

Metals

Nickel or cobalt in concentrations up to 1 mg/L do not interfere. Eliminate the interference from up to 20 mg/L copper and 5 mg/L iron by adding the contents of one HexaVer Chelating Reagent Powder Pillow to the sample and then mixing before adding the CyaniVer 3 Cyanide Reagent powder Pillow in Step 5. Prepare a reagent blank of demineralized water and reagents to zero the instrument in Step 15.

Acid Distillation

For USEPA reporting purposes, samples must be distilled. All samples to be analyzed for cyanide should be treated by acid distillation except when experience has shown that there is no difference in results obtained with or without distillation. With most compounds, a one–hour reflux is adequate.

If thiocyanate is present in the original sample, a distillation step is absolutely necessary as thiocyanate causes a positive interference. High concentrations of thiocyanate can yield a substantial quantity of sulfide in the distillate. The "rotten egg" smell of hydrogen

sulfide will accompany the distillate when sulfide is present. The sulfide must be removed from the distillate prior to testing.

If cyanide is not present, the amount of thiocyanate can be determined. The sample is not distilled and the final reading is multiplied by 2.2. The result is mg/L thiocyanate.

The distillate can be tested and treated for sulfide after the last step of the distillation procedure by using the following lead acetate treatment procedure.

a) Place a drop of the distillate (already diluted to 250 mL) on a disc of hydrogen sulfide test paper that has been wetted with pH 4.0 Buffer Solution.

b) If the test paper darkens, add 2.5 N Hydrochloric Acid Standard Solution drop–wise to the distillate until a neutral pH is obtained.

c) Add a 1–g measuring spoon of lead acetate to the distillate and mix. Repeat Step a.

d) If the test paper continues to turn dark, keep adding lead acetate until the distillate tests negative for sulfide.

e) Filter the black lead sulfide precipitate through filter paper and funnel. This sample should now be neutralized to pH 7 and analyzed for cyanide without delay.

Distillation Procedure
The following steps describe the distillation process using apparatus offered by Hach:

a) Set up the distillation apparatus for cyanide recovery, leaving off the thistle tube. Refer to the *Hach Distillation Apparatus Manual.* Turn on the water and make certain it is flowing steadily through the condenser.

b) Fill the distillation apparatus cylinder to the 50–mL mark with 0.25 N Sodium Hydroxide Standard Solution.

c) Fill a clean 250–mL graduated cylinder to the 250–mL mark with sample and pour it into the distillation flask. Place a stirring bar into the flask and attach the thistle tube.

d) Arrange the vacuum system as shown in the *Hach Distillation Apparatus Manual*, but do not connect the vacuum tubing to the gas bubbler. Turn on the water to the aspirator to full flow and adjust the flow meter to 0.5 SCFH.

e) Connect the vacuum tubing to the gas bubbler, making certain that air flow is maintained (check the flow meter) and that air is bubbling from the thistle tube and the gas bubbler.

f) Turn the power switch on and set the stir control to 5. Using a 50–mL graduated cylinder, pour 50 mL of 19.2 N Sulfuric Acid Standard Solution through the thistle tube and into the distillation flask.

g) Using a water bottle, rinse the thistle tube with a small amount of demineralized water.

h) Allow the solution to mix for three minutes; then add 20 mL of Magnesium Chloride Reagent through the thistle tube and rinse again. Allow the solution to mix for three more minutes.

i) Verify that there is a constant flow of water through the condenser.

j) Turn the heat control to 10.

k) It is very important to monitor the distillation flask at this point in the procedure. Once the sample begins to boil, slowly lower the air flow to 0.3 SCFH. If the contents of the distillation flask begin to back up through the thistle tube, increase the air flow by adjusting the flow meter until the contents do not back up through the thistle tube. Allow the sample to boil for one hour.

l) When one hour is up, turn the still off but maintain the air flow for 15 minutes.

m) After 15 minutes, remove the rubber stopper on the 500–mL vacuum flask to break the vacuum and turn off the water to the aspirator. Turn off the water to the condenser.

n) Remove the gas bubbler/cylinder assembly from the distillation apparatus. Separate the gas bubbler from the cylinder and pour the contents of the cylinder into a 250–mL, Class A volumetric flask. Rinse the gas bubbler, cylinder and J–tube connector with demineralized water and add the washings to the volumetric flask.

o) Fill the flask to the mark with demineralized water and mix thoroughly. Neutralize the contents of the flask and analyze for cyanide.

SUMMARY OF METHOD

The pyridine–pyrazolone method used for measuring cyanide gives an intense blue color with free cyanide. A sample distillation is required to determine cyanide from transition and heavy metal cyanide complexes.

REQUIRED REAGENTS

	Cat. No.
Cyanide Reagent Set (100 Tests)	22428–00
Includes: (1) 14039–69, (1) 14040–99, (1) 14041–69	

Description	Quantity Required Per Test	Units	Cat. No.
CyaniVer 3 Cyanide Reagent Powder Pillows	1 pillow	100/pkg	14039–69
CyaniVer 4 Cyanide Reagent Powder Pillows	1 pillow	100/pkg	14040–99
CyaniVer 5 Cyanide Reagent Powder Pillows	1 pillow	100/pkg	14041–69

REQUIRED APPARATUS

Clippers, for opening powder pillows	1	each	968–00
Cylinder, graduated, 25 mL	1	each	508–40
Stoppers, rubber	1	12/pkg	2118–01

OPTIONAL REAGENTS

Acetic Acid Solution, 10%	500 mL	14816–49
Ascorbic Acid	100 g	6138–26
Bromine Water	29 mL	2211–20
Buffer Solution, pH 4.0	500 mL	12223–49
Hexanes, ACS	3.78 L	14478–17
HexaVer Chelating Reagent Powder Pillows	100/pkg	243–99
Hydrochloric Acid Standard Solution, 2.5 N	100 mL MDB	1418–32
Lead Acetate, trihydrate, ACS	500 g	7071–34
Magnesium Chloride Solution	1000 mL	14762–53
m–Nitrophenol Indicator	100 mL MDB	2476–32
Potassium Iodide Solution, 30 g/L	100 mL DB	343–32
Sodium Arsenite Solution, APHA	100 mL MDB	1047–32
Sodium Cyanide, ACS	28 g	184–20
Sodium Hydroxide Standard Solution, 0.25 N	1000 mL	14763–53
Sodium Hydroxide Standard Solution, 5.0 N	1 L	2450–53
Starch Indicator Solution	100 mL MDB	349–32
Sulfuric Acid Standard Solution, 19.2 N	1000 mL	2038–53
Water, demineralized	4 L	272–56

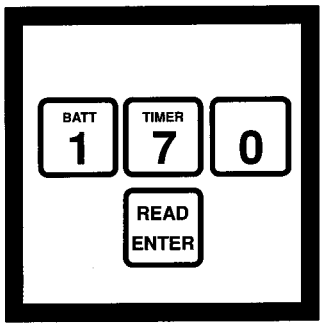
OPTIONAL APPARATUS

Beaker, glass, 600 mL	each	500–52
Bottle, wash, 500 mL	each	620–11
Cylinder, graduated, 50 mL	each	508–41
Cylinder, graduated, 250 mL	each	508–46
Distillation Apparatus, cyanide accessories	each	22658–00
Distillation Apparatus, general purpose accessories	each	22653–00
Distillation Apparatus Heater and Support Apparatus, 115 Vac, 60 Hz	each	22744–00
Distillation Apparatus Heater and Support Apparatus, 230 Vac, 50 Hz	each	22744–02
Dropper, plastic	each	6080–00
Filter Paper, folded, 12.5 cm	100/pkg	1894–57
Flask, volumetric, 1000 mL	each	547–53
Flask, volumetric, Class A, 250 mL	each	14574–46
Funnel, poly, 65 mm	each	1083–67
Funnel, separatory, 500 mL	each	520–49
Hydrogen Sulfide Test Papers	100/pkg	393–33
pH Meter, EC10, portable	each	50050–00
Pipet, volumetric, Class A, 1 mL	each	14515–35
Pipet, volumetric, Class A, 2 mL	each	14515–36
Pipet, volumetric, Class A, 5 mL	each	14515–37
Pipet Filler, safety bulb	each	14651–00
Pour–Thru Cell Assembly Kit	each	45215–00
Scoop, double ended	each	12257–00
Spoon, measuring, 1.0 g	each	510–00
Support Ring, 4"	each	580–01
Support Stand	each	563–00

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

CYANURIC ACID (0 to 50 mg/L)

Turbidimetric Method



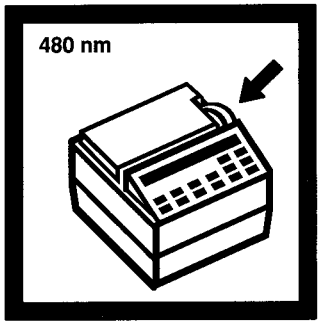
1. Enter the stored program number for cyanuric acid.

Press: **1 7 0 READ/ENTER**

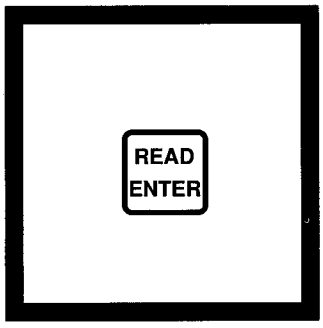
The display will show:
DIAL nm TO 480

Note: DR/2000s with software versions 3.0 and greater will display "P" and the program number.

Note: Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.

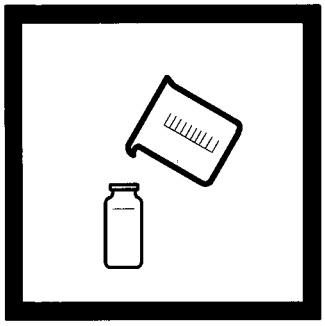


2. Rotate the wavelength dial until the small display shows:
480 nm



3. Press: **READ/ENTER**

The display will show:
mg/l CYANURIC.A



4. Fill the sample cell with 25 mL of sample.

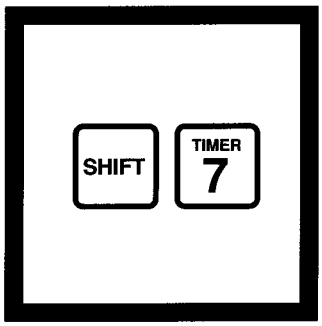
Note: Filtering is required for highly turbid samples.

Note: The Pour–Thru Cell cannot be used with this procedure.

Note: For proof of accuracy, use a 20 mg/L cyanuric acid standard solution (preparation given in the Accuracy Check*) in place of the sample.*

5. Add the contents of one Cyanuric Acid 2 Reagent Powder Pillow (the prepared sample). Swirl to mix.

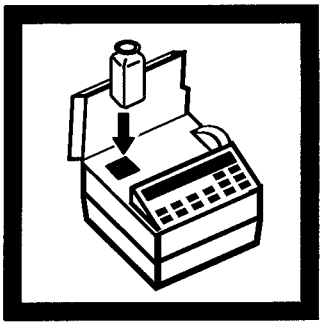
Note: A white turbidity will form if cyanuric acid is present.



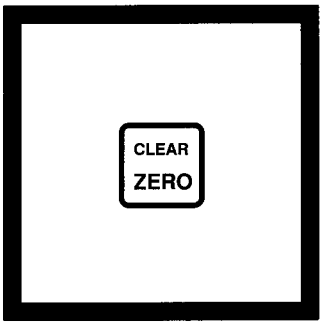
6. Press: **SHIFT TIMER**

A 3–minute reaction period will begin.

Note: While the timer is running, continue with Step 7.



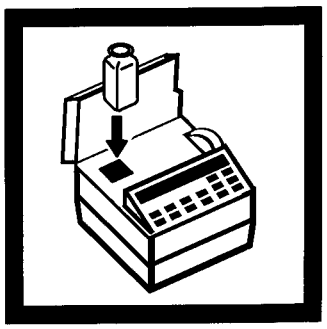
7. Fill a second sample cell with 25 mL of sample (the blank) and place it into the cell holder.



8. When the timer beeps, the display will show:
mg/l CYANURIC.A

Press: **ZERO**

The display will show:
WAIT
then:
0. mg/l CYANURIC.A

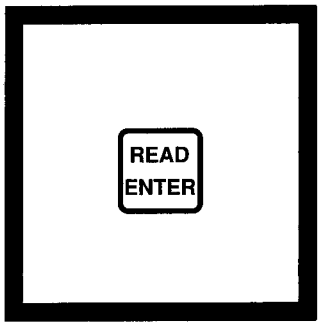


9. Within 7 minutes after the timer beeps, place the prepared sample into the cell holder.

Note: Readings should be taken within 5 minutes of the previous blank. If not, the instrument will display:

ZERO SAMPLE

The user may re-zero or read the sample.



10. Press: **READ/ENTER**

The display will show:

WAIT

and then the results in mg/L cyanuric acid will be displayed.

Note: In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display value stabilizes, read the result.

Note: Clean sample cells with soap, water and a brush soon after each test to avoid a white film forming.

SAMPLING AND STORAGE

Collect samples in clean plastic or glass bottles. Samples must be analyzed within 24 hours.

ACCURACY CHECK

Standard Solution Method

a) Dissolve 1.000 gram of cyanuric acid in 1 liter of demineralized water to make a 1000 mg/L solution. This solution is stable for several weeks.

b) Dilute 2.00 mL of the 1000 mg/L solution to 100 mL with demineralized water to make a 20 mg/L solution. Prepare fresh daily.

c) Testing the 20 mg/L solution should give test results of about 20 mg/L cyanuric acid.

PRECISION

In a single laboratory, using a standard solution of 25 mg/L cyanuric acid and two lots of reagent with the DR/2000, a single operator obtained a standard deviation of ±1 mg/L cyanuric acid.

SUMMARY OF METHOD

The test for cyanuric acid uses the turbidimetric method. Cyanuric Acid 2 Reagent precipitates any cyanuric acid present and holds it in suspension. The amount of turbidity caused by the suspended particles is directly proportional to the amount of cyanuric acid present.

REQUIRED REAGENTS AND APPARATUS

Description	Quantity Required Per Test	Units	Cat. No.
Cyanuric Acid 2 Reagent Powder Pillow	1 pillow	50/pkg	2460–66
Clippers, for opening powder pillows	1	each	968–00

OPTIONAL REAGENTS

Cyanuric Acid		25 g	7129–24
Water, demineralized		4 L	272–56

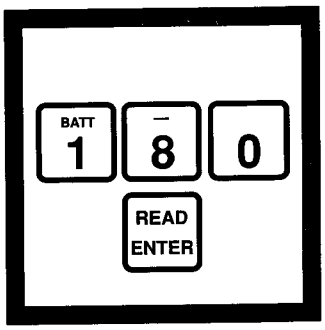
OPTIONAL APPARATUS

Filter Paper, folded 12.5 cm		100/pkg	1894–57
Flask, volumetric, 100 mL		each	547–42
Flask, volumetric, 1000 mL		each	547–53
Funnel, poly, 65 mm		each	1083–67
Pipet, volumetric, Class A, 2.00 mL		each	14515–36

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

DEHA (N,N-Diethylhydroxylamine) (0 to 450 µg/L)

Iron Reduction Method for Oxygen Scavengers



1. Enter the stored program number for diethylhydroxylamine (DEHA).

Press: **1 8 0 READ/ENTER**

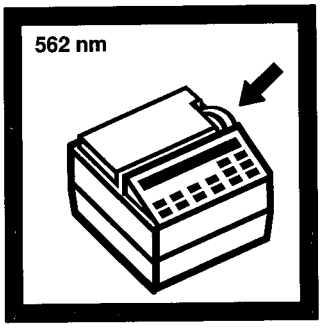
The display will show:
DIAL nm TO 562

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

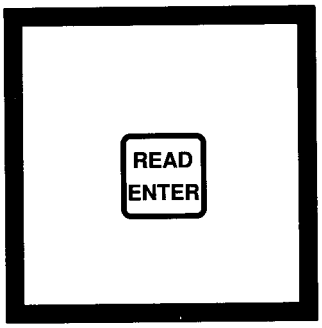
Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

Note: *Samples must be analyzed immediately and cannot be stored for later analysis.*

Note: *Other oxygen scavengers may be determined by this method if the result is multiplied by the appropriate factor. See* Other Oxygen Scavengers *following these steps.*

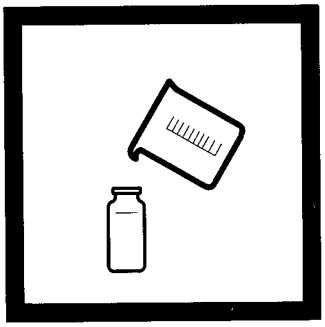


2. Rotate the wavelength dial until the small display shows:
562 nm



3. Press: **READ/ENTER**

The display will show:
µg/l DEHA



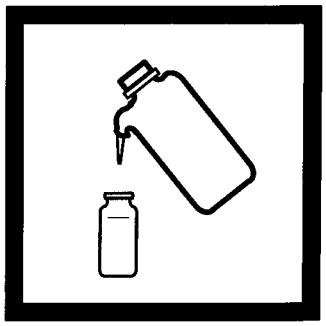
4. Fill a sample cell (the prepared sample) with 25 mL of sample.

Note: *Rinse glassware with 1:1 Hydrochloric Acid Solution. Rinse again with demineralized water. These two steps will remove iron deposits which can cause slightly high results.*

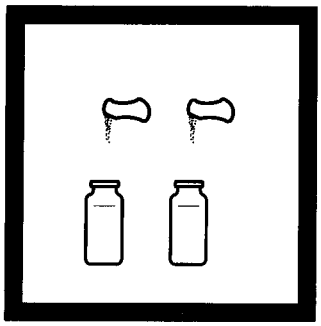
Note: *The sample temperature should be 25 ±3 °C (77 ±5 °F).*

Note: *The Pour–Thru Cell can be used with this procedure.*

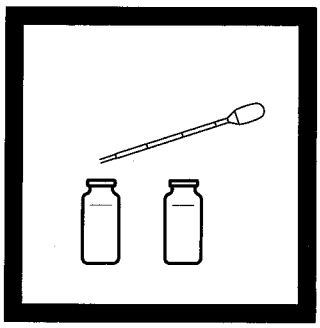
*Adapted from Ishii and Koh, *Bunseki Kagaku*, 28 473 (1979)



5. Fill a second sample cell (the blank) with 25 mL of demineralized water.

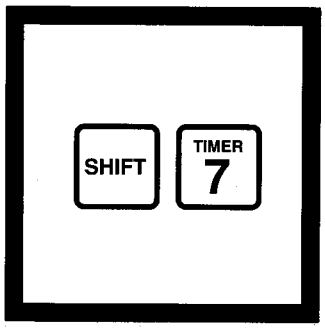


6. Add the contents of one DEHA Reagent 1 Powder Pillow to each sample cell. Swirl to mix.



7. Add exactly 0.5 mL of DEHA Reagent 2 Solution to each sample cell. Mix. Place both sample cells in the dark.

Note: A purple color will slowly develop if DEHA is present.

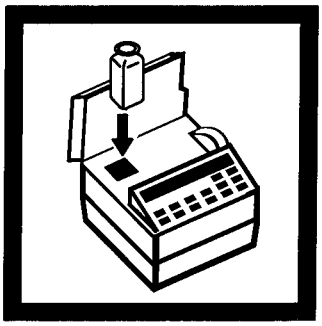


8. Immediately, press: **SHIFT TIMER**

A 10–minute reaction period will begin.

Note: *Both sample cells must remain in the dark during the 10–minute period.*

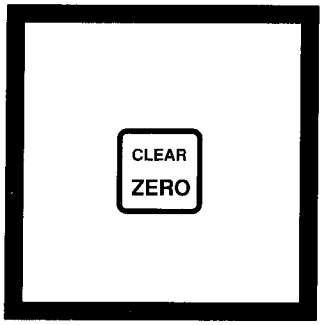
Note: *Temperature and reaction time affect the results. Be sure these factors are controlled as described.*



9. When the timer beeps, the display will show:

µg/l DEHA

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



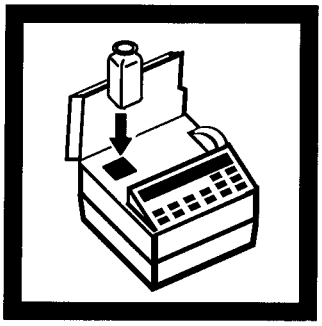
10. Press: **ZERO**

The display will show:

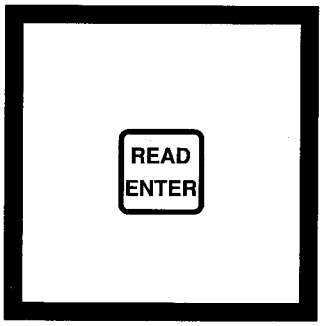
WAIT

then:

0. µg/l DEHA



11. Immediately place the prepared sample into the cell holder. Close the light shield.



12. Press: **READ/ENTER**

The display will show:

WAIT

then the result in µg/L DEHA will be displayed.

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

Note: *Repeat the above procedure, omitting Step 7, to determine the ferrous iron concentration in the sample. Subtract this result from those obtained in Step 12 to determine the actual DEHA concentration.*

Note: *To determine other oxygen scavenger compounds, see* Other Oxygen Scavengers *below.*

OTHER OXYGEN SCAVENGERS

To determine other oxygen scavengers, perform the test as directed above; then multiply the DEHA result by the appropriate factor:

	Factor
Erythorbic Acid (Iso–ascorbic acid)	3.5
Hydroquinone	2.5
Methylethylketoxime	4.1
Carbohydrazide	1.3

When determining those compounds which react quickly with oxygen at room temperature, it may be necessary to stopper the cell containing the prepared sample in Steps 4 to 9 to exclude air.

PRECISION

In a single laboratory, using standard solutions of 150 µg/L DEHA and two representative lots of reagent with the DR/2000, a single operator obtained a standard deviation of ±2.3 µg/L DEHA.

INTERFERENCES

Substances which reduce ferric iron (such as other oxygen scavengers) will interfere. Substances which complex iron strongly may also interfere. The following may interfere when present in concentrations exceeding those listed below:

Borate (as $Na_2B_4O_7$)	500 mg/L
Cobalt	0.025 mg/L
Copper	8.0 mg/L
Hardness (as $CaCO_3$)	1000 mg/L
Lignosulfonates	0.05 mg/L
Manganese	0.8 mg/L
Molybdenum	80 mg/L
Nickel	0.8 mg/L
Phosphate	10 mg/L
Phosphonates	10 mg/L
Sulfate	1000 mg/L
Zinc	50 mg/L

Light interferes with the color development.

SUMMARY OF METHOD

Diethylhydroxylamine (DEHA) or other oxygen scavengers present in the sample react with ferric iron in DEHA Reagent 2 Solution to produce ferrous ion in an amount equivalent to the DEHA concentration. This solution then reacts with DEHA 1 Reagent, which forms a purple color with ferrous iron. Using this procedure other oxygen scavengers can be determined by multiplying the DEHA results by the appropriate multiplier.

REQUIRED REAGENTS

Description	Quantity Required Per Test	Units	Cat. No.
DEHA Reagent 1 Powder Pillows	2 pillows	100/pkg	21679–69
DEHA Reagent 2 Solution	1 mL	500 mL	21680–49
Water, demineralized	5 mL	4 L	272–56

REQUIRED APPARATUS

Clippers, for opening powder pillow	1	each	968–00
Dropper, 0.5 and 1.0–mL marks	1	10/pkg	21247–10

OPTIONAL REAGENTS

Hydrochloric Acid, 1:1 (6 N)		500 mL	884–49

OPTIONAL APPARATUS

Cylinder, graduated, polypropylene, 25 mL		each	1081–40
Pour–Thru Cell Assembly Kit		each	45215–00
Stopper, hollow, poly, No. 0		6/pkg	14480–00
Thermometer, –20 to 105 °C		each	1877–01

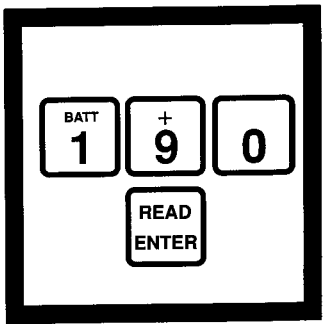
For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

FLUORIDE (0 to 2.00 mg/L F^-)

For water, wastewater and seawater

SPADNS Method* (Reagent Solution or AccuVac Ampuls); USEPA accepted for reporting wastewater and drinking water analysis (distillation required; *See Section I*)**

USING SPADNS REAGENT SOLUTION



1. Enter the stored program number for fluoride (F^-).

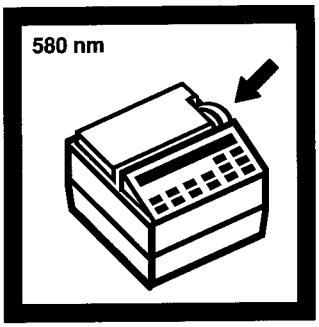
Press: **1 9 0 READ/ENTER**

The display will show:
DIAL nm TO 580

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

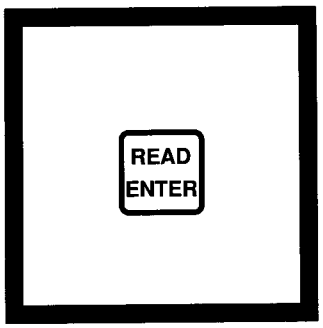
Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

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



2. Rotate the wavelength dial until the small display shows:
580 nm

Note: *Approach the wavelength setting from higher to lower values.*



3. Press: **READ/ENTER**

The display will show:
mg/l F^-

4. Measure 25.0 mL of sample into a dry sample cell (the prepared sample).

Note: *Use a graduated cylinder or pipet.*

Note: *For proof of accuracy, use a 1.0 mg/L fluoride standard solution (listed under* Optional Reagents*) in place of the sample.*

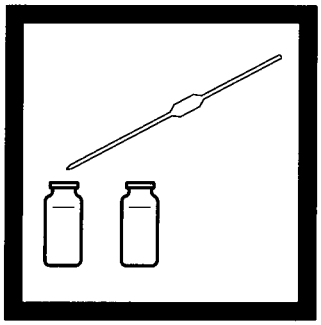
*Adapted from *Standard Methods for the Examination of Water and Wastewater.*

**Procedure is equivalent to USEPA method 340.1 for drinking water and wastewater.

5. Measure 25.0 mL of demineralized water into a second dry sample cell (the blank).

Note: *Use a graduated cylinder or pipet.*

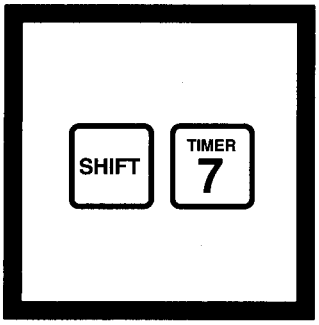
Note: *The sample and demineralized water should be at the same temperature (±1 °C). Temperature adjustments may be made before or after reagent addition.*



6. Pipet 5.00 mL of SPADNS Reagent into each cell. Swirl to mix. Use a pipet filler.

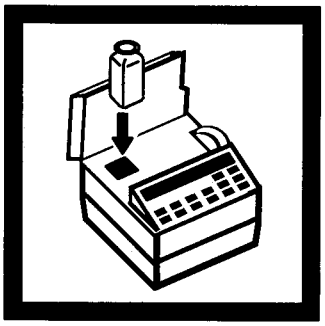
Note: *SPADNS Reagent is toxic and corrosive; use care while measuring.*

Note: *The SPADNS Reagent must be measured accurately.*



7. Press: **SHIFT TIMER**

A 1-minute reaction period will begin.

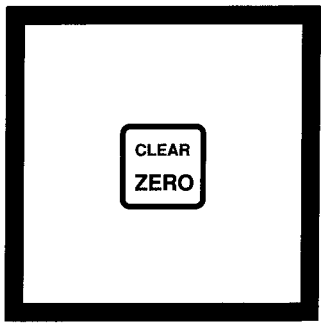


8. When the timer beeps, the display will show:

mg/l F^-

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

Note: *The Pour-Thru Cell cannot be used with this procedure.*



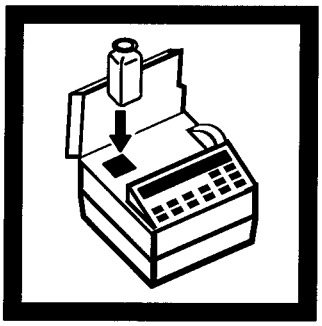
9. Press: **ZERO**

The display will show:

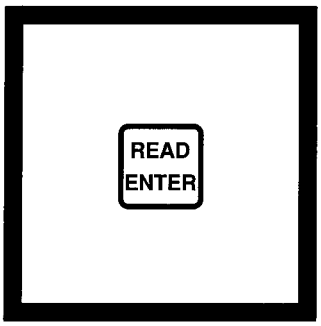
WAIT

then:

0.00 mg/l F^-



10. Place the prepared sample into the cell holder. Close the light shield.



11. Press: **READ/ENTER**

The display will show:

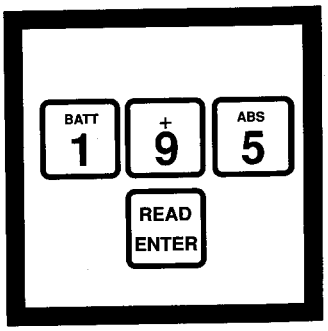
WAIT

then the result in mg/L F^-.

Note: *If the instrument shows OVER-RANGE, dilute the sample with an equal volume of demineralized water and repeat the test, using this solution in Step 4. Multiply the result by 2.*

Note: *In the constant-on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

USING ACCUVAC AMPULS



1. Enter the stored program number for fluoride (F^-) AccuVac ampuls.

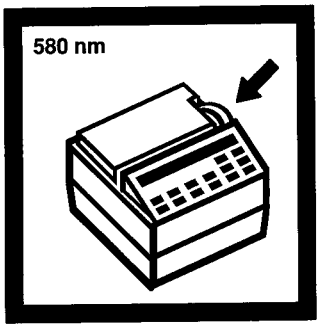
Press **1 9 5 READ/ENTER**

The display will show:
Dial nm TO 580

Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

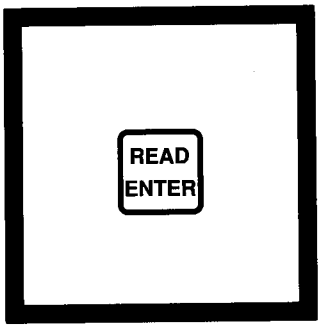
Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed with Step 4.*

Note: *If samples cannot be analyzed immediately, see* Sampling and Storage *below.*



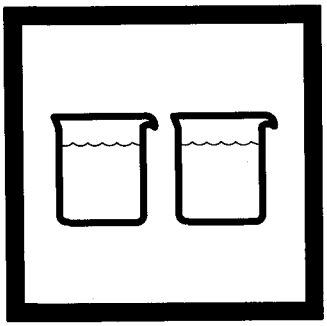
2. Rotate the wavelength dial until the small display shows:
580 nm

Note: *Approach the wavelength setting from higher to lower values.*

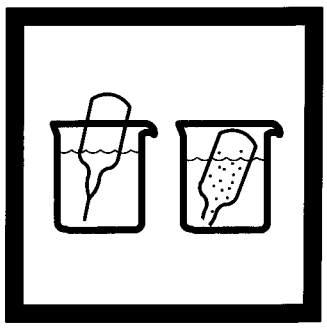


3. Press: **READ/ENTER**

The display will show:
mg/l F^- amp



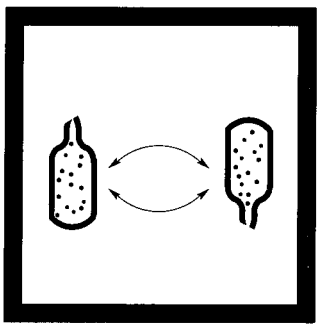
4. Collect at least 40 mL of sample in a 50–mL beaker. Pour at least 40 mL of demineralized water into a second beaker.



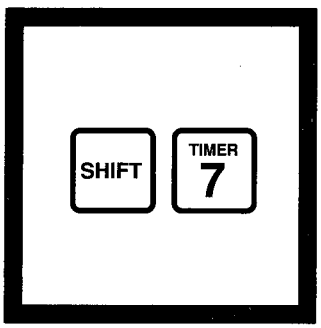
5. Fill a SPADNS Fluoride Reagent AccuVac Ampuls with sample by breaking the tip on the bottom of the beaker. Fill a second AccuVac ampul with demineralized water (the blank) in the same manner.

Note: *Keep the tip immersed while the ampul fills completely.*

Note: *For proof of accuracy, use a 1.0 mg/L fluoride standard solution (listed under* Optional Reagents*) in place of the sample.*

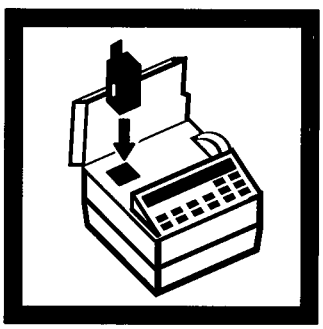


6. Quickly invert the ampuls several times to mix. Wipe off any liquid or fingerprints.



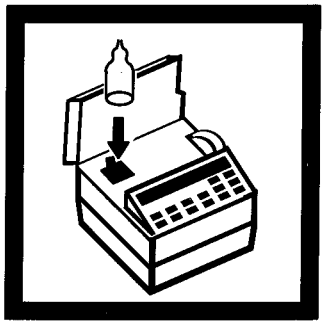
7. Press: **SHIFT TIMER**

A 1–minute reaction period will begin.

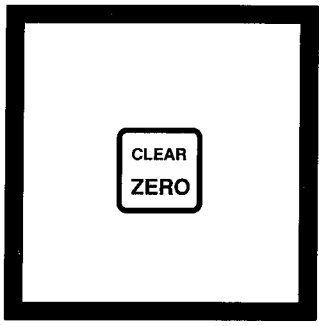


8. Place the AccuVac Vial Adapter into the cell holder of the instrument.

Note: *Place the grip tab at the rear of the cell holder.*

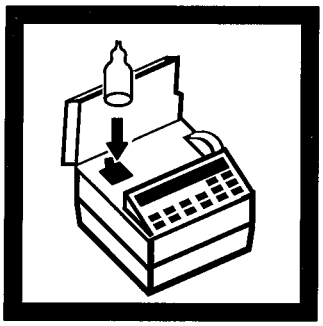


9. When the timer beeps, the display will show:
mg/l F^- amp
Place the blank into the cell holder. Close the light shield.

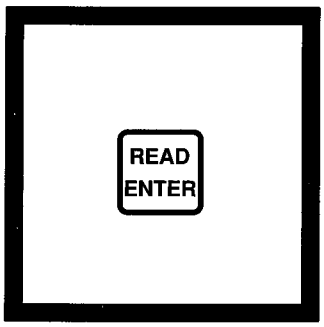


10. Press: **ZERO**

The display will show:
WAIT
then:
0.00 mg/l F^- amp



11. Place the AccuVac ampul containing the sample into the instrument. Close the light shield.



12. Press: **READ/ENTER**

The display will show:
WAIT
then the result in mg/L F^- will be displayed.

Note: *If the instrument shows OVER–RANGE, dilute a fresh sample. Repeat the test. Multiply by the appropriate dilution factor.*

Note: *In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.*

SAMPLING AND STORAGE

Samples may be stored in glass or plastic bottles for at least seven days when cooled to 4 °C (39 °F) or lower. Warm samples to room temperature before analysis.

ACCURACY CHECK

Standard Solution Method

A variety of standard solutions covering the entire range of the test is available from Hach. Use these in place of sample to verify technique. Minor variations between lots of reagent become measurable above 1.5 mg/L. While results in this region are usable for most purposes, better accuracy may be obtained by diluting a fresh sample 1:1 with demineralized water and retesting. Multiply the result by 2.

PRECISION

In a single laboratory, using standard solutions of 1.00 mg/L fluoride and two lots of SPADNS Reagent with the DR/2000, a single operator obtained standard deviations of ±0.02 mg/L fluoride.

INTERFERENCES

This test is sensitive to small amounts of interference. Glassware must be very clean. Repeating the test with the same glassware is recommended to ensure that results are accurate.The following substances interfere to the extent shown:

	Concentration	Error
Alkalinity (as $CaCO_3$)	5000 mg/L	–0.1mg/L F^-
Aluminum	0.1 mg/L	–0.1 mg/L F^-
Chloride	7000 mg/L	+0.1 mg/L F^-
Iron, ferric	10 mg/L	–0.1 mg/L F^-
Phosphate, ortho	16 mg/L	+0.1 mg/L F^-
Sodium Hexametaphosphate	1.0 mg/L	+0.1 mg/L F^-
Sulfate	200 mg/L	+0.1 mg/L F^-

SPADNS Reagent contains enough arsenite to eliminate interference up to 5 mg/L chlorine. For higher chlorine levels, add one drop of Sodium Arsenite Solution to 25 mL of sample for each 2 mg/L of chlorine.

To check for interferences from aluminum, read the concentration one minute after reagent addition, then again after 15 minutes. An appreciable increase in concentration suggests aluminum interference. Waiting two hours before making the final reading will eliminate the effect of up to 3.0 mg/L aluminum.

Most interferences can be eliminated by distilling the sample from an acid solution as described below:

a) Set up the distillation apparatus for the general purpose distillation. See the *Hach Distillation Apparatus Manual.* Turn on the water and make certain it is flowing through the condenser.

b) Measure 100 mL of sample into the distillation flask. Add a magnetic stirring bar and turn on the heater power switch. Turn the stir control to 5. Cautiously measure 150 mL of StillVer Distillation Solution (2:1 Sulfuric Acid) into the flask. If high levels of chloride are present, add 5 mg silver sulfate for each mg/L chloride present.

c) Turn the heat control to setting 10, with the thermometer in place. The yellow pilot lamp shows when the heater is on.

d) When the temperature reaches 180 °C (about one hour), turn the still off. Analyze the distillate by the above method.

SUMMARY OF METHOD

The SPADNS Method for fluoride determination involves the reaction of fluoride with a red zirconium–dye solution. The fluoride combines with part of the zirconium to form a colorless complex, thus bleaching the red color in an amount proportional to the fluoride concentration. This method is approved by the EPA for NPDES and NPDWR reporting purposes when the samples have been distilled. Seawater and wastewater samples require distillation. See *Optional Apparatus* for distillation apparatus listing.

REQUIRED REAGENTS (Using Solution)

Description	Quantity Required Per Test	Units	Cat. No.
SPADNS Reagent for Fluoride	10 mL	500 mL	444–49
Water, demineralized	25 mL	4 L	272–56

REQUIRED APPARATUS (Using Solution)

Cylinder, graduated, 25 mL	1	each	508–40
Pipet Filler safety bulb	1	each	14651–00
Pipet, volumetric, Class A, 5.00 mL	1	each	14515–37
Thermometer, –20 to 105 °C	1	each	1877–01

REQUIRED REAGENTS (Using AccuVac Ampuls)

SPADNS Fluoride Reagent AccuVac Ampuls	2 ampuls	25/pkg	25060–25
Water, demineralized	varies	4 L	272–56

REQUIRED APPARATUS (Using AccuVac Ampuls)

Adapter, AccuVac vial	1	each	43784–00
Beaker, 50 mL	2	each	500–41

OPTIONAL REAGENTS

Fluoride Standard Solution, 0.2 mg/L F^-	473 mL	405–02
Fluoride Standard Solution, 0.4 mg/L F^-	473 mL	405–04
Fluoride Standard Solution, 0.5 mg/L F^-	473 mL	405–05
Fluoride Standard Solution, 0.6 mg/L F^-	473 mL	405–06
Fluoride Standard Solution, 0.8 mg/L F^-	473 mL	405–08
Fluoride Standard Solution, 1.0 mg/L F^-	946 mL	291–16
Fluoride Standard Solution, 1.0 mg/L F^-	473 mL	291–11
Fluoride Standard Solution, 1.2 mg/L F^-	473 mL	405–12
Fluoride Standard Solution, 1.4 mg/L F^-	473 mL	405–14
Fluoride Standard Solution, 1.5 mg/L F^-	473 mL	405–15
Fluoride Standard Solution, 1.6 mg/L F^-	473 mL	405–16
Fluoride Standard Solution, 1.8 mg/L F^-	473 mL	405–18
Fluoride Standard Solution, 2.0 mg/L F^-	473 mL	405–20
Silver Sulfate, ACS	113 g	334–14
Sodium Arsenite Solution	100 mL MDB	1047–32
StillVer Distillation Solution	500 mL	446–49

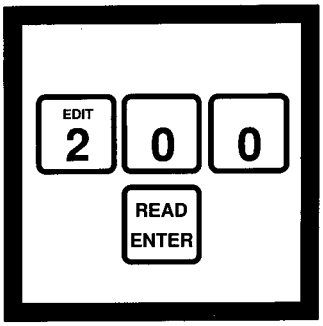
OPTIONAL APPARATUS

AccuVac Snapper Kit	each	24052-00
Cylinder, graduated, 100 mL	each	508–42
Cylinder, graduated, 250 mL	each	508–46
Distillation Heater and Support Apparatus Set, 115 V, 50/60 Hz	each	22744–00
Distillation Heater and Support Apparatus Set, 230 V, 50/60 Hz	each	22744–02
Distillation Apparatus General Purpose Accessories	each	22653–00
pH/ISE Meter, EC20, portable	each	50075–00
Pipet, Volumetric, 25 mL	each	515–40

For additional ordering information, see final section.
In the U.S.A. call 800–227–4224 to place an order.

FORMALDEHYDE (0 to 350 µg/L)

MBTH Method*



1. Enter the stored program number for formaldehyde (CH_2O).

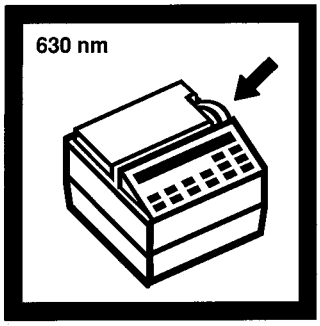
Press: **2 0 0 READ/ENTER**

The display will show:
DIAL nm TO 630

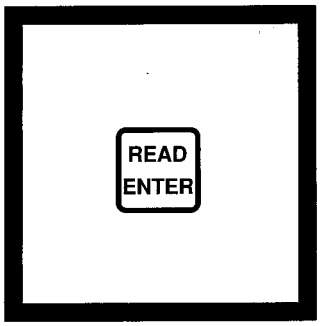
Note: *DR/2000s with software versions 3.0 and greater will display "P" and the program number.*

Note: *Instruments with software versions 3.0 and greater will not display "DIAL nm TO" message if the wavelength is already set correctly. The display will show the message in Step 3. Proceed to Step 4.*

Note: *Samples must be analyzed immediately and cannot be stored for later analysis.*

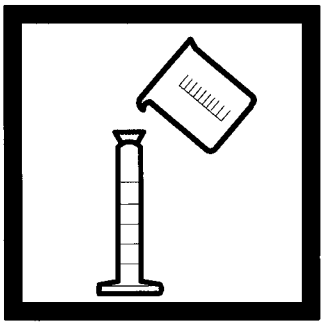


2. Rotate the wavelength dial until the small display shows:
630 nm



3. Press: **READ/ENTER**

The display will show:
µg/l CH_2O



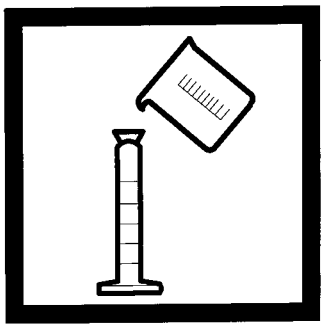
4. Accurately measure 25 mL of sample in a 50–mL mixing cylinder (the prepared sample).

Note: *Wash glassware with chromic acid cleaning solution to remove trace contaminants.*

Note: *Time and temperature are very important in this test. The sample should be at 25 ±1 °C, and the times specified below must be followed precisely. A temperature controlled water bath is recommended for better accuracy.*

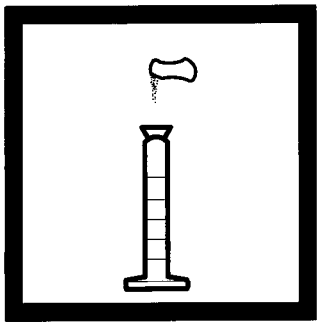
Note: *For proof of accuracy, use a 320 µg/L formaldehyde standard solution (preparation given in the* Accuracy Check*) in place of the sample.*

*Adapted from Matthews, T.G. and Howell, T.C., *Journal of the Air Pollution Control Association*, 31 (11) 1181–1184 (1981)

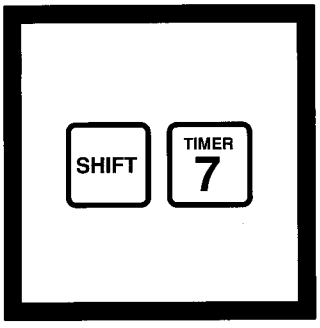


5. Accurately measure 25 mL of formaldehyde–free water in a second 50–mL mixing cylinder (the blank).

Note: Obtain formaldehyde–free water by distilling water from alkaline permanganate (4 g sodium hydroxide, 2 g potassium permanganate per 500 mL water). Discard the first 50 to 100 mL of distillate.

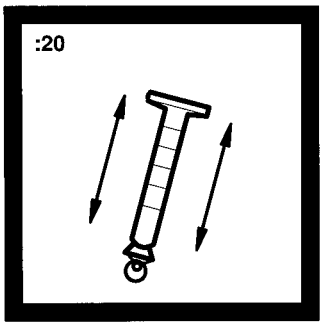


6. Add the contents of one MBTH Powder Pillow to the blank. Stopper the cylinder.



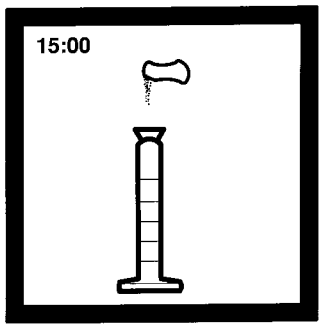
7. Immediately press:
SHIFT TIMER

A 17–minute reaction period will begin.

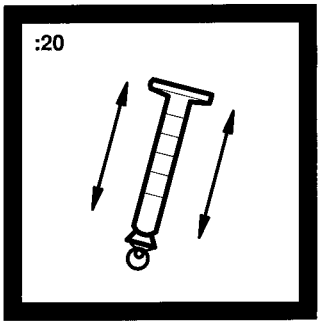


8. Immediately after the reaction period starts, shake the cylinder vigorously for 20 seconds.

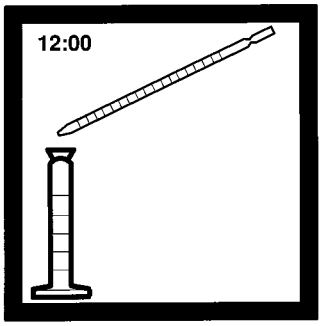
Note: Do not wait for the timer to beep.



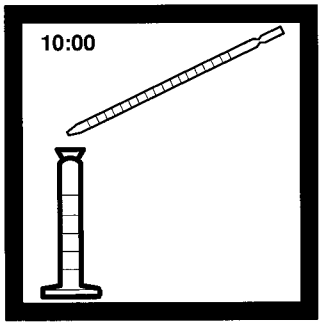
9. Add the contents of one MBTH Powder Pillow to the prepared sample when the timer shows 15:00. Stopper the cylinder.



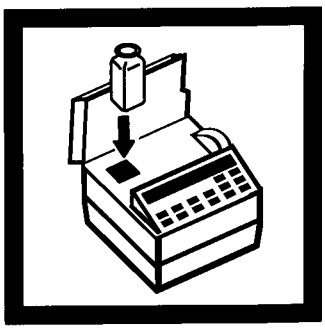
10. Shake the cylinder vigorously for 20 seconds.



11. Add 2.5 mL of Developing Solution For Low Range Formaldehyde to the blank when the timer shows 12:00. Stopper. Invert to mix.



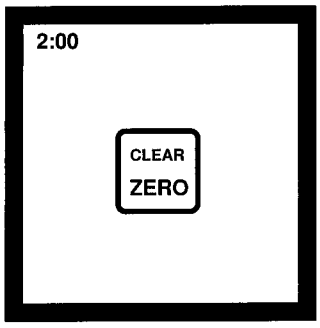
12. Add 2.5 mL of Developing Solution For Low Range Formaldehyde to the prepared sample when the timer shows 10:00. Stopper. Invert to mix.



13. Pour the blank into the sample cell just before the timer shows 2:00. Place the blank into the cell holder. Close the light shield.

Note: Pouring the solution slowly into the cell will avoid bubble formation on the cell walls. If bubbles form, swirl the cell to dislodge them.

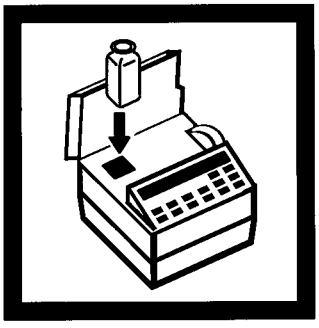
Note: The Pour–Thru Cell cannot be used with this procedure.



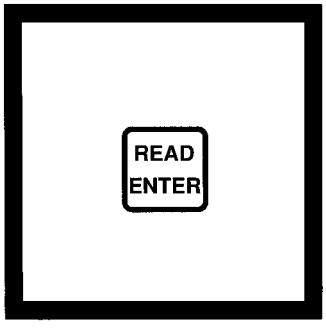
14. When the timer shows 2:00, press: **ZERO**

The display will show:
WAIT
then:
0. µg/l CH_2O

Note: If desired, return the display to the timer mode by pressing SHIFT TIMER.



15. Pour the prepared sample into a sample cell. Place it into the cell holder. Close the light shield.



16. When the timer beeps, the display will show:
µg/l CH_2O
Immediately press:
READ/ENTER

The display will show:
WAIT
then the result in µg/L formaldehyde (CH_2O) will be displayed.

Note: In the constant–on mode, pressing READ/ENTER is not required. WAIT will not appear. When the display stabilizes, read the result.

ACCURACY CHECK

Standard Additions Method

a) Snap the neck off a Formaldehyde Voluette Ampule Standard Solution, 4000 mg/L.

b) Use the TenSette Pipet to add 0.2 mL of standard to a 100 mL volumetric flask. Dilute to volume with formaldehyde–free water. Mix well. Prepare daily. This is an 8 mg/L formaldehyde standard solution.

c) Use the TenSette Pipet to add 0.1 mL, 0.2 mL and 0.3 mL of diluted standard (8 mg/L) to three 25–mL water samples. Mix each thoroughly.

d) Analyze each sample as described above. The formaldehyde concentration should increase 32 µg/L for each 0.1 mL of standard added.

e) If these increases do not occur, see *Standard Additions* in *Section I* for more information.

Standard Solution Method

Prepare a 320 µg/L formaldehyde standard by pipetting 1.0 mL of the 8 mg/L solution from the Accuracy Check into a 50–mL mixing cylinder. Dilute to 25.0 mL with formaldehyde–free water. Run the test directly on this sample.

INTERFERENCES

The following may interfere when present in concentrations exceeding levels listed below.

Acetate	1000 mg/L
Ammonium (as N)	10 mg/L
Aniline	10 mg/L
Bicarbonate	1000 mg/L
Calcium	3500 mg/L
Carbonate	500 mg/L
Chloride	5000 mg/L
Copper	1.6 mg/L
Cyclohexylamine	250 mg/L
Ethanolamine	33 mg/L
Ethylenediamine	1.5 mg/L
Glucose	1000 mg/L
Glycine	1000 mg/L
Iron (Fe^{3+})	12 mg/L
Lead	100 mg/L
Manganese	500 mg/L
Mercury	70 mg/L
Morpholine	0.36 mg/L
Nitrate	1000 mg/L
Nitrite	8 mg/L
Phenol	1050 mg/L
Phosphate	200 mg/L
Silica	40 mg/L

Sulfate	10000 mg/L
Urea	1000 mg/L
Zinc	1000 mg/L

Other aldehydes give a positive interference.

PRECISION

In a single laboratory, using standards of 146 µg/L formaldehyde and two lots of reagent with the DR/2000, a single operator obtained a standard deviation of ±3.1 µg/L formaldehyde.

SUMMARY OF METHOD

Formaldehyde reacts with MBTH (3–methyl–2–benzothiazoline hydrazone) and a developing solution to form a blue color in proportion to the formaldehyde concentration.

REQUIRED REAGENTS

	Cat. No.
Formaldehyde Reagent Set (100 Tests)	22577–00
Includes: (1) 22571–69, (1) 22572–49	

Description	Quantity Required Per Test	Units	Cat. No.
Developing Solution For Low Range Formaldehyde	5 mL	500 mL	22572–49
MBTH Powder Pillows	2 pillows	100/pkg	22571–69

REQUIRED APPARATUS

Clippers, for opening powder pillow	1	each	968–00
Cylinder, mixing, graduated 50 mL	2	each	1896–41
Pipet, serological, 5 mL	1	each	532–37
Pipet Filler, safety bulb	1	each	14651–00

OPTIONAL REAGENTS

Chromic Acid Cleaning Solution	500 mL	1233–49
Formaldehyde Standard Solution, Voluette ampule, 4000 mg/L	10 mL	16–pkg	22573–10
Potassium Permanganate, ACS	454 g	168–01
Sodium Hydroxide, pellets, ACS	500 g	187–34

OPTIONAL APPARATUS

Ampul Breaker Kit	each	21968–00
Pipet, TenSette, 0.1 to 1.0 mL	each	19700–01
Pipet Tips, for 19700–01 TenSette Pipet	50/pkg	21856–96
Thermometer, –20 to 105 °C	each	1877–01
Water bath, 120 Vac, 60 Hz, 5 gal (19 L)	each	24638–00
Water bath, 240 Vac, 50 Hz, 5 gal (19 L)	each	24638–02

For additional ordering information, see final section.
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